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CONTENTS

THE EFFECT OF Ag$^+$ AND Cu^{2+} ADDED TO BIOGLASS® ON RESULTS OF *IN VITRO* TEST
Opavová K., Peroutková K., Pánová K.

CERAMIC PROTECTION OF ANTI-CORROSION LAYERS OF 3-GLYCIDYLOXYPROPYL-TRIETHOXYSILANE ON STEEL
Pokorny P., Prodanović N., Janata M., Brožek V.

COMPARISON OF INORGANIC BINDERS POROSITY MEASURING METHODS
Pulcová K., Šídlová M., Šulc R., Formáček P.

RESISTOMETRIC METHOD FOR CORROSION MONITORING
Reiser M., Kouřil M.

OIL, PETROCHEMICALS, BIOFUELS

KEY TRENDS AND STRATEGIES IN THE OIL AND PETROCHEMICAL INDUSTRY
H. Kittel

SLUDGE FORMATION DURING LONG-TERM STORAGE OF VARIOUS TYPES OF CRUDE OIL
Lyko Vachková E., Maxa D., Straka P., Váchová V.

ZERO EMISSION REFINERY: REALITY OR DREAM?
Souček I., Kittel H., Minařík Z.

POTENTIAL FOR USE OF SIDE STREAMS IN THE PRODUCTION OF DICYCLOPENTADIENE
Waňousová S., Herink T., Perrot A., Hyršl J., Bandžuch J., Černý R., Kunrtová D.

ORGANIC TECHNOLOGY

PRODUCTION OF 4-AMINO-4H-1,2,4-TRIAZOLE AND ITS APPLICATION AS THE NITRIFICATION INHIBITOR
Kelemen P., Majerníková J., Tokár Z., Kučera M.

INFLUENCE OF THE REACTION CONDITIONS ON 3-CARENE EPOXIDATION
Rejzková A., Vyskočilová E.

STUDY OF UNCATALYZED LOW TEMPERATURE OXIDATION OF CYCLOHEXYLAMINE WITH AIR IN LIQUID PHASE – EFFECT OF REACTION TEMPERATURE AND CONCENTRATION OF WATER
Valeš R., Kukučková A., Dvořák B., Krupka J.

POLYMERS COMPOSITES

MODELING OF GAS-PHASE POLYMERIZATION PROCESS OF PROPYLENE – REACTION KINETICS
Grůza J., Skoumal M.

PRODUCTION AND APPLICATION OF GROUND TYRE RUBBER: A WAY TO INCREASE THE CIRCULARITY OF RUBBER MATERIALS
Hrdlička Z., Brejcha J.

EFFECT OF CATALYTIC SYSTEM ON THE STRUCTURE OF ETHYLENE/PROPYLENE COPOLYMERS
Kolomazník V., Buráň Z., Skoumal M.

POLYOLEFIN STRUCTURE MODIFICATION: FROM BASIC MATERIALS TO POLYMER SPECIALITIES
Kotyza O., Sokolohorskyj A., Merna J.

VOLATILE COMPOUNDS RELEASED FROM PVC WIRE COATING
Uřičář J., Pilnaj D., Kalousková R., Veselý P., Slavíková A., Dušek K., Brožek J.

SYNTHESIS AND PRODUCTION OF DRUGS

DETERMINATION OF CYTOTOXIC EFFECTS OF DERIVATIVES OF BETULONIC AND PLATANIC ACID ON CELL LINES HepG2 AND HEK 293T
Černá L., Lovecká P.

COMBINING DIFFERENT POWDER UNIAXIAL COMPRESSION ARRANGEMENTS TO BETTER PREDICT POWDER COMPRESSIBILITY BEHAVIOUR DURING THE ROLLER COMPACTION PROCESS
Marinko N., Zámostný P., Budková V., Krpelan T.

TECHNOLOGY FOR ENVIRONMENTAL PROTECTION

DIESEL EXHAUST FLUID QUALITY IMPEDANCE MEASUREMENT SYSTEM
Seidl J., Černý P., Pelikán P., Scholtz V.

ECONOMICS OF CHEMICAL INDUSTRY

POSSIBILITIES OF IMPLEMENTATION OF CIRCULAR ECONOMY PRINCIPLES IN MEDIUM-SIZED ENTERPRISES OF THE CHEMICAL INDUSTRY IN THE CZECH REPUBLIC
Benda A., Munzarová S.

SUSTAINABLE HUMAN RESOURCES MANAGEMENT
Botek M., Charvátová D.

WAYS TO IMPROVE THE COLLECTION AND RECYCLING OF SEPARATE WASTE IN THE SELECTED REGION – CASE STUDY
Branská L., Paták M., Dostálová A., Pecinová Z.

THE LOGISTICS IN THE CHEMICAL INDUSTRY
Kostalek J., Kotatkova Stranska P.

CIRCULAR ECONOMY IN ENTERPRISES OF THE CZECH CHEMICAL INDUSTRY
Kutnohorská O., Strachotová D.

ONLINE REPUTATION MANAGEMENT IN COMPANIES OPERATING IN THE CHEMICAL INDUSTRY IN THE CZECH REPUBLIC
Poppelová E., Jelínková M.

INDICATORS OF SUSTAINABLE PRODUCTION IN CHEMICAL ENTERPRISES
Vávra J., Vrbická T.

IMPLEMENTATION OF ENERGY SAVING PROJECTS IN CHANGING ENVIRONMENT
Vytlačil D.

BIOTECHNOLOGY AND BIOREFINERY

REDIRECTION OF METABOLIC FLUXES IN CLOSTRIDIUM BEIJERINCKII AS A RESPONSE TO LIGNOCELLULOSE INHIBITORS

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Abstract

Lignocellulose biomass represents a promising renewable source of utilisable saccharides for biotechnology upon hydrolysis. Any efficient treatment of this recalcitrant material leads inevitably to the production of chemicals that hinder cell growth or production. Solventogenic clostridia such as e.g., *Clostridium beijerinckii* can transform a range of inhibitors and growth in their presence; nevertheless, changes in product ratio to the disadvantage of solvents are a frequent undesirable phenomenon. Seven common inhibitors (vanillic acid, 4-hydroxy-benzoic acid, syringaldehyde, coumaric acid, ferulic acid, furfural, and hydroxymethyl furfural) were tested and their impacts on growth, acids and solvents production were evaluated for *Clostridium beijerinckii* NRRL B-598. A considerable decrease in solvent production was observed under sublethal inhibitor concentrations in the presence of syringaldehyde, coumaric acid, and ferulic acid, while it was accompanied by a significant increase in butyric acid formation only for cultures challenged by coumaric acid. In the case of ferulic acid and syringaldehyde, rather the ability to fully utilise available glucose was negatively influenced, suggesting different mechanisms of impact of inhibitors on fluxes through central metabolism.

Key words: lignocellulose inhibitors, Clostridium beijerinckii, solventogenic clostridia

Introduction

Solvent production employing microbial producers has gained increased attention mainly in connection with sustainable production of biofuels, while the most profound molecule for this purpose is bio butanol, the primary metabolite of the fermentation metabolism of solventogenic clostridia. Today, electricity and hydrogen are rather considered for the replacement of fossil fuels in transportation, while bio butanol remains a focus mainly as a precursor for synthetic biofuels and as a bio solvent. A group of microorganisms capable of production of butanol and other solvents belong to the genus *Clostridium* and, owing to their fermentation profile, they are called solventogenic clostridia. Among the most promising species for industrial production belong *C. acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum,* and *C. diolis* which differ slightly in a spectrum and ratio of produced metabolites and by substrate utilization preferences with the strongest carbon catabolite repression observed for *C. acetobutylicum*[1]. This feature is important because of the increased requirements for sustainable production from renewable sources that are naturally composed of multiple components. Lignocellulose biomass belongs to the most promising substrate for the biotechnological production of bulk chemicals; however, its utilisation requires overcoming many issues. It is an abundant and readily available material produced as part of plant biomass. It consists of cellulose, hemicellulose, lignin, and other less represented components. The main bottleneck is its recalcitrance caused by the tight interconnection of these molecules and thus complicated processing of their separation and consequent hydrolysis. Many different procedures have been developed to obtain fermentable substrates from lignocellulose biomass[2] however, those sufficiently efficient inevitably produce a wide range of chemicals hindering microbial growth or production, these are collectively referred to as inhibitors. From a chemical point of view, they are mainly furans, phenols, organic acids, and inorganic salts. When lignocellulose hydrolysates are fermented by solventogenic clostridia, these inhibitors can cause a decrease in and a delay in culture growth and severe intervention to the metabolic pathways of solvent production[3]. Generally, the metabolism of solventogenic clostridia consists of two stages. First, the acidogenic one, which is characterised by rapid population growth, production of high titres of acids, acetic and butyric and gases with high content of hydrogen. The decrease in pH of the fermentation medium together with the accumulation of acids and some factors that have not yet been revealed lead to the metabolic switch to the second phase, solventogenesis. In the solventogenesis, the carbon source is predominantly converted to butanol, acetone, ethanol, and eventually isopropanol[4]. At the same time, acids formed in the first stage are reutilised to solvents too. Unfortunately, until now, the exact mechanism and regulation of the metabolic switch have not been revealed. The presence of lignocellulose inhibitors in fermentation media often led to a prolonged stay in the acidogenic stage, decreased reutilization ability of acids, or total loss of solvent production, all of them leading to lower titres of desired solvents[5]. One of the reasons for the observed phenomenon might be the altered redistribution of intermediates into branches of the central metabolic pathway due to the changed availability of reduced cofactors NADH and NADPH. These could be used in a detoxification reaction[6] in which the inhibitors present in hydrolysates are reduced to a less toxic compound.

In this study, our objective was to reveal whether the presence of sublethal concentrations of the most common inhibitors will result in a different production profile or in general deterioration in growth and production performance caused by adverse conditions.

Materials and methods

All experiments were performed with the strain *Clostridium beijerinckii* NRRL B-598 obtained from ARS collection and cultivated in Erlenmeyer flasks in an anaerobic chamber Concept 400 (Ruskin). Cultivation medium used was P2 (glucose 45 g/L, yeast extract 1 g/L, the following solutions were sterilized separately by filtration and completed prior to cultivation; acetate buffer: KH2PO4 0.5 g/L, K2HPO4 0.5 g/L, ammonium acetate 2.2 g/L; vitamins: para-amino-benzoic acid 0.001 g/L, thiamine 0.001 g/L, biotin 0.00001 g/L; minerals: MgSO4.7H2O 0.2 g/L, MnSO4.7H2O 0.01 g/L, FeSO4.7H2O 0.01 g/L, NaCl 0.01 g/L). Inhibitors were diluted in DMSO and added prior inoculation that was carried out via pipetting the overnight culture prepared from spore stocks as described previously[7].

Optical density was measured after appropriate dilution in 1 mL volume cuvettes using Varian Cary 50 (Agilent) spectrophotometer and wavelength 600 nm. Glucose concentration and primary metabolite quantification was performed as described in[8].

Results and discussion

Seven inhibitors were tested in static cultures in which inhibitors were added to the medium prior to inoculation and the final profile of the metabolites and the biomass formed were analysed after 96 h of fermentation. Because clostridia very often show a high variability in behaviour depending on very small fluctuations in culture conditions[8,9], each batch was supplemented with its own control culture without the addition of an inhibitor. A comparison of these parameters for all inhibitors tested is shown in Figures 1 and 3–5. Figure 1 shows the overall growth of the culture and indicates that, except for furan derivatives, the presence of all other inhibitors decreased the optical density (OD) that were finally reached. It should be noted that, in the case of clostridia, the decrease in OD might be caused by entering the culture to the sporulation cycle[10], which changes the optical properties of the cell suspension and together the absorbance values. However, the presence of inhibitors rather decreases the sporulation rate[11] therefore in this case we can assume the OD drop to be proportional to the decreased ability to reach a certain cell density. The lower sporulation rate was also observed in our experiments, where it was accompanied by a change in cell morphology, which, instead of the short rods observed under control conditions, showed rather filamentous-like growth after the addition of the inhibitor; see Figure 2.

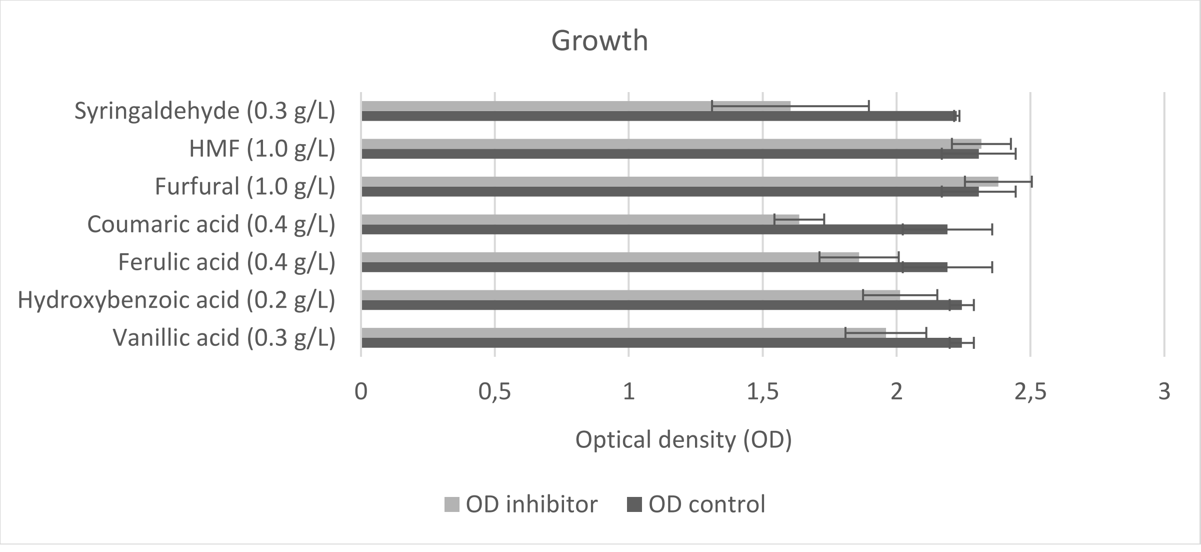

Figure 1. Values of optical density reached after 96 h of cultivation of *C. beijerinckii* NRRL B-598 in the presence or without inhibitors (control). The values are means of three biological replicates and error bars represent standard deviation.

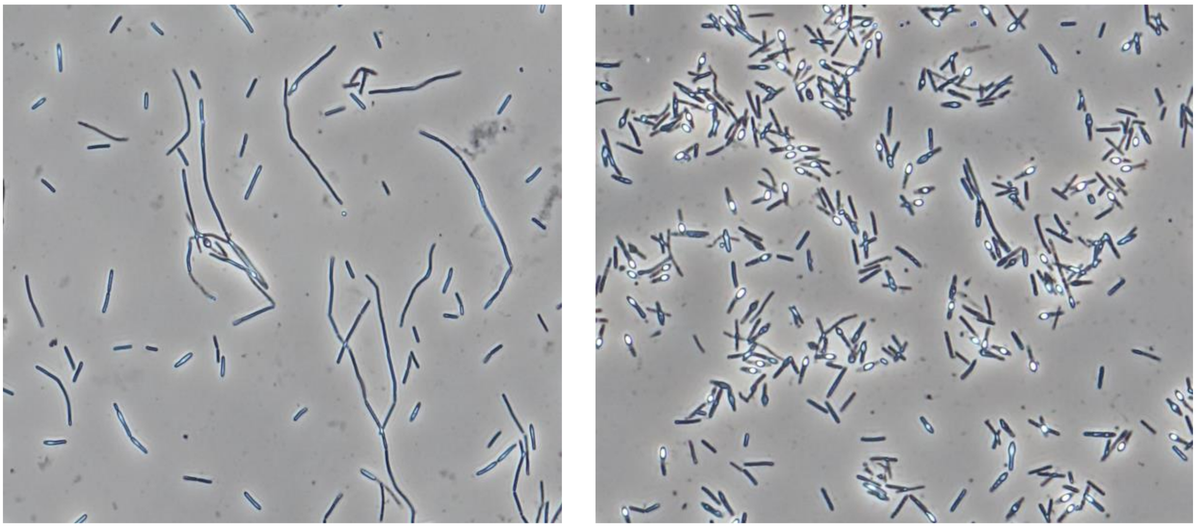

Figure 2. Changes in cell morphology of *C. beijerinckii* NRRL B-598 in the presence (Left) or without inhibitors (Right). Samples were withdrawn after 96 h of cultivation and observed using phase contrast microscopy, Olympus BX51.

Glucose consumption (Figure 3) was calculated from the initial and final concentrations of glucose in medium. The approximate initial concentration was set at 45 g/L. The addition of all inhibitors decreased the amount of glucose utilised in the batch experiment. The accumulation of acids and solvents causes a decrease in the viability of the production culture with an early cessation of the fermentation process[9,12]. Inhibitors present in the culture medium, or their less toxic forms could contribute to the overall toxicity of the medium[6] with an additive or synergistic effect[13] resulting in lower glucose utilisation. Due to the fact that the rapid viability assay at the single cell level is complicated in the case of solventogenic clostridia[14,15], the direct impact of inhibitors on their viability was studied very scarcely. Nevertheless, viability, growth, and substrate consumption are significantly influenced by the instantaneous culture/individual cell state.

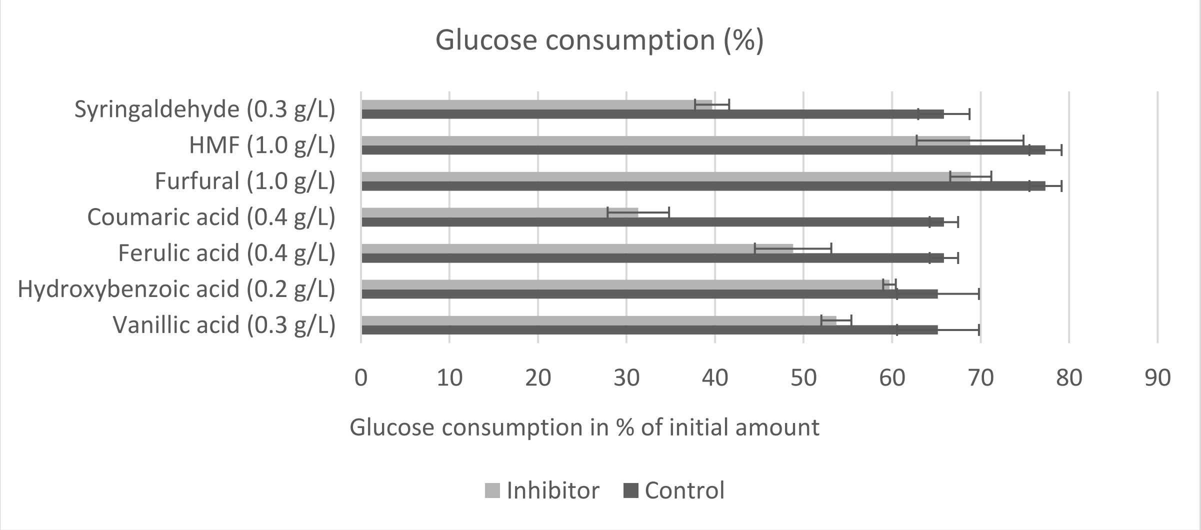

Figure 3. Glucose consumption in percent calculated from initial values and concentrations after 96 h of cultivation of *C. beijerinckii* NRRL B-598 in the presence or without inhibitors (control). The values are means of three biological replicates and error bars represent standard deviation.

Figs. 4 and 5 show the titres of butyric acid and butanol levels after the fermentation. Other products are not shown due to chromatographic overlap of retention time of acetone with DMSO used to solubilize solid inhibitors. Ethanol is formed in negligible concentrations in strain *C. beijerinckii* NRRL B-598[16] and acetate is already present in the optimized culture medium for solventogenic clostridia. Nevertheless, both butyric acid and butanol represent two metabolic branches: acidogenic and solventogenic. Moreover, solvents are often formed in a fixed ratio. It is apparent that except for culture challenged by coumaric acid, butyric acid formation was promoted only marginally, while a decrease in butanol production is clearly demonstrated.

Comparing this observation with Figure 6, where the calculated values for butanol yield are depicted, it can be concluded that except for coumaric acid and potentially syringaldehyde, no redirection of metabolites was detected and the decrease in butanol production can be attributed to the disruption of the second solventogenic phase of fermentation. This is evidenced by lower consumption of glucose but comparable yields ($Y_{butanol / glucose}$).

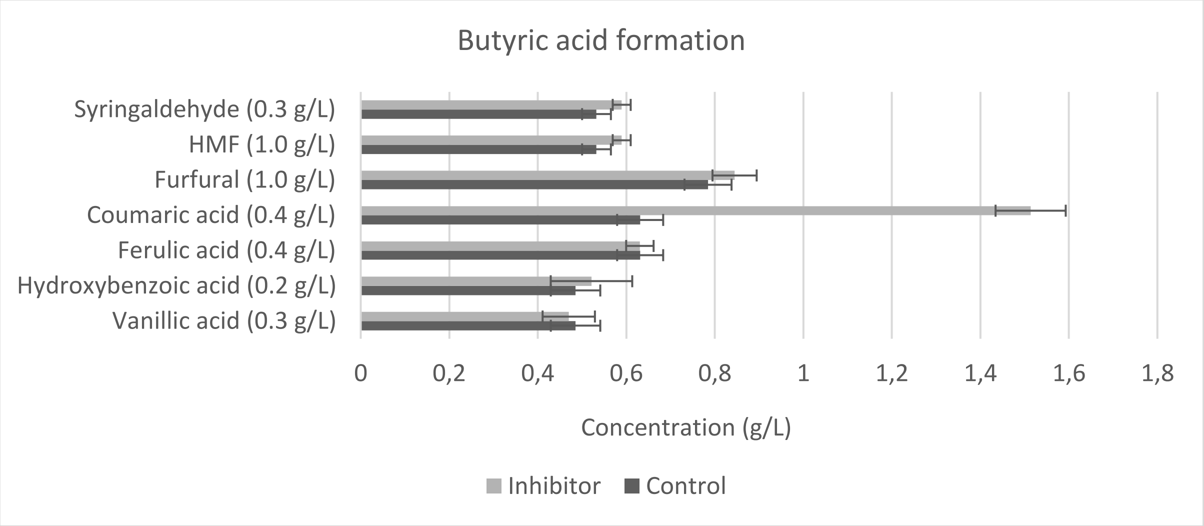

Figure 4. Butyric acid concentrations after 96 h of cultivation of *C. beijerinckii* NRRL B-598 in the presence or without inhibitors (control). The values are means of three biological replicates and error bars represent standard deviation.

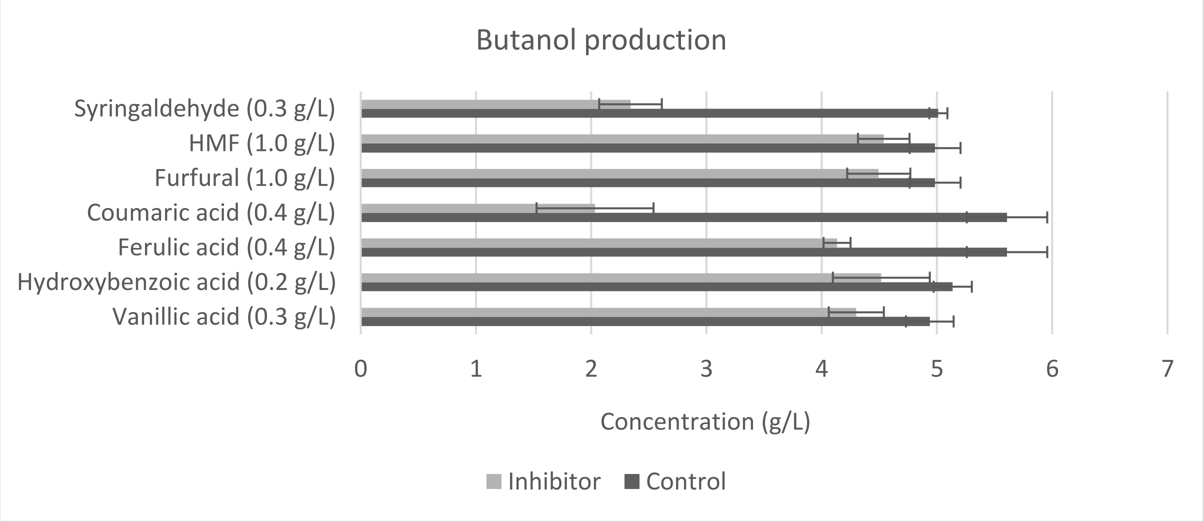

Figure 5. Butanol concentrations after 96 h of cultivation of *C. beijerinckii* NRRL B-598 in the presence or without inhibitors (control). The values are means of three biological replicates and error bars represent standard deviation.

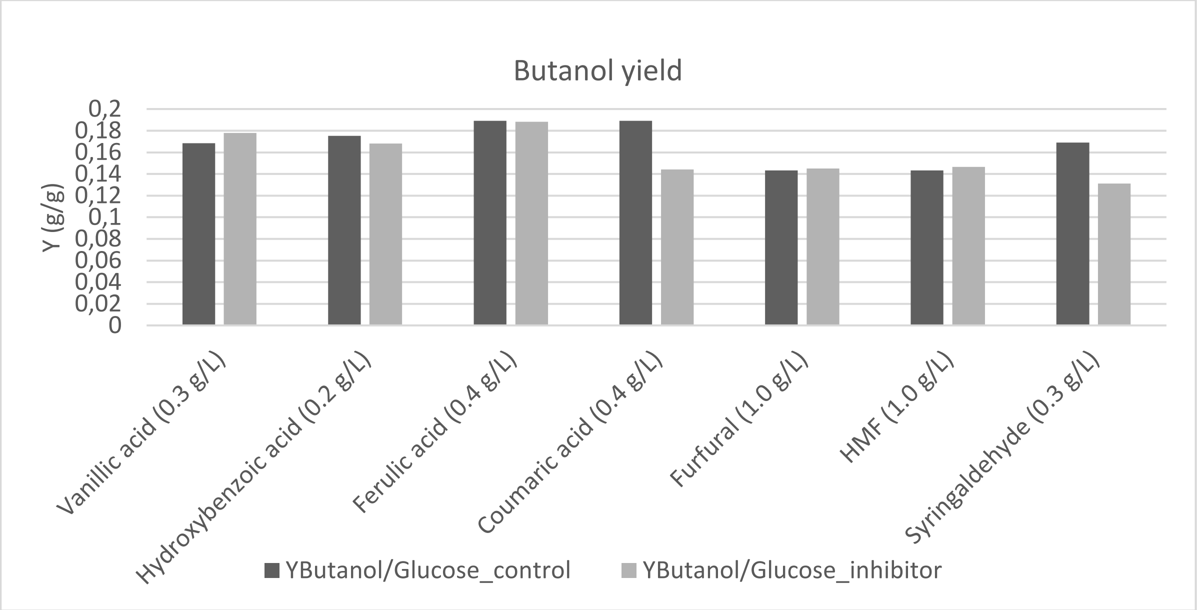

Figure 6. Yields of butanol calculated from initial (t0h) and final (t96h) values. Y (g/g) were calculated as the ratio of butanol produced to glucose consumed.

The production pattern of the culture challenged with coumaric acid revealed significant differences compared to the other inhibitors. Acid production was more than doubled, and butanol production was poor. Such a phenomenon can be observed when lignocellulose hydrolysates are utilised for butanol production. Another study suggested that the main reason for the preferential production of acids at the expense of solvents could be attributed to the action of formic acid[17] that is sometimes present in hydrolysates. However, in our experiments pure chemicals were used instead of real hydrolysates. Luo et al. 2020[11] described a decreased rate of acid reutilization upon the addition of inhibitors to the growing culture, which could also contribute to the increased butyric acid concentration. A low butanol concentration was also reached in case of syringaldehyde addition, but no alteration in acid concentration was observed. It suggests an additional (or synergistic) effect of acids, solvents, and inhibitor[6,13].

Conclusion

Of the seven inhibitors tested, a redirection of metabolic flux to butyric acid was observed only in the case of coumaric acid for *C. beijerinckii* NRRL B-598. The presence of all inhibitors led to decreased production of butanol, nevertheless except for coumaric acid and syringaldehyde, the yield remained unchanged in comparison to the control, suggesting rather a reduction in the overall metabolic activity.

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References

1. Ren C., Gu Y., Hu S., Wu Y., Wang P., Yang Y., Yang C., Yang S., Jiang W. Identification and Inactivation of Pleiotropic Regulator CcpA to Eliminate Glucose Repression of Xylose Utilization in Clostridium Acetobutylicum. Metab. Eng. 2010, doi:10.1016/j.ymben.2010.05.002.
2. Guo Y., Liu Y., Guan M., Tang H., Wang Z., Lin L., Pang H. Production of Butanol from Lignocellulosic Biomass: Recent Advances, Challenges, and Prospects.RSC Adv. 2022, doi:10.1039/d1ra09396g.
3. Birgen C., Degnes K.F., Markussen S., Wentzel A., Sletta, H. Butanol Production from Lignocellulosic Sugars by Clostridium Beijerinckii in Microbioreactors. Biotechnol. Biofuels 2021, 14, doi:10.1186/S13068-021-01886-1.
4. Sedlar K., Vasylkivska M., Musilova J., Branska B., Provaznik I., Patakova P. Phenotypic and Genomic Analysis of Isopropanol and 1,3-Propanediol Producer *Clostridium diolis* DSM 15410. Genomics 2021, 113, 1109–1119, doi:10.1016/j.ygeno.2020.11.007.
5. Birgen C., Dürre P., Preisig H.A., Wentzel A. Butanol Production from Lignocellulosic Biomass: Revisiting Fermentation Performance Indicators with Exploratory Data Analysis., Biotechnol. Biofuels. 2019 doi:10.1186/s13068-019-1508-6.

6. Zhang Y., Han B., Ezeji T.C. Biotransformation of Furfural and 5-Hydroxymethyl Furfural (HMF) by *Clostridium acetobutylicum* ATCC 824 during Butanol Fermentation. N. Biotechnol. 2012, 29, 345–351, doi:10.1016/J.NBT.2011.09.001.
7. Vasylkivska M., Jureckova K., Branska B., Sedlar K., Kolek J,. Provaznik I., Patakova P. Transcriptional Analysis of Amino Acid, Metal Ion, Vitamin and Carbohydrate Uptake in Butanol-Producing *Clostridium beijerinckii* NRRL B-598. PLoS One 2019, 14, doi:10.1371/journal.pone.0224560.
8. Branska B., Vasylkivska M., Raschmanova H., Jureckova K., Sedlar K., Provaznik I., Patakova P. Changes in Efflux Pump Activity of *Clostridium beijerinckii* throughout ABE Fermentation. Appl. Microbiol. Biotechnol. 2021, 105, 877–889, doi:10.1007/s00253-020-11072-2.
9. Branska B., Pechacova Z., Kolek J., Vasylkivska M., Patakova P. Flow Cytometry Analysis of *Clostridium beijerinckii* NRRL B-598 Populations Exhibiting Different Phenotypes Induced by Changes in Cultivation Conditions. Biotechnol. Biofuels 2018, 11, 99, doi:10.1186/s13068-018-1096-x.
10. Diallo M., Kengen S.W.M., López-Contreras A.M. Sporulation in Solventogenic and Acetogenic Clostridia. Appl. Microbiol. Biotechnol. 2021, 105, 3533–3557 doi:10.1007/S00253-021-11289-9.
11. Luo H., Zheng P., Bilal M., Xie F,. Zeng Q., Zhu C., Yang R., Wang Z. Efficient Bio-Butanol Production from Lignocellulosic Waste by Elucidating the Mechanisms of *Clostridium acetobutylicum* Response to Phenolic Inhibitors. Sci. Total Environ. 2020, 710, 136399 doi:10.1016/j.scitotenv.2019.136399.
12. Kolek J., Branska B., Drahokoupil M., Patakova P., Melzoch K. Evaluation of Viability Metabolic Activity and Spore Quantity in Clostridial Cultures during ABE Fermentation. FEMS Microbiol. Lett. 2016 363 fnw031 doi:10.1093/femsle/fnw031.
13. Luo H., Zheng P., Xie F., Yang R., Liu L., Han S., Zhao Y., Bilal M. Co-Production of Solvents and Organic Acids in Butanol Fermentation by *Clostridium acetobutylicum* in the Presence of Lignin-Derived Phenolics. RSC Adv. 2019 doi:10.1039/c9ra00325h.
14. Linhova M., Branska B., Patakova P., Lipovsky J., Fribert P., Rychtera M., Melzoch K., Linhová M., Branská B., Patáková P. Rapid Flow Cytometric Method for Viability Determination of Solventogenic Clostridia. Folia Microbiol. (Praha). 2012, 57, 307–311, doi:10.1007/s12223-012-0131-8.
15. González-Peñas H., Lu-Chau T.A., Moreira M.T., Lema J.M. Assessment of Morphological Changes of *Clostridium acetobutylicum* by Flow Cytometry during Acetone/Butanol/Ethanol Extractive Fermentation. Biotechnol. Lett. 2015, 37, 577–584, doi:10.1007/s10529-014-1702-3.
16. Sedlar K., Kolek J., Gruber M,. Jureckova K., Branska B., Csaba G., Vasylkivska M., Zimmer R., Patakova P., Provaznik I. A Transcriptional Response of *Clostridium beijerinckii* NRRL B-598 to a Butanol Shock. Biotechnol. Biofuels 2019, 12, doi:10.1186/s13068-019-1584-7.
17. Wang S., Zhang Y., Dong H., Mao S., Zhu Y., Wang R., Luan G., Li Y., Formic Acid Triggers the "Acid Crash" of Acetone-Butanol-Ethanol Fermentation by *Clostridium acetobutylicum*. Appl. Environ. Microbiol. 2011, 77, 1674–1680

CHITIN-DEGRADING ISOLATES POTENTIALLY USABLE AS THE BASIS OF A BIOPREPARATION

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Abstract

The development and application of biopreparation are currently key environmentally focused projects to minimize the negative impact of human activity on the environment. The registered preparation must not be phytotoxic, must effectively protect the plant from phytopathogens and/or promote its growth. In other words, it must have biopesticide and/or biostimulant effects. This work focuses on the isolation and study of chitin-degrading microorganisms that would be the basis (an active ingredient) of a preparation with biostimulatory and/or biopesticidal effects. The identified isolates had to be tested for potential phytotoxicity and enzyme production with a focus on chitinases. Eight individual procaryotic isolates with high chitinase activity were successfully obtained. All isolates were non-phytopathogenic. The enzyme profile of *Arthrobacter stackebrandtii* with the highest biomass growth was the most diverse and rich in proteases, esterizes and other hydrolases. Although the highest chitinase activity was fluorometrically determined in the case of one strain *Pseudomonas gessardii*.

Introduction

The increase in human population, and therefore the associated increase in demand for food, together with inappropriate agricultural practices, is contributing to the gradual reduction in soil fertility and degradation of the land under cultivation[1]. The agricultural sector is often threatened by improper and excessive use of agricultural land, resulting in the creation of nutritional deficiencies in the soil[2]. Yield maximization (plant productivity) is often mediated by the use of a range of expensive agrochemicals of non-microbial origin, which are a burden on the environment[3]. The aforementioned negative aspects of intensive farming approach can be mitigated by more environmentally friendly biotechnological practices. The problem of soil nutrient deficiency can be solved by the application of non-hazardous biopreparations, which would additionally enhance the vitality and fertility of economically important plants. Biodegradable, non-naturally persistent products that effectively repel potential plant pests have significant potential to replace synthetic, chemical sprays[4]. The development and optimization of the production process of biostimulant and biopesticide products based on chitin-degrading microorganisms is rightly ranked among the main pillars of modern environmentally oriented approaches in (intensive) agriculture in today's consumer society, and therefore this topic will be the main focus of this project.

Microbial communities inhabiting (not only) the soil ecosystem have an irreplaceable influence on the cycling of basic elements in the biosphere[5]. They have a huge biodegradation and therefore production potential thanks to their ability to synthesize a rich enzyme apparatus (chitinases, proteases, lipases...). From the point of view of the development of a biopreparation intended for plant protection or growth promotion, the study of microbial producers capable of synthesizing and producing hydrolytic enzymes, surfactant molecules, siderophores and other bioactive components is very important. All aforementioned active ingredients would constitute the active cellular or non-cellular component of a potential biopreparation[6]. In order to maximize the increase in biomass or production of biologically active molecules and minimize the cost of the final product, it is always necessary to design the optimal culture conditions and course of downstream processes.

A product with antifungal, insecticidal or biostimulant properties must meet strict criteria to be approved and placed on the market. The microbial biopreparation (active ingredient of the biostimulant or biopesticide) must not be pathogenic, phytotoxic or otherwise harmful to the environment or humans. However, the approval process with subsequent registration of the biopreparation (biopesticide, biostimulant) needs to be set within a standardised legislative framework that is currently being developed[7]. Specific examples of registered biopesticides routinely used in the Czech Republic are the biopesticide named Polyversum®, whose active ingredient is the mycoparasitic oomycete *Pythium oligandrum*, or the biostimulant Tonivit®, whose active ingredient is an extract of the alga *Ascophyllum nodosum*[8]. The success of expanding the list of registered biopreparations will be crucial to meet the ever-increasing demand for livelihoods by an unstoppably growing human population, but not at the cost of increasing environmental contamination.

Material and methods

Isolation of microorganism

The source for the isolation of microorganisms was compost. The isolation process was carried out by enrichment culturing in an Erlenmeyer flask in basal salt medium (BSM) with neutral pH. Culture process was carried out at 20 °C. The medium included crushed, boiled shrimp exoskeletons (10 g/l), which served here as a source of chitin (inducer of chitinase synthesis) and as a carrier of biofilm predominantly formed by chitin-degrading microorganisms. Always after 14 days of culture, only the exoskeletons (the biofilm on the surface was the source of inoculum) were transferred to fresh BSM and cultured again. This process was repeated. The final step was the release of cells from the exoskeleton surface into fresh BSM using vortex. The medium – cell suspension – was then added onto DEV agar. After colony formation, single, morphologically distinct colonies were separately inoculated onto fresh agar until only homogeneous colonies grew on the agar. In this way, individual microbial isolates were isolated and tested in more detail in this study. The described procedure is partly based on several studies[9].

The effect of carbon source on isolates growth

Before starting to test individual isolates, it was necessary to determine the most suitable carbon and energy source in terms of growth. Glucose, glycerol and ethanol (750 mg/l) were chosen for this purpose. The isolates were cultured in wells of a microtiter plate containing BSM (pH = 7) and the specific carbon and energy source. The initial OD value was 0.1. The plates with filled wells were placed in a Bioscreen C (Dynex, Czech Republic). Cultivation was carried out at 20 °C for 48 h. Before each measurement, the contents of the wells were homogenized by gentle shaking.

Preparation of cell suspension for future analyses

Cell suspensions of all isolates were produced for subsequent analyses. The most suitable carbon and energy source (based on Bioscreen C results) was used with a concentration of 2 g/l for culture of specific isolate. Cultivation was carried out in an Erlenmeyer flask with BSM at a temperature of 20 °C and for a period of 3 days. The initial OD value was 0.2. Shrimp exoskeletons were also part of the medium. After the end of cultivation, untreated cell suspensions and supernatants obtained by centrifugation of the original suspension (10,000 rpm, 5 min) were studied.

Phytotoxicity tests

All isolates, including their metabolites, had to be tested for their potential phytotoxic effect on plant growth and fitness. For this purpose, a modified method described in the study by Salvatore et. al. was used[10]. The cell suspension and supernatant representing the specific isolate were applied (4 ml each) to the steriled seeds of lettuce (*Lactuca sativa* L. var. *capipatata* L.), which are very sensitive to the presence of toxic substances. The seeds were first treated with sterile distilled water, and then placed on sterile filter paper placed at the bottom of a Petri dish. Fresh sterile BSM served as a negative control. After 4 days of cultivation in the dark, an evaluation was carried out consisting in measuring the length of the shoots (image analysis of the captured image using ImageJ software) and gravimetric analysis of fresh and dried plant biomass.

Screening testing of the enzyme profile of isolates

In the case of non-phytotoxic isolates, a preliminary screening of their enzyme profile was performed. For this purpose, specific diagnostic solid agars were used, which contained a substrate (Tween 20 or 80, casein, colloidal chitin, urea) intended for the detection of a specific enzyme. For more detailed testing, the API ZYM® semi-quantitative diagnostic kit was used, which is designed to detect the presence of 19 different enzymes[11]. Productivity was shown only as "–" (no production), "+" (low production) and "++" (high production) according to the visual evaluation of the coloration of the wells (release of coloured product into the medium from chromogenic substrate due to the presence of the enzyme), which was compared with the evaluation sheet.

Chitinase activity measurement

In this study, the chitinase activity in the medium after the end of cultivation was tested in detail. A fluorometric assay was used for this purpose[12]. The measurement principle consists in the detection of emitted fluorescent radiation by an enzymatically cleaved product (fluorophore – excitation: 360 nm, emission: 465 nm). The substance 4-metylumbelliferyl-N-acetyl-β-D-glucosaminid was used as substrate and metylumbelliferol was the fluorescent product. Based on the measured emitted intensity, it was possible to calculate the enzyme activity given in µmol/l/h (amount of released product per time and well volume).

Specifically, the time dependence of chitinase production and chitinase activity at a specific time (after 3.5 h of cultivation) were measured. In the second case, the cell suspension and supernatant of all isolates were studied. In this way it was possible to detect cell-associated chitinases with free extracellular ones (cell suspension) and free extracellular chitinases only (supernatant). The measurement was carried out in a microtiter plate placed in the reader INFINITE F200 (Tecan, Switzerland).

Results and discussion

Isolation of microorganism

Eight prokaryotic isolates were successfully isolated, preliminarily characterized (morphology and G^+/G^-) and identified (16S r-RNA analysis). These were specifically: *Pseudomonas brenneri* (2x), *Pseudomonas gessardii* (3x), *Arthrobacter stackebrandtii*, *Glutamicibacter uratoxydans* and *Stenotrophomonas maltophilia*. Some of the isolates were identical in terms of identification. For the time being, all of them will be tested, as even identically classified microorganisms may have different behaviour – different production of biologically active metabolites (enzymes...).

The effect of carbon source on isolates growth

The resulting values of specific growth rates (including standard deviations) indicated that glucose was the most suitable source of carbon and energy compared to the other sources (see Table I). In the case of *A. stackebrandtii* and *G. uratoxydans*, glycerol was also a very good source in terms of growth. On the other hand, ethanol was the least suitable source in most cases.

Table I.
The resulting average specific growth rates represent the growth of isolates in the presence of a given carbon and energy source.

	Specific growth rate (h^{-1})		
Isolate	Glucose	Glycerol	Ethanol
P. brenneri I	0.110 ± 0.006	0.079 ± 0.002	0.067 ± 0.003
P. brenneri II	0.123 ± 0.003	0.080 ± 0.004	0.069 ± 0.006
P. gessardii I	0.099 ± 0.002	0.008 ± 0.002	0.079 ± 0.003
P. gessardii II	0.120 ± 0.002	0.081 ± 0.009	0.060 ± 0.010
P. gessardii III	0.099 ± 0.008	0.072 ± 0.003	0.060 ± 0.003
A. stackebrandtii	0.101 ± 0.006	0.103 ± 0.004	0.081 ± 0.002
G. uratoxydans	0.047 ± 0.005	0.045 ± 0.007	0.000 ± 0.000
S. maltophilia	0.078 ± 0.004	0.062 ± 0.002	0.065 ± 0.004

Phytotoxicity tests

Comparison of shoot lengths and fresh and dried plant biomass weights with those of the control (seeds treated with BSM only) indicated that all isolates and their supernatants were non-phytotoxic (see Figure 1). This finding is very important in terms of their applicability as the basis of a biopreparation that has no negative effect on plant growth. No apparent biostimulatory effect on seed germination and plant growth was observed for any of the isolates (within this method). However, this property will be studied more thoroughly using more sophisticated methods.

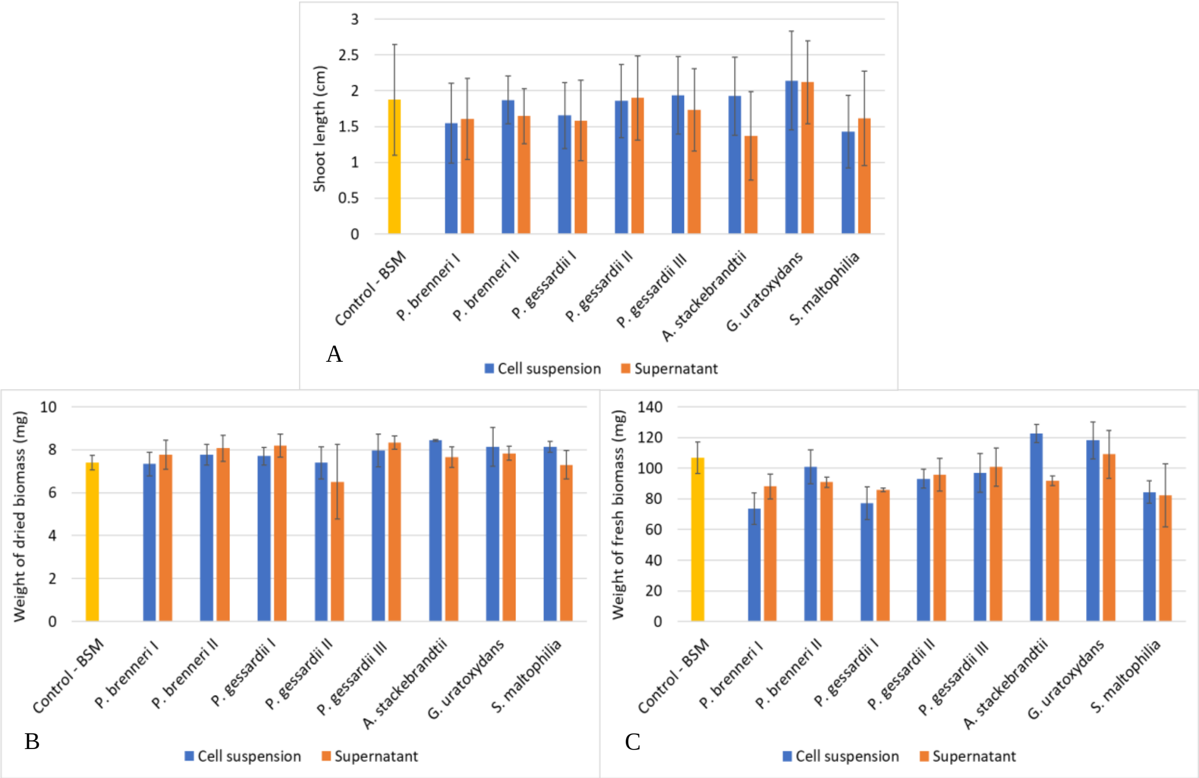

Figure 1: Phytotoxicity testing of a cell suspension (OD = 0.1) and a supernatant representing aparticular isolate against sensitive lettuce seeds: A – shoot length, B – dried plant biomass weight and C – fresh plant biomass weight

Screening testing of the enzyme profile of isolates

The resulting enzyme profiles of the studied isolates detected by using diagnostic solid agar and by the semi-quantitative diagnostic kit API ZYM® are included in the summary Table II. All isolates produced esterase, phosphatase (acid and alkaline), urease, trypsin or naphthol-phosphohydrolase. *S. maltophilia* was the only isolate found to produce chitinases using diagnostic solid agar containing colloidal chitin. N-acetyl-β-glucosaminidase activity was detected in *P. brenneri* II, *P. gessardii* III and *A. stackebrandtii*. The enzyme profile of *A. stackebrandtii* was the most diverse.

Table I.

The enzyme profiles obtained from the evaluation of the diagnostic solid agar and the API ZYM® diagnostic stripe

	***P. brenneri* I**	***P. brenneri* II**	***P. gessardii* I**	***P. gessardii* II**	***P. gessardii* III**	***A. stackebrandtii***	***G. uratoxydans***	***S. maltophilia***
	Diagnostic solid agar							
Lipase I (Tween 80)	+	+	+	+	+	+	+	+
Lipase II (Tween 20)	+	+	+	+	+	–	+	+
Protease (Casein)	+	+	+	+	+	+	+	+
Chitinase (Col. chitin)	–	–	–	–	–	–	–	+
Urease (Urea)	+	+	+	+	+	+	+	+
	Diagnostic stripe API ZYM®							
Alkaline phosphatase	++	++	++	++	++	++	++	++
Esterase (C 4)	+	+	+	+	+	+	+	++
Lipase esterase (C 8)	+	+	+	+	+	+	+	+
Lipase (C 14)	–	+	–	–	+	+	+	–
Leucinarylamidase	+	+	+	+	+	++	++	+
Valinarylamidase	+	+	+	+	+	+	+	+
Cystinarylamidase	–	–	–	–	–	–	–	–
Trypsine	+	+	+	+	+	++	+	+
apha-chymotrypsine	–	–	–	–	–	–	–	–
Acid phosphatase	++	++	++	++	++	++	++	++
Naphtol-AS-BI-phosphohydrolase	++	++	++	++	++	++	++	++
alpha-galactosidase	–	–	–	–	–	+	–	–
beta-galactosidase	–	+	–	–	+	++	–	–
beta-glucuronidase	–	–	–	–	–	–	–	–
alpha-glucosidase	+	+	–	–	+	++	+	–
beta-glucosidase	+	+	–	–	+	++	+	+
N-acethyl-beta-glucosaminidase	–	+	–	–	+	+	+	–
alpha-mannosidase	–	–	–	–	–	++	+	–
alpha-fucosidase	–	+	–	–	+	++	–	–

Note: "–" = no production, "+" = low production, "++" = high production

Chitinase activity measurement

The kinetics of chitinase production, expressed as the increase in chitinase activity over 24 h of culture in a microtiter plate, are shown in Figure 2. During 24 h, the highest increase in chitinase activity was observed for *P. gessardii* II (fluorometric assay).

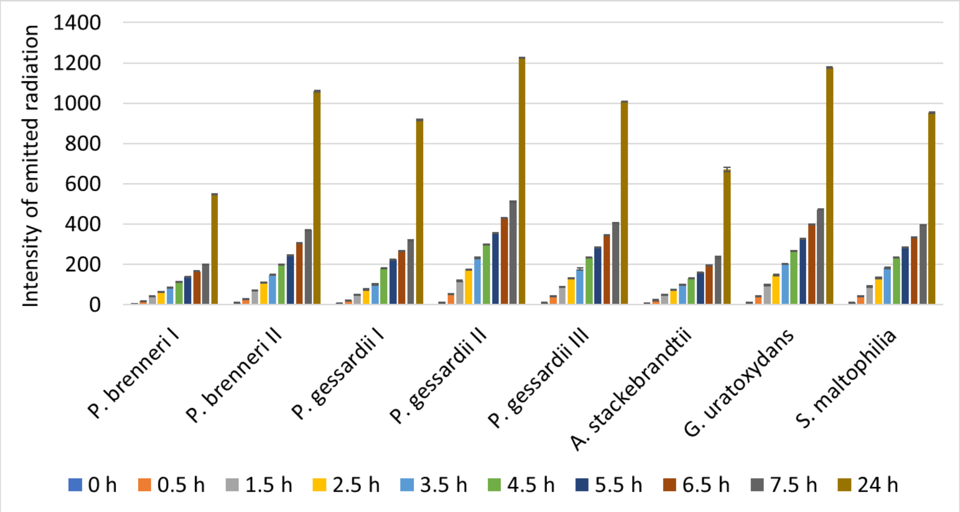

Figure 2: Kinetics of chitinases production within 24 h

Comparison of measured values of chitinase activities after 3.5 hours of culture in microtiter plate in case of supernatants and cell suspensions. The highest values were measured in the case of *P. gessardii* II – cell suspension = 0.44 ± 0.01 µmol/l/h and supernatant = 0.36 ± 0.02 µmol/l/h. In the cases of *P. gessardii* I, *P. gessardii* II and *S. maltophillia*, the majority of chitinases belonged to the group of extracellular free enzymes.

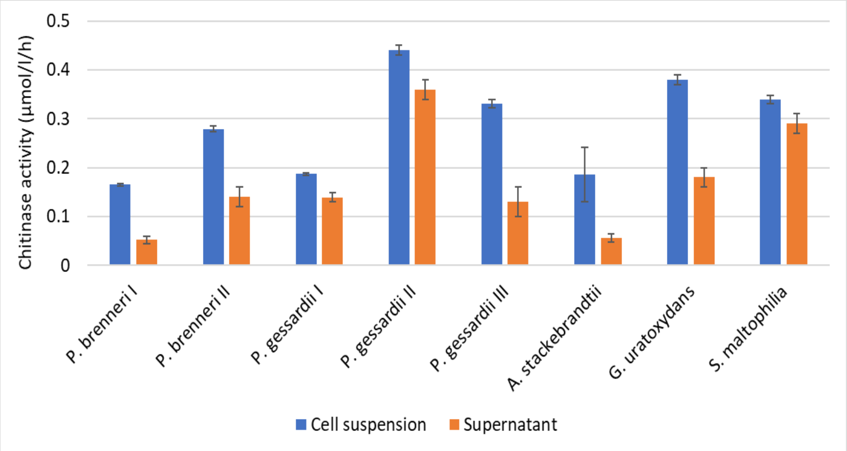

Figure 3: Values of chitinase activities in culture medium samples – cell suspension and its supernatant – at a specific time (3.5 h)

Conclusion

The resulted data, obtained in this study, will help with the selection of isolates for their potential to be a suitable basis for a biopreparation with biopesticide and/or biostimulant effect. All key results are summarised in the following sections:

- Successful isolation of eight isolates with high chitinase activity
    - *Pseudomonas brenneri* (2x), *Pseudomonas gessardii* (3x), *Arthrobacter stackebrandtii*, *Glutamicibacter uratoxydans* and *Stenotrophomonas maltophilia*
- Glucose was the most suitable carbon source for all isolates.
- No phytotoxic effect of the isolates against the model plant was observed.
- *Arthrobacter stackebrandtii* had the most diverse enzyme profile.

- *Pseudomonas gessardii* II shown the highest chitinase activity (fluorometric assay).
    - Chitinase activity after 3.5 h – cell suspension = 0.44 ± 0.01 µmol/l/h and supernatant = 0.36 ± 0.02 µmol/l/h
- Determined chitinase activity depends a lot on used method – testing on real plant pests will be necessary.

References

1. Cuffaro N.: World Dev. *25*, 7 (1997).
2. Hartemink A. E.: Adv. Agron. *89*, 5 (2006).
3. Singh G., Bhalla A., Bhatti J., Chandel S., Rajput A., Abdullah A., Andrabi S. and Kaur P.: Research & Reviews: J. Microbiol. Biotechnol. *3*, 10 (2013).
4. Copping L. G. and Menn J. J.: Pest Manag. Sci. *56*, 8 (2000).
5. Chen G., Zhu H. and Zhang Y.: Res. Microbiol. *154*, 6 (2003).
6. Ahmed E. and Holmström S. J. M.: Microb. Biotechnol. *7*, 3 (2014); Veliz E. A., Martínez-Hidalgo P. and Hirsch A. M.: AIMS Microbiol. *3*, 3 (2017).
7. Chandler D., Bailey A. S., Tatchell G. M., Davidson G., Greaves J. and Grant W. P.: Philos. Trans. R. Soc. Lond., B, Biol. Sci. *366*, 1573 (2011).
8. Pisarčik M., Hakl J. and Hrevušová Z.: Crop Prot. *127*, 11 (2020).
9. Gary R. L. and James T. H.: Aquat. Microb. Ecol. *42*, 3 (2006); A S., Divatar M., Gajare S., Ahmed S. and Lingappa K.: J. Adv. Sci. Res. *7*, 2 (2016).
10. Di Salvatore M., Carafa A. M. and Carratù G.: Chemosphere *73*, 9 (2008).
11. Goswami G., Bora S. S., Parveen A., Chandra Boro R. and Barooah M.: J. Ethn. Foods *4*, 3 (2017).
12. Marx M. C., Wood M. and Jarvis S. C.: Soil Biol. Biochem. *33*, 12 (2001).

CIRCULATING ECONOMY

ZINC ASH WASTE TRANSFORMATION TO FERTILIZERS – SUITABLE FORM FOR PLANTS

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Abstract

Zinc is well-known microelement, in a short time essentially needed in fertilizers and food. Zinc is necessary for the human immune system – it works as an activator and stabilizer of many enzymes. Zinc plays the role in biosynthesis of chlorophyl and protein stabilization. Plants take up zinc as Zn^{2+} ions. Zinc is mainly needed by corn, cereal crops, winter rapeseed, hops, poppy, grapevine…

Waste from car bodyshells is processed by remelting of such parts in Slovakia. This process produces waste zinc ash. As a part of the task, we solved the possibility of processing this waste into a form suitable for plants. The composition of waste was analyzed during 2 years from individual campaigns. Individual types of raw materials entering the process were analyzed for a presence of lead. As a part of laboratory research, zinc ash was processed into a form suitable for plants. This product was then added into the fertilizer and the effect on fertilizer properties was monitored. The production was tested in a small scale quarter-operational production before the operational trial itself. 3.3 ton of zinc ash were processed into nitrate form. It was necessary to develop an analytical method to determine the end of the zinc nitrate formation reaction. 1,000 ton of such fertilizer was produced at the plant. The impact of zinc introduction into the fertilizer on the production processes at the plant was evaluated. Problems that will need to be solved were identified. The effect of zinc on the produced fertilizer was monitored and this fertilizer was compared with fertilizer without zinc. Part of the fertilizer was stored in the big bags. In order to determine the effect of time on the fertilizer, 2 big bags are taken out and checked at regular intervals.

Introduction

Zinc is one of the important micronutrients for plants. Zinc is an activator and stabilizer of many enzymes and in many cases has similar function as the Mg a Cu, which it can also replace. It also affects the creation of biologically active substances such as the synthesis of tryptophan. In the case of Zn deficiency, the synthesis of RNA, proteins and starch decreases and the formation of chlorophyl is impaired. In the Central Europe there are many zinc deficient soils. Plants receive zinc in the form of Zn^{2+}. Zinc has the beneficial impact on the immune system of the human body. Its decreased content in the soil results in a lower content in plants and thus also decreased intake by the human body, and therefore it is necessary to supplement it by the nutritional supplements. Zinc is mainly needed by: corn, cereal crops, winter rapeseed, hops, poppy, grapevine...

Waste from car bodyshells is processed by remelting of such parts in Slovakia. During processing of this waste, 150 tons per year of zinc ash are currently produced. The plan for the future is to process double amount of car bodyshells waste, which would produce 300 tons of zinc ash waste per year. Currently, 150 tons of zinc ash would be enough to produce of 55,000 tons of fertilizer with a zinc content of 0.2 wt.%, which is by agronomic the effective recommended dose content in fertilizers. We had been monitoring the composition of zinc ash over the course of 2 years. We received the samples of zinc ash from individual campaigns regularly and we traced the composition in individual bodyshells types. Based on this, we specified the dose of zinc ash should be added to the fertilizer and an influence of zinc content inhomogeneity on the final content in the fertilizer. The content of Cd, Pb, Hg, As and Cr was monitored to see if, after being incorporated to the fertilizer, they would not exceed the legally permitted levels for the content of heavy metals according to Regulation of the European Parliament and the Council No. 2019/1009. In the case of carbon content, the limits for saltpeter fertilizers are set in terms of explosiveness, and the presence of F and Cl in large quantities can affect the technology (especially by corrosion). All these elements are within the limits with a sufficient margin to start thinking about the use of these raw materials in fertilizers.

Table I.
Minimal and maximal content of selected elements in zinc ash monitored over 2 years

Zinc	Zn	C	Cd	Pb	Hg	As	Cr	F	Cl
ash	wt. %		ppm						
min	74.5								
max	79.5	1.61	5	4000	2	2	10	1000	600

Laboratory research

Zinc in zinc ash is found in the form of ZnO, which is not the most suitable form for plants. A more suitable form is sulfate or zinc nitrate, which are water soluble. The project continued with laboratory research on the transformation of ZnO into these forms. Decomposition of zinc ash by using nitric or sulphure acid:

$ZnO + 2\,HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$ (1)

$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$ (2)

A problem with the presence of free ammonia, which is used in the production of fertilizers and causes the formation of a non-soluble zinc form:

$3\,Zn(NO_3)_2 + 4\,NH_3 + 4\,H_2O \rightarrow \mathbf{Zn_3(OH)_4(NO_3)_2} + 4\,NH_4NO_3$ (3)

$4\,ZnSO_4 + 6\,NH_3 + 6\,H_2O \rightarrow \mathbf{Zn_4SO_4(OH)_6} + 3\,(NH_4)_2SO_4$ (4)

Laboratory research was oriented to determining the conditions for maximum conversion and, in the case of the nitrate form, also minimizing the formation of NOx. Under the right conditions, 97–99% conversion was reached without the free acid, or almost 100% conversion with a certain excess of acid. The next step was the incorporation of these forms into fertilizers with minimal formation of non-soluble form. After the decomposition of the zinc ash by sulfuric/nitric acid, a suspension, which was added to the slurries of individual fertilizers, was formed. We prepared the fertilizers ASN+Zn (N-total = 26%; S-total = 13% and Zn-water = 0.2%) and CAN+Zn (N-total = 27%; CaO-total = 6.5%; MgO-total = 4.1% and Zn-water = 0.2%) on a twin-screw granulator (Figure 1). The fertilizers prepared from zinc sulphate suspension had slightly better physicochemical properties, but due to lower corrosion when using nitric acid, we chose zinc nitrate suspension for further using.

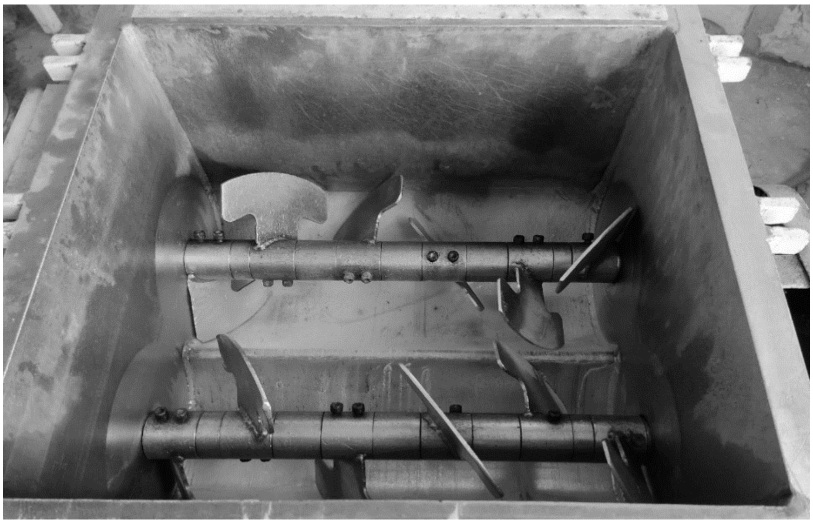


Figure 1. Twin-screw granulator

We measure the size of the particles, bulk properties of zinc ash and compared the bulk properties with ground dolomite (Table II). Dolomite is commonly used raw material in this field, and it is easier for technologist to imagine what individual data mean for the point of view of storage and transport. The particle size of zinc ash is up to 50 µm without ultrasound (Figure 3) and up to 10 µm with ultrasound (Figure 2), which means that the raw material is fine – it will become dusty during the transport and storage, but it is also very reactive. In the case of zinc ash, the initial bulk density and tapped density are about 3 times lower than those of dolomite, which means that this raw material takes up 3 times more space in the warehouse, one truck takes away one third of an amount, an since it has such low values of size and is extremely fine, it will be very dusty. Angle of repose is an important data during storage, means which type of hill the raw material will create (zinc ash will slide and the hill will be lower, that means, also in the warehouse it will takes up more of space in width in comparison with dolomite). Dumping angle and angle of slide are important when unloading trucks, but most important is the fact that the siding must be raised 6° higher than with dolomite. Arching is an important parameter when transporting raw materials through various overflows, bends... from this point of view, zinc ash and dolomite behave similarly.

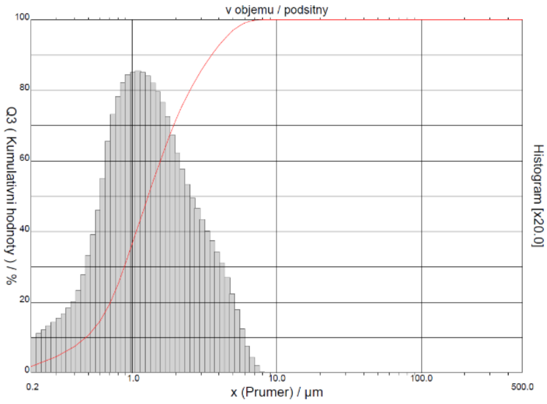


Figure 2. Zinc ash May 2022 measurement with ultrasound

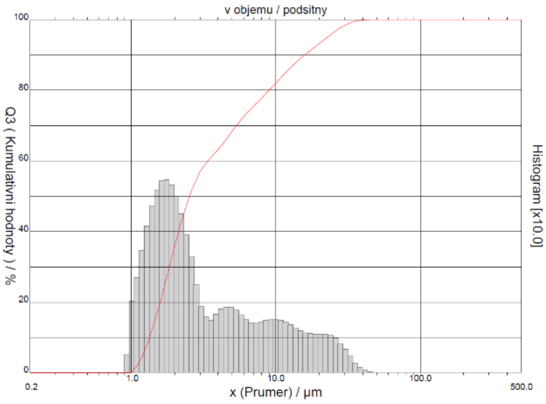


Figure 3. Zinc ash May 2022 measurement without ultrasound

Table II.
Bulk properties dolomite and zinc ash

Parameter	Unit	Dolomite	Zinc ash
Initial bulk density	kg/m^3	1173	360
Tapped density	kg/m^3	1435	430
Angel of repose	°	41.9	33.7
Dumping angle	°	54.8	60.6
Angel of slide	°	37.7	44.7
Arching		1-7	1-7

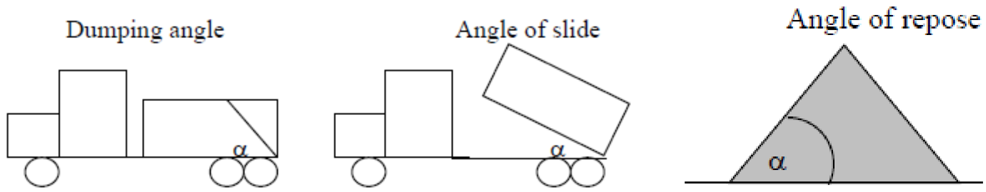


Figure 4. Dumping angle, angle of side and angle of repose

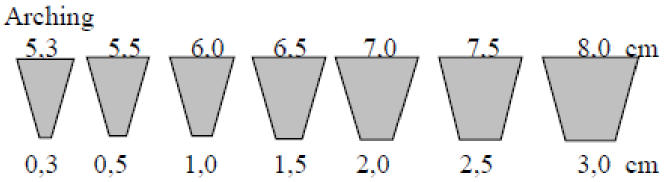


Figure 5. Arching

Operational trial

After the end of the laboratory research, we moved on to the preparation of the operational trial. In the first step, a batch suspension of zinc nitrate was prepared in a 5 m^3 reactor. It was done twice. In the first case, the suspension was prepared so that all nitric acid reacts (excess of zinc ash) and in the second case, on the contrary, so that a minimum of unreacted nitric acid remains. For determination of the content of nitric acid in this complex suspension, we developed a methodology by potentiometric titration with sodium acetate. The differences between suspensions have been prepared are mainly in the contents of undissolved ZnO, pH and free acid content. Compared to the laboratory research, we gained a lower conversion achieved in much longer time (the laboratory reaction takes minutes, the reaction in the reactor takes an hours). In comparison of these processes, we found that this was probably caused by the significantly lower mixing intensity of the large reactor and by different shape of the stirrers. We then measured physical properties in the samples (unfiltered/filtered) on the reason of storability and transport. Filtration was considered in case a solution of zinc nitrate was used instead of suspension. The viscosity of these solutions was around 10 mPa.s at standard pumps performance, which is very good indicator, and at low shear rates up to 100 mPa.s, which is important for example in the case of pump failure, or in the case of start mixing of the suspension in the tank. Density and crystallization temperate were measured. Regarding the crystallization temperature, it was found that if the suspension contains the small amount of free acid, the crystallization temperature is about 8 °C lower which is important during storage.

Table III.
The amount of produced suspension, the content of zinc nitrate, manganese nitrate, insoluble components, pH and content of free nitric acid

	$Zn(NO_3)_2$ – June 2022	$Zn(NO_3)_2$ – July 2022
Mass (kg)	6250	7000
Zn-total (wt. %)	19.91	18.7
Zn-water (wt. %)	18.53	18.2
$Zn(NO_3)_2$ (wt. %)	53.67	52.72
$Mg(NO_3)_2$ (wt. %)	0.96	1.09
Insoluble residue in water (wt. %)	2.42	2.75
Water (wt. %)	42.95	43.44
Free nitric acid (wt. %)	0	0.04
pH	2.6	0.3

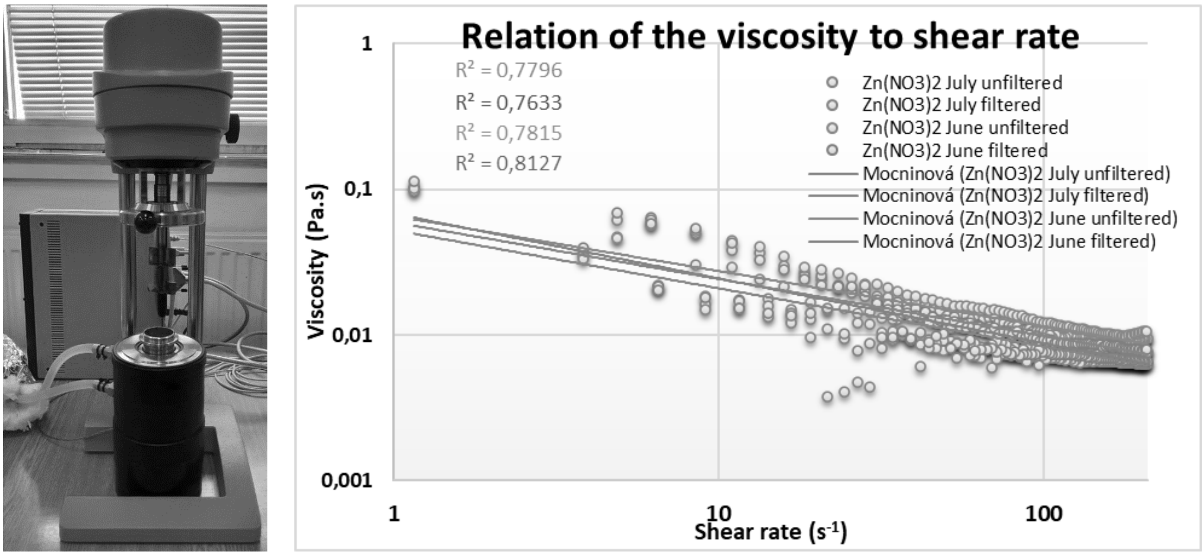


Figure 6. Used viscosimeter and measured viscosities

Table IV.
Density and crystallization temperature of prepared suspension and suspension filtrates

	$Zn(NO_3)_2$- unfiltered June	$Zn(NO_3)_2$ – filtered June	$Zn(NO_3)_2$ – unfiltered July	$Zn(NO_3)_2$ – filtered July
Density (kg/m^3)	1648	1620	1640	1614
Crystallization temperature (°C)	8	6	*	-2

*It cannot be clearly measured

The prepared suspensions were used for an operational trial with the aim to produce 1000 tons of ASN fertilizer with 0.2 wt.% Zn by the universal granulation line. A tank of 10 m3 was filled with suspensions. The fertilizer ASN without zinc was produced on one day and fertilizer ASN with zinc on the next day. After the end of the operational trial, the process was evaluated and the occurred problems during the production of the new product with need to solve summarized:

- Since this was the first such production, it will be necessary to solve the quality control (chemical analysis). Here the problem occurred with the poorly chosen calibration curve for this new product and the results obtained at the time of production differed from the real ones (determined by repeated measurement).

- The addition of zinc suspension disturbs the water balance in the fertilizer and thus the recycling ratio must be changed in favor of recycling, which resulted in a reduction of production by approx. 3 wt.% and simultaneously increases the granulometry, which had to be corrected by changing of operating parameters. It is necessary to repeat the experiment, where the parameters will be adjusted correctly so that the granulometry will be identical with the fertilizer without zinc (a longer operational time is needed) and the reduced production will probably remain.

The fertilizer without and with zinc was compared and the effect of zinc addition was evaluated:

- Zinc had no effect on dust formation and mechanical resistance of fertilizer (Table V.).
- There is an indication that the granule hardness of ASN with zinc fertilizer increases with the time => the fertilizer matures (Table VI.). (the higher value the better)
- Zinc free ASN fertilizer has a lower caking tendency, even with increasing time it increases. In the case of zinc fertilizer, it can be seen that caking tendency is higher, but decreases with the time => the fertilizers mature (Table VI.). (lower value is better)
- Zinc nitrate reacts in fertilizer to $(NH_4)_2Zn(SO_4)_2.6H_2O$ (Figure 8)

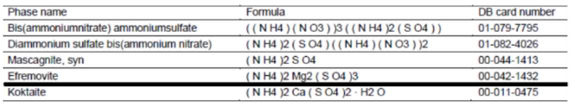
$2\ (NH_4)_2SO_4 + Zn(NO_3)_2 + 6\ H_2O \rightarrow (NH_4)_2Zn(SO_4)_2.6H_2O + 2\ NH_4NO_3$ (5)

Table V.
Dust formation and mechanical resistance of ASN fertilizer without/with zinc

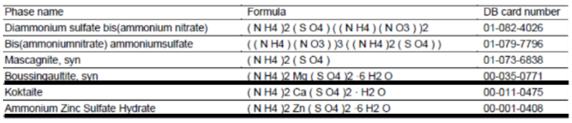
	Dust formation (wt. %)			Mechanical resistance (wt. %)		
	Within 24 hours	Next week	Next month	Within 24 hours	Next week	Next month
ASN 7:00 10.11.	0.01	0.03	0.02	0.13	0.02	0.03
ASN 11:00 10.11.	0.01	0.02	0.02	0.02	0.03	0.04
ASN 6:00 11.11.	0.01	0.01	0.02	0.04	0.02	0.03
ASN 8:00 11.11.	0.01	0.02	0.02	0.03	0.03	0.05
Average	**0.01**	**0.02**	**0.02**	**0.06**	**0.03**	**0.04**
ASN+Zn 12:00 11.11.	0.01	0.03	0.03	0.01	0.03	0.04
ASN+Zn 14:00 11.11.	0.01	0.02	0.03	0.05	0.02	0.03
ASN+Zn 16:00 11.11.	0.02	0.03	0.03	0	0.02	0.02
ASN+Zn 20:00 11.11.	0.02	0.02	0.02	0.01	0.03	0.04
ASN+Zn 0:00 12.11.	0.01	0.02	0.03	0.02	0.01	0.02
ASN+Zn 4:00 12.11.	0.02	0.02	0.02	0.03	0.01	0.02
Average	**0.01**	**0.02**	**0.03**	**0.02**	**0.02**	**0.03**

Table VI.
Granule hardness and caking tendency of ASN fertilizer without/with zinc

	Granule hardness (N)			Caking tendency (N)		
	Within 24 hours	Next week	Next month	Within 24 hours	Next week	Next month
ASN 7:00 10.11.	96.3	92	122	51.4	68.1	83.2
ASN 11:00 10.11.	128.3	132.7	101.3	48.9	73.6	76.6
ASN 6:00 11.11.	120.1	122.5	99.5	30.6	34.1	45
ASN 8:00 11.11.	110.4	113.6	103.8	43.4	48.3	56.7
Average	**113.8**	**115.2**	**106.7**	**43.6**	**56**	**65.4**
ASN+Zn 12:00 11.11.	111.5	108.4	92.8	81.9	74.1	69.1
ASN+Zn 14:00 11.11.	116.8	110.1	126.4	54.8	90.6	64.5
ASN+Zn 16:00 11.11.	116.4	123	138.9	76.9	74	62.9
ASN+Zn 20:00 11.11.	109.1	118.7	119.6	78.9	93.1	73.2
ASN+Zn 0:00 12.11.	108.7	110.3	116.5	98.1	92	74.8
ASN+Zn 4:00 12.11.	97.4	105.3	110.8	90.3	101.1	69.2
Average	**110**	**112.6**	**117.5**	**80.2**	**87.5**	**69**



Phase name	Formula	DB card number
Bis(ammoniumnitrate) ammoniumsulfate	$((NH_4)(NO_3))_3((NH_4)_2(SO_4))$	01-079-7795
Diammonium sulfate bis(ammonium nitrate)	$(NH_4)_2(SO_4)((NH_4)(NO_3))_2$	01-082-4026
Mascagnite, syn	$(NH_4)_2SO_4$	00-044-1413
Efremovite	$(NH_4)_2Mg_2(SO_4)_3$	00-042-1432
Koktaite	$(NH_4)_2Ca(SO_4)_2 \cdot H_2O$	00-011-0475



Phase name	Formula	DB card number
Diammonium sulfate bis(ammonium nitrate)	$(NH_4)_2(SO_4)((NH_4)(NO_3))_2$	01-082-4026
Bis(ammoniumnitrate) ammoniumsulfate	$((NH_4)(NO_3))_3((NH_4)_2(SO_4))$	01-079-7796
Mascagnite, syn	$(NH_4)_2(SO_4)$	01-073-6838
Boussingaultite, syn	$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	00-035-0771
Koktaite	$(NH_4)_2Ca(SO_4)_2 \cdot H_2O$	00-011-0475
Ammonium Zinc Sulfate Hydrate	$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$	00-001-0408

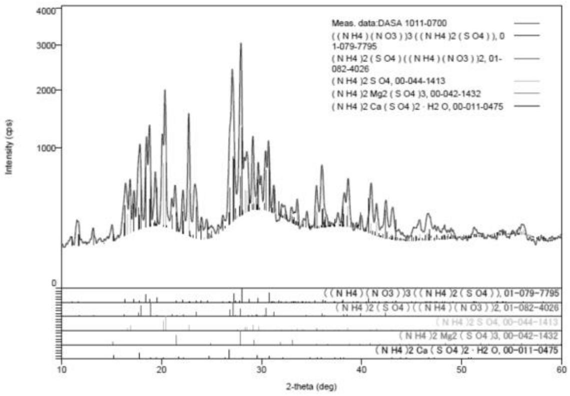


Figure 7. XRD ASN

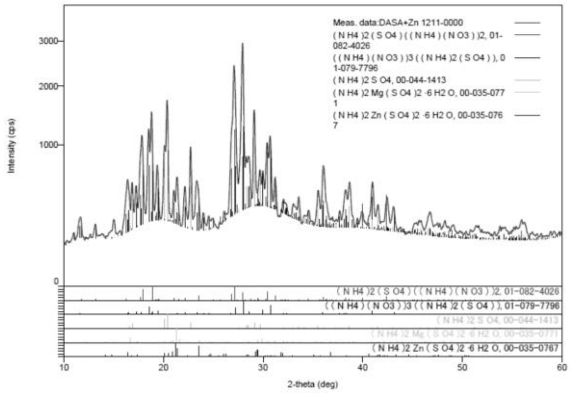


Figure 8. XRD ASN + Zn

Conclusions

- It was possible to specify successfully the conditions for the preparation of zinc nitrate/sulphate with maximum conversion and, in the case of nitrate, also minimize the formation of NO_x by laboratory way.
- Bigger amount of suspension for operational trial was prepared and the importance of stirring intensity and suitable option of stirrer has been established.
- The properties necessary for the introduction of this process into real production were measured.
- The ASN fertilizer with zinc was successfully granulated by universal granulation line and the problems with need to be solved before permanent introduction of this product were identified.
- The impact of zinc on product quality was identified.

A process to treat the waste generated by the recycling of bodyshells waste in the automotive industry has been developed.

Continuation of this project

- Production of the intermediate product $Zn(NO_3)_2$ by decomposition of ZnO with nitric acid in the continuous process
- Granulation 8,000 tons ASN + Zn in universal granulation line with the goal to solve all the problems brought by the addition of zinc nitrate to suspension to the process.
- Stock tests after 3 and 6 months

Nomenclature

ASN – ammonium sulphate with ammonium nitrate,
CAN – ammonium nitrate with calcium carbonate

Acknowledgment

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ISOLATION AND IDENTIFICATION OF BACTERIA UTILIZING MICROBIALLY INDUCED CALCITE PRECIPITATION (MICP) FOR THE RECYCLING WASTE CONCRETE FINES

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Abstract

During concrete production, large quantities of carbon are released into the environment. A promising route to a more sustainable construction industry involves the use of microbially induced calcite precipitation (MICP) in concrete recycling. Here, we investigated utilizing the ureolytic activity of the alkaliphilic bacterium *Sporosarcina pasteurii* DSM 33 and other strains isolated from the sand as potential candidates for MICP. Powder samples of old waste concrete fines (WCF) were mixed with urea–$CaCl_2$ solution, in which ureolytic bacteria can precipitate $CaCO_3$ crystals and support their formation in WCF. Scanning electron microscopy was used to characterize the crystals according to their properties. Thus, our results suggest that MICP-prepared WCF composites could be an effective way of recycling old concrete, thereby reducing the industry's carbon footprint.

Introduction

The continuous increase in global temperatures has led to a surge in the frequency and intensity of extreme weather phenomena such as floods, hurricanes, wildfires, and heat waves. Carbon dioxide (CO_2) overproduction contributes significantly to this – global warming, leading to various climate and societal impacts. In response to these challenges, the Paris Climate Agreement was established in 2015, requiring countries to reduce especially CO_2 emissions and achieve carbon neutrality by 2060–2080.

Nowadays, the reduction of carbon footprint is primarily accomplished through the implementation of the circular economy concept. This approach revolves around the recycling and valorization of waste materials, such as those generated in the food industry (Stiborova et al., 2020) or the construction industry (Nežerka et al., 2023a), in order to recover their value.

The construction sector is a major contributor to greenhouse gas emissions, primarily through cement production. Concrete, widely used construction materials composed of cement, aggregate, and water, poses challenges in terms of waste generation and high energy demands. Recycling waste concrete, particularly waste concrete fines (WCF), is essential for achieving a circular economy. Current recycling methods involve crushing the concrete and using recycled aggregates in various applications. However, WCF, which accounts for a significant volume of crushed concrete, faces challenges in storage and handling (Nežerka et al., 2023b). Microbially induced calcite precipitation (MICP) offers a potential solution for the reuse of WCF. The biomineralization process utilizes microorganisms to precipitate minerals, including calcium carbonate. Through the application of MICP with ureolytic bacteria, effective binding of WCF particles can be achieved, resulting in crack healing and improved durability.

In this study, we employed an enrichment method to isolate unknown microbial isolates from sand which were subsequently identified. All isolates were found to be ureolytically active and involved in the precipitation of calcium carbonate crystals by utilizing urea and calcium ions. By comparing the isolate with the highest urease activity to the highly ureolytic *Sporosarcina pasteurii* DSM33, we investigated the bio cementation and binding capabilities of WCF particles. Three different types of WCFs were chosen to test their abilities in MICP. The obtained results effectively demonstrated the potential of ureolytic bacteria in promoting sustainable concrete recycling through MICP and the utilization of WCF.

Methods and materials

Isolation bacteria with ureolytic activity

The isolation of bacteria with ureolytic activity involved this protocol: 32 g of the sand specimen and 7 g of WCF (gutter) were initially treated with a solution comprising 10 ml of saline and 10 ml of biocementation (MICP) solution, followed by incubation at 28 °C for 48 hours. Next, 10 ml of MICP solution was added to the samples every 48 hours, maintaining the same incubation conditions. This process was repeated five times, resulting in five bio cementation solution additions. After the incubation, two samples were collected — a sample of mineralised material and a sample of leachate (the solution that passed through the sand). Each sample was inoculated onto a Tryptic Soy Agar (TSA) supplemented with urea (final concentration of 20 g l^{-1}) and incubated at 28 °C for 72 hours. Visually different bacterial cultures were separated by streaking them onto separate TSA supplemented with urea. As a result, nine bacterial strains were obtained and named: U1, U2, U3, U4a, U4b, U5, U6, U7, U8 (Ux = Ureolytic + name of an isolate).

Measuremen of urease activity

The evaluation of urease activity involved both qualitative and quantitative analyses.

The qualitative analysis of urease activity was performed by mixing 1 ml of the bacterial suspension (OD_{600} = 5) with 4 ml of the bio cementation solution and incubating at 28 °C for 48 hours. The crystal formation was assessed visually.

In the case of quantitative analysis, the determination of urease activity involved the utilization of the phenol-hypochlorite assay. The absorbance of the samples was measured at a wavelength of 620 nm. The urease assay was conducted in the following way: the bacteria were inoculated into large vessels containing Tryptone Soya Broth (TSB) supplemented with urea (final concentration of 20 g l^{-1}) and incubated at 28 °C for 72 hours. Within this period, urease activity was measured. The urease activity was calculated using the standard curve obtained by measuring the optical density (OD) of ammonium chloride at different concentrations at 620 nm.

DNA isolation and identification of isolated bacteria

DNA isolation was performed with the InstaGene Matrix kit (Bio-rad Laboratories, Inc., USA). The resulting liquid supernatant containing the extracted DNA was stored at a temperature of -20 °C.

The identification of the isolates was based on the sequence of the marker gene (16S rRNA) and two-steps PCR. The final samples were concentrated using the Genomic DNA Clean & Concentrator kit (Zymo Research, USA). The concentration of the DNA was measured using the Nanodrop One (Thermoscientific, USA). As the concentration of the DNA after the first PCR was too low (the required quantity was 10–40 ng µl^{-1}), the second PCR was conducted. Subsequently, the accuracy of both the DNA isolation and PCR reaction was confirmed through electrophoresis. The resulting genetic material was sent to SeqMe s.r.o. for Sangers sequencing.

Preparation of the WCF samples and biomineralization process

The WCF samples, obtained as a powder from various concrete facilities, were used in the study. The initial WCF suspension was prepared the following way: 7 g of WCF was combined with 10 ml of saline and 10 ml of bacterial suspension (OD_{600} = 5). The pH value of the WCF suspension was adjusted to a final value of 6.8 ± 0.2. The final WCF composites involved a specialized apparatus illustrated in Figure 1. This apparatus consisted of a plastic cup with a hole at the bottom covered with filter paper. Two pipette tips provided air access to a second cup, which was placed under the filter; the same function had a hole in the lid. The WCF suspension was added to this prepared plastic cup, allowing the bio cementation solution (containing Nutrient Broth of 3.2 g l^{-1}, urea at 20 g l^{-1} and $CaCl_2$ at 2.8 g l^{-1}) to be filtered through the WCF mixture, resulting in $CaCO_3$ precipitation. All WCF samples were incubated at 28 °C during the whole experiment. The bio cementation solution was added every 48–72 hours for a total of 28 days. Subsequently, the WCF samples were dried for 28 days at 28 °C.

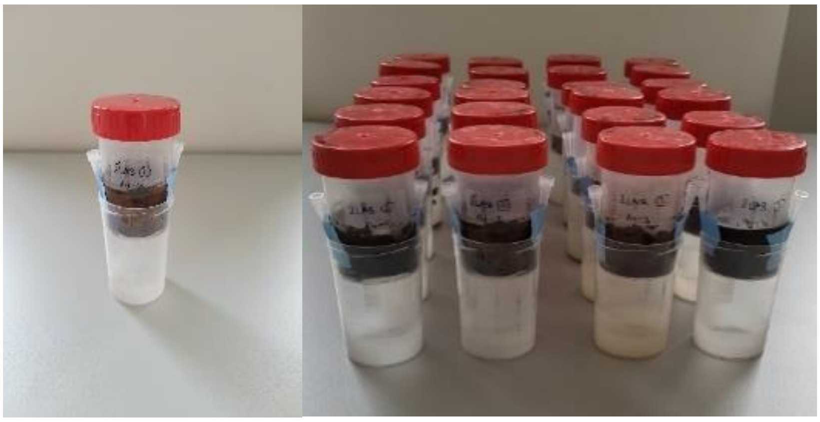

Figure 1. The filter apparatus (with WCF samples)

Results and discussion

A total of nine bacterial strains were isolated using the enrichment method with urea-containing medium. The strains were named, U1, U2, U3, U4a, U4b, U5, U6, U7, U8 (Ux = Ureolytic + name of an isolate).

After the qualitative urease activity test, an additional bacterial strain was isolated, so isolate U3 was divided into U3a and U3b. Each isolate had the specific smell of ammoniac, confirming the existence of an ureolysis process. Bacteria with ureolytic activity are commonly found in various environments. For example, in the study of Bibi et al. (2018), ureolytic bacterial strains were isolated from soil, which was collected in different locations around Doha City, Qatar. The growth of ureolytic bacteria in these samples was initially stimulated using the enrichment solution containing urea. Ureolytic strains were determined with the indicator culture medium and then isolated. In total, more than half of the isolated strains had ureolytic activity.

Additionally, our study also confirms the presence of bacteria with urease activity in building materials. The identification of the isolates is shown in Table I.

Table I.
Identification of bacterial isolates (U1–U8) with urease activity

Sample	Identification	Percent identity [%]
U1	*Sporosarcina* sp.	99.0
U2	*Sporosarcina jiandibanonis* LAM9210	99.2
U3a	*Sporosarcina* sp.	98.3
U3b	*Sporosarcina* sp.	99.0
U4a	*Sporosarcina terrae* LZ2	96.5
U4b	*Bacillus subtilis* IAM12118	99.1
U5	*Siminovitchia acidinfaciens*	99.3
U6	*Sporosarcina terrae* LZ2	98.5
U7	*Sporosarcina newyorkensis*	98.7
U8	*Sporosarcina* sp.	98.2
-	*Sporosarcina pasteurii* DSM33	99.9

Measurement of urease activity

To validate the potential of the isolated strains of capability of the MICP process, the qualitative test for urease activity was performed. Following the incubation of the reaction mixture, all samples contained calcite (visibly and clearly detected), the qualitative test confirmed the positive urease for each isolate. The visual results of the qualitative test can be observed in Figure 2.

Figure 2. Results of qualitative test of urease activity

Following the evaluation of the MICP capabilities of the isolated strains, a quantitative urease activity test was conducted at a specific time point. The cultivation time chosen for the experiment was 72 hours, allowing the isolates to complete the exponential phase and enter their stationary phase. The phenol-hypochlorite method of measuring urease activity was taken from the research conducted by Kim and Youn (2016). The results revealed that *Sporosarcina pasteurii* DSM 33 exhibited the highest urease activity (0.62 µkat), followed by *Sporosarcina terrae* U6 (0.35 µkat) and *Sporosarcina jiandibaonis* U2 (0.22 µkat). For these strains, the urease activity was further evaluated at different time intervals.

Table II. presents the data, indicating that after 48 hours, *Sporosarcina jiandibaonis* U2 had the highest enzymatic activity (0.219 µkat), followed by *Sporosarcina terrae* U6 after 53 hours (0.199 µkat), and

Sporosarcina pasteurii DSM33 after 30 hours (0.270 µkat). In previous studies on urease activity, *S. pasteurii* also note that the cultivation time beyond 24 hours is optimal for higher enzymatic activity (Achal et al. 2009, Omoregie et al. 2017, Zhao et al. 2019). Following the urease activity test, the isolate exhibiting the highest urease activity (*S. jiandibaonis* U2) was selected for a comparative analysis of its calcium carbonate precipitation ability with the MICP of *S. pasteurii* DSM33. According to the results of the previous experiment, a cultivation time of 48 hours at 28 °C was considered optimal for both selected bacterial strains.

Table II.
Bacterial isolates with their urease activity

Sample	Identification	Urease activity [µkat]	Time of the highest activity [h]	Urease activity [µkat]
U1	*Sporosarcina* sp.	0.12	-	-
U2	*Sporosarcina jiandibanonis* LAM9210	0.22	48	0.219
U3a	*Sporosarcina* sp.	0.15	-	-
U3b	*Sporosarcina* sp.	0.15	-	-
U4a	*Sporosarcina terrae* LZ2	0.12	-	-
U4b	*Bacillus subtilis* IAM12118	0.09	-	-
U5	*Siminovitchia acidinfaciens*	0.14	-	-
U6	*Sporosarcina terrae* LZ2	0.35	53	0.199
U7	*Sporosarcina newyorkensis*	0.18	-	-
U8	*Sporosarcina* sp.	0.21	-	-
-	*Sporosarcina pasteurii* DSM33	0.62	30	0.270

Biomineralization of WCF

The experiment with WCF lasted 28 days, which was followed by an additional 28-day period of sample drying at 28 °C. Original WCF samples are presented in Figure 3. Visually, these samples had slightly different colour; the Column WCF had the most crumbly texture, while the Gutter WCF was less crumbly textured and less homogenous, the Highway WCF fell in between the previous samples in regards to all the observed qualities. The impact of the structure of granular media (mostly soils) on the bacterial viability was discussed in a few papers.

Figure 3. Powdery WCF (Gutter, Highway, and Column from left to right).

The effectiveness of MICP greatly influenced by the initial material properties (Nain et al. 2019, Amer Algaifi et al. 2020, Metwally et al. 2020). One potential solution to address this issue is the utilization of an immobilising agent. This agent creates a porous structure that provides the space for bacterial cells and necessary substances.

Figure 4 and 5 illustrate the appearance of the dried samples on the filters at the end of the experiment. At first sight, the WCF samples mineralised by *S. jiandibaonis* U2 and *S. pasteurii* DSM33 appeared similar. The presence of calcite crystals on the sample surface indicates the occurrence of the MICP process. The mineralized samples of Highway WCF and Column WCF looked more like common concrete, while Gutter WCF was very cracked regardless of the strain.

Figure 4. The WCF samples mineralised by *S. jiandibaonis* U2 (Gutter, Highway, and Column from left to right; top row — samples with 2x addition of bacteria; bottom row — only initial addition of bacteria)

Figure 5. The WCF samples mineralised by *S. pasteurii* DSM 33 (Gutter, Highway, and Column from left to right; top row — samples with 2x addition of bacteria; bottom row — only initial addition of bacteria)

The appearance of the resulting mineralised WCF samples can be observed in Figure 6. All the samples except Gutter WCF samples relatively compact. Although the Column samples were solid, they were very brittle as well. The samples of Highway WCF exhibited the highest integrity. And all of the above, we can conclude that the initial texture of the WCF should not be too powdery (Column WCF) or too nonhomogeneous (Gutter WCF).

Figure 6. The mineralised WCF samples (Gutter, Highway, and Column from left to right; top row — samples mineralised by *S. pasteurii* DSM 33; bottom row — mineralised by *S. jiandibaonis* U2)

If we compare the MICP abilities of different bacteria, then the samples mineralised by *S. pasteurii* DSM 33 were visually without cracks than the samples treated by *S. jiandibaonis* U2. The study by Metwally et al. (2020) reveals the benefits of bacterial concrete. Researchers were comparing the compressive strength of common concrete cubes and concrete cubes treated by *S. pasteurii*. The results showed that the compressive strength of the concrete with the addition of bacteria was higher from 11 to 79%, depending on the ratio of water and solid matter (Kadapure et al. 2017, Alonso et al. 2018).

According to SEM photos, in Figure 7 (left) the sterile sample of WCF (Highway) did not contain any significant traces of the MICP process. The small formation of crystals that can be observed in Figure 7 (in the middle) are most likely products of the carbonation of concrete. However, crystals of calcium carbonate are clearly visible in Figure 7 (right), where needle crystals are probably aragonite, while the rest of the crystal formations are calcite.

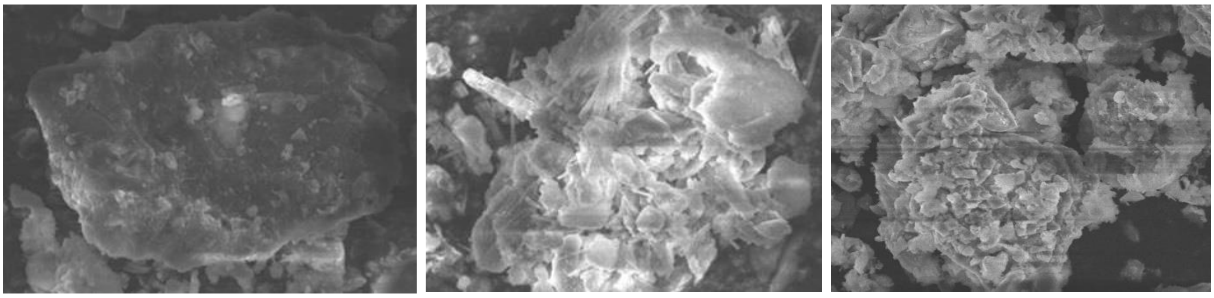

Figure 7. SEM photos of the sterile Highway WCF (left); Crystals formed by *S. jiandibaonis* U2 (in the middle) and by *S. pasteurii* DSM33 (right) (magnification 10 000x)

Conclusion

Ten bacterial strains were isolated using the enrichment method with a medium containing urea. Isolated microorganisms were identified based on the sequence of the marker gene (16S rRNA) using Sanger sequencing. The results of the quantitative urease activity, measured after 72 hours of cultivation, indicated that the highest enzymatic activity was detected in strains *S. jiandibaonis* U2, *S. terrae* U6 and *S. pasteurii* DSM33. The bio cementation of three different WCF types was performed using strains *S. jiandibaonis* U2 and *S. pasteurii* DSM33. The selected cultivation time of bacteria was at 28 °C for 48 hours. Both strains had enough MICP activity to mineralise the WCF samples. However, the WCF samples treated by *S. pasteurii* DSM33 showed higher stability of formed composite samples. The WCF samples with two additions of the bacterial suspension did not show significant differences from the samples with one addition of the bacterial suspension. Among the three types of WCF, the most visually stable samples were made of WCF (Highway), which has an intermediate texture between powdery WCF (Column) and inhomogeneous WCF (Gutter), but mechanical properties will be tested in the next study.

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References

1. Stiborova, H., Kronusova, O., Kastanek, P., Brazdova, L., Lovecka, P., Jiru, M., Belkova, B., Poustka, J., Stranska, M., Hajslova, J. and Demnerova, K.: J. Chem. Technol. Biotechnol., 95, 985 (2020).
2. Nežerka, V., Holeček, P., Somr, M., Tichá, P., Domonkos, M., Stiborová, H.: Rev Environ Sci Biotechnol 22, 427 (2023a).
3. Nežerka, V., Prošek, Z., Trejbal, J., Pešta, J., Ferriz-Papi, A., Tesárek, P.: J. of Cleaner Prod., 385, 135711 (2023b).
4. Bibi, S., M. Oualha, M. Y. Ashfaq, M. T. Suleiman and N. Zouari: RSC Advanc. 8, 5854 (2018).
5. Kim, G., & Youn, H.: Microbial. Materials (Basel), 9, (2016).
6. Achal, V., A. Mukherjee, P. C. Basu and M. S. Reddy: J. of ind. Microb. & Biotech. 36, 981 (2009).
7. Omoregie, A. I., G. Khoshdelnezamiha, N. Senian, D. E. L. Ong and P. M. Nissom: Ecol. Eng. 109, 65 (2017).
8. Zhao, Y., Z. Xiao, J. Lv, W. Shen and R. Xu: Geomicrob. J. 36, 819 (2019).
9. Nain, N., R. Surabhi, N. V. Yathish, V. Krishnamurthy, T. Deepa and S. Tharannum: Constr. and Build. Mat. 202, 904 (2019).
10. Amer Algaifi, H., S. Abu Bakar, A. Rahman Mohd. Sam, M. Ismail, A. Razin Zainal Abidin, S. Shahir and W. Ali Hamood Altowayti: Constr. and Building Mat. Mat. 254, 119258 (2020).
11. Metwally, G., M. Mahdy and A. El-Raheem: Civil Eng. J. 6, 1443 (2020).
12. Kadapure, S. A., G. S. Kulkarni and K. B. Prakash: Arabian J. Sc. and Eng. 42, 1039 (2017).
13. Alonso, M. J. C., C. E. L. Ortiz, S. O. G. Perez, R. Narayanasamy, G. d. J. Fajardo San Miguel, H. H. Hernandez and N. Balagurusamy: Envir. sc. and pollut. res. int. 25, 21451 (2018).

THE WASTE RECYCLING

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Abstract

Waste recycling is nowadays a high priority in all industrialized countries. It is the result of the action of a number of factors at once. If we create a new resource from waste, we achieve cost savings and at the same time help the environment. We reduce the amount of waste that would be placed in a waste dump or otherwise disposed of. And we are also creating a substitute with which to replace the input raw material. EU countries in particular are characterized by high industrial development on the one hand and low sources of input raw materials on the other. The absence of our own raw materials implies the need to import them from other countries, which is associated with transport costs, the covid period also brought a disruption in the logistics chains and this was reflected in the failure of their supplies and an increase in their prices, and even now the situation has not completely returned to normal. This is also due to the overall geopolitical instability. That is why the EU in particular puts a high emphasis on activities connected with the re-use of waste raw materials as resources for production of all kinds in various sectors. Which, in addition to economic and ecological positives, will also bring a reduction in raw material dependence of EU states on other countries. This basic idea can be called by different terms such as "circular economy", "reverse logistics", etc.

E.g., if 1 ton of steel scrap is reused, savings are achieved: 1,100 kg of iron ore, 630 kg of coal, 55 kg of limestone and a reduction in CO_2 emissions of 58%. If 1 ton of wastepaper is reused, 3.5 m^3 of waste dump space is saved, burning this amount of paper would generate 750 kg of CO_2 emissions, 270 litres of oil, 26,000 litres of water, 4,000 kilo watt hours of energy and 31 trees are saved.

Despite all these arguments, there are a number of reasons why the transformation of waste raw materials into input raw materials for new production is not at a much higher level.

The aim of our paper is to describe this issue in time and data and to popularize the circular economy.

Introduction

The waste recycling means reusing waste as a resource that replaces the primary raw material. Most European countries, including the Czech Republic, have a developed industry that consumes a large amount of raw materials and energy. At the same time, most European countries have very low raw material resources or have already extracted them in the past. Another problem is in the strict legislation regarding the extraction and processing of primary raw materials in Europe. That is why the idea of a circular economy, where waste would be used as a resource of raw materials, is very current. The waste would not end up in waste dumps or incinerators but would be used as a new resource. Waste recycling has a long history. For example, in the 18th century in Sweden, there was a royal decree and citizens were forbidden to throw away old paper and old clothes. They were obliged to collect these raw materials and hand them over for further production[2]. In 1900, residents of the Charlottenburg district of Berlin were required to sort their household waste into ash, food waste and other waste, and these raw materials were further used[2].

The prices of primary raw materials are constantly rising, their resources are running out in the world, and they often have to be imported over long distances. The processing of primary raw materials is often energy-intensive, and energy prices are also rising. Thanks to this, recycling is increasingly being used. Another important factor is the use of new recycling technologies, and thanks to this, we are able to economically use even waste that previously had no use. The main recycled raw materials are: glass, paper, plastics, iron and steel and precious metals. Energy savings compared to the use of primary raw materials are 74% for iron and steel, 95% for aluminium, 85% for copper, 64% for paper and 80% for plastics[1].

Secondary raw materials and their recycling

Paper

The average consumption of paper in the world is 55 kg per person per year, in developed countries it is higher, e.g., in Germany it is 230 kg per person per year and in the Czech Republic 126 kg per person per year[1]. The primary raw material for paper production is wood. The primary raw material can be replaced with old, collected paper. In the long term, paper production in the Czech Republic shows a ratio of approximately 75% wood and only 25% wastepaper, while in EU countries it is approximately 54% waste paper and 46% wood[6].

Plastics

Plastics are a very useful material due to their properties and relatively low material costs; they are used in a wide variety of industries. Plastics are divided into thermoplastics (these occupy the largest share of the total world production, approximately 80%) and reactive plastics. Thermoplastics are further divided into polyethylene (32% of total production), polypropylene (20% of total production), polyvinyl chloride (17% of total production), etc.[1] The production of plastics in the world is increasing every year[7], see Figure 1. In 2017, 348 million tons of different types of plastics were produced worldwide, consumption of plastics in the Czech Republic this year was 1.25 million tons[6]. It is true that some plastic components and products have a long life and therefore become waste only after a longer time interval, but some plastic products are only for one use, e.g., bottles, packaging, etc. A large production of plastics implies a large amount of plastic waste. Therefore, different forms of recycling are important so that plastic waste does not pile up on the planet. Recycling of plastics can be: energy-based – burning and use of the generated heat, chemical – plastics are destroyed into monomers and used in chemical production, mechanical – plastics are crushed and melted and used for the production of new plastic products. Different types of plastics require different recycling technologies[1,3].

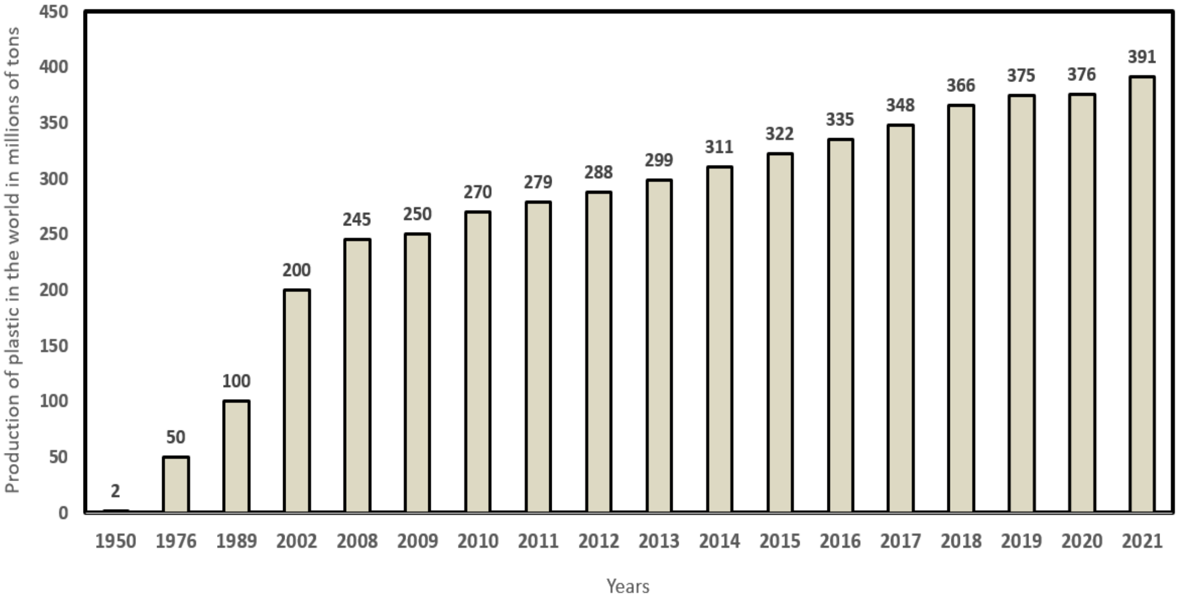

Figure 1. Global plastics production over time
Source: https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/ [7]

Metals

Metal consumption in industrialized countries averages more than 10 tons per inhabitant, of which 98% is the share of the five most important metals: iron, aluminium, copper, zinc and manganese[1]. Metal recycling is of great importance because the production of metal from scrap metal is associated with much lower energy consumption and lower CO_2 emissions. Compared to production from primary raw materials (metal ores), which are in short supply and must be imported over long distances. The production technology itself is simpler and cheaper when using scrap metal. Investment costs for operations processing metal waste are approximately 20% of investment costs for operations processing metal ores[5]. Iron is used in conjunction with other elements, the carbon content is important, if it is lower than 2.14% it is steel, if it is higher than 2.14% it is cast iron. World steel production is 1,700 million tons per year, but steel scrap production is only 500 million tons per year[6], so the production of steel from crude iron, which has to be produced by energy-intensive processes from iron ore, predominates. In the Czech Republic, steel and cast-iron waste is recycled almost 100% [6]. The production of non-ferrous metals such as aluminium, copper, zinc, lead, etc. is very energy-intensive, and the energy savings when using waste metals compared to the production of these metals from ores is over 90% [5]. Approximately 5 million tons of ferrous metal waste (steel, cast iron) and 150 to 200 thousand tons of non-ferrous waste[6] are collected and recycled in the Czech Republic each year. In recent years, the recycling of rare metals such as: platinum, gallium, indium, germanium, cobalt, etc. has been very important for Europe, because the sources of their primary raw materials are very limited worldwide. At the same time, these raw materials are used in the automotive industry and in the production of electrical appliances. It is therefore important to sort waste and separate electrical appliances of all kinds and use their components for recycling. Furthermore, it is important to adjust the design and construction of products in such a way that they allow easy disassembly and the possibility of separating these materials, which will facilitate their recyclability and use.

Glass

The primary raw material for glass production consists of glass sand, dolomite, limestone, and other ingredients. The glass industry produces three types of glass that differ according to their use. Bottles, glasses, and window glasses are made from the first type of glass. Other types of glass are used in the production of vases, kitchen and laboratory glass. The largest volume of separated glass intended for recycling is precisely the first type of glass, where there are mainly non-returnable bottles. This also includes glass from car wrecks and window glass (the trend in the Czech Republic is to replace old windows with plastic ones). This type of glass is cleaned of impurities and then recycled by melting and mixing with the primary raw material. The addition of recycled glass has several advantages: The melting temperature is lower and therefore the energy consumption is lower. Melted recycled glass releases less gas than the primary raw material. And one kilogram of recycled glass produces more melt than one kilogram of primary raw material. New glass, which is created by adding old glass, has the same properties and parameters as glass made only from the primary raw material[1]. Specifically, the energy consumption for the production of one ton of window glass is 9.1 to 10.1 Gigajoules. When 1% recycled glass is added to the primary raw material, energy consumption is reduced by 0.25% per ton. Approximately 595 kg of CO_2 is produced during the production of one ton of window glass. When 1% of recycled glass is added to the primary raw material, the amount of CO_2 is reduced by 0.42% per ton. The energy consumption to produce one ton of bottle glass is approximately 5 Gigajoules. When 10% recycled glass is added to the primary raw material, energy consumption is reduced by 2.5% per ton. During the production of one ton of bottle glass, 350 to 400 kg of CO_2 is produced. When 35% recycled glass is added to the primary raw material, the amount of CO_2 is reduced by 18.5% per ton. The amount of waste glass added is different for different production situations, but it is usually tens of percent, and this implies significant savings in energy and CO_2 emissions. In 2017, 150,000 tons of glass were recycled in this way in the Czech Republic[6].

The easiest way to recycle glass is with glass bottles that are backed up and customers return them to stores. In the Czech Republic, these are mainly beer bottles that just need to be washed and can be immediately reused. Bottle washing creates waste when the labels are washed off the bottles. An interesting fact is that this waste is used, e.g., in the Radegast brewery, for the production of compost[4].

An interesting fact is that the following amount of waste is generated from one discarded passenger car: 30 kg of tires, 760 kg of ferrous metals, 31 kg of non-ferrous metals, 23 kg of plastic, 38 kg of glass and other types of waste. In the Czech Republic alone, more than 150,000 old cars are scrapped each year[6].

Coal combustion products (CCPs)

Another example is the by-products of energy that are produced in thermal power plants and heating plants when coal is combusted. It is mainly about fly ash, gypsum and cinder. Ash is produced during the combusting of coal, where it is subsequently captured using filters. This material is used in the production of concrete, where it is able to partially replace cement[5]. Which is advantageous economically and also ecologically. In the Czech Republic, the price of fly ash is approximately ten times lower than the price of cement. During the production of one ton of cement, 0.8 tons of CO_2 [3] are released into the atmosphere. The quality of fly ash depends on the type of coal combusted. Some quality fly ash can be used for cement production[6]. Gypsum is created during the desulfurization process and is widely used in the production of plasterboard, it is also used as a substitute for natural gypsum, in the production of cement. Lower-quality energy gypsum is mixed with fly ash and water to form a mass that hardens and is very hard and solid, so it is used as a solid base, for example, in road construction. Cinder is a solid substance that remains after combusting coal and is used in the construction industry. Fly ash, gypsum and cinder, which are not suitable for further processing, are used in the reclamation of the landscape, where they backfill places after mined coal.

In 2017, the following were produced in the Czech Republic: 7,322,239 tons of fly ash, 1,287,574 tons of cinder and 1,952,843 tons of gypsum. (In addition to these main products, others are created, e.g., fly ash, which is created by combusting biomass, etc.). Of this production of coal combustion products, 1,008,162 tons were used for the production of concrete, cement and bricks. 55,199 tons were used for the production of the mentioned solid sub-surface for road construction, 395,256 tons were used for the production of plasterboard, gypsum and cement, 5,240,694 tons were used for surface mine backfilling, 30,904 tons were used for underground mine backfilling, and 4,739 612 tons were used for landscape reclamation[6]. Fly ash is widely used abroad as a raw material for the production of concrete panels, mortars, bricks, tiles, etc. It is proven that fly ash improves some chemical and mechanical parameters of concrete[3].

Conclusion

Waste recycling has great economic and environmental potential because raw materials obtained by recycling waste are much cheaper than primary raw materials and their acquisition is associated with lower energy requirements and environmental burden. An important factor is also the increase in the cost of storing waste in waste dumps, as well as legislation restricting waste landfilling and a ban on dumping waste in waste dumps in the near future. Every ton of waste that is recycled does not take up to a waste dump. The share of sorted raw materials has been constantly increasing in recent years. New procedures, methods and technologies for recycling waste are emerging. Apart from economic benefits or legislative regulations, many companies use recycled materials as part of green marketing. Companies try to ensure that their production does not burden the environment, they use recycled raw materials as production inputs, products and packaging materials are designed in such a way that they can be easily recycled. Informed customers and business partners prefer products from manufacturers who develop these environmentally friendly activities. Business partners and customers carefully monitor whether the company has a certificate, for example EN ISO 14001, proving that the company deals with environmental management or whether their products meet the criteria for labelling as environmentally friendly (Ecolabelling). Such companies gain a competitive advantage over companies that do not have these certificates. This is a trend for the 21st century in developed countries, for example in Australia 90% of customers prefer companies that behave socially responsibly, in Western Europe it is 50% of customers[4]. Nevertheless, there is still a great possibility for increasing the share of recycled waste in the future.

References

1. Kuraš M.: Odpady a jejich zpracování. Vodní zdroje Ekomonitor, Chrudim 2014.
2. Mikoláš J.: Recyklace průmyslových odpadů. SNTL, Praha 1988.
3. Verma S., Khan R., Mili M., S. A. R. Hashmi, Kumar A. S.: Advanced Materials from Recycled Waste. Elsevier, 2023.
4. Tetřevová L., Vávra J., Bednaříková M., Munzarová S., Košťálová J.: Společenská odpovědnost firem společensky citlivých odvětví. Grada, Praha 2017.
5. Voštová V., Altmann V., Fries J., Jeřábek K.: Logistika odpadového hospodářství. ČVUT, Praha 2009.
6. Analýza současného stavu vybraných komodit druhotných surovin a jejich zdrojů včetně vize rozvoje daného odvětví. Ministerstvo průmyslu a obchodu ČR, 2018. https://www.mpo.cz/ [6_6_2023]
7. Global plastics production https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/ [6_6_2023]

DECARBONISATION AND ECONOMIC ASPECTS OF THE TRANSFORMATION OF THE CHEMICAL INDUSTRY

ASSESSMENT OF HYDROGEN PRODUCTION: IS GREEN HYDROGEN COMPETITIVE?

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Abstract

Hydrogen production is on a rise every year, but the production is majorly via Steam Methane Reforming (SMR) method (around 96% of the total hydrogen production). This technology utilises natural gas as a feedstock to produce hydrogen which is environmentally detrimental producing on an average around 7 kg of carbon dioxide per kilogram of hydrogen produced. The most environmentally conscious form of hydrogen is green hydrogen, which is produced via electrolysis of water, using renewable energy sources as feedstock. The issue with green hydrogen is the viability and economic sustainability of the production process. Review of the economic viability of the green hydrogen contributes to the right investment decisions. Sensitivity analysis answers the "What If" scenario by changing input variables like electricity prices, selling price of green hydrogen and CAPEX investment. A comparison with steam methane reforming provides the view on competitiveness of green hydrogen.

Introduction

The rapid increase in population and urbanisation has increased the demand for energy extensively[1]. The dependence of the world on fossil fuels as a source of energy can no longer be sustainable given their limited quantity and environmental crisis associated with their extraction, use and emissions of greenhouse gases. Carbon dioxide in the atmosphere which is the leading cause of global warming, accelerating climate change[2]. One of the renewable secondary energy sources gaining traction is green hydrogen. The renewable energy sources release less Carbon dioxide in the atmosphere but their upfront/establishment cost is more as compared to that of non-renewable sources[3].

The amount of investment countries around the World are making towards green hydrogen production and development of supportive infrastructure, this development can be termed as a "Dawn of the Era of Green Hydrogen". The future of energy system is sustainable, clean, and based on energy, which is renewable, readily available and can be stored for future utilisation[2].

Need for Hydrogen

Hydrogen is a versatile alternative energy carrier or secondary energy source which can be produced by both renewable and non-renewable clean/green energy sources[4]. The need of alternative energy is influenced by ongoing wars, geo political tension between oil producing countries, price volatility, climate change and energy shortage and security within Europe[5]. Hydrogen economy is inching towards reality, with more and more countries investing towards energy independence. Energy independence is the ability of a country to be self-sufficient in supporting its energy sector rather than be too dependent on export from other countries. The investment and the governmental incentives involved in green hydrogen has led to expansion of domain from just involvement of scientist and researchers to politicians and businesses[6]. The main reason for green hydrogen being in spotlight is decarbonization potential that it holds over the energy sector[7]. This would be a great ally in the fight against climate change and temperature rise around the globe as stated in Paris Agreement (2015), where around 194 member countries are parties to the accord agreeing to limit the temperature rise to around 1.5 degree Celsius by 2050[7]. The only by-product of hydrogen after combustion is water, unlike other fossil fuels no greenhouse gases are released. Due to this reason, it can be used as a viable non-polluting feedstock, a fuel and an energy carrier which can be utilized for storage, having many applications across industries for example chemical, transport, power generation[8]. The big bet on hydrogen is being placed on the outlook that it would be a sustainable replacement for hydrocarbons as an energy vector for future energy systems[9]. One of the major advantages of hydrogen over fossil fuels is that it can be produced almost everywhere in the world unlike fossil fuels which are exhaustive in nature and only present in certain locations around the world[10].

Application of Hydrogen

Hydrogen can be used to power turbines, internal combustion engines along with fuel cells as well as a supply in households for kitchen, heating[11]. Hydrogen's versatility helps it to be used with other fuels as mixtures to enrich their energy and have a wider range of flammability to provide higher combustion power to engines[11]. Hydrogen is used by NASA to power the space shuttle's main engine along with fuel cells to provide electricity onboard the space shuttle[12]. Hydrogen is mostly used in chemical industries to produce ammonia, methanol synthesis, hydrogenation of fossil hydrocarbons, fats and oils along with many other[12], with around 49% being used in ammonia production, 37% in petroleum refining, methanol production took around 8% hydrogen production and other miscellaneous uses took up 6% of the total production[13]. In transport industry, hydrogen is a promising alternative to fossil fuel, heavy-duty trucks, large passenger vehicles with long-range and long-distance coaches with the use of hydrogen and fuel cell technologies can achieve cost parity between 2025–2030[14].

Production Method of Hydrogen

At present the most developed method is SMR with around 48% of hydrogen being produced by this method followed by Partial Oxidation of crude oil residues with a share of 30% and then 18% by Coal Gasification[13]. So in nowadays, almost 96% of the hydrogen produced in the world is via hydrocarbons and the remaining 4% is via Electrolysis of Water[15].

The issue with production of hydrogen with hydrocarbons and other non-renewable as feedstock is that the hydrogen produced is of low purity and high amount of pollution due to release of greenhouse gases[16]. Whereas hydrogen produced with renewable resources termed as green hydrogen is seen as more sustainable and environmentally friendly. The disadvantage of water electrolysis for the production is that the efficiency of production is low, requires sufficient and reliable supply of green electrical energy and it is not economically competitive with fossil fuel-based methods[17].

Hydrogen production can be classified in colours, the colour of Hydrogen produced is given based on feedstock/primary energy source used to produce it[18].

SMR is a well-established method with low-cost hydrogen production cost[18] and Hydrogen produced via SMR is termed as Grey Hydrogen. The equation 1 and equation 2 define the reaction, which goes through for production of Grey Hydrogen. SMR has an efficiency of 74–85% while maintaining the purity of Grey Hydrogen produced in the range 97–99%.

$CH_4 + H_2O \longrightarrow CO + 3H_2$ [Equation 1]

$CO + H_2O \longrightarrow CO_2 + H_2$ [Equation 2]

The Carbon Dioxide produced in equation 2 is separated from Hydrogen via absorption.

Water electrolysis's principle is quite simple, the water molecule is divided into Hydrogen and Oxygen with the application of direct electric current. The direct current acts like an input energy source for the endothermic reaction that breaks the electrolyte (raw material) into Hydrogen and Oxygen. Equation 3 define the overall reaction of hydrogen production via electrolysis.

$2H_2O \longrightarrow O_2 + 2H_2$ [Equation 3]

Water electrolysis can be classified in various types based on their electrolyte, operating conditions, and ionic agents, however operating principles are same in all the cases17. Figure 1 states the type of Electrolysis used for Green Hydrogen production.

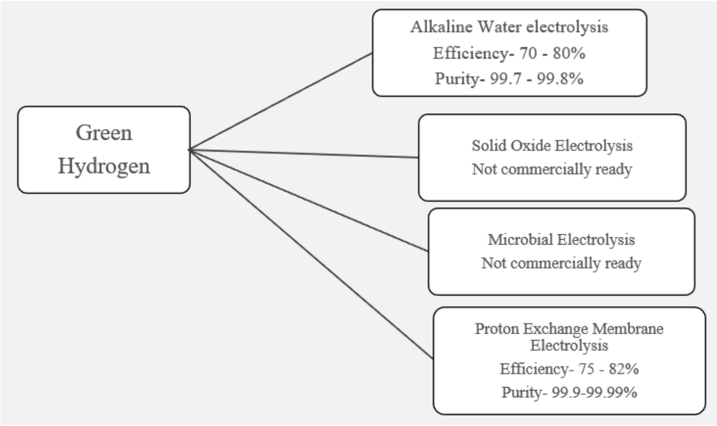

Figure 1. Types of Electrolysis for Green Hydrogen Production along with their efficiency and Purity17.

Practical setup

The practical part of the article is focused on economic of green and grey hydrogen production. The setup based on use of financial tools like Net Present Value (NPV), Break Even Point (BEP) and Internal rate of Return (IRR) would be used to implore the financial implication of the investment decisions and draw conclusion based on interpretation of resulting calculations.

Figure 2 illustrates the setup of green hydrogen production plant with a production capacity of 5,4 kt/year with the assumption that the electrolyser works with 100% efficiency and capacity. The cost of photovoltaic plant is included in the CAPEX and the discount rate is taken around 8% in accordance with industry standard. Another assumption is that the working capital is considered certain percentage of the revenue and is maintained positive for modelling purposes. The feedstock for electrolysis is deionized water which is obtained by purification and deionization of drinking water through reverse osmosis. The prices used for sensitivity analysis are external prices of electricity incase our internal photovoltaic system fails during functioning and thus the scenario was created. Also, the electricity market is turbulent and depends upon demand and production aspect in order to find the correct pricing for electricity. Figure 3, Figure 4 and Figure 5 are the graphical depiction of sensitivity analysis while changing inputs like electricity prices (scenario 1), selling price of green hydrogen (scenario 2) and changing CAPEX (scenario 3).

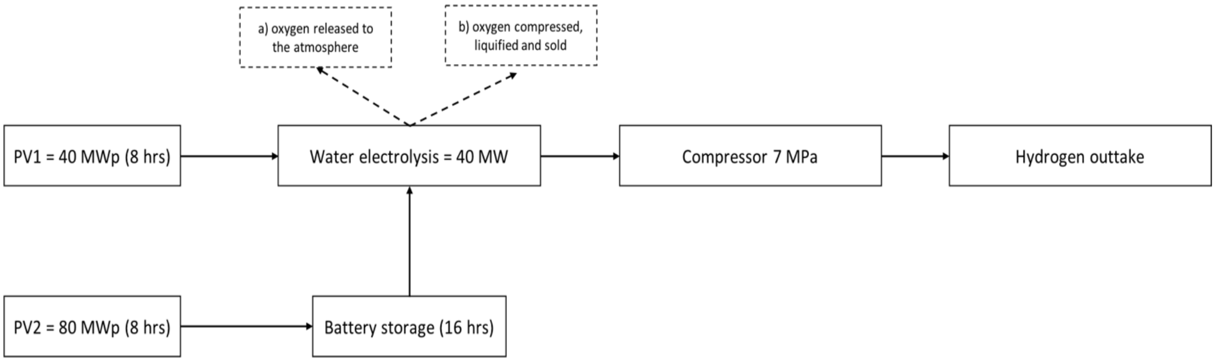

Figure 2. Illustrative setup of green hydrogen production plant

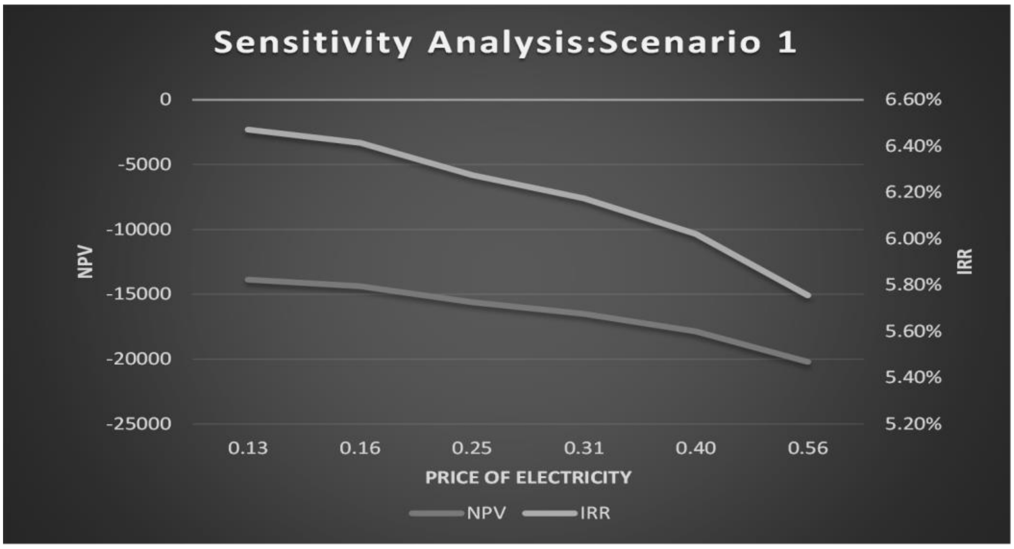

Figure 3. Sensitivity Analysis Scenario 1

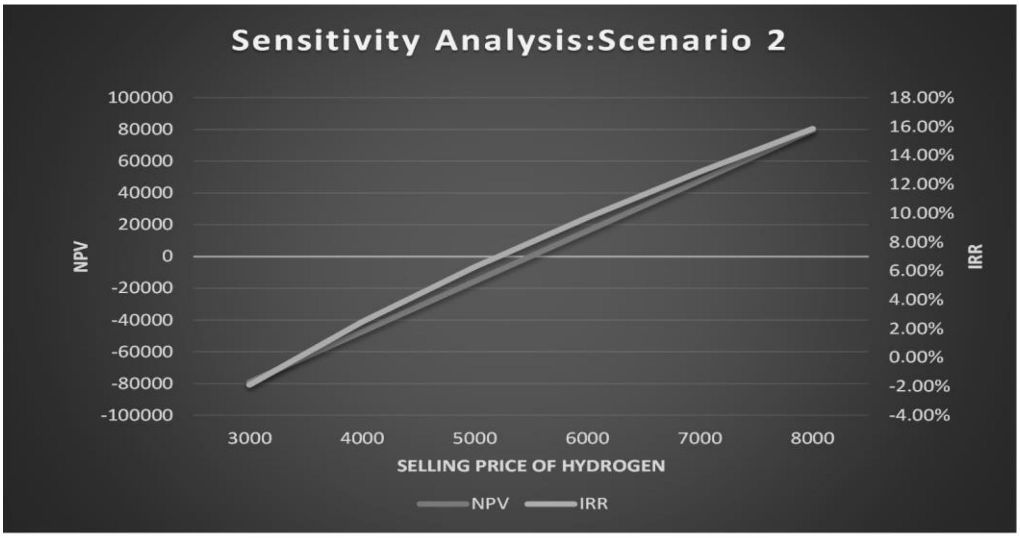

Figure 4. Senstivity Analysis Scenario 2

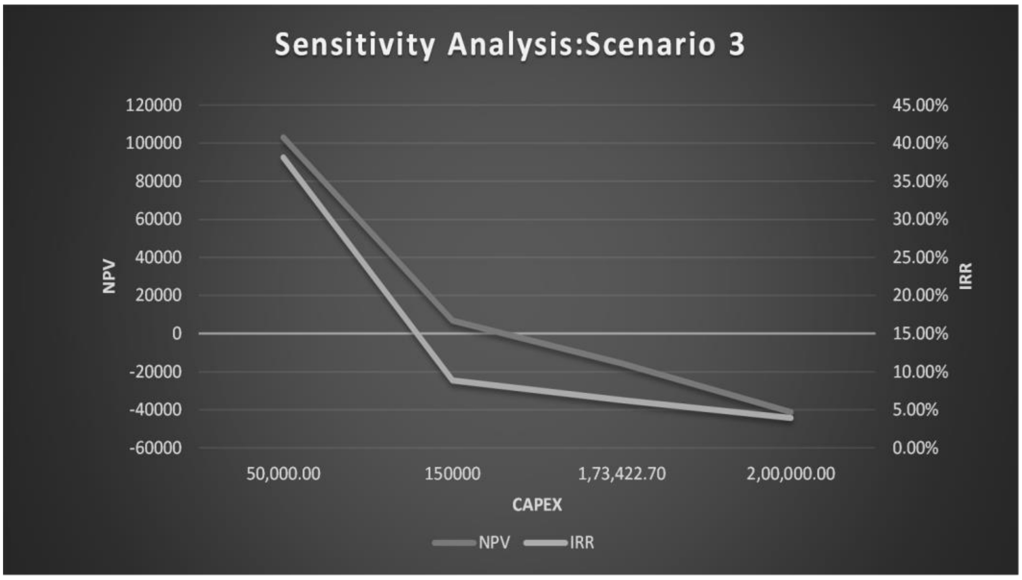

Figure 5. Sensitivity Analysis Scenario 3

Discussion and result analysis

The result is that under base conditions of CAPEX 173,423,000 Euros, input price of renewable electricity of 0.247 EUR/MWh and the green hydrogen selling price of 5,000 EUR/tonne the NPV is negative (-15,623,000 Euros) and the IRR is less that the discount rate that the market offers of a round 6.3%. This leads us to the result that the investment in production plant is not economically viable at that price of green hydrogen. The Break-even point of the hydrogen price (BEP) leads us to the result that the economically feasible selling price of green hydrogen should be higher than 5.492 EUR/Kg.

The sensitivity analysis is performed for 3 scenarios respectively:

1.The input price of electricity is changed while all the other input conditions are maintained constant. In the Figure 3, with the increase in electricity prices the NPV and IRR decreased and vice versa, but overall, the impact of electricity prices on NPV and IRR was not that profound. The lowest selected electricity price of 0.13 EUR/KWh could not produce a positive NPV and IRR greater than the discount rate. (Scenario 1)

2.The input selling price of green hydrogen is changed while all the other input conditions are maintained constant. In the Figure 4, with the increase in selling price of hydrogen the NPV and IRR increased and vice versa. The NPV remained negative for the prices below the BEP price of 5.492 EUR/Kg and the IRR remained lesser than the industry offered discount rate making the investment not feasible but once the prices were above BEP the NPV and IRR bother showed result which would be worth investing. (Scenario 2)

3.The CAPEX is varied while all the other input are maintained as the base case with electricity prices of 0.247 EUR/KWh and selling price of hydrogen at 5,000 EUR/tonne. The change in CAPEX has a big impact on the result of NPV and IRR. The lesser the CAPEX expenditure higher is the NPV, through the input data we found out that with a decrease of CAPEX by 1% NPV increases by around 10%. The CAPEX expenditure plays an important role in investment decision. The higher the CAPEX expenditure, higher is the requirement of the free cash flow in order to produce NPV which is positive and IRR above industry standard. Please refer Figure 5 (Scenario 3).

The CAPEX can also change with the advancement of technology with more R&D, the CAPEX would decrease with the biggest expenditure of electrolyser cost decreasing. It is possible in the few years that the cost of electrolysers would reduce drastically decreasing the CAPEX expenditure.

The SMR methodology is dependent upon the price of natural gas for the production to be viable and economically sound. The prices of natural gas are turbulent given the geo-political issues arising across the world. These can be wars, low production volume, decrease in export by the natural gas producing country or decrease in demand or over supply. The cost of production of hydrogen increases with increase in prices of natural gas and vice versa. The Figure 6 illustrates graphically the cost of hydrogen produced with varying price of natural gas. The Figure 6 can also be used to compare the selling price of green hydrogen (BEP) with that of the price of hydrogen produced via SMR (grey hydrogen). This comparison is important from the point of view that it shows that green hydrogen prices can be comparable to the prices of grey hydrogen provided there is a certain benchmark of natural gas prices which if breached and the prices start trending upwards then green hydrogen is competitive with the grey hydrogen prices. Based on the calculations green hydrogen becomes a better option than grey hydrogen once the prices of natural gas reach above and beyond 100 EUR/MWh.

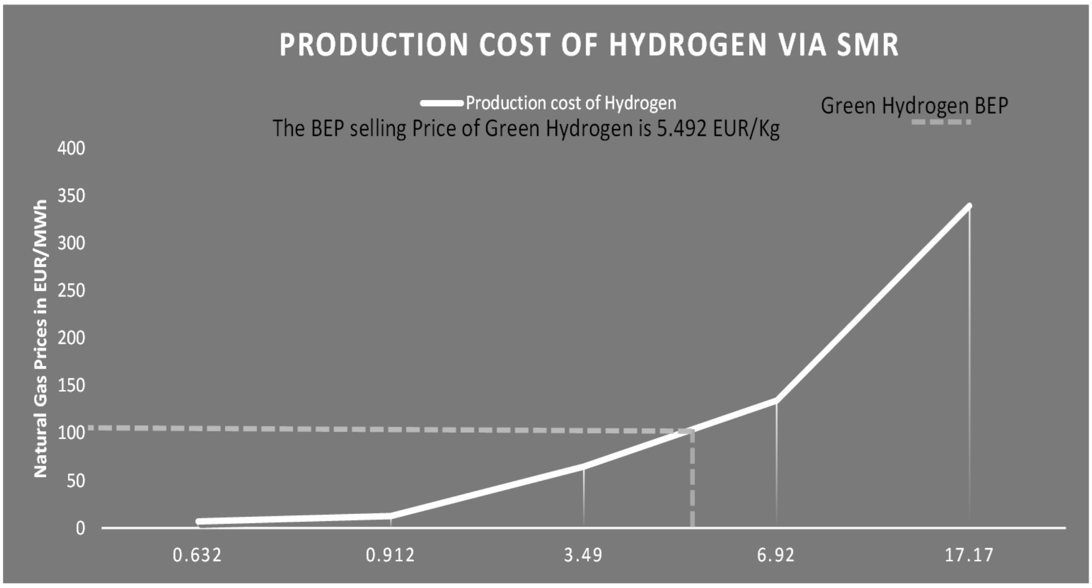

Figure 6. Production cost of hydrogen via SMR with marking of selling price (BEP) of green hydrogen

Conclusion

Green hydrogen is being seen as a saviour towards the issue of global warming and rightly so, it produces no emission while being produced and no emission during its combustion. The resources utilized are renewable and do not burden the planet with overuse.

Green hydrogen can best be described by idiom “Every cloud has a silver lining”, in which it seems hopeful that it would be the fuel of future with the silver lining being the governments around the world are acknowledging the virtues and attributes of green hydrogen and are actively framing policies and incentives towards its mainstream utilisation. The progress is visible in the sense that whenever the World talks about Carbon-Neutral future, green hydrogen is on top of the list to move towards sustainability and achieve the goal. Like there are pros to green hydrogen its biggest cons are that it is still a technology which needs to be widely commercialised and is dependent on availability of green electrical energy. That it is still expensive compared to grey hydrogen which makes it is a slower to switch. The initial investment is higher and the plant components like electrolysers are expensive but positive side being that R&D developments are already driving the cost down.

Green hydrogen can be a gamechanger, but it would need a lot of government support, cheap green electrical energy availability and industry acceptance.

References

1. Furat Dawood, Martin Anda, G.M.Shafiullah. Hydrogen production for energy: An overview. *Int J Hydrog Energy*. Published online December 10, 2019. https://doi.org/10.1016/j.ijhydene.2019.12.059
2. Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. *Renew Sustain Energy Rev*. 2017;67:597-611. doi:10.1016/j.rser.2016.09.044
3. Dong F, Qin C, Zhang X, et al. Towards Carbon Neutrality: The Impact of Renewable Energy Development on Carbon Emission Efficiency. *Int J Environ Res Public Health*. 2021;18(24):13284. doi:10.3390/ijerph182413284
4. Dutta S. A review on production, storage of hydrogen and its utilization as an energy resource. *J Ind Eng Chem*. 2014;20(4):1148–1156. doi:10.1016/j.jiec.2013.07.037
5. Dillman KJ, Heinonen J. A ‘just’ hydrogen economy: A normative energy justice assessment of the hydrogen economy. *Renew Sustain Energy Rev*. 2022;167:112648. doi:10.1016/j.rser.2022.112648
6. Dunn S. Hydrogen futures: toward a sustainable energy system. *Int J Hydrog Energy*. 2002;27(3):23 –264. doi:10.1016/S0360-3199(01)00131-8
7. *Geopolitics of the Energy Transformation: The Hydrogen Factor*. International Renewable Energy Agency; 2022.
8. EUROPEAN COMMISSION. *A Hydrogen Strategy for a Climate-Neutral Europe*.; 2020. https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52020DC0301&from=EN
9. Møller KT, Jensen TR, Akiba E, Li H wen. Hydrogen – A sustainable energy carrier. *Prog Nat Sci Mater Int*. 2017;27(1):34–40. doi:10.1016/j.pnsc.2016.12.014
10. U.S. Department of Energy, 1000 Independence Avenue, S.W., Washington, D.C. 20585-0121. *Progress Report for Hydrogen, Fuel Cells, and Infrastructure Technologies Program*.; 2002. www.eren.doe.gov/hydrogen
11. Mazloomi K, Gomes C. Hydrogen as an energy carrier: Prospects and challenges. *Renew Sustain Energy Rev*. 2012;16(5):3024–3033. doi:10.1016/j.rser.2012.02.028
12. Abdelaal H, Sadik M, Bassyouni M, Shalabi M. A new approach to utilize Hydrogen as a safe fuel. *Int J Hydrog Energy*. 2005;30(13–14):1511–1514. doi:10.1016/j.ijhydene.2005.07.007
13. Balat M. Potential importance of hydrogen as a future solution to environmental and transportation problems. *Int J Hydrog Energy*. 2008;33(15):4013–4029. doi:10.1016/j.ijhydene.2008.05.047
14. Hydrogen Council. *Path to Hydrogen Competitiveness A Cost Perspective*.; 2020. https://hydrogencouncil.com/wp-content/uploads/2020/01/Path-to-Hydrogen-Competitiveness_Full-Study-1.pdf
15. Minet R, Desai K. Cost-effective methods for hydrogen production. *Int J Hydrog Energy*. 1983;8(4): 285–290. doi:10.1016/0360-3199(83)90139-8
16. Md Mamoon Rashid, Mohammed K. Al Mesfer, Hamid Naseem, Mohd Danish. Hydrogen Production by Water Electrolysis: A Review of Alkaline Water Electrolysis, PEM Water Electrolysis and High Temperature Water Electrolysis. *Int J Eng Adv Technol IJEAT*. 2015;4(3).
17. Shiva Kumar S, Himabindu V. Hydrogen production by PEM water electrolysis – A review. *Mater Sci Energy Technol*. 2019;2(3):442–454. doi:10.1016/j.mset.2019.03.002
18. Ajanovic A, Sayer M, Haas R. The economics and the environmental benignity of different colours of hydrogen. *Int J Hydrog Energy*. 2022;47(57):24136-24154. doi:10.1016/j.ijhydene.2022.02.094

CCU SOLUTIONS VS. ADDITIONAL ENERGY REQUIREMENTS

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Abstract

The issue of global warming and the role that fossil fuel emissions are playing is subject of political and technical disputes. This work is demonstrating the concept of elimination of CO_2 emissions from fossil source emitting CO_2. This CO_2 could be converted to methanol. In order to convert CO_2 to methanol, the green hydrogen production should be established. This amount of hydrogen could be produced by electrolyser with significantly high installed capacity. The interdependence of balance of production streams (water, hydrogen, CO_2, oxygen for gas turbine operation and methanol) was analysed and balance model has been developed. This work identifies that green solution are significantly dependent on large amount of green electricity. Nevertheless, this concept could be used in situations of large access of the electricity from renewable sources converting CO_2 it into products for final use or accumulating energy into products which are easy to store.

Introduction

The European Green Deal represents a manifestation of the European Union's intention to become carbon-neutral by 2050. This ambition ought to be accomplished by supporting innovative environmentally friendly technologies. The most promising way to decarbonize energy intensive industries such as chemical, cement and steel-making industry, energy sector and a whole lot of mobility segments is "green hydrogen way".

Energy source such as gas turbine emitting CO2 could be used as source of CO2 for subsequent chemical production such as methanol.

Case study

Case study is demonstrating the concept of elimination of CO_2 emissions from small gas turbine with capacity of 0,3 MW consuming 3,5 kt of natural gas per year and emitting 9,5 kt of CO_2 per year. This amount of CO_2 could be converted to 6,9 kt methanol per year. In order to convert CO_2 to methanol, the green hydrogen production should be established. The amount of green hydrogen needed for defined quantity of methanol is about 1,3 kt/y. This amount of hydrogen could be produced by electrolyser with installed capacity 10 MW.

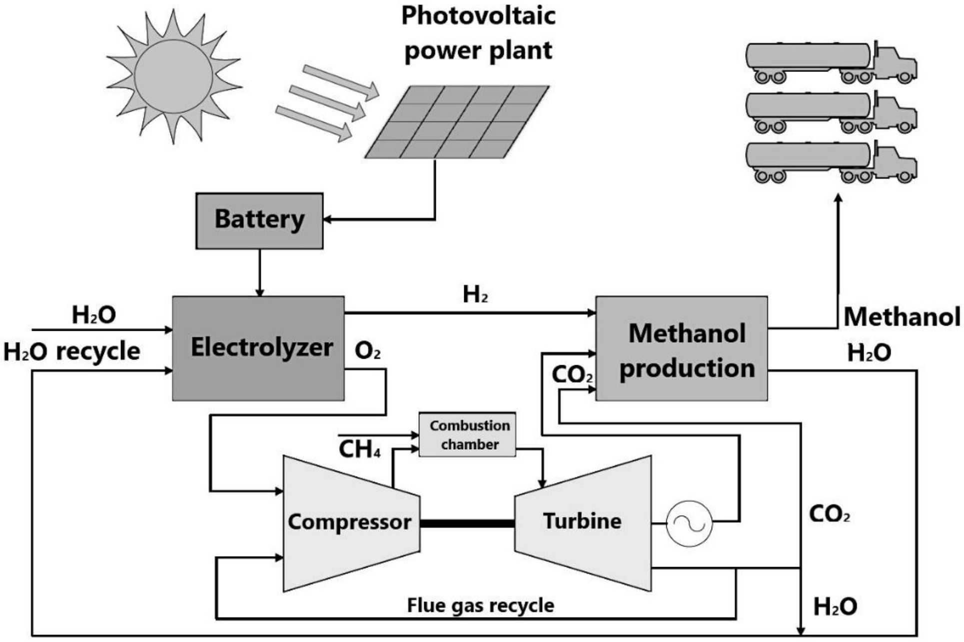

Figure 1. Simplified concept lay-out.

Hydrogen production

Hydrogen has been produced from various renewable and non-renewable energy resources such as fossil fuels, especially steam reforming of methane, oil/naphtha reforming, coal gasification, biomass, biological sources, and water electrolysis.

In order to produce green hydrogen, it is vital that the electricity used in the electrolytical production process for water decomposition comes from renewable source of energy. For this case study, as the main renewable source of energy for the green hydrogen production is considered PV plant.

The basic chemical equation of water electrolysis is:

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2$$

For purpose of this case study, the hydrogen is utilised for methanol synthesis when oxygen is used for CO_2 production at gas turbine.

As indicated in the Figure 2, production of hydrogen is available at the utilization rate of the electrolyzer equals 100%. The source of electricity is PV with the installed power 40 MWp, which covers 8 hours of electricity supply. Further 80 MWp will be installed to generate renewable electricity, which will be stored in the battery storage. The stored renewable electricity will provide the electricity supply for the rest of the day i.e., 16 hours of insufficient sunshine for generation of solar electricity to secure the 100% utilization rate of the electrolyzer. The electrolyzer's power is 10 MW. Produced hydrogen will by compressed to 7 MPa and supplied to methanol production. The oxygen produced during the electrolysis is supplied to gas turbine for "pure CO_2 production".

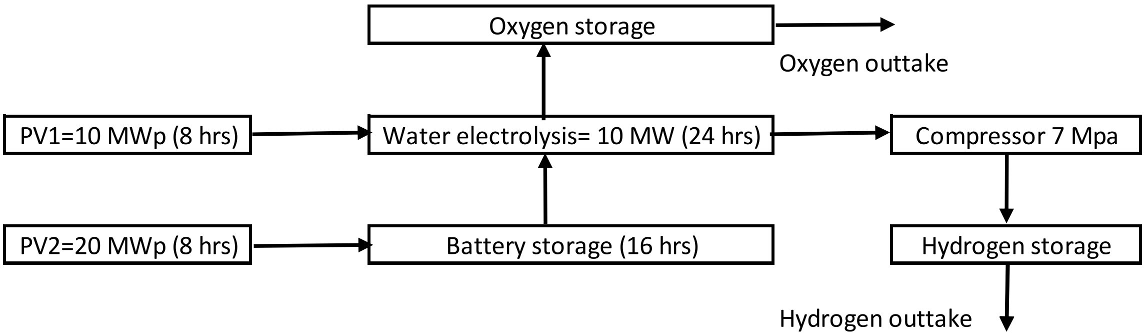

Figure 2: Hydrogen production scheme

Oxyfuel gas turbine

Oxyfuel gas turbine is considered due to the following reasons:

1. Utilisation of water electrolysis by-product – oxygen
2. Production of "pure" CO_2

The concept of using oxyfuel technology is based on using pure oxygen instead of air in the combustion process. It means that the inlet to the combustion chamber consists of two mediums (methane and oxygen). Using this technology help to avoid mixing nitrogen with products of combustion, so there is no need to use any high-tech CO_2 separation units. Flue gases consist just of carbon dioxide and water steam. To separate water from carbon dioxide the water steam should be just condensed [1].

Methanol production concept

The methanol economy [2], based on green-methanol synthesis pathways, has been proposed in contrast to the hydrogen economy, which requires a deep change in energy storage and transportation means.

Methanol is promising and widely synthesized chemicals. History of producing methanol is based on the 1920s into German, where methanol was used as a cheap motor fuel [3]. The Catalyst used in synthesis was ZnO/Cr_2O_3, which operated at high pressures of 25–35 MPa and a temperature of 320–450 °C. In the 60s was high temperature process changed. Nowadays, is the most widely used low pressure process (5–10 MPa) catalysed by ZnO/CuO, supported on alumina and the temperature is in the range of 200–300 °C[4].

Methanol synthesis is one way of dealing with carbon dioxide produced from fossil fuels. The chemical processes occurring in the reactor could be summed by equations:

$$CO + 2H_2 \leftrightarrow CH_3OH$$
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

From the first equation it follows that the one mole of carbon monoxide and two moles of hydrogen must be used to produce one mole of methanol. And from the second equation fellows that one mole of carbon dioxide and three moles of hydrogen must be used to produce one mole of methanol and water.

Balance model

In order to decarbonise fossil fuel gas turbine was made balance model. All the important data are summarized in Table I. Let's assume that a photovoltaic power plant with a power of 10 MW will be connected to an electrolyzer and all the oxygen will be consumed to burn methane in oxyfuel gas turbine. So, the produced amount of carbon dioxide will be 9506 ton per year. Hydrogen produced (1728 ton per year) from electrolyzer should cover the consumption of hydrogen in methanol synthesis reactor to store all the carbon dioxide to methanol. And there will be still 422 ton per year of hydrogen left. Amount of water that is necessary to add to this process to run electrolysis will be 436 ton per year. Assuming that water from process of burning methane and water separated from methanol synthesis reactor will be recycled in electrolyzer. Then we can produce 6921 tons of green methanol per year.

Table I.
Process mass balance

Medium	Input	Output	Difference	Unit
Carbon dioxide	9506	9506	0	t/year
Oxygen	13823	13823	0	t/year
Water	1742	1306	-436	t/year
Methane	3465	0	-3465	t/year
Hydrogen	1306	1728	422	t/year
Methanol	0	6921	6921	t/year

Conclusion

This work identifies that green solution are significantly dependent on large amount of green electricity. Nevertheless, this concept could be used in situations of large access of the electricity from renewable sources converting CO2 it into products for final use or accumulating energy into products which are easy to store.
Hydrogen can be potentially synthesized by reforming or partial oxidation of different carbon-based materials. Economic considerations typically suggest which raw materials are more suitable for use, even though long-term availability, political considerations, energy consumption and environmental aspects play an important role in the final decision as well[5]. This option requires much less electrical energy supply compared to Case study scheme. Nevertheless the „green economy“ (deriving to decarbonisation of fossil sources) is becoming the main goal for 2050 due to the danger of un-controlled global warning. Methanol is also expected to be a potential solution to the partial deployment of fossil source-based economies. Moreover, it is a recognized energy carrier that is better than other alternatives in terms of transportation, storage and reuse[6].

References

1. Sundkvist, S. G.; Dahlquist, A.; Janczewski, J.; Sjödin, M.; Bysveen, M.; Ditaranto, M.; Langørgen, Ø.; Seljeskog, M.; Siljan, M. Concept for a combustion system in oxyfuel gas turbine combined cycles. J Eng Gas Turbines Power 2014, 136 (10), 1–10. https://doi.org/10.1115/1.4027296.
2. Vita, A.; Cristiano, G.; Italiano, C.; Pino, L.; Specchia, S. Syngas production by methane oxy-steam reforming on Me/CeO2 (Me=Rh, Pt, Ni) catalyst lined on cordierite monoliths. Appl Catal B Environ 2015, 162, 551–563. https://doi.org/10.1016/j.apcatb.2014.07.028.
3. Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and chemical recycling of solid plastic waste. Waste Manag 2017, 69, 24–58. https://doi.org/10.1016/j.wasman.2017.07.044.
4. Dieterich, V.; Buttler, A.; Hanel, A.; Spliethoff, H.; Fendt, S. Power-to-liquid via synthesis of methanol, DME or Fischer–Tropsch-fuels: a review. Energy Environ Sci 2020, 13 (10), 3207–3252. https://doi.org/10.1039/d0ee01187h.
5. Haid, J.; Koss, U. Lurgi’s Mega-Methanol technology opens the door for a new era in down-stream applications. Stud Surf Sci Catal 2001, 136, 399–404. https://doi.org/10.1016/s0167-2991(01)80336-0.
6. Bozzano, G.; Manenti, F. Efficient methanol synthesis: Perspectives, technologies and optimization strategies. Prog Energy Combust Sci 2016, 56, 71–105. https://doi.org/10.1016/j.pecs.2016.06.001.

INORGANIC TECHNOLOGY

MINERAL FERTILIZER WITH NATURAL ANHYDRITE – CONNECTION OF LABORATORY AND PRODUCTION PRACTICE

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Abstract

Controlled nutrition of plants consists in systematic replacement of mineral substances necessary for the healthy development of crops in the soil. Industrial fertilizers should help to balance and maintain the equilibrium of nutrients in the soil, possibly in plants. The elements used in plant nutrition are called biogenic. Main nutrients, or macro elements, are considered as essential in the cultivation of agricultural crops[1].

These include sulfur, which is present in all crops and plays an important metabolic role. It is essential for the formation of proteins, amino acids, vitamins and enzymes. It supports the creation of specific substances with influence on the taste, smell, aroma and by this also the specific properties of plants and plant products. Sulfur is becoming an increasingly important nutrient due to the combination of lower sulfur emissions, the increasing prevalence of fertilizers and higher cropping intensity.

The form of sulphates is the most accessible source of sulfur in the soil for plants. Sulphates enter to the metabolism of plants already in the roots or they are transported to the leaves, where, together with nitrogen, participate in the formation of proteins. Increasing of winter resistance and drought tolerance are other positive properties of sulfur-containing fertilizers. Leguminous plants, oilseeds, plants from the cabbage-family, hops, onions and root crops have the greatest requirements for sulfur[2,3].

One of sulphates applied to granular fertilizers, that serve as a source of sulfur, is calcium sulphate. The raw material for the future fertilizer with a content of 24% N and 6% S is anhydrite, anhydrous calcium sulphate - a natural raw material from Gemerská Hôrka.

Introduction

The crystal modification of calcium sulfate particles has different effects on the properties of the melt during the preparation of NS – fertilizer and on the whole technological process of granulation. The different types of $CaSO_4$ crystals obtained behave very differently when added to water or to a hot ammonium nitrate melt. The contact of calcium sulfate dihydrate and ammonium nitrate ends in unstable granulation, due to a highly viscous melt, although with a high-water content. Calcium sulfate dihydrate cannot be used direct for the production of granular ammonium nitrate containing $CaSO_4$. Gypsum dihydrate is transformed in an environment of increased temperature into different types of hemihydrates, alpha (α) or beta (β), and subsequently into different types of anhydrous calcium sulfate[4]. Heating the dihydrate in the presence of high-water vapor pressure produces an α - hemihydrate, while in the presence of atmospheric pressure, a β-hemihydrate[5] is formed. In its natural form, it occurs as the mineral bassanite[6].

In addition to calcium sulfate hydrates, there are two types of anhydrous calcium sulfate, the hexagonal (γ- $CaSO_4$) and orthorhombic (β- $CaSO_4$) forms. The γ- form is formed by dehydration of hydrates and is considered metastable[7]. The natural raw material consists of the β- form of $CaSO_4$.

The aim of this work is to verify the possibility of preparing granulated NS – fertilizer from ammonium nitrate with the addition of natural anhydrite and to compare its qualitative properties with granulated ammonium nitrate and dolomite.

Characteristic of anhydrite

Anhydrite as a natural raw material comes from the Gemerská Hôrka locality in Slovakia. Based on XRD – phase analysis, the following components were identified in the anhydrite: anhydrous calcium sulfate $CaSO_4$, calcium sulfate dihydrate $CaSO_4.2H_2O$ and dolomite $CaMg(CO_3)_2$. Phases were identified in ground dolomite: dolomite $CaMg(CO_3)_2$, quartz SiO_2 and magnetite Fe_3O_4.

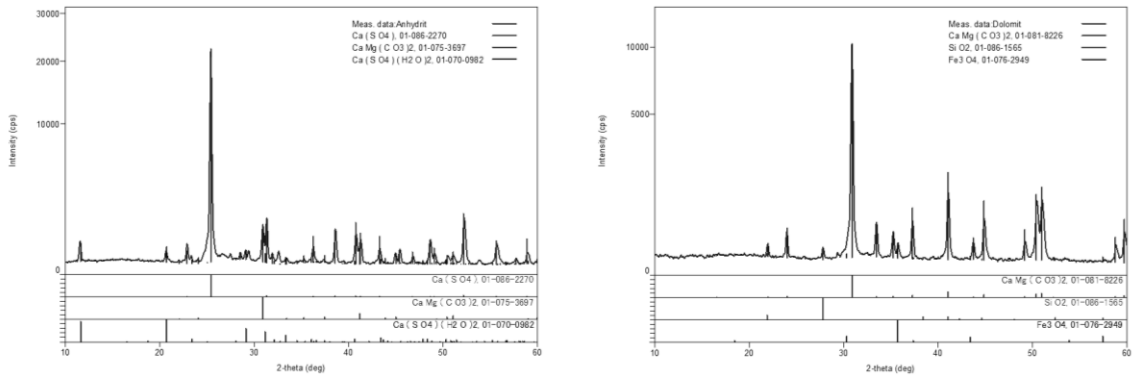

Figure 1. X-ray diffraction analysis (XRD) of anhydrite (on the left) and dolomite (on the right)

Used ammonium nitrate was with a concentration of 98%. The ground anhydrite and dolomite were applied for preparation of the fertilizer, where the particle size distribution was measured.

Table I.
Particle size distribution of anhydrite and dolomite

Particle size distribution	Anhydrite		Dolomite	
	with ultrasound	without ultrasound	with ultrasound	without ultrasound
Diameter at 10%, µm	1.56	1.51	2.27	2.59
Diameter at 50%, µm	16.44	16.03	20.18	25.87
Diameter at 90%, µm	51.29	52.26	63.02	81.05
Mean diameter, µm	22.026	22.08	27.41	35.26

Fertilizer preparation

Granulated fertilizers ammonium nitrate with dolomite (LAD) containing 27% nitrogen and ammonium nitrate with anhydrite containing 24% nitrogen, 6% sulfur were prepared by screw granulation of the melt and the recycle. The temperature of the melt before granulation was 150 °C. Granulation of the melt with the recycle was followed after the addition of dolomite or anhydrite. Drying of the granulate was at a temperature of 105 °C for the same time of 60 minutes. It is important to compare the physicochemical parameters of the anhydrite – containing fertilizer with the LAD quality that corresponds to the standard product.

Table II.
Chemical analysis of fertilizer

Chemical analysis	Fertilizer samples					
	LAD 1.gran.	LAD 2.gran	LAD 3.gran.	NS 1.gran.	NS 2.gran.	NS 3.gran.
N_{total}, %	26.69	26.71	26.71	24.08	24.05	23.99
$N_{ammon.}$, %	13.29	13.26	13.34	11.83	11.84	11.88
S_{total}, %	0.112	0.108	0.119	5.8	5.77	5.87
$S_{water\ soluble}$, %	0.106	0.106	0.116	3.69	3.87	3.82
Ca_{total}, %	5.04	4.93	4.85	7.96	7.93	7.96
$Ca_{water\ soluble}$, %	1.52	1.79	1.63	5.05	5.03	4.92

Contents of the water-soluble calcium and sulfur were determined based on procedures for the determination of water-soluble components according to EN regulations[8]. In NS – fertilizer with anhydrite, the content of water – soluble sulfur is 63–67% in relation to its total content. In the case of the content of water-soluble calcium, considering its total content, it is approximately 61–63%.

Subsequently, measurements of physicochemical parameters of the fertilizer samples were made: content of water in the product, dustiness, fertilizer abrasion, point strength and caking.

Table III.
Qualitative parameters of fertilizers

Quality parameter	Fertilizer samples					
	LAD 1.gran.	LAD 2.gran	LAD 3.gran.	NS 1.gran.	NS 2.gran.	NS 3.gran.
H_2O, %	0.20	0.12	0.22	0.32	0.28	0.27
Dustiness, %	0.02	0.03	0.02	0.02	0.02	0.03
Abrasion, %	0.71	0.96	0.73	0.06	0.52	0.53
Point strength, N	63.9	73.7	73.2	91.7	91.8	92.3
Caking, N	174.5	141.95	139.5	113.5	144.8	168.2

The water content in the fertilizer with the application of natural anhydrite is higher due to the presence of calcium sulfate dihydrate in the raw material. A significant improvement in the quality of NS – fertilizer was noted in the case of high point strength, dustiness and abrasion were reduced. The caking of NS – fertilizer is considered or lower than LAD. The effect of increased water content in the product, compared to ammonium nitrate with dolomite, was not manifested in the quality of the fertilizer with anhydrite.

Thermal cyclization of granular ammonium nitrate with dolomite and with anhydrite

One of the most important factor that affects the quality of fertilizers with a high ammonium nitrate content is the fertilizer's resistance to temperature attacks.
Ammonium nitrate shows by default 7 crystallographic modifications with phase transition temperatures (°C): 125,2 (I-II), 84,2 (II-III), 32,3 (III-IV), -18 (IV-V), -103 (V-VI), -170 (VI-VII).

Table IV.
Phase transitions of ammonium nitrate, temperature, and related changes in volume[9]

Changes	Phase transition				
	Liquid -> I	I →II	II →III	III → IV	IV → V
Temperature, °C	169.9	125.2	84.2	32.3	-16.9
Volume change, %		1.9-2.1	1.3-1.6	3.4-3.6	0.9-2.9
ΔH, $J.g^{-1}$	73.7	52.6	15.5	18.4	5.9
Direction of volume change		Decrease	Increase	Decrease	Increase

For testing the fertilizer against temperature fluctuations during storage, the procedure for thermal stress cycles for fertilizers with a high nitrogen content according to EN 2003/2003[8] was applied. The tests are carried out at a temperature of 50°C. The fertilizer is placed in a closed container so that the influence of external moisture is excluded.
100 g of fertilizer is poured into a 250 ml Erlenmeyer flask. The granulometry of the used fertilizer is 3.15 mm and 4 mm in a weight ratio of 1:1. We place the banks with fertilizer in a drying oven at a temperature of 50 °C for 2 hours, then take them out and let them cool down at a temperature of 25 °C. The procedure is repeated 6 times. 1 cycle lasts 4 hours (2 hours heating, 2 hours cooling). After thermal cycling test of the sample, we measure the granulometry and abrasion.

Table V.
Sieve analysis of granular fertilizer before and after LAD fertilizer thermal cycling test

The content of the fraction on the site, %	Fertilizer samples					
	LAD 1.gran.		LAD 2.gran.		LAD 3.gran.	
Number of cycles	0	6	0	6	0	6
The bottom	0.00	0.17	0.01	0.15	0.01	0.15
0.560 mm	0.00	0.08	0.00	0.07	0.00	0.27
1 mm	0.00	0.16	0.00	0.20	0.00	0.19
2 mm	2.00	1.22	3.49	2.44	2.42	1.22
3.15 mm	48.48	42.95	48.95	47.95	49.24	43.43

4 mm	48.29	47.84	47.05	46.96	45.81	49.61
Over the sieve 5 mm	1.23	7.58	0.50	2.23	2.51	5.14
Under the sieve 2 mm	0.00	0.41	0.01	0.42	0.01	0.61

Table VI.
Sieve analysis of granulated fertilizer before and after the NS – fertilizer thermal cycling test

The content of the faction on the site, %	Fertilizer samples					
	NS 1.gran.		NS 2.gran.		NS 3.gran.	
Number of cycles	0	6	0	6	0	6
The bottom	0.00	0.03	0.00	0.05	0.00	0.01
0.56 mm	0.00	0.01	0.00	0.04	0.00	0.01
1 mm	0.00	0.03	0.00	0.10	0.00	0.01
2 mm	1.93	0.26	2.77	0.67	6.07	2.48
3.15 mm	49.74	43.07	49.07	42.71	49.37	46.14
4 mm	47.10	49.51	47.04	50.17	43.92	45.79
Over the sieve 5 mm	1.23	7.09	1.12	6.25	0.63	5.56
Under the sieve 2 mm	0.00	0.07	0.00	0.19	0.00	0.03

The abrasion resistance and the granulometry of the fertilizers are tested after thermal cycling test. They describe how the fertilizer will behave during further handling, how resistant the fertilizer will be. When the fertilizer is handled, not only dust particles are peeled off, that is why the percentage content of the shares under the 0.560 mm sieve and under the 1 mm sieve are indicated.

Table VI.
The results of abrasion of LAD and NS fertilizer after thermal cycling test, content of the shares under sieve 0.560 mm and 1 mm

Abrasion of fertilizer, %	Fertilizer samples					
	LAD 1.gran.	LAD 2.gran	LAD 3.gran.	NS 1.gran.	NS 2.gran.	NS 3.gran.
Under the sieve 0.560 mm	4.721	2.388	1.535	0.488	1.762	0.722
Under the sieve 1 mm	4.916	2.562	1.616	0.530	1.809	0.780

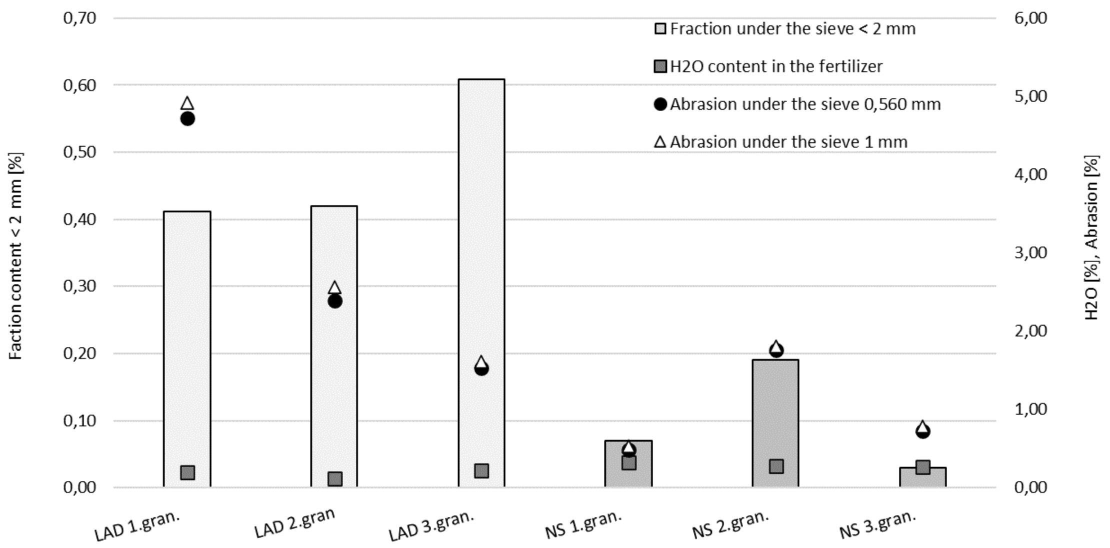

Figure 2. Content of the fraction under the 2 mm sieve after sieve analysis after thermal cycling test, abrasion of the fertilizer under the 1 mm and 0.560 mm sieves, water content in the product

Discussion and result analysis

The increased water content in NS – fertilizer is caused by the presence of calcium sulfate hemihydrate $CaSO_4.0.5H_2O$ in the product. It was formed by dehydration of $CaSO_4.2H_2O$ in an ammonium nitrate environment at a temperature of 150 °C.

Calcium sulfate is included in the production of fertilizers with a high content of ammonium nitrate among the additives that have a stabilizing effect against explosiveness. They are often used to increase the strength of the particles and improve resistance to the phase transition of ammonium nitrate[10].

This was confirmed in the case of NS – fertilizer granulation, where the application of natural anhydrite increased the point strength of the granules by approx. 30%. The fertilizer has excellent resistance to thermal attacks and abrasion. In general, there was a significant improvement in quality parameters compared to ammonium nitrate with dolomite.

Conclusion

The contribution describes the application properties of anhydrite as part of granular NS – fertilizers. As a source of sulfur and calcium, anhydrite was often applied in the agricultural area in the form of so-called superphosphate. Nevertheless, the fact that anhydrite is considered a relatively stable material, it leaches into the soil in 6 weeks and the release rate depends on the particle size[11].

It is possible to prepare a high-quality fertilizer containing nitrogen, calcium and sulfur from natural anhydrite. Compared to classic granular ammonium nitrate, despite the higher water content, the fertilizer has comparable or even better-quality parameters. A more significant difference in favour of NS – fertilizer is in the results of measurement of abrasion. The fertilizer is more abrasion-resistant, which was also evident after the thermal cycling test.

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References

1. Jäger J., Hegner P.: Kvalita tuhých průmyslových hnojiv, SNTL, Praha, 1987
2. Fertilizer International, Number 497, July / August 2020
3. Fecenko J., Ložek O.: Výživa a hnojenie poľných plodín, SPU v Nitre, 2000
4. Vanmarcke L., Verhaegen P., Elderson R., Stevens R.: Process for producing a ns-fertilizer, Intl. Patent Appl. Publ. WO 2001098233A1
5. Kuthadi S. K.: Laboratory Scale Study of Calcium Sulfate Hydration Forms, Western Kentucky University, 2015
6. Clifton J. R.: Thermal Analysis of Calcium Sulfate Dihydrate and Supposed, α and β Forms of Calcium Sulfate Hemihydrate from 25 to 500 °C, Institute for Applied Technology, Washington, D.C.,1971
7. Ballirano P., Melis E.: The thermal behaviour of γ-CaSO4, Phys Chem Minerals, 2009
8. EN 2003/2003
9. Kiiski H.: Properties of Ammonium Nitrate based fertilisers, University of Helsinki – Finland, Helsinki 2009
10. Laurent B., Kemira S.A., Belgium: Straight Ammonium Nitrate Granule-Prill Fertilizer Stabilization: Theoretical Possibilities, IFA Technical Conference, Chennai, India, 2022
11. Lobb W. R., Rothbaum H. P.: The use of anhydrite as a fertiliser, New Zealand Journal of Agricultural Research, Volume 12, 1969

MATERIALS ENGINEERING

BIOACCUMULATION OF ZINC FROM OZONATED TIRE GRANULATE BY TERRESTRIAL ORGANISMS

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Abstract

Waste tires from traffic can be used for many purposes, including insulation materials in building engineering. An interesting possibility seems to be their application as granules. Ozonation can be one of the ways to better break down tires and get granules from them. However, various organic or inorganic substances can be released from them during their production or use. It can lead to a risk for both environment and humans. Zinc belongs to important potential toxic elements. For that reason, the toxicity and bioaccumulation of zinc from ozonated tire granules were studied on earthworms *Eisenia fetida* (28 days-bioassay) and on mustard plant species *Sinapis alba* (4 day-bioassay). The results indicated no mortality for earthworms. The toxicity for plants was though observed; it was manifested in the form of root inhibition. Bioaccumulation of zinc was confirmed for both organisms. The measured amounts of zinc were higher in earthworms than in plants. The use of rainwater in the plant test was found to decrease the toxicity and bioaccumulation, as compared with distilled water.

Introduction

Waste human products represent an important emission of pollutants into the environment, the end-of-life tires (ELTs) from traffic being a characteristic example in that respect. Such waste tires are produced in the amount of many tones during a year[1] and there is necessary to get rid of them in an ecological way or to use them as a filling of recycled materials. They can be used for example at the production of asphalt, as a filler in cement composites, or for insulation materials by using rubber crumb produced by tire crushing[2,3,4].

Polycyclic aromatic hydrocarbons, amines and inorganic elements are the most danger substances that can be often found in them during their life cycle[5]. For this reason, there is necessary to verify that no dangerous substances are released when they are reused in practical applications. While the analysis of PAHs is very demanding due to their volatility and the presence of many structurally very similar substances or their N/O/S-heterocycles (their analysis requires various combinations of expensive chromatographic methods), the analysis of elementary zinc is usually very simple using ICP or AAS[6,7,8,9,10].

There is also suitable to use various biological methods as additional supplement of chemical analysis. Biological assays include ecotoxicological tests and bioaccumulation tests. The ecotoxicity tests indicate if the samples or their eluates or tested compounds can be dangerous for environment, especially for microorganisms, plants or animals[11]. Ecotoxicity of zinc was confirmed for many aquatic and terrestrial organisms. There are more than four thousand papers in the Web of Science on that topic. Zinc effects were recognized from several ng to mg in dependence on tested species and cultivated medium[12-17].

One of the most used organisms are earthworms, thanks to their high importance in soil ecosystems. The used plants include mainly some grasses and cultivated crops and fodder species. One of such plant group are cruciferous plants (*Brasicacae*), which have been proven to be able to accumulate zinc and can thus also be used for remediation[15,17].

The bioaccumulation of zinc has not been studied frequently in the past and its uptake from ELTs has been analyzed very rarely[5,12,15]. All studies used also moistening by distilled water in the case of contact tests or as a solution for some substances or preparation of eluates. However, nobody has been tried to use rainwater instead of distilled water in such types of studies. Scientific papers interested in a toxicity of rubber tire products have been also very rare[19-25].

In this paper, the ecotoxicity and bioaccumulation of ELTs in a form of small ozonated granules prepared for further use in building industry were studied on earthworms (Eisenia fetida) and terrestrial plants (Sinapis alba). These two organisms belong to the most often used model organisms in terrestrial ecotoxicology and they such combine adequate approaches for testing of tires granules for terrestrial application. The mortality of adults was analysed after 28 days of exposure and prolongation of plant roots after 4 days of exposure. Accumulation of zinc in both organisms was analysed after finishing the testing periods.

Simulation and experiment

Materials

Rubber crumbs originating from ELTs were used as tested materials. The rubber crumb particles having a diameter up to 10 mm were studied. The granules are shown on the Figure 1. The chemical analyses of the tested granulates are described in Fořt et al.[5]. The process of ozonation is described in[26].

Figure 1. Ozonated tire-granulates sample.

Biological assays

Test with earthworms

Adult earthworms of species *Eisenia fetida* were purchased from Zoo Braník Ltd., Prague. The test on earthworms was performed according to the appropriate OECD guideline[27] but some modifications were done. The LUFA 2.2 soil II (Speyer Ltd., Germany) was used as a control substrate. 100 g of dry control or tested substrate was put into square plastic test vessels. The substrates were adjusted to 50% humidity by distilled water or rainwater. The next day, 10 adult earthworms were added into each test vessel. The earthworms were fed by a special food Wormňam (1 g/test vessel)[28] once a week. Three replicates were prepared for control and for tested samples. The experiment lasted 28 days and after this period, the adult earthworms were removed from control or the tested substrate. They were rinsed in distilled water from the substrate and gently dry with a paper tissue. They were weighed (all earthworms from one test container together), then placed into a plastic bag and frozen at -80°C for chemical analysis.

Test with plant species (mustard)

Seeds of species *Sinapis alba* were purchased from Aros-osiva, Ltd., Prague. Inhibition of roots was the measured endpoint after 96 hours of exposure [29]. The test was performed as an aquatic test with filter paper moistened by distilled water or rainwater as control media or by the eluate (5 ml of aquatic solution) from tire granulates as test medium. Ten pre-germinated seeds were inserted on the filtrate papers in each Petri dish (10 cm in a diameter). Petri dishes were then closed by lids, wrapped in foil and placed in the thermostat at (20 ± 2) °C in dark. After finishing the test, the plants were removed from Petri dishes and length of their roots was measured by a rule (in mm). They were then weighed (all plants from one test dish together), then placed in a plastic bag and frozen at -80°C for chemical analysis.

Preparation of leachates

Two types of leachates were prepared for chemical analysis:
Leachate of rubber articles (the eluate was also used in the biological test with plants)
Leachate of control soil (the bioassay with earthworms).

100 g of rubber particles or control soil was used to prepare 1 l of leachate. The prepared mixtures were stirred for 24 hours on a head-to-heel shaker Reax 20/4. After 24 hours, the extracts were filtered through paper filter (Whatman, grade 6) and used for the chemical analysis or for the ecotoxicity test (*S. alba* test). All types of leachates were prepared for adjustment by distilled water or rainwater.

The rainwater was of natural origin, it was collected a week before the start of the experiments in a sterile plastic canister in the courtyard of the Faculty of Civil Engineering. It was kept in a refrigerator before use in tests and before a chemical analysis. Pure distilled water and the rainwater were analyzed as backgrounds.

Chemical analyses of zinc

Biological samples (earthworms, plants) were vacuum freeze dried in Christ Alpha 1–4 and digested in mixture of nitric acid and peroxide (v/v 5:1). High pressure digestion was performed in microwave station Milestone Ethos Touch Control. After digestion samples were diluted to the volume 10 ml. The eluates from tires were stabilized by nitric acid (0.1 ml of acid into 100 ml of sample) and kept refrigerated. For the analysis of Zn, atomic absorption spectrometry with flame atomization (AAS iCE 3500Z Thermo Scientific) was used. Calibration standard was prepared from Certified Reference Materials CPAChem, Ltd.

Statistical analyses

Ecotoxicological data were expressed as inhibition of measured endpoint of 100% eluate or 100% solid mixture in a comparison with the control value according to the equation

$$\mathrm{I}\ (\%) = \frac{(\mathrm{C{-}N})\ .100}{C} \quad (1)$$

where:
I … inhibition,
C … measurable value for control medium,
N … measurable value for medium containing tire particles or for leachate.

The selected ecotoxicological data were evaluated using the one-way analysis of variance (ANOVA), by means of the GraphPad InStat software (InStat version 3, San Diego, CA, USA). The multiple-comparison Tukey–Kramer test was performed at 0.05 significance level.

Results and discussion

Ozonated tire granulates were not toxic for earthworms, no mortality or 1% inhibition of surviving was found. On the other hand, inhibition of plant roots was observed – 81% for granulates moistened by distilled water and 17% for granulates moistened by rainwater (Figure 1). The ecotoxicity of tire-granulates moistened by distilled water (TG-DW) in plant test was statistically significant in comparison with the other samples. Our results cannot be adequately compared with data from the other published studies because ozonated granulate has been firstly studied just in the present study. Nevertheless, previously published data indicate that earthworm *E. fetida* exposed to zinc grew slower than control worms, matured later and produced fewer or no cocoons[13]. 100% mortality of earthworms was also found for species *Eisenia fetida* but only 31% inhibition of root prolongation of species *S. alba*[5] if tires were not destructed by ozone process.

In another study the authors found that aged crumb rubber and new crumb rubber appeared to pose similar toxic risks to earthworms[30]. The accumulation of zinc especially from rubber was also described for plants [31], but not for *S. alba*. There a rubber ash was used as a source of Zn having the ability to increase yield of rice and at the same time decrease Cd accumulation from soil. This fact is important in the comparison of granulates moistened by rain and distilled water in the present study. Rainwater probably contains various elements that could affected bioavailability of zinc to *S. alba* leading to lower toxicity (Figure 1). A similar toxic effect of zinc was confirmed also in a study of[17], where the author tested aquatic solutions of zinc. In any case, there is necessary to say that the toxicity of rubber can be affected by many factors, especially by rubber chemical composition, its ageing when volatile compounds can be released from them to air and by specific conditions of used bioassays or model organisms. The discrepancies in toxicity between rain and distilled water are more evident if the pure eluate is used (the plant bioassay) instead of the solid test with earthworms where a lower effectivity of rainwater composition can be expected.

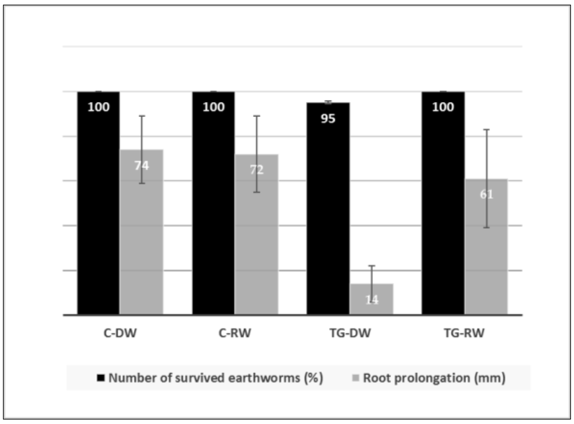

Figure 2. Ecotoxicity of tire granulates for earthworms *E. fetida* and seeds of *L. sativa*: C-DW = control medium moistened by distilled water, C-RW = control medium moistened by rainwater, TG-DW = tire granulates moistened by distilled water, TG-RW = tire granulates moistened by rain water.

The AAS analysis of solid and liquid samples confirmed the presence of zinc in all samples with the exception of distilled water and food for earthworms (see Table I.). It is generally known that rainwater can contain many organic and inorganic substances from the environment, but it is impossible to detect the presence of all theoretical chemicals found there. For this reason, only zinc was detected not only in rainwater, but in all tested matrices. If we know the levels of elements in biota, we can estimate the zinc concentration based on the weight of used organisms (see Table II. and Table III.). The earthworms' data show that "pure" earthworms contained relatively high amounts of zinc before the use in the present experiment (Table I.). Nevertheless, they were able to accumulate also the zinc from the tire granulates (Table III.). It is evident that earthworms contained at least zinc in control LUFA soil moistened by distilled water. The zinc concentration in such earthworms was negligible. The other biota samples had two orders of magnitude higher zinc concentration than this baseline control. The control LUFA soil moistened by rainwater had numerically lower zinc level than tire granulate with rainwater, and tire granulate with distilled water contained the highest amount of zinc. Nevertheless, the toxicity of samples was not found and so we can conclude that such zinc concentration, together with the other leached chemicals from tire granulates, was not the limiting factor for surviving of earthworms in the present study.

Table I.
AAS analysis of Zn in background samples – distilled water, natural rainwater and the eluates of control LUFA 2.2 soil and tire sample, earthworms purchased from a firm before use in an experiment. Purchased food for earthworms, 5 g of soil, earthworms, granules or food was added to 50 ml volume of solution.

Distilled water	Rainwater	Eluate from LUFA 2.2 soil	Eluate from waste tires	Earthworms (after purchase)	Food for earthworms
(mg/L)					
< 0.001	0.063	0.032	19.452	0.528	< 0.001
(mg/kg)					
-	-	0.320	194.520	87.405	< 0.001

Table II.
Mean weight of earthworms (*E. fetida*) after 28 days of exposure.

Replicate	Control – Distilled water (g)	Control – Rainwater (g)	Granulates + Rainwater (g)	Granulates + Distilled water (g)
1	4.80	5.15	3.90	4.25
2	4.88	4.76	3,73	4.01
3	4.96	5.59	4.40	4.02
Mean weight of ten earthworms (g)/test vessel	4.09	5.17	4.01	4.13
SD	0.08	0.42	0.35	0.14
Mean weight of one earthworm	0.41	0.52	0.40	0.41

Table III.
Zinc mean values of earthworms (*E. fetida*) measured by AAS.

Replicate	Control – Distilled water (mg/kg)	Control – Rainwater (mg/kg)	Granulates + Rainwater (mg/kg)	Granulates + Distilled water (mg/kg)
1	96.176	334.046	469.965	370.294
2	84.989	240.224	423.752	574.721
3	88.716	263.000	307. 432	428.977
Mean values	89.960	279.090	400.383	457.997
SD	5.696	48.937	83.749	105.258
Zn mean value minus Zn concentration in worms before sta of the test (mg)	2.555	191.685	312.978	370.592
Zn – mean level in c earthworm (mg)	0.001	0.099	0.126	0.153

Roots of species *S. alba* were weighed (see Table IV.) and these were used for the determination of zinc concentration in plants (Table V.). It is evident that numerically the lowest residues were found in the rank order: control – distilled water < control – rainwater < tire granulates – rainwater < tire granulates – distilled water (Table V.) but the values were relatively similar in comparison to the values from the earthworm's test (Table III.). Order-of-magnitude similar zinc values in mustard roots were observed in the study[32] where the zinc residues in roots were in a range from 64 to 138 mg/kg in different soil samples. The data confirmed that this mustard species was generally able to intake similar zinc levels from soil as from tire granulates. The authors of[33] described that *S. alba* plants accumulated less Mn a Zn in the presence of sulfur. It indicated antagonistic effects of individual substances leading probably to lower competition of various substances in tire eluates or directly in rainwater (see Figure 1 and Table V).

Table IV.
Mean weight of plants (*S. alba*) + their standard deviations (SDs) after 72 hours of exposure. 10 plants were used for each the dish.

Replicate	Control – Distilled water (g)	Control – Rainwater (g)	Granulates + Rainwater (g)	Granulates + Distilled water (g)
1	0.963	0.975	0.945	0.995
2	0.960	0.957	0.922	0.968
3	0.979	0.944	0.925	1.013
Mean values/dish	0.967	0.959	0.931	0.992
SD	0.010	0.016	0.013	0.023
Mean weight of one plant	0.097	0.096	0.093	0.099

Table V.
Zinc mean values in plants (*S. alba*) + their standard deviations (SDs) measured by AAS. 10 plants were used for each the dish.

Replicate	Control – Distilled water (mg/kg)	Control – Rainwater (mg/kg)	Granulates + Rainwater (mg/kg)	Granulates + Distilled water (mg/kg)
1	49.677	85.831	137.142	237.899
2	102.033	151.187	121.343	267.416
3	99.843	76.603	109.186	240.683
Mean values	83.851	104.540	122.557	248.666
SD	29.616	40.660	14.018	16.298
Zn - mean level in one plant (mg)	0.008	0.010	0.011	0.025

Conclusions

Ecotoxicity and bioaccumulation of zinc from ozonated tire granulate was analyzed in the solid test with earthworm species *E. fetida* and in the aquatic test with plant species *Sinapis alba*. The tire granulates did not have any effect on the surviving of earthworms. Zinc was accumulated by both organisms; the higher zinc residues were found in earthworms. The use of rainwater in the aquatic solution in the plant test decreased the toxicity and bioaccumulation in a comparison with distilled water.

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References

1. Bianco I., Panepinto D., Zanetti M.: Appl. Sci. *11*, 3599 (2021).
2. Landi D., Gigli S., Germani M., Marconi M.: Waste Manag. *75*, 187 (2018).
3. Strukar K., Sipos T. K., Milicevic I., Busic R.: Eng. Struct. *188*, 452 (2019).
4. Wang J. Q., Du B.: J. Build. Eng. *32*, 7 (2020).
5. Fořt J., Kobetičová K., Böhm M., Podlesný J., Jelínková V., Vachtlová M., Bureš F., Černý R.: Polymers *14*, 1416 (2022).
6. Saljooghi A. S., Fatemi S. J., Afzali D.: Bull. Chem. Soc. Ethiop. *24*, 127 (2010).

7. Taverniers I., Loose M. D., Bockstaele E. V.: Trends Anal. Chem. *23*, *535* (2004).
8. Ardestani M. M., van Straalen N. M., van Gestel C. A. M.: Environ. Pollut. *193*, 277 (2014).
9. Peijnenburg W. J. G. M., Posthuma L., Zweers P. G. P. C., Baerselman R., de Groot A. C., Van Veen R. P. M.: Ecotoxicol. Environ. Saf. *43*, 170 (1999).
10. Posthuma L., Baerselman R., Van Veen R. P. M., Dirven-Van Breemen E. M.: Ecotoxicol. Environ. Saf. *38*, 108 (1997).
11. Filser J., Koehler H., Ruf A., Römbke J.: Basic Appl. Ecol. *9*, 346 (2008).
12. Smit, C. E.; Van Gestel, C. A. M. Environ. Toxicol. Chem. *17*, 1132 (1998).
13. Reinecke A. J., Reinecke S. A.: Pedobiol. *40*, 439 (1996).
14. Sestinova O., Findorakova L., Hancul'ak J., Fedorova E., Spaldon T.: Terrestrial Eco-Toxicological Tests as Screening Tool to Assess Soil Contamination in Krompachy Area. In: IOP Conference Series-Earth and Environmental Science, Prague, Czech Republic, 5–9. September 2016.
15. Fargasova A.: Biol. Plant *44*, 471 (2001).
16. Kral'ova K., Masarovicova E., Gyoryova K.: Inhibition of photosynthetic electron transport in spinach chloroplasts and chlorella vulgaris and reduction of *Sinapis alba* L. growth by some Zn(II) compounds. In: 7th Regional Meeting of the Central and Eastern European Section, Brno, Czech Republic, 14–16 October, 2002.
17. Fargasova A.: Plant Soil Environ. *50*, 33 (2004).
18. Vasile G. G., Tenea A. G., Dinu C., Iordache A. M. M., Gheorghe S., Mureseanu M., Pascu L. F.: Int. J. Environ. Res. Public Health *18*, 12947 (2021).
19. Rhodes E. P., Ren Z. Y., Mays D. C.: Environ. Sci. Technol. *46*, 12856 (2012).
20. Wik A., Nilsson E., Kallqvist T., Tobiesen A., Dave G.: Chemosphere *77*, 922 (2009).
21. Fahad S., Hussain S., Khan F., Wu Ch., Saud S., Hassan S., Ahmad N., Gang D., Ullah A., Huang J. L.: Environ. Sci. Pollut. Res. *22*, 12439 (2015).
22. Gualtieri M., Andrioletti M., Mantecca P., Vismara C., Camatini M.: Fibre Toxicol. *2*, 1 (2005).
23. Capolupo M., Sorensen L., Jayasena K. D. R., Booth A. M., Fabbri E.: Water Res. *169*, 115270 (2020).
24. Lu F. X., Su Y., Ji Y., Ji R.: *Bull. Environ. Contam. Toxicol*. *107*, 651 (2021).
25. Marwood C., McAtee B., Kreider M., Ogle R. S., Finley B., Sweet L., Panko J.: Ecotoxicol. *20*, 2079 (2011).
26. Fořt J., Zámyslický J.: Alternative production of rubber crumb by accelerated aging of waste tires by ozone. In AIP Conference Proceedings 2275, Melville, NY: AIP Publishing, APL, the American Institute of Physics, 2020.
27. OECD 2015, OECD Earthworm Reproduction Test (*Eisenia fetida*/*Eisenia andrei*), Paris, France.
28. Wormňam. Available online: https://www.zizaly.com/products/wormnam/(accessed on 22. December 2022).
29. OECD 2006, OECD Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test. Paris, France.
30. Pochron S., Nikakis J., Illuzzi K., Baatz A., Demirciyan L., Dhillon A., Gaylor T., Manganaro A., Maritato N., Moawad M.: *Environ. Sci. Pollut. Res*. *25*, 11376 (2018).
31. Fahad S., Hussain S., Khan F., Wu C., Saud S., Hassan S., Ahmad N., Gang D., Ullah A., Huang J. L.: *Environ. Sci. Pollut. Res*. *22*, 12439 (2015).
32. Vasile G. G., Tenea A. G., Dinu C., Iordache A. M. M., Gheorghe S., Mureseanu M., Pascu L. F. Int. J. Environ. Res. Public Health *18*, 12947 (2021).
33. Jankowski K. J., Budzynski W. S., Kijewski L., Klasa A.: Plant Soil Environ. *60*, 364 (2014).
34. Price G. A. V., Stauber J. L., Holland A., Koppel D. J., Van Genderen E. J., Ryan A. C., Jolley D. F.: Environ. Sci.: Processes Impacts *24*, 783 (2004).
35. Di Toro D. M., Allen H. E., Bergman H. L., Meyer J. S., Paquin P. R., Santore R. C.: Environ. Toxicol. Chem. 20, 2383 (2001).

ECOTOXICITY AND BIODEGRADATION OF GLUE ON THE BASE OF ISOCYANATE

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Abstract

In the area of adhesive intended for load-bearing wooden elements, the priority is currently to use adhesive with the lowest possible impact on the environment, which at the same time do not contain formaldehyde. One option is to use polyurethane glue. However, adhesives are generally materials for which ecotoxicity or biodegradation has been practically very poorly studied, and their environmental assessment is usually based only on theoretical calculations of the toxicity of the individual substances in the adhesive. The aim of this work was therefore to test the ecotoxicity/biodegradation of the selected glue after its hardening (Lignofix D4, STACHEMA CZ) on green algae (*Desmodesmus subspicatus*) and yeasts (*Saccharomyces cerevisae*). Toxicity was evaluated in aquatic tests on the prepared leachate from the glue and the water containing the tested glue. The results indicated any toxicity of eluates for yeasts and algae but toxicity of solution containing own glue for algae (31%). Biodegradaton and biocolonisation of hardened isocyanate glue is so probably possible by microorganisms according to the results of the present study.

Introduction

There is a large number of adhesives available on the market, which differ from each other not only in terms of use, but also in composition. The basic division is into natural (vegetable and animal) and artificial glues. A special group consists of one-component, isocyanate-based adhesives. These adhesives are produced by polyaddition of a polyol with an excess of isocyanate. These adhesives harden due to air humidity[1]. While the composition of adhesives for their useful properties are mostly described by the manufacturer to a sufficient extent, their toxicity is usually described on the basis of the toxicity of the individual components that make up the adhesive. This actually evaluates the liquid glue in the packet of the given composition. After its application and hardening, however, the toxic effects of solid adhesives are unknown and have not yet been described by manufacturers.

For this reason, one of the isocyanate adhesives available on the market was selected and tested in two ecotoxicity tests in this study. The first test is a test with freshwater algae to investigate the effect of glue on the amount of biomass in a 4-day experiment. The second model organism was the yeast Saccharomyces cerevisae, in which the influence of the adhesive on viability was evaluated after 24 hours of exposure. Both organisms were exposed to glue leachate as well as exposure to glue mixture with distilled water directly.

The aim of this study was to determine the toxicity of the glue for both organisms, to compare their sensitivity and also to compare the toxic effect of the leachate and the mixture of glue in water. The results were discussed with the toxicity of the individual components from the safety data sheet[2] of the given adhesive.

Adhesives are also used for gluing of building elements, the isocyanate one is often used for gluing wood[3,4,5]. However, wood is one of the materials that can be subject to biological degradation[6,7,8]. For this reason, in addition to ecotoxicity, the effect on potential biodegradation was also discussed, as both model organisms (algae, yeasts) represent groups of organisms that can participate in the colonisation of wooden building structures together with other organisms (bacteria, fungi, moulds, lichens).

Experiment

Chemicals

Glue called Lignofix D4 was purchased from the STACHEMA CZ, Czech Republic). It composes of diphenylmethan-2,4; isocyanate; and its isomers and homologs[2]. Buffer and 3-[4,5-dimethylthiazol-2-yl]-2,5-difenyltetrazolium bromide (5 g/L) were purchased from the company Merck Life Science, Ltd. (Czech Republic).

Preparation of leachates

Hardened and cut glue was used to prepare the leachate (in a ratio 1:10 for the sample: the distilled water). The prepared mixture was stirred on a head-to-heel shaker Reax 20/4 for 24 hours. After that, the extract was filtered through paper filter (Whatman, grade 6) and used for the chemical analysis or for the ecotoxicity tests.

Figure 1. Cured glue

Organisms

Yeasts (strain *Saccharomyces cerevisae*) were donated by the Research Institute of Brewing and Malting (Prague, Czech Republic). The algal species *Desmodesmus subspicatus* was purchased from the Botanical Institute of AV CR (Třeboň, Czech Republic).

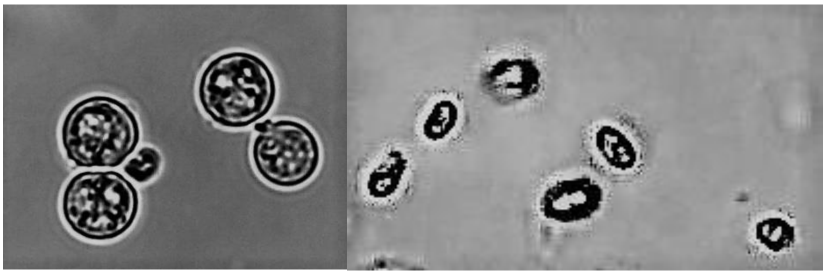

Figure 2. Yeasts of species *Saccharomyces cerevisae* (in the left) and green algal species *Desmodesmus subspicatus* (in the right).

Bioassay with algae

The appropriate amount of algal biomass corresponding to the concentration 10,000 cells/ml was added to each test flask with the whole volume 25 ml of solution[9]. The concentration of algal cels was calculated on the base of microscopical observation under a light videomicroscope DSM. Five replicates of control (nutrient medium with algal inoculum), of eluate (the eluate with incolum) and distilled water with glue (with inoculum) were prepared. The flasks were stored in an incubator with light regime 12:12 (light:dark) at 20 ± 2 °C for 96 hours. The measured endpoint was algal biomass. The algal biomass was recorded as absorbance values spectrometrically at wavelength 750 nm and its inhibition was expressed in %s.

Bioassay with yeasts

The MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide) viability assay was performed according to the tested procedures[10] and was modified for the purposes of the present study. A 0.5 mL volume of yeasts (10,000 cells/ml) + 0.15 mL of phosphate buffer + 0.25 mL of sample (eluate or distilled water with own glue) or buffer (control) were mixed in one glass tube. Duplicates were performed for the control, the eluate and the suspension. The samples were incubated in the thermostat (30 ± 2 °C) in the dark for 24 hours. 3-[4,5-dimethylthiazol-2-yl]-2,5-difenyltetrazolium bromide (TTB) was added as a substrate (0.1 mL/tube) and the samples were incubated for one hour in the dark. A 9 mL volume of ethanol was then added into each tube. The blue product formazan was extracted after the next 24 h. The formazan is a product of microorganismal metabolism. Dead microorganisms are not able to produce it and its production is thus an indicator of microorganismal fitness and viability. The levels of formazan were measured spectrophotometrically at 485 nm (Jenway 6300 spectrophotometer).

Measuring of acidity and conductivity

Multimeter PC70$^+$ DHS (Italy) was used for measuring of pH values and conductivity of samples.

Measuring of inorganic elements

The quantity of leached elements in the water was done using inductively coupled plasma optical emission spectrometer Agilent 5110 SVDV (ICP-OES). The device was equipped with a SeaSpray glass concentric nebulizer and Autosampler SPS 4 (Agilent Technologies, USA). The general settings of the device were as follows: radio frequency power 1.2 kW; sample uptake delay 18 s; rinse time 18 s; peristaltic pump rate 80 rpm. Pure argon was used for the measurement (99.996%, Linde Gas, Prague) and the measurement conditions were as follows: replicates 3; stabilization time 15 s; replicate read time 10 s; peristaltic pump rate 12 rpm; plasma gas flow 12 L·min^{-1}; nebulizer flow 0.7 L·min^{-1}; auxiliary argon flow 1 L·min-1. The instrument was calibrated before the measurement using TUNE calibration solutions supplied by ANALYTIKA (Prague, Czech Republic) for the following elements: B, Ba, Cd, Co, Cr, Cu, Fe, Ca, Si, Mg, K, Hg, Mn, Ni, Al, Pb, Si, U, Zn. The quantification limits were determined as 10 times the relative standard deviation. ICP Expert Software v. 7.4 (Agilent Technologies, USA) was used for the evaluation.

Statistical analyses

Ecotoxicological data were expressed as inhibition of measured endpoint of 100% eluate or 100% solid mixture in a comparison with the control value according to the equation

$$\mathrm{I}\ (\%) = \frac{(\mathrm{C}-\mathrm{N})\,.100}{C} \qquad (1)$$

Where:
I … inhibition,
C … measurable value for control medium,
N … measurable value for medium containing glue or for leachate.

Discussion and result analysis

The results of the algal test indicate that the eluate caused stimulation of algal growth in comparison to control. On the other hand, the glue sample in distilled water caused 31% inhibition for algae (Table I.). The yeasts were not sensitive to presence of glue in solution as well the own eluate. They showed stimulation in growth and viability in comparison to control (Table II.). It seems that yeasts were less sensitive to glue than algae. This could be also caused probably shorter time of experiment (only 24 hours). It is possible that longer presence of glue pieces in water lead to a higher involving of possible toxic organic substances into the solution. The other reason of higher algal sensitivity could be a fact that algae are photosynthesizing organisms and need light to live. Thus, the presence of pieces of glue in the water probably led to light shielding, which was reflected in a lower algal biomass increase compared to the control and leachate. The reduced abundance values in the sample with glue could also be obtained due to the fact that part of the algae settled directly on the glue. This was observed and confirmed for yeasts, where pieces of glue were also stained purple after the addition of the MTT reagent (see Figure 3).

The pH value were not significantly different at the end of the experiment (Table III.), conductivity of all studied solutions were very low (Table III.). Chemical analysis (ICP) did not confirm presence of analysed elements (B, Ba, Cd, Co, Cr, Cu, Fe, Ca, Si, Mg, K, Hg, Mn, Ni, Al, Pb, Si, U) in the solution. They levels were under limit a detection. Only zinc residues were analysed in the samples, the most level was found in the sample containing glue and we can suppose that zinc was leached from glue in water (Table III.).

Authors Güclü and Ertan[11] described EC_{50} value for zinc and species *Desmodesmus subspicatus* as 2.26 mg/L. The same authors also describe that this species was able to remove around 40% of zinc from cultivated medium[11]. These conclusions are similar to the inhibition of algal growth in te ixture with glue where zinc levels were increased on 2.15 mg/L and the reduction of zinc in the eluate at the end of the test (compare Table I. and Table III.). However, ecotoxicity of cured glue has never been described and so we are not able to compare our results with data from the literature. The tested glue compost of isocyanates and their homologs or isomers and we can also suppose that some isocyanate units can be involve into the solution. In the present study, we did not analyzed cyanate residues in samples because it is very complacted thanks to polymer character of the tested sample. Toxicity of isocyanates to some organisms has been tested only in one study[12]. The authors tested toxicity of isocyanates on nematode Caenorhabditis elegans in various assays and found lethality, reproduction.

These additives caused lethality of nematodes lowest LC_{50} value at µg.L^{-1} levels, various degrees of inhibitions in body volumes and longevity, changes in DNA, oxidative stress, inhibition in locomotor and food intake/excretion behaviour and neurotoxicity.

Biodegradation of glue in polymer form is not possible to excluded in general, mainly if glues will be exposed for long times to the water environment. Some isocyanate units can be then involved into a water and caused some negative effects, but this aspect was not studied in the present research. It would be good to give more attention to this in further research.

Table I.
The absorbance values and evaluated inhibition (%) in the algal bioassay

Replicate	Absorbance		
	Control	Eluate	Sample
1	0.162	0.366	0.106
2	0.110	0.322	0.095
3	0.185	0.262	0.125
4	0.132	0.375	0.107
5	0.182	0.382	0.098
mean	0.154	0.341	0.106
Standard deviation (SD)	0.033	0.050	0.012
Inhibition	–	-1.214	0.311
Inhibition (%)	–	-121	31

Table II.
The absorbance values and evaluated inhibition (%) in the yeast bioassay

Replicate	Absorbance		
	Control	Eluate	Sample
1	0.168	0.429	0.318
2	0.290	0.464	0.210
mean	0.229	0.447	0.264
Standard deviation (SD)	0.086	0.025	0.076
Inhibition	–	-0.950	-0.153
Inhibition (%)	–	-95	-15

Figure 3. Photo of glue covered by yeasts confirmed by MTT assay (glue covered by live cells were coloured in violet, because the yeasts produced violet formazan).

Table III.
The properties (pH values, conductivity, zinc residues) of studied samples (demi water, the pure eluate of glue, the mixture of glue and demi water).

Property				
	Demi water	Pure Eluate	Eluate (96 hours)	Sample (96 hours)
pH value	7.02	7.10	6.96	6.80
Conductivity (μS/m) ± SD	7.71 ± 0.1	5.85 ± 0.2	4.34 ± 0.2	8.71 ± 0.1
Zinc (mg/L), SD = 0.23	0.00	0.06	0.03	2.15

Conclusion

- Eluates of glue caused positive effect on algal growth in comparison to water with presented solid sample (own glue) where toxicity around 31% was observed.
- Eluates and suspension of glue caused positive effect on yeasts – their viability.

- There is evident that selection of test design (eluate versus presence of solid sample) could have significant effect on the results and interpretation of toxicity.
- Durations of assays (24 hours-lasting yeast assay versus 96 hours-lasting algal assay) caused different toxicity (stimulation versus 31% inhibition), probably thanks to dilution of higher levels of zinc in water containg glue during testing and mechanical shielding with glue.
- The biodegradation of the test glue is possible thanks to the absence of toxicity. In addition, the glue samples were coloured to violet after addition of the reactant. This is an evidence of yeast attachment to the surface of pieces of cured glue in solution and their aliving directly on the glue.

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References

1. Tao X., Tian D., Liang S., Zhang L., Li S., Fu F.: Polym. Compos. *44*, 1331 (2023).
2. Data Safety Sheets.: Lignofix D4. BL-Lignofix-D4.pdf, Stachema, s.r.o. (2022).
3. Ong C. B.: Wood Composites, 123 (2015).
4. Frihart C. R.: For Prod. J. *65*, 4 (2015).
5. Lubis M. A. R., Park B. D., Lee S. M.: Int. J. Adhesion Adhes. *100*, 102599 (2020).
6. Gabriel J., Švec K.: Fungal Biol. Rev. *31*, 212 (2017).
7. Elam J., Bjordal Ch.: Int. Biodeterior. Biodegradation *148*, 104913 (2020).
8. Atiwesh G., Parrish Ch. C., Banoub J., Le T.-A. T.: Biotechnol. Prog. *38*, e3226 (2021).
9. OECD guideline No. 201: Freshwater Alga and Cyanobacteria, Growth Inhibition Test. Geneva, Switzerland (2011).
10. Stockert J. C., Horobin R. W., Colombo L. L., Blázquez-Castro A.: *Acta Histochem.* 120, 159 (2018).
11. Güçlü Z., Ertan Ö.: Turk. J. Fish. Aquat. Sci. *12*, 309 (2012).
12. Li X., Chen Y., Gao W., Mo A., Zhang Y., Jiang J., He D.: J. Hazard. Mater. *442*, 130051 (2023).

STUDY OF THE ALKALI-SILICA REACTION OF PROCESSED FLY ASH AND BOTTOM ASH

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Abstract

Development of alkali-silica reaction (ASR) in concretes and mortars is, among others, a possible cause of concrete construction failure. However, there are admixtures which can significantly mitigate ASR. Admixtures with such ability are generally pozzolans, moreover, energy by-products (CCPs) give very good results. This work aims to study the effect of the addition of fly ash (FA) and bottom ash (BA) as well as investigate the influence of CCPs particle size on ASR development. The ASR was studied using an accelerated dilatometric test according to ASTM 1260, complemented by an assessment of mechanical properties after immersion of tested samples into 1 M NaOH solution for 28 days. Experiments were performed on hardened samples containing 10 wt.% CCPs in 3 different grinding finenesses and with the addition of glass (size fraction 2–4 mm). Experiments performed on hardened samples with FA and BA indicate their positive effect on ASR elimination. The results showed that higher grinding finenesses of the admixtures resulted in minimal changes in the expansion reactions.

Introduction

The alkali-silica reaction (ASR) is a common cause of concrete constructions failure[1]. It is induced by concrete exposition to an alkali-rich and humid environment. The exposed concrete, however, must contain reactive forms of silicon oxide in certain amounts, which are usually introduced as concrete aggregate. The ASR was first described in the 1940s by Thomas E. Stanton as a result of extensive research on the causes of frequent building collapses. Moreover, he described the occurrence of reactive silica in opal and volcanic glass[1,2].

The general mechanism is based on silicate dissolution in highly alkaline solutions, which are in concrete often present. By action of OH- ions, the silicates are broken down into hygroscopic mass known as a silicagel. As water absorption in the silicagel occurs, the volume of the gel progressively grows. This makes the concrete inner strain to increase and, in the end, it may result in severe damage to the concrete body[1].

By the nature and common application of concrete constructions, it seems impossible to completely avoid ASR. However, there are still possibilities how to reduce its destructive impact[3]. The first reasonable precaution is to select the aggregate with a minimal amount of reactive silica in any form. Furthermore, it was found that using aggregate containing small particle size fractions or the addition of specific admixtures is an effective approach in terms of mitigation of the ASR. The first type of admixtures are those containing miscellaneous lithium and aluminium compounds. Lithium acts as a substitute for alkali ions in hygroscopic gel, which makes it dramatically less expansive, thus reducing the internal stress[4]. Aluminium, on the other hand, prevents damages caused by expansive silica gel with a different strategy. Aluminium-containing powders induce the development of porosity, which creates plenty of space where silicagel can expand without further internal stress increase. The downside of the first type of admixtures is their price. The second type of admixtures are more known as pozzolans, but ASR-mitigating effects were observed also at energy by-products (CCPs). The energy by-products are generally products from the combustion of solid fuels in thermal power plants. Composition and thus the effect differs with the combustion technique and used fuel. Ordinarily, CCPs from thermal power plants are distinguished as fly ash (FA) and bottom ash (BA)[5,6]. Mechanism of action consists of ion mobility, water permeability and calcium availability reduction. Generally speaking, the higher the pozzolan activity is, the more effective is the material in ASR reduction[3,4,5,6,7].

Materials and methods

The prepared prisms were composed of five input materials – Cement CEM 42,5 R from Českomoravský cement, závod Mokrá (CEM), aggregate of fraction 0.125–4 mm from sand mine Dobříň (AG), Fly ash (FA) and Bottom ash (BA) from coal power plant Tušimice and float glass shards of fraction 2–4 mm from TGK - Technika, sklo a umění s.r.o. (GS). All input materials were characterized by X-ray fluorescence (Table I.), X-ray diffraction (Table II.), and granulometry (Table III.). Fly ash and Bottom ash were mechanically treated by grinding to three different fineness at different time intervals. Based on the degree of grinding (fineness) the sets of prisms were named FA (0), FA (I), FA (IV), BA (0), BA (I) and BA (IV) – (0) is unground raw material, (I) is ground material for 7 min and (IV) is ground for 45 min.

X-ray fluorescence (XRF), which determines the chemical composition of the sample was performed on an X-ray spectrometer ARL 9400 XP (Thermo ARL, Switzerland). X-ray diffraction (XRD) determines the phase composition of the sample. The measurement was performed on a θ-θ X'Pert3 Powder diffractometer (PANanalytical, Netherlands). Samples for XRD were measured by semi-quantitative analysis, but also by quantitative Rietveld analysis. The semi-quantitative analysis does not consider the amorphous binder phase, while the quantitative Rietveld analysis also determines the amorphous binder phase using internal standard ZnO (10%). The results were evaluated using HighScore Plus 4.0 software. The particle size distribution (PSD) was measured on a laser particle size analyser Bettersizer ST (Dandong Bettersize Instruments Ltd., China).

Table I.
Chemical composition of input materials, XRF [%]

Material	**Na_2O**	**MgO**	**K_2O**	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**SO_3**	**Others**
CEM	0.36	1.34	0.89	64.99	18.62	4.77	3.49	0.29	4.66	0.59
AG	1.86	0.95	2.86	1.33	77.77	11.72	2.34	0.68	0.03	0.46
FA	0.58	1.21	1.81	2.04	49.73	33.20	9.25	1.17	0.51	0.50
BA	0.56	1.13	1.66	1.96	47.90	32.52	9.95	1.23	2.44	0.65
GS	15.55	4.04	0.35	9.52	69.08	1.06	0.08	0.03	0.24	0.05

Table II.
Phase composition of input materials, XRD [%]

Material	**C_3S**	**C_2S**	**C_4AF**	**C_3A**	**$CaSO_4 \cdot ½ H_2O$**	**Amorph.**
CEM	56	19	11	2	2	10

Materials	**SiO_2**	**Albite**	**Muscovite**	**Ortoklase**	**Mullite**	**Fe_2O_3**	**Anorthite**	**Amorph.**
AG	80	10	5	5	-	-	-	-
FA	10	-	-	-	26	1	1	62
BA	10	-	-	-	19	1	-	70

Table III.
PSD of input materials [μm]

Material	**D10**	**D50**	**D90**
CEM	2.52	14.11	44.19
FA (0)	4.84	45.03	148.40
FA (I)	1.77	14.06	59.80
FA (IV)	1.44	10.16	45.52
BA (0)	13.75	125.60	320.40
BA (I)	3.17	37.91	123.10
BA (IV)	1.68	12.65	48.05

The prepared prisms contained 1 part by weight of binder (cement), 2.25 parts by weight of aggregate (sand/glass), and water to binder ratio of 0.47. A total of 7 sets of prisms were prepared according to the standard ASTM 1260[8], the composition of mixtures is described in the table (Table IV.). For all sets of prisms, the 2–4 mm fraction aggregate (AG) was replaced by 10 wt.% glass (GS) of 2–4 mm fraction. The reference set of prisms contained cement, aggregate, glass and water in the above mentioned water to binder ratio mentioned above (REF). For the experiment, three sets of prisms with fly ash (FA) and bottom ash (BA) were prepared. All of the above mentioned CCPs replaced 10% of the cement in the prisms.

Dry homogenization was carried out after the raw materials were weighed according to Table IV. After one minute of homogenization, water was added and the mixture was stirred twice for 90 seconds. In the middle of the time intervals (after the first 90 seconds), the mixture was removed and stirred manually. After stirring, the mixture was placed into molds of sizes 25x25x285 mm according to ASTM 1260. The forms with the mixtures were placed in a moist cabinet (20 ± 2 °C) for 24 hours. After 24 hours prisms were demoulding and they were placed into containers with water at laboratory temperature so that they were completely submerged and had as little contact with themselves and the bottom of the container as possible. The containers with the prisms were placed in a preheated drying oven (80 ± 2 °C) for 24 hours. After 24 hours, "first" zero values were measured with a dilatometer. Measurements of the length expansions due to ASR according to the ASTM 1260 expansion test were performed on a dilatometric device mod. S382-01 (MATEST S.p.A, Italy).

Table IV.
Composition of mixtures REF, FA and BA [g]

Material	**CEM**	**AG**	**GS**	**CCPs**	**Water**
REF	375.5	759.4	84.4	0	176.3
FA (0)	375.5	759.4	84.4	37.5	176.3
FA (I)	375.5	759.4	84.4	37.5	176.3
FA (IV)	375.5	759.4	84.4	37.5	176.3
BA (0)	375.5	759.4	84.4	37.5	176.3
BA (I)	375.5	759.4	84.4	37.5	176.3
BA (IV)	375.5	759.4	84.4	37.5	176.3

After measuring zero values the prisms were placed as quickly as possible in containers with 1 mol/l NaOH solution at 80 ± 2 °C. The containers with the prisms were placed back in the drying oven (80 ± 2 °C). A further measurement was taken 24 hours after the zero measurements to record a value for the lengths of the prisms after the first day of the test. For the following days, the next values were always recorded at the same time with a maximum deviation of 15 minutes.

As the samples are heated to 80 °C, their temperature drops very rapidly in laboratory conditions in the air (20 ± 2 °C) and so does the length of the prisms. For consistent results, it is essential to conduct measurement within 15 seconds after removing the prisms from the warm solution. For each prism, three length expansions were recorded each day. The first value was always taken from the marked starting position, a second value was obtained by turning the body 90° to the left and a third value was taken at a further 45° to the left. Between each measurement of the prisms, the length of the LEtal standard was measured and used to reset the dilatometer.

The measurement result is the relative length expansion of the prisms calculated by the relation:

$$L = \frac{L_x - L_0}{G_x \times 100}, \tag{1}$$

where:

L_x is the length of the prism read from the display of the x-th measurement,
L_0 is the value of the zero measurement,
G_x = 250 mm, which represents the length of the prism determined by the ASTM 1260.

The riskiness of the measured relative length expansions is described by standard TP 137[9], where expansion below 0.1% is characterized as low risk, expansion in the range of 0.1–0.2% as medium risk and expansion above 0.2% as high risk due to the development of ASR reaction. These limits are highlighted in the following graphs.

After 28 days of length measurement, the prisms were tested for compressive and tensile bending strength.

Results and discussion

The results of the expansions of the fly ash prisms according to the ASTM 1260 test are shown in Figure 1. The curves show a constant increase in expansion at 28 days. After the fourteenth day of the test, all prism sets FA (0), FA (I), and FA (IV) showed expansions in the 0.119–0.123% range which is in the medium risk limit according to TP 137. After twenty-eight days, FA (I) achieved the highest expansion value of 0.258%, FA (0) and FA (IV) achieved the lower expansion value of 0.242% and 0.247%. All values are above the 0.2% limit. However, compared to the reference sample (REF), there is a decrease in relative expansion by approximately 0.05%. Based on the results, it can be stated that fly ash has an inhibiting effect on ASR reaction. The effect of different grinding fineness's on the expansion of the prisms due to ASR was not observed.

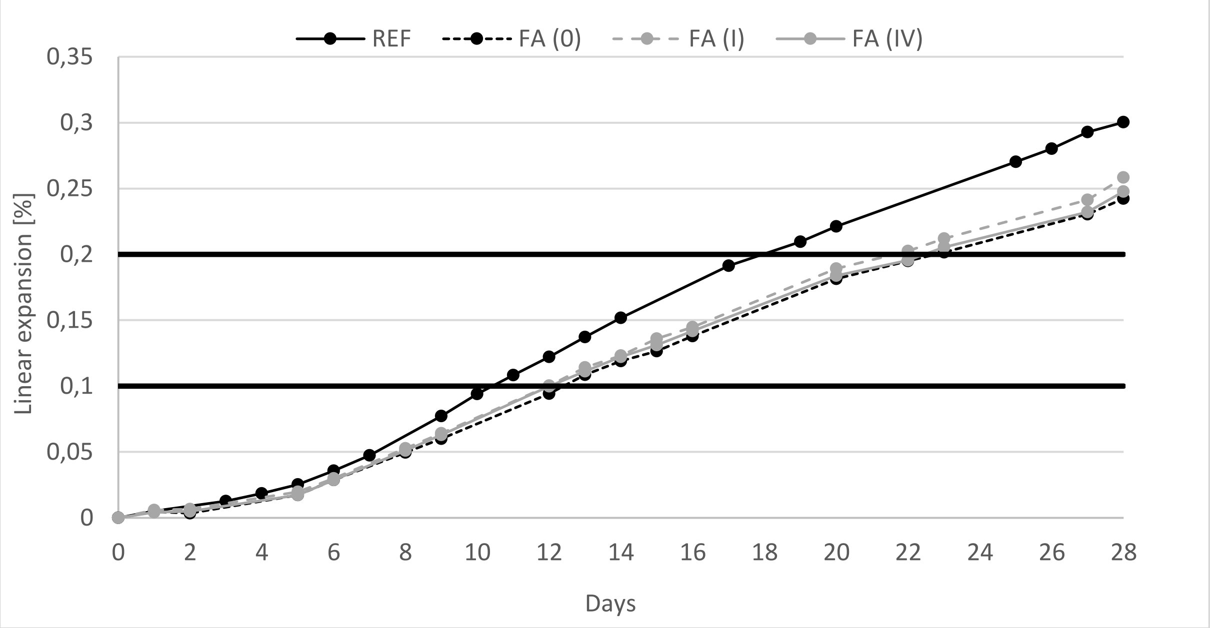

Figure 1: Relative elongation of the samples FA over a period of 28 days

The results of the ASTM 1260 expansion tests for the bottom ash prisms are recorded in Figure 2. It can be seen that within the first 8 days, the curves show a constant increase in expansion and this expansion is similar for all prisms (BA (0) – 0.047%, BA (I) – 0.042% and BA (IV) – 0.045%). After 8 days, the expansion of the BA (I) prism is constantly lower in comparison with another two sets of prism. After 14 days the expansions are above 0.1% and constantly grow until 28 days. After 28 days, BA (I) achieved the lowest expansion value of 0.201%, BA (0) achieved the higher expansion value of 0.225% and BA (IV) achieved the highest expansion value of 0.237%. All values are above the 0.2% limit, samples BA (I) is on the border of this limit. In comparison with the reference sample (REF) there is a decrease of more than 0.05% for BA (0) and BA (IV). For the sample BA (I) this decrease is 0.1%. Based on the results, it can be stated that bottom ash has an inhibiting effect on the ASR reaction. The effect of different grinding fineness's on prisms due to ASR was observed for sample BA (I) compared to samples BA (0) and BA (IV).

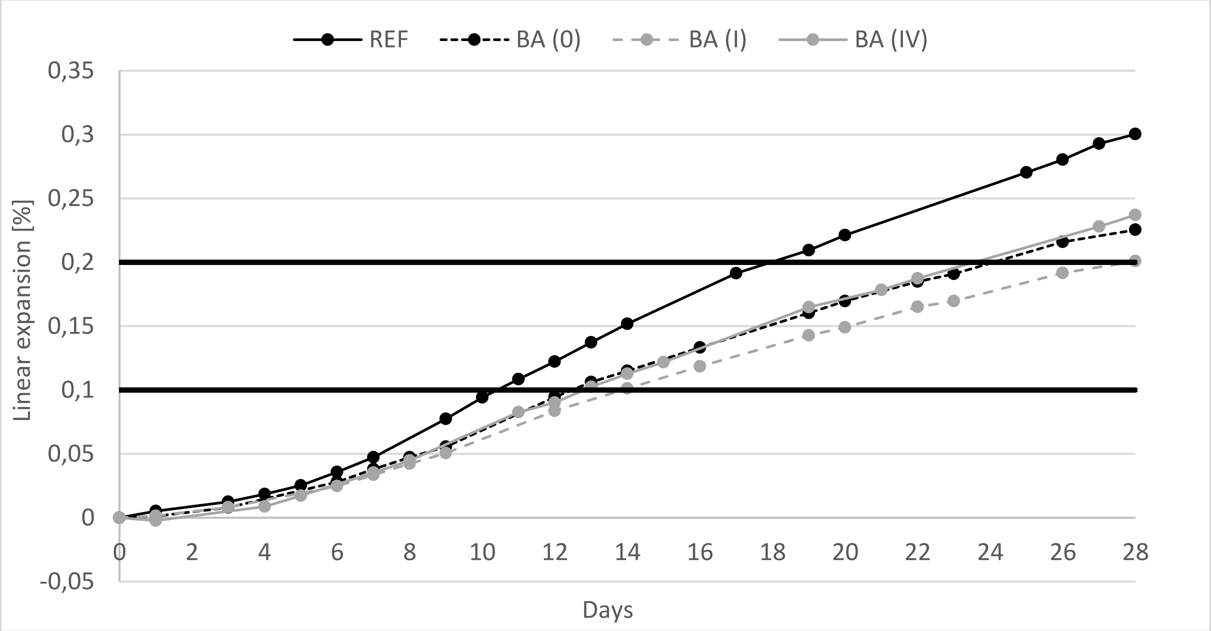

Figure 2: Relative elongation of the samples BA over a period of 28 days

From Figure 3 and Figure 4, the compressive strengths and tensile bending strengths of the sets of prisms with fly ash and bottom ash can be observed.

From compressive strengths for FA and BA of the prisms with the addition of different fineness materials, it can be seen that the compressive strength increases for sample ground for 7 min in comparison to each other. Compared to the reference sample (REF), the strengths for FA (I) are lower and for BA (I) are the same. In general, the compressive strengths of BA prisms, regardless of different grinding fineness's, are higher than the strengths of FA prisms.

Prisms mechanically tested for tensile bending strengths get similar values compared with the referent sample (REF). The best results of mechanical properties were achieved for the samples with additions (FA and BA) ground for 7 minutes.

From Figure 3 and Figure 4 it can be noticed for both evaluated strengths BA prisms show higher values than FA in comparison with each other.

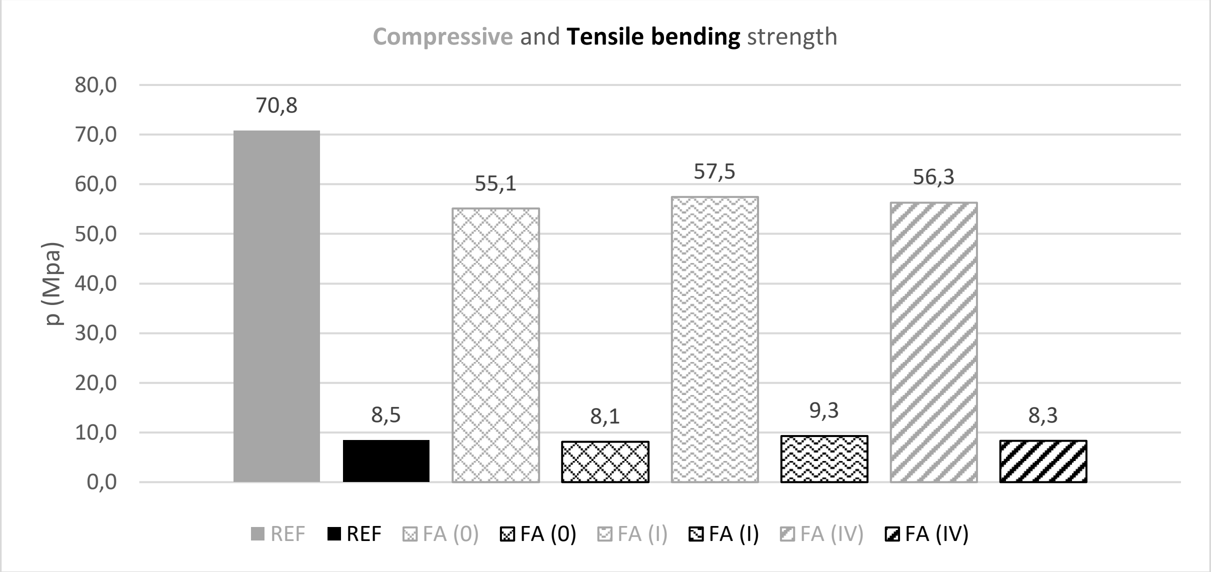

Figure 3: Compressive strength and tensile bending strength of hardened binder after 28 days – FA

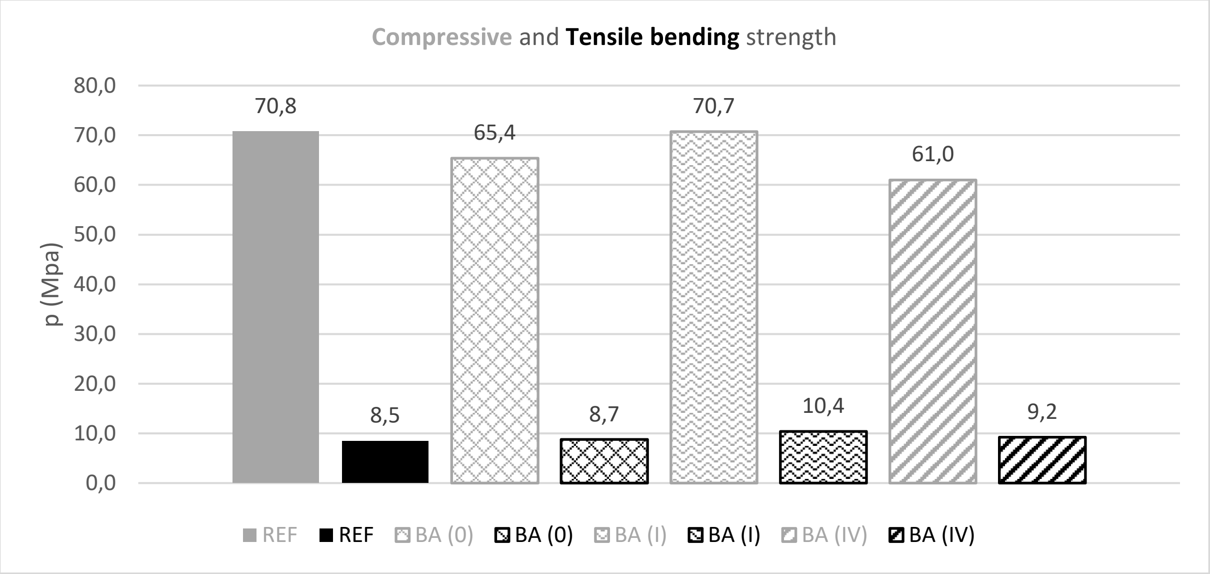

Figure 4: Compressive strength and tensile bending strength of hardened binder after 28 days – BA

Conclusion

It was found that the utilization of CCPs into concrete mixtures (10% CCPs cement replacement) is the efficient solution for the alkali-silica reaction mitigation.

The fining of CCPs seems to have no significant effect on the development and mitigation of the ASR. Due to dilatometric tests, no effect of fineness on length changes was observed for fly ash, whereas length changes over time were observed for different fineness for bottom ash.

Mechanical properties are affected by CPPs particle size. The best results of mechanical properties (compressive and tensile strengths) were obtained for the samples with CPPs ground for 7 minutes. However, this effect is most likely not associated with ASR but is due to other physico-chemical processes.

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References

1. Lukschová, Š.; Alkali-silica reaction of aggregates in real concrete and mortar specimens, no. 18, pp. 79–86, 2009.
2. Škvára, F.; Technologie anorganických pojiv II, VŠCHT Praha, 1995.
3. Pertold, Z. a. kol.; Alkalicko-křemičitá reakce v České republice a možnosti její eliminace, Mater. a technol., vol. 2, 2014.
4. Mo, X.; Yu, C.; Xu, Z.; Long-term effectiveness and mechanism of LiOH in inhibiting alkali-silica reaction, Cem. Concr. Res., vol. 33, no. 1, pp. 115–119, 2003, doi: 10.1016/S0008-8846(02)00934-1.
5. Farny, J.; Kosmatka, S. H; Concrete Diagnosis and Control of Alkali-Aggregate Reactions in Concrete, Concr. Technol., pp. 1–23, 1997.
6. R. Hay and C. P. Ostertag, “New insights into the role of fly ash in mitigating alkali-silica reaction (ASR) in concrete,” Cem. Concr. Res., vol. 144, p. 106440, Jun. 2021, doi: 10.1016/J.CEMCONRES.2021.106440.
7. S. Chatterji, “The role of Ca(OH)2 in the breakdown of Portland cement concrete due to alkali-silica reaction,” Cem. Concr. Res., vol. 9, no. 2, pp. 185–188, Mar. 1979, doi: 10.1016/0008-8846(79)90024-3.
8. ASTM C1260-21, Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method). ASTM International, West Conshohocken, PA, 2021.
9. M. dopravy, Editor; Technické podmínky 137 – Vyloučení alkalické reakce kameniva v betonu na stavbách pozemních komunikací, 2016, p. 26.

THE NEED FOR COMPREHENSIVE STANDARDS FOR MORE PROPER TESTING OF BIPOLAR PLATES MATERIALS AND THEIR COMPARISON

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Abstract

PEMFCs are a promising source of electricity for transport that could help to partially replace fossil fuel engines. One of the main parts in fuel cells are bipolar plates, which serve as current collectors, gas distributor, the body of the fuel cell etc. Therefore, there are big demands on BPPs and their properties. In this work there are tested two substrates AISI 316L and Titanium Grade 2 (7), two single layer coatings 316L+Au and 316L+CrNi, one surface treatment TiGr7-enriched and one nickel based alloy Hastelloy C. All materials are tested according to DOE test at recommended conditions. The objective of this work is to show that representative test conditions are necessary for BPP testing. It is also necessary to develop more comprehensive standards with long term testing under appropriate conditions and desired objectives to be followed by most authors to achieve comparable results.

Introduction

Transportation using internal combustion engines is one of the sources of a pollution and bad environmental conditions. Therefore, there is a big demand to decrease the use of fossil fuels and invent or incorporate an alternative solution. Such alternative is an electromobility using batteries or produce the electricity in the vehicle via fuel cell. One of the most promising seems a Proton Exchange Membrane Fuel Cell (PEMFC). PEMFC offers advantages, such as low noise, quick commissioning, low operating temperature (80–100°C), high efficiency and low emissions. The most limiting factor for bigger commercial use is the initial cost of the PEMFC. The main sources of high cost are the Membrane Electrode Assembly (MEA), and the Bipolar Plates (BPP). BBPs serves several very important roles in the fuel cell, collect current, distribute gasses, dissipate heat, hold the stack together and help with water outflow. Hence, BPPs should have good electrical and thermal conductivity, mechanical properties, hydrophobicity and high corrosion resistance[1,2,3,4].

Global standards for bipolar plates and desired properties are missing. There are only targets given by EU or U.S. Department of Energy (DOE). DOE targets are listed with the measurements methods and conditions, which should be followed. In the corrosion point of view the most important the corrosion limit are: anode corrosion ($j< 1\ \mu A\cdot cm^{-2}$ + no passivation peak) at potentiodynamic scan, cathode corrosion ($j< 1\ \mu A\ cm^{-2}$) at potentiostatic scan and Interfacial Contact Resistance (ICR <$10\ m\Omega\cdot cm^2$)[5].

Comprehensive standards would help researches to compare materials better and avoid unnecessary mistakes and testing under non-representative conditions. PEMFC operates at elevated temperature 80–100 °C, therefore corrosion tests should be performed at same or at least similar temperature, around 80 °C. Comparing materials tested at ambient conditions might lead to overestimation. The opposite trend is in aggressiveness of the testing solutions. In situ testing shows that the corrosive ions, mostly leached from membrane, are HCO_3^-, HSO_4^-, SO_4^-, F^- etc., and pH of the solutions varies from 3 to 7. However, testing at 1M H_2SO_4 is very common, such solution have pH around 0. In situ testing also shows decoupling of potentials between bipolar plate and Pt electrode, due to high ionic resistive discontinuous water films in GDL. A discontinuous aqueous environment is desirable, too much water could flood the distributing channels and cause problems with gas distribution. Potential range required for testing is limited by the decoupling, where on anode the potential would be around 0 V/SHE and on cathode max around 1 V/SHE. Therefore, testing up to 2 V/SHE, together with too aggressive solutions might lead to a great underestimation of the properties and behaviour in real PEMFC[6,7,8].

Graphite is the main material for bipolar plates for stationary use, unfortunately it lacks mainly the mechanical properties to serve also in transportation. Candidates for replacing graphite are conductive polymers (composites) or metallic materials. Stainless steel and titanium plates are the most favoured ones and even practically used with coatings[9]. Both metals have adequate corrosion resistance in PEMFC environment, very close to DOE targets, thanks to forming of passive layer on the surface. The passive layer protects the material, but significantly reduce conductivity, thus the ICR increase. Those two parameters go against each other and are the most important from corrosion point of view[10]. Metal cations originating from corrosion could poison the membrane and together with an increase in ICR could lead to a decrease in performance. Therefore, wide range of coatings, surface treatments and their combinations are tested to achieve better and better results. Coating are usually carbides (CrC, NbC), nitrides (TiN, CrN), amorphous carbon and precious metals (Au, Pt) deposited by numerous methods. Surface treatments try to enrich the surface in some element, Cr in case of 316L or Pd in case of TiGr 7. The goal is to produce defect free layer with desired properties[11,12].

Experiment

Material

There were several materials chosen for this work, most used stainless steel AISI 316L without coating and coated with CrNi and Au. The gold coated steel serves in most cases as a reference. There was also a representative of nickel materials in form of Hastelloy C and two titanium alloys, Titanium grade 2 (TiGr2) and Titanium grade 7 (TiGr7). Samples were either machined from a rod in the form of circles or cut from a sheet as squares. All coating were deposited on the final shaped and adequately prepared substrates. The TiGr7 was surface treated in hot sulphuric acid, details are written in[3].

Electrochemical measurements

All electrochemical measurements were done in the 3-electrode connection. Reference electrode was silver/silver chloride electrode (ACLE), counter electrode was platinum wire and the working electrode was the tested material. The tests were performed in cell with sample pressed in from a side with o-ring sealing the cell and setting the measuring area to 1 cm^2. As a testing solution was chosen diluted sulphuric acid 1 mmol l^{-1} with 1 ppm of F$^-$ added from a solution of NaF. Measurements were performed at elevated temperature 80 °C using a water thermostat. For each measurement the solution was prepared fresh and only used once.

There were two types of sequence measurements, where anodic consisted of measuring open circuit potential (OCP) for 1 hour, followed by potetiodynamic scan (PD) with potentials ranging from -400mV/ACLE to +600 mV/ACLE with scan rate of 0.1 mV·s^{-1} in deaerated solution. Cathodic sequence consisted of measuring OCP for 1 hour followed by potentiostatic scan (PS) at +600 mV/ACLE for 24 hours, in aerated solution, all according to DOE. All measurements were performed on the Zahner Zehnium workstation and data were evaluated using Thales Analysis.

Interfacial contact resistance

ICR was measured on ground samples in case of AISI 316L, TiGr2 and Hastelloy C. Surface treated TiGr7 and all coated samples were only rinsed with water, ethanol and dried with air. ICR was measured before PS and immediately after. Test setup is shown at Figure 1, where the samples is placed between two sheets of GDL (Sigracet 28 BC) and pressed by two copper cylinders using universal testing machine FPZ 100/1. The compacting force ranged from 0–200 N·cm^{-2}. The overall resistance R was recorded by GOM-805 DC Miliohm-Meter connected to the cylinders. The measuring area is 0.8 cm^2, had to be slightly smaller than area exposed at PS. The final value of ICR is then calculated at 140 N·cm^{-2} using equating 1 and converted to mΩ·cm^2. Where $R_{S/CP}$ represents the required ICR of the sample-GDL interface, R_{total} is the measured resistance of the whole setup including sample and $R_{CP/CU}$ is measured without the sample. Each measurement uses new GDLs without previous compression. $R_{CP/CU}$ was measured at the start of measurements, two times at least.

PEMFC test

AISI 316L, AISI316L+Au, TiGr7 and TiGr7-Enriched were tested in PEMFC. Rectangular samples with 5 cm^2 active area were prepared for this test. Fuel cell consisted of the catalyst coated membrane (CCM) prepared using Nafion 212 membrane, coated with catalyst HiSPEC 4000 using ustrasonic spray and ionomer Nafion D521 with Pt loading of 0.3 mg·cm^{-2}. Sigracet 28BC served as GDL and carbon felt Mersen 3mm replaced the role of the gas distribution channels. Tested materials served as the current collectors.

The fuel cell was operated for several days at 0.5 A·cm^{-2} at ambient temperature, which increased by the heat produced during operation. Hydrogen and oxygen were supplied in double excess to stoichiometry without humidification. The fuel cell was characterized by EIS at different voltages (0.9; 0.8; 0.7; 0.6 and 0.5 V) and load curves in the range from OCP to 0.25 V with 5 mV·s^{-1} scan rate at workstation Autolab PGSTAT302N with 20 A booster.

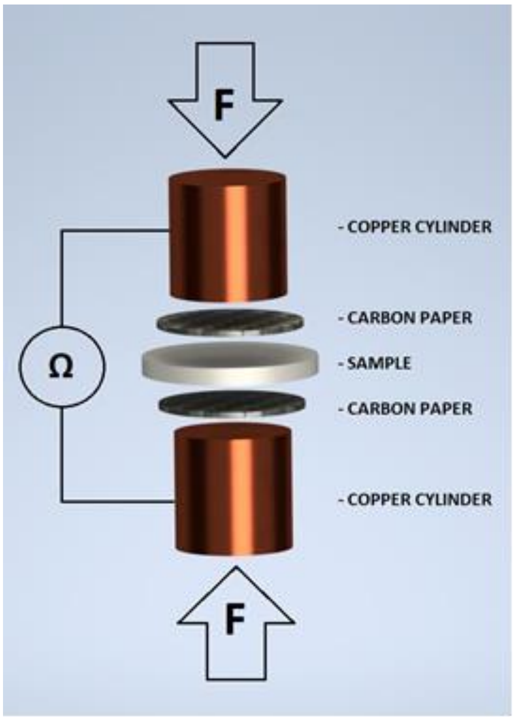

Figure 1 Schematic arrangement of ICR measurement

$$R_{S/CP} = \frac{1}{2}(R_{total} - R_{CP/CU}) \quad (1)$$

Results and Discussion

Potentiodynamic curves, measured according to DOE standards, offers fast and quite easily achievable comparison of materials at the beginning of a research. All PD curves are shown in Figure 2. There is no materials which meet all the DOE targets schemed for this test. All materials exceed the current limit of 1 $\mu A \cdot cm^{-2}$ at the end of the polarization. Hastelloy C shows the passivation peak and with 316L+CrNi achieve the highest current density. Passivation peak is visible also in the case of 316L+Au, where it is response from the substrate due to some damage or defects in the Au coating. AISI 316L itself is corrosion resistant in the simulated PEMFC environment, but there is a risk of crevice corrosion under the o-ring. Titanium Grade 2 has the most negative E_{corr} of all materials and exceeds the DOE limit at around 0.1 V/ACLE, but then it is more or less constant and reaches current density of 1.2 $\mu A \cdot cm^{-2}$, similar to most of the tested materials. TiGr7-Enriched exhibits the highest current density at cathodic region and also the most positive E_{corr}, both thanks to enriched surface in Pd. As for the potentiostatic test, all the materials meet the DOE target for the test. All corrosion properties are sum up in Table I. together with ICR values. Only the gold coated 316L meet the DOE target for ICR. The ICR measurement is in dry conditions unlike the PD test, therefore, there is no response of the substrate, even though there is a path to the substrate present. 316L+ CrNi exceeds the limit at the beginning due to passivation in natural atmosphere and could not been grinded for obvious reasons, contrary to other materials. In the case of TiGr7-Enr there is no negative impact of the fast enrichment before PS on the ICR value. AISI 316L and 316L+CrNi reach similar results after PS due to similar composition of passive layer, even though 316L is slightly worse because of iron oxides in the layer. Gold does not corrode or passivate in the PEMFC environment so the conductivity is retained even after PS. ICR of Hastelloy increases also after PS but less than expected and reaches the value of 120 $m\Omega \cdot cm^2$. ICR of TiGr2 increases significantly and reaches the highest value of all over 1.1 $\Omega \cdot cm^2$. On the other hand enriched TiGr7 has lower ICR after PS, proving that the enrichment in Pd helps to keep the surface more conductive.

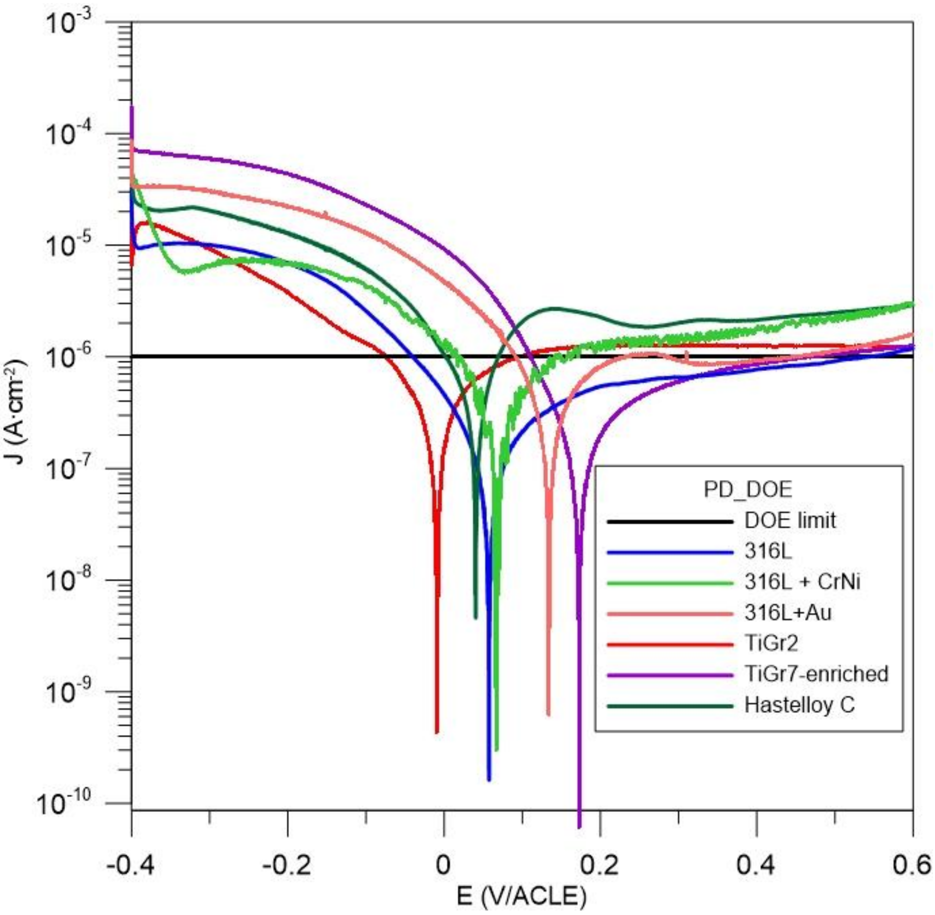

Figure 2 Potentiodynamic curves of tested materials in simulated PEMFC environment at 80 °C

Table I.
ICR values and corrosion properties of tested materials

Material	ICR before	ICR after PS	Ecorr	J (PD)	J (PS)
	mΩ·cm^2	mΩ·cm^2	mV/ACLE	µA·cm^2	µA·cm^2
316L	2	454	45	1.1	0.16
316L+Au	< 1	< 1	130	1.3	0.11
316L+CrNi	300	380	65	2.9	0.28
TiGr2	3	1157	-10	1.2	0.41
TiGr7-Enr	2	330	172	1.2	0.05
Hastelloy C	4	120	40	2.5	0.10

Samples of 316L+CrNi and Hastelloy C were excluded from PEMFC simulation test, due to worst performance at PD testing. There was also change in case of TiGr2, which was replaced by untreated TiGr7, which has the same chemical composition except containing 0.15% Pd. Figure 3 shows results from PEMFC test after one day, just for very easy comparison. Stainless steel 316L performs very poorly, followed by untreated TiGr7. Both materials passivate and their conductivity decrease, leading to loss of performance of the PEMFC. Therefore, both are intended to be coated or surface treated in the commercial use. TiGr7-enriched performs better, thanks to increased Pd content in the surface. It is getting closer to the best performing Au coated 316L, which served as the reference.

Although, no material met all the DOE targets, some performed quite well, even in the PEMFC simulation test. The need of more complex testing is taken into account together with testing in PEMFC at high temperature. There is also demand for the standardization of the testing methods and conditions, which might help to compare materials in more representative way. DOE tests are good but not entirely sufficient for complex comparison. It lacks longer exposition tests and their objectives should be explained. ICR measurements should also see some changes or at least more detailed description as it measures one of the most important parameter for PEMFC functionality and performance during the lifetime.

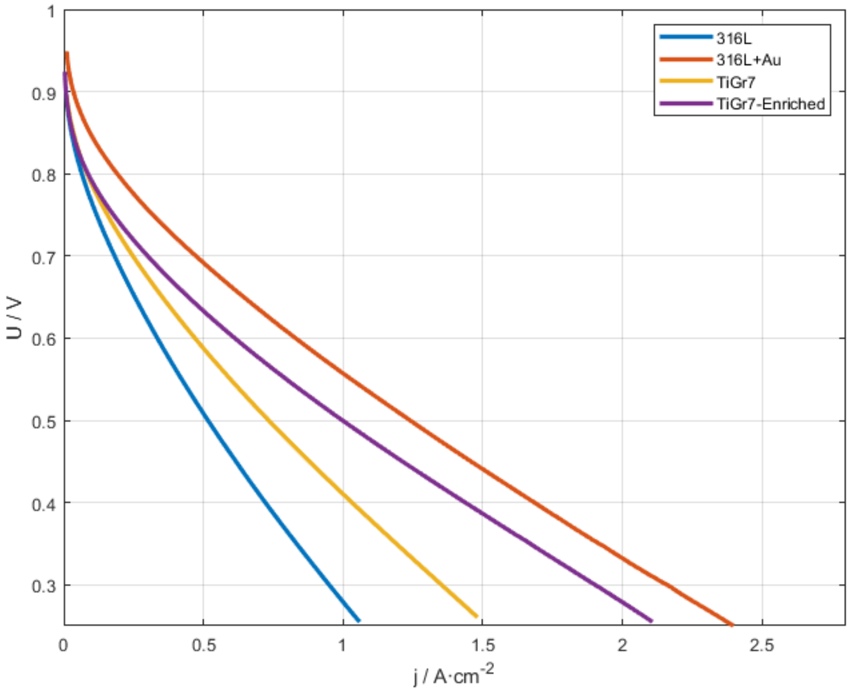

Figure 3 Comparison of load curves of tested materials in PEMFC after 1 day

Conclusion

In potentiodynamic scan the 316L, 316L+Au, TiGr2 and TiGr7-Enr performed quite well and exceeded the limit by a little bit. ICR testing remains very important for evaluating BPPs materials. There are significant changes even after short-time potentiostatic polarization and no materials except gold reached values lower than 10 mΩ·cm^2. However, PS is done at aqueous and ICR at completely dry conditions. The real PEMFC works under much more complicated conditions with high humidity and discontinuous aqueous phase for example. Despite quite high values of ICR (330 mΩ·cm^2) and J(PD) of 1.2 µA·cm^{-2}, the sample of TiGr7-Enr performed quite well in the PEMFC test and got closer to the performance of gold coated stainless steel.

Among tested materials, there was no final candidate for PEMFC, however that was not the goal of this work. The objective was to show that representative conditions such as temperature, environment and others are meaningful and might help in future, together with complex and global standards, to avoid unnecessary mistakes, misjudging and overall better comparison of materials for bipolar plates of Proton Exchange Membrane Fuel Cells.

Acknowledgement

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References

1. Tawfik, H., Y. Hung, and D. Mahajan, Metal bipolar plates for PEM fuel cell – A review. J. Power Sources, 2007. 163(2): p. 755–767.
2. Asri, N.F., Husaini, T., Sulong, A.B., Malan, E.H. and Daud, W.R.W. Coating of stainless steel and titanium bipolar plates for anticorrosion in PEMFC: A review. International Journal of Hydrogen Energy, 2017. 42(14): p. 9135–9148.
3. Bohackova, T., J. Ludvik, and M. Kouril, Metallic Material Selection and Prospective Surface Treatments for Proton Exchange Membrane Fuel Cell Bipolar Plates-A Review. Materials (Basel), 2021. 14(10).
4. Daud, W. R. W., Rosli, R. E., Majlan, E. H., Hamid, S. A. A.,Mohamed, R. and Husaini, T. et al., PEM fuel cell system control: A review. Renewable Energy, 2017. 113: p. 620–638.
5. DOE limits. 2020; Available from: https://www.energy.gov/eere/fuelcells/doe-technical-targets-polymer-electrolyte-membrane-fuel-cell-components.

6. Hinds, G., On the choice of applied potential in ex situ testing of bipolar plate materials. 2023.
7. Hinds, G. and E. Brightman, Towards more representative test methods for corrosion resistance of PEMFC metallic bipolar plates. International Journal of Hydrogen Energy, 2015. 40(6): p. 2785–2791.
8. Prestat, M., Corrosion of structural components of proton exchange membrane water electrolyzer anodes: A review. Journal of Power Sources, 2023. 556.
9. Wang, Y. and D.O. Northwood, Effects of O2 and H2 on the corrosion of SS316L metallic bipolar plate materials in simulated anode and cathode environments of PEM fuel cells. Electrochimica Acta, 2007. 52(24): p. 6793–6798.
10. Mølmen, L., Fast, L., Lundblad, A., Eriksson, P. and Leisner, P. Contact resistance measurement methods for PEM fuel cell bipolar plates and power terminals. Journal of Power Sources, 2023. 555.
11. Gabreab, E.M., Hinds, G., Fearn, S., Hodgson, D., Millichamp, J., Shearing, P.R. and Brett, D.J.L. An electrochemical treatment to improve corrosion and contact resistance of stainless steel bipolar plates used in polymer electrolyte fuel cells. Journal of Power Sources, 2014. 245: p. 1014–1026.
12. Alo, O.A., Otunniyi, I. O., Pienaar, HCvZ and Iyuke, S. E. Materials for Bipolar Plates in Polymer Electrolyte Membrane Fuel Cell: Performance Criteria and Current Benchmarks. Procedia Manufacturing, 2017. 7: p. 395–401.

THE EFFECT OF Ag^+ AND Cu^{2+} ADDED TO BIOGLASS® ON RESULTS OF *IN VITRO* TEST

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Abstract

This study investigates the *in vitro* behaviour of bioactive glasses modified with Ag^+ and Cu^{2+} ions to impart antibacterial properties. Bioactive glasses are widely used in medical applications due to their biocompatibility and ability to form a hydroxyapatite layer, facilitating bonding with bone tissue. The modification with 1 wt.% of Ag and Cu ions was chosen to address the risk of infection near implants and the increasing bacterial resistance to antibiotics. *In vitro* testing was conducted according to international standards, examining the apatite-forming ability of the modified glasses in simulated body fluid over 14 days. pH levels and the concentration of Si^{IV}, Ca^{2+}, and $(PO_4)^{3-}$ ions were monitored through spectrometry, while the formation of new layers was observed using microscopy and X-ray diffraction. The results indicate that the introduction of metallic ions not only influenced the interaction rate but also affected the composition of the newly formed layers.

Introduction

Nowadays, bioactive glasses are one of the most desirable materials in the field of tissue engineering used as an implant device to repair diseased or damaged bones (e.g. bone filling, dental cement, *scaffolds*). Thanks to their biodegradability, osteoconductivity and high biocompatibility, during their interaction with physiological fluids (*in vivo*/*in vitro*), they can induce the formation of hydroxyapatite on their surface, allowing the implant to bond tightly with the surrounding bone tissue[1,2]. Bioglass 45S5 is the most widely used type of Bioglass® which was first developed in 1972. The composition of Bioglass (Figure 1) is usually based on silicate glasses with a variable content of sodium, calcium and phosphorus ions. These elements (Na, Ca, P) are a natural part of the human body. It is assumed that when a Bioglass® implant is exposed to the environment of body fluids, a SiO_2-CaO/P_2O_5 gel layer is formed, on which hydroxyapatite subsequently precipitates. The composition of this layer closely resembles the bone hydroxyapatite matrix and allows osteoblast differentiation and the formation of new bone[3,4].

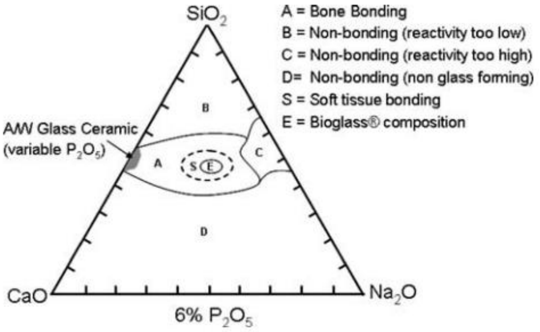


Figure 1. Diagram showing the effect of Bioglass composition on the ability to bond, with human bone[5]

Monitoring the bioactive behaviour is a crucial part of the comprehensive testing that all biomaterials have to undergo before they can be used in medical practice. The initial testing is carried out *in vitro* in simulated body fluid (SBF) that is designed to mimic the composition of the inorganic part of human blood plasma and is conducted according to ISO standard (ISO 23317:2014). These tests provide a first insight into how the material interacts with the environment of living organism[6]. *In vitro* tests can take place under static (ISO 23317:2014), static-dynamic or dynamic conditions, which best corresponds to the processes taking place in the human body and precede the *in vivo* tests on animals[7,8].

Current clinical practice is facing the problem of increasing bacterial resistance to common antibiotics in the hospital environment. Infections and inflammation present a possible risk in every surgery and can lead to implant failure and subsequent reoperation. It is necessary to find alternative methods to provide an antibacterial effect. Given the fact that infection around implants is dangerous for the patient and can negatively affect the healing process, new methods are being developed to grant the materials themselves sufficient antibacterial properties. One of the methods is the incorporation of metal ions such as silver or copper. However, it is necessary to monitor their concentration due to the possibility of cytotoxicity of the material. A huge advantage of these methods enhancing the antibacterial properties of the implant is that the surrounding tissue has enough time to regenerate, the acceptance of the implant is improved, and the amount of antibiotics that represent a heavy burden on the patient's organism can be reduced[9-11].

Experiment

Preparation of the samples

Three types of glasses based on Bioglass 45S5 (Figure 2, Table I.) – bioglass (BG), bioglass with 1 wt.% of Ag (BG-Ag), bioglass with 1 wt.% of Cu (BG-Cu) were prepared by melting at 1280 °C for 3 hours. Subsequently, they were tempered at 500 °C for 1 hour and cooled at 5 °C/min until the next day. The glasses were cut into cubes and adjusted with SiC grinding papers with grit sizes P120 and P600 to a uniform shape. Then, the samples were cleaned in ethanol in an ultrasonic bath twice for 10 minutes and dried at laboratory temperature.

Figure 2. Prepared BG (white), BG-Ag (orange), and BG-Cu (blue)

Table I.

[wt.%]	SiO_2	Na_2O	CaO	P_2O_5	Ag	Cu
Bioglass 45S5	45.0	24.5	24.5	6.0	-	-
Bioglass + 1 wt.% Ag	45.0	24.5	24.5	6.0	1.0	-
Bioglass + 1 wt.% Cu	45.0	24.5	24.5	6.0	-	1.0

Testing of bioactivity

The bioactive ability was tested in SBF under static *in vitro* test, according to the international standard (ISO 23317:2014), for 14 days and compared against the non-modified bioglass samples[7]. Both the materials and the solutions were sampled at pre-arranged times – 1st, 3rd, 7th, 10th, and 14th day. After the interaction, the samples were air-dried, and their surfaces were observed and characterized by an optical and scanning electron microscope and XRD method to determine the chemical and mineralogical composition of newly formed phases. The pH levels and the concentration of silicon, phosphate, and calcium ions in the solutions were determined using AAS and UV-VIS spectrometry. The concentration of released silver and copper ions was measured by the ICP-OES method.

Antibacterial tests

Antibacterial tests were performed against *Escherichia coli* to confirm the antibacterial effect of the metallic ions incorporated into bioglass. The glass samples were submerged into a testing suspension (physiological solution (9 $g \cdot l^{-1}$ NaCl) with a concentration of bacteria 10^4 $cell \cdot ml^{-1}$) at laboratory temperature for 4 and 24 hours. After the end of the interaction, 100 µl of each reacted suspension was spread on a Petri dish with agar and incubated at 36.5 °C in a biological thermostat for 24 hours. Afterwards, the Petri dishes were photographed, and the colonies of surviving bacteria were counted using the computer program NIS-Elements AR 3.10. The entire process ran in a sterile environment of Flow-box.

Discussion and result analysis

The interaction of bioglass samples with SBF

The changes in pH (Figure 3) are the primary indicator of the interaction of bioactive glasses with the solution. The most significant change in pH occurred for the sample BG-Ag from the 3rd day of the experiment. Overall, the pH levels had a similar trend – increasing until the 7th day and then descending for all three types of bioglass samples.

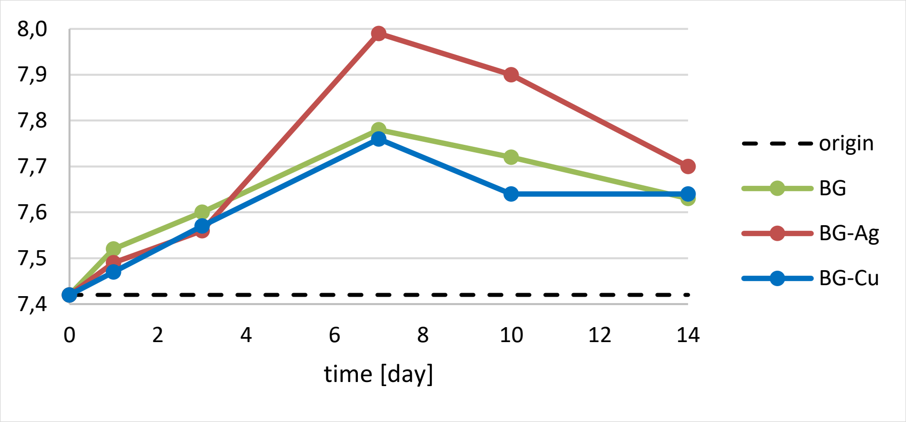


Figure 3. Changes in pH during the 14 day exposition of bioglass samples in SBF

Figures 4–6 show the concentration of silicon, calcium, and phosphate ions in the solution during the entire experiment. An increase in the concentration of these ions in the solution indicates the dissolution of the glass material, and a decrease in concentration suggests the depletion of ions from the solution and the precipitation of new phases.

The greatest dissolution of the silica network occurred in the case of the samples containing silver (BG-Ag). This is also confirmed by the analysis of the calcium ions. On the other hand, the bioglass with copper (BG-Cu) behaves very similarly to the original bioglass (BG). Both glasses dissolved up to the 3rd day but then the dissolution stopped.

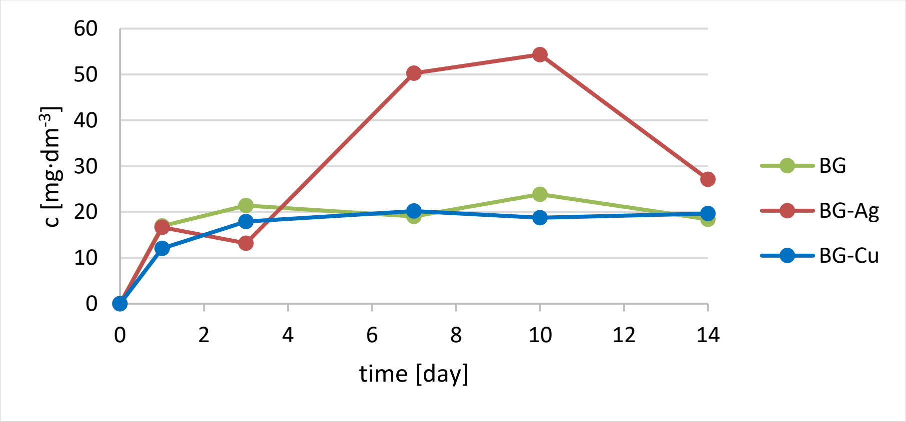


Figure 4. The concentration of Si^{IV} during the 14 day interaction

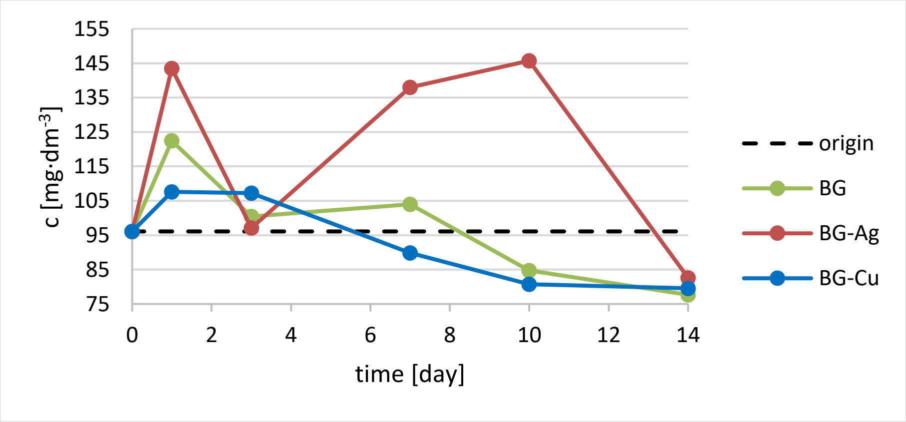


Figure 5. The concentration of Ca^{2+} during the 14 day interaction

From Figures 5 and 6, it is clear that Ca^{2+} ions were released from the glass samples and phosphate ions were pumped out at the same time on the first day of interaction. We can explain it by the initial fast reaction of samples with SBF. The concentration of calcium ions in the solutions was basically the same in BG and

BG-Cu. From the third day of interaction, both phosphate and calcium ions were gradually pumped out from the solution for all samples. It indicates a gradual formation of new layers, the presence of which was subsequently confirmed by observing the samples using a scanning electron microscope.

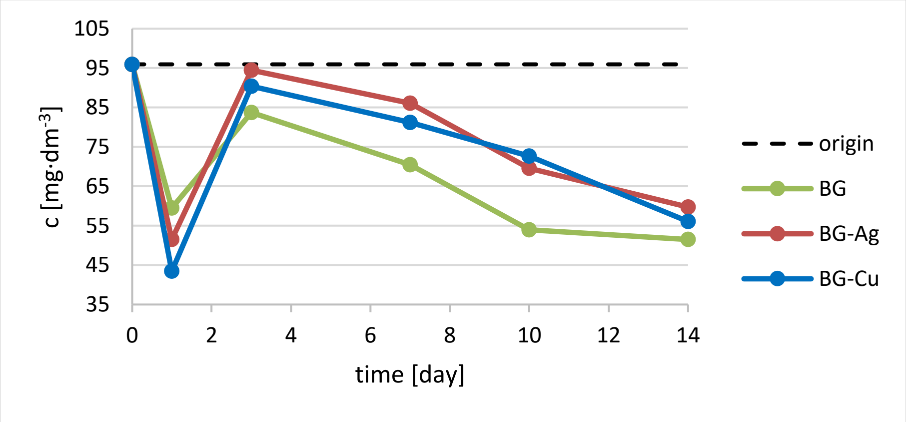


Figure 6. The concentration of $(PO_4)^{3-}$ during the 14 day interaction

Figure 7 showing the concentration of silver and copper ions in leachates indicates that in the case of the samples BG-Ag, there was a lower amount of metallic ions released into the solution than in the case of samples BG-Cu. The concentration of Cu^{2+} ions remained almost constant from the 3rd day of interaction. On the other hand, the concentration of Ag^+ ions slowly increased during the entire experiment.

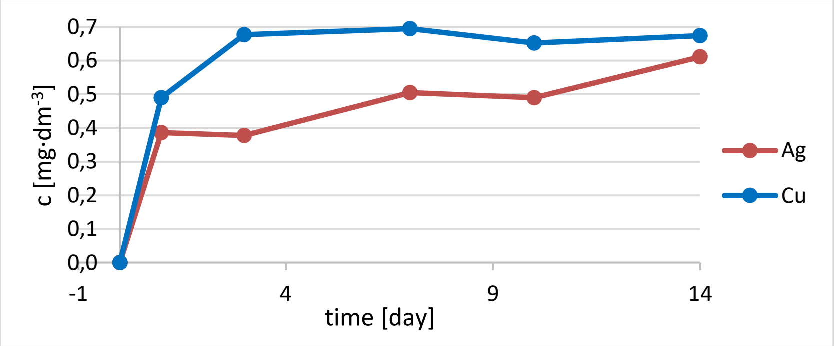
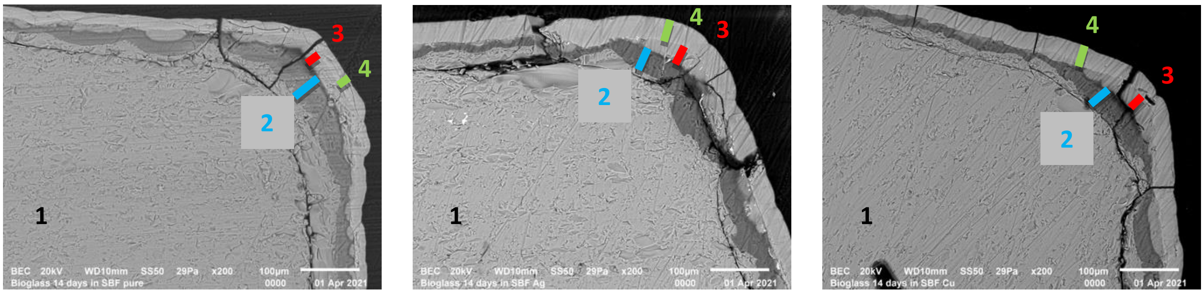


Figure 7. The concentration of Ag and Cu during the 14 day interaction

1. <u>Formation of corrosion and precipitated layers on the surface of bioglass samples</u>

Monitoring of the formation and chemical composition of new phases was observed and analysed by SEM-EDS. Figure 8a–c shows cross-sectional images of bioactive glasses after 14 days of *in vitro* bioactivity test. These images show the morphology of the samples and different layers can be seen – the native glass (area 1), SiO_2-rich layers (corroded layers) (area 2), some interlayers (area 3) and new precipitated Ca-P layers (area 4), which were identified by XRD as hydroxyapatite. In the case of bioglasses with the addition of metallic ions, the outer layer was not formed only by hydroxyapatite but it was also combined with AgCl (BG-Ag) or Cu (BG-Cu).



a) b) c)

Figure 8. Cross-sectional images 14th day of experiment by SEM a) BG, b) BG-Ag, c) BG-Cu

Figure 9a–c shows a visual representation of the thickness of newly precipitated layers on the surface of the samples. The rate of formation of new layers is different for bioactive glasses with and without incorporated metallic ions. The hydroxyapatite layer formed faster on BG-Ag and BG-Cu than on BG. For all three types of samples, between the 10th and 14th day of interaction, the solution was probably depleted, or the layer peeled off, which caused the reduction in the layers' thickness.

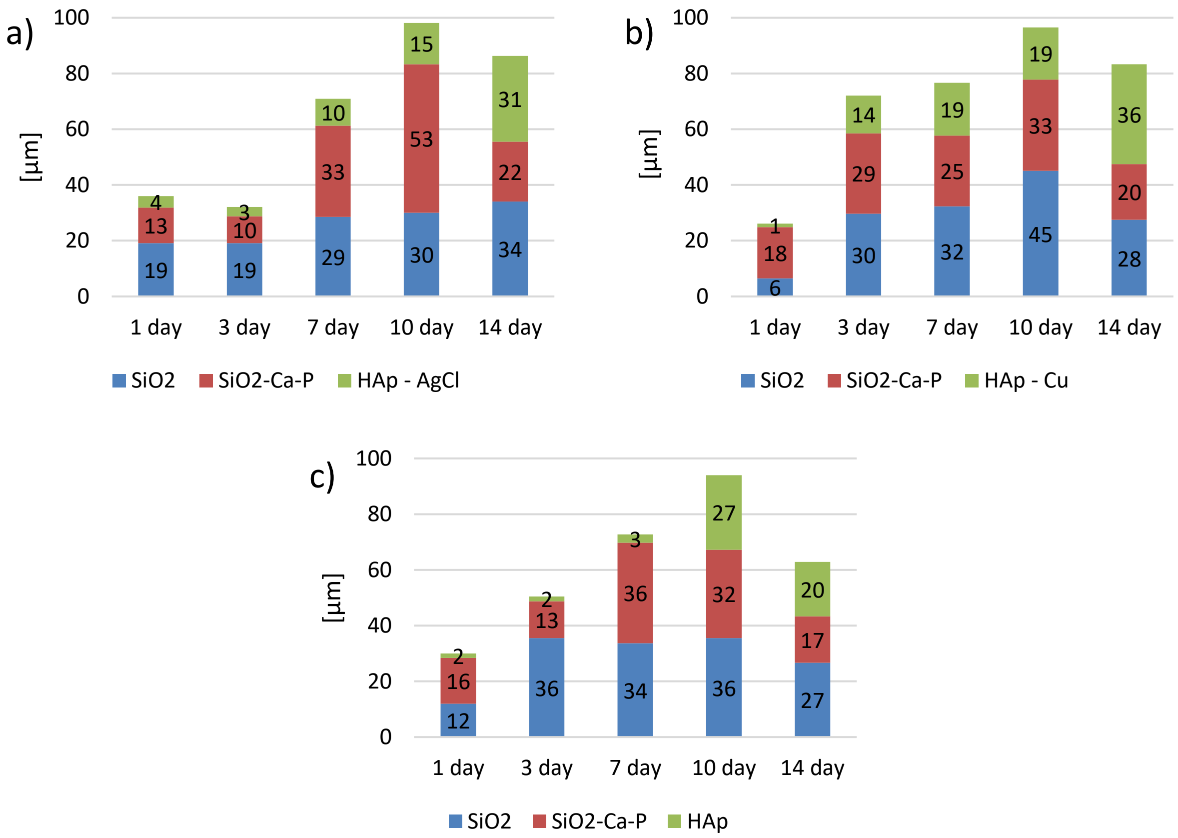


Figure 9. precipitated layers a) Bioglass-Ag, b) Bioglass-Cu, c) Bioglass

2. Antibacterial ability of the modified bioglass samples

The bioactive glasses were modified with metallic ions (Ag^+ and Cu^{2+}) to grant them antibacterial properties. Table II. shows that the antibacterial effect against *E. coli* is partial (58% and 30%) after 4 hours in the case of BG-Ag and BG-Cu only. For Bioglass without metallic ions, the effect is very low after 4 hours (~9%), which was expected. After 24 hours, all glass samples showed full (BG-Ag and BG-Cu) or almost full (BG) antibacterial effect, which was surprising in the case of non-modified bioglass samples (BG).

Table II.
Antibacterial effect after 4 and 24 hours against *Escherichia coli*

	4 hours	**24 hours**
Bioglass	8.8 %	97.7 %
Bioglass – Ag	58.2 %	100.0 %
Bioglass – Cu	30.4 %	100.0 %

Conclusion

The results showed that the introduction of metallic ions affected not only the rate of dissolution but their presence in bioactive glasses had a significant impact on the mechanism of precipitation and composition of the newly precipitated layers. The results obtained by analysing the leachates correspond nicely with the samples' morphology observed via SEM-EDS. Metallic ions improved the antibacterial properties of bioglass within 4 hours.

Acknowledgement

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References

1. Chen Q. Z., Thompson I. D., Boccaccini A. R.: Biomaterials *27*, 2414 (2006)
2. Spirandeli B.R., Ribas R. G., Amaral S. S., Martins E. F., Esposito E., Vasconcellos L. M. R., Campos T. M. B., Thim G.P., Trichęs E. S.: Mater. Sci. Eng. C *131* (2021)
3. Kokubo T., Takadama H.: Biomaterials *27*, 2907 (2006)
4. Krishnan V., Lakshmi D.: J. Adv. Pharm. Technol. Res. *4*, 78 (2013)
5. Hench L. L.: J. Mater. Sci.: Mater. Med. *17*, 967 (2006)
6. Rohanová D., Horkavcová D., Helebrant A., Boccaccini A. R.: J. Non-Cryst. Solids *432*, 53 (2016)
7. ISO 23317:2014 (2014)
8. Bandyopadhyay A., Shivaram A., Mitra I., Bose S.: Acta Biomater. *96*, 686 (2019)
9. Aftab M., Butt M. Z., Ali D., Bashir F., Aftab Z. H.: Ceram. Int. *46*, 5037 (2020)
10. Horkavcová D., Novák P., Fialová I., Černý M., Jablonská E., Lipov J., Ruml T., Helebrant A.: Mater. Sci. Eng. C *76*, 25 (2017)
11. Batebi K., Khazaei B. A., Afshar A.: Surf. Coat. Technol. *352*, 522 (2018)

CERAMIC PROTECTION OF ANTI-CORROSION LAYERS OF 3-GLYCIDYLOXYPROPYL-TRIETHOXYSILANE ON STEEL

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Abstract

There are various variations on the problem of steel reinforcement bond strength in concrete. Along with geometrical considerations, corrosion performance of steels with varying chemical compositions in interaction with variable chemical compositions of concrete are crucial. One approach is to cover steel surfaces with organosilane compounds, which increases the reinforcement resistance to corrosion in both acidic and alkaline conditions but, on the other hand, may weaken the reinforcement bond strength on concrete. The issue is resolved by intentionally forming a thin-walled, highly adhering corundum layer that is highly porous and impregnated with 3-glycidyloxypropyltriethoxysilane. This procedure also includes testing the adhesion properties between the ceramic and the metal and the cement prior to conducting a corrosion test in a chloride environment.

Introduction

A major issue that severely reduces the service life of reinforced concrete structures, which are primarily designed for construction underwater or beneath the sea, is corrosion of typical concrete reinforcing bars. The cost of rehabilitation efforts places a heavy load on many states and construction firms budgets.[1,2] There are several options for anti-corrosion protection, such as cathodic protection with the attachment of a DC protective current source or with the use of a sacrificial anode. However, this anti-corrosion treatment is quite costly and cannot be utilized everywhere.[3,4] For the prolonged service life, the application of corrosion inhibitors is equally unreliable.[5] The construction industry can enhance the service life of reinforced concrete structures by coating the surface of traditional reinforcement. Epoxy-based coatings have particularly established themselves from this perspective.[6,7] Using organosilane to cover traditional reinforcement is yet another cutting-edge method of surface protection.[8] A novel method of indirect corrosion prevention for concrete reinforcement may include the use of organosilane solutions to reduce the porosity of ordinary concrete (OPC). Reactive suspensions of organosilanes can make traditional concrete more resistant to penetration of chloride anions as well as carbonation, lengthening the serice life of reinforced concrete structures that are typically used for underwater or sea-level structures. The potential for an immediate reaction between organosilanes and the hydrated form of ordinary portland cement (with C_3A compound), which is conceivable given their unique reactivity, is quite intriguing.[9] The state or future of materials that have not yet been utilized in the building process, i.e., their storage and premature mechanical manipulation, which have detrimental effects primarily on the mechanical and chemical resistance of protective layers, are not, however, taken into consideration by any of these variations. This issue can be resolved by applying a high-strength ceramic coating to a steel surface that guarantees mechanical or abrasion resistance while also preserving low mechanically robust organosilane anti-corrosion coatings.

Experiment

The least expensive commercial corundum AH240 of F 240 mesh (see Table I. and Figure 1) was used for the ceramic coating of conventional carbon steel type 10 216 (chemical composition, see Table I.). Blasting with a corundum abrasive to a value of R_a 5.2–5.6 µm was used to initially roughen the steel substrates (see Table II.).

Table I.
Basic specifications of steel 10 216 and corundum AH240 were used for further experiments

Composition of substrate steel 10 216 (wt.%)			Composition of alumina powder AH240 (wt.%)		
Fe	99.332	0.6	Al_2O_3	85.77	0.10
Si	0.042	0.01	MgO	0.56	0.02
P	0.050	0.02	SiO_2	5.32	0.07

S	0.029	0.005	Fe_2O_3	1,22	0.03
Cr	0.073	0.01	CaO	0.65	0.02
Mn	0.410	0.04	TiO_2	5.50	0.07
			Cr_2O_3	0.02	0.004

Table II.
Surface roughness of metal surface (steel 10 216) and corundum AH240, coating 230 µm thickness (CSN EN ISO 4288)

Surface roughness of metal substrate (steel 10 216)			Surface roughness of corundum (AH240) coating		
R_a	R_q	R_z	R_a	R_q	R_z
5.609	8.884	31.833	7.029	6.574	58.326
5.282	6.802	39.437	6.096	9.397	29.895

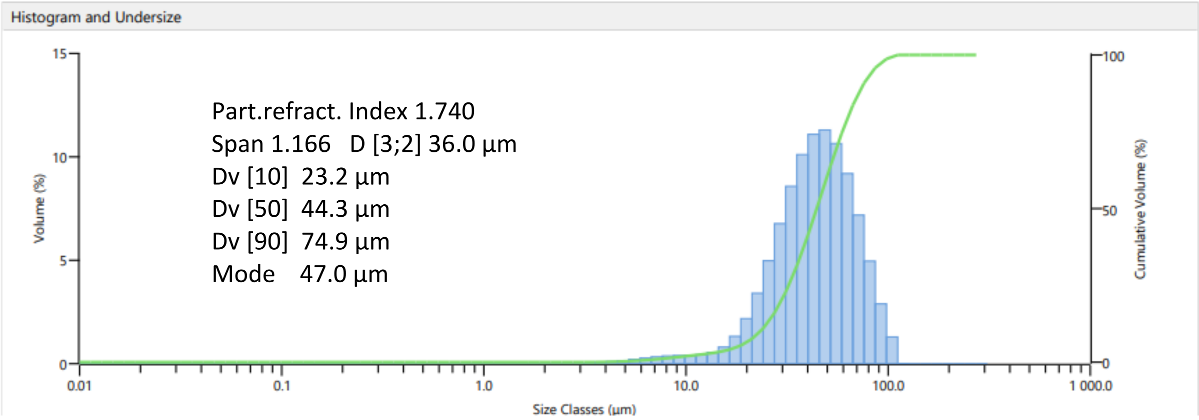


Figure 4. Granulometry Al_2O_3 AH240

After blasting with corundum abrasive, an XRF study of the steel surface revealed the presence of up to 8% securely embedded corundum crystals that could not be removed even by an ultrasonic batch treatment. The WSP®-H 500 hybrid plasma torch with water stabilization was subsequently used to plasma spray additional corundum coatings of thicknesses 120 µm and 230 µm (Figure 2). This gadget, created at the IPP CAS Prague, generates 150 kW of electricity at 500 A of direct current. The plasma arc, which is burning between the revolving anode with external cooling and the tungsten cathode, travels behind the exit nozzle and through a stabilization channel with a water vortex. Its temperature is around 25 000 K, and its flow rate may reach 7 m/s. The resultant plasma has an enthalpy of around 300 MJ/kg. A heated stream made of plasma is blasted out of the nozzle, melting and dragging the powder that has been injected from outside the device. The plasma spray characteristics were made more porous in order to more effectively penetrate ceramics utilizing the aforementioned organosilane compound GPTES. A value of 500 A was specified for the DC current source. The spraying distance of the WSP-H torch from the coated rod was SD = 450 mm, and the distance at which powdered corundum was fed into the plasma jet was FD = 75 mm. Bar-shaped samples were clamped in a chuck head and rotated by a robotic arm equipped with a WSP-H torch that scrolled up and down vertically. The rods were chilled using compressed air to a temperature of 110°C between each stage of Al_2O_3 injection. Figures 3 and Figure 4 depict the coating microstructure.

Figure 5. Illustration of plasma coating with a WSP®-H 500 torch

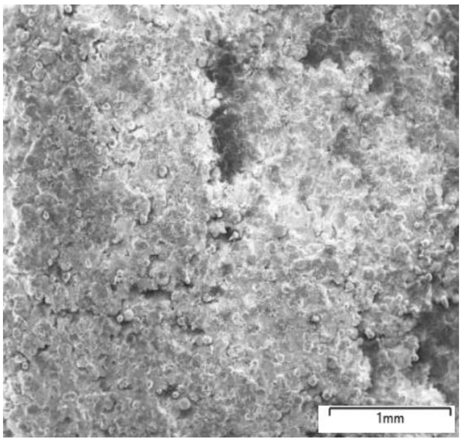


Figure 6. Photograph of the surface structure of the corundum coating on 10 216 steel

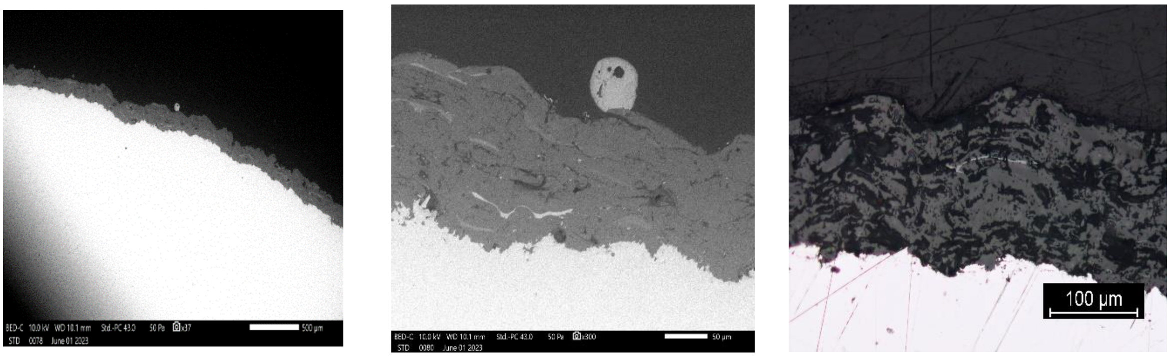


Figure 7. Cross-sectional structure of Al_2O_3 AH240 coating on 10 216 steel

Abrasion and tear tests were used to determine the mechanical strength of the corundum coatings and how well the coating adhered to the substrate. The technique depicted in Figure 5. was used to measure mechanical strength, or abrasive resistance to mechanical force.

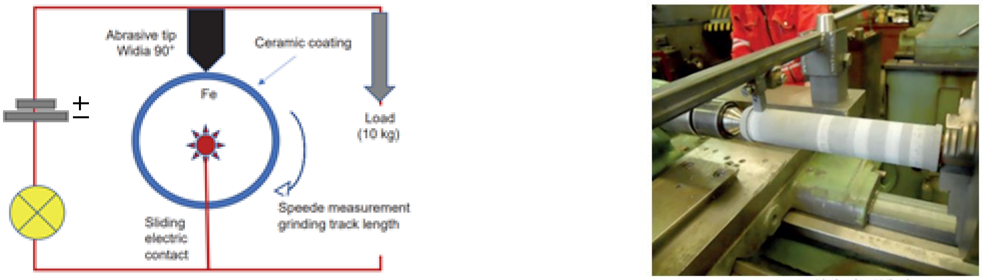
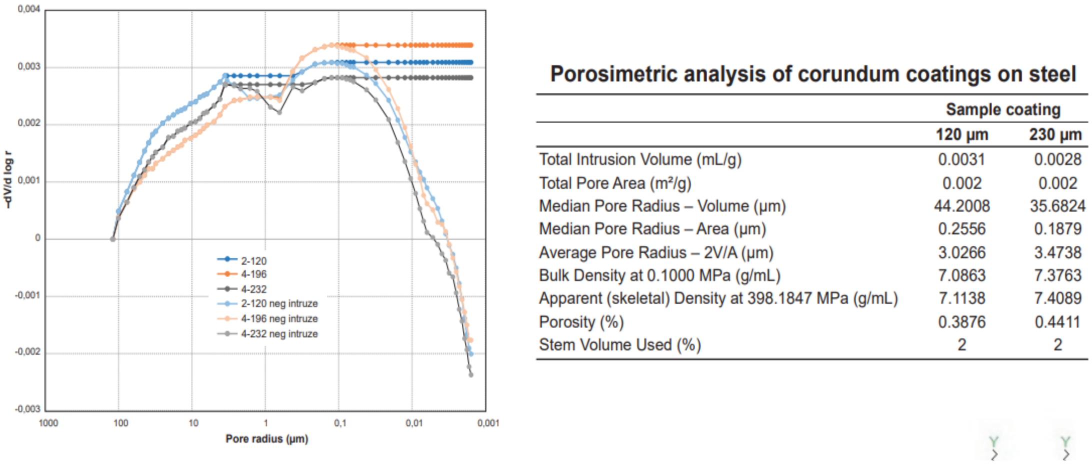


Figure 8. Measurement of the abrasive resistance of cylindrical corundum coatings with a thickness of 230 µm

Length of abrasion path up to the time of electric breakdown:
Tip with cutting edge 1 mm …….. 12 ÷ 15 cm
Tip with cutting edge 5 mm …….. 70 ÷ 80 cm

Mercury porosimetry (AutoPore IV 9500 Micromeritics) was used to determine the structural features of the coatings. The study was conducted in the vicinity of macropores and mesopores at pressures between 0.01 and 400 MPa, or for pore radius between about 10^{-4} and $1.5 \cdot 10^{-9}$ m (Figure 6).



Porosimetric analysis of corundum coatings on steel

	Sample coating	
	120 µm	**230 µm**
Total Intrusion Volume (mL/g)	0.0031	0.0028
Total Pore Area (m²/g)	0.002	0.002
Median Pore Radius – Volume (µm)	44.2008	35.6824
Median Pore Radius – Area (µm)	0.2556	0.1879
Average Pore Radius – 2V/A (µm)	3.0266	3.4738
Bulk Density at 0.1000 MPa (g/mL)	7.0863	7.3763
Apparent (skeletal) Density at 398.1847 MPa (g/mL)	7.1138	7.4089
Porosity (%)	0.3876	0.4411
Stem Volume Used (%)	2	2

Figure 9. Porosimetric analysis of corundum coating on steel 10 216

The samples were weighed once the porosimetric measurement was complete, and all the mercury was then extracted in a vacuum oven at 360°C (the boiling point of mercury is 356.7°C). According to the values of the overall incursion volume, the results allowed for a control calculation of the volume of open pores. The mean value of the open pore volume was 1.18 mm^3 per 1 cm^2 of the corundum-coated surface of the metallic steel substrate, which is supposed to have zero porosity, for coatings with a thickness of 230 m. This made it possible to impregnate the coating with 3-glycidyl-oxypropyl-triethoxysilane (GPTES) in a concentration of 1.025 mm^3/cm^2 (respectively 1.03 mg/cm^2).The strength of the anchoring of the silane thus depends on the formation of a chemical connection with the substrate, not only because of its wettability and surface tension but also because it protects an exposed metal surface from corrosion in open holes (cracks) (see Figure 7).

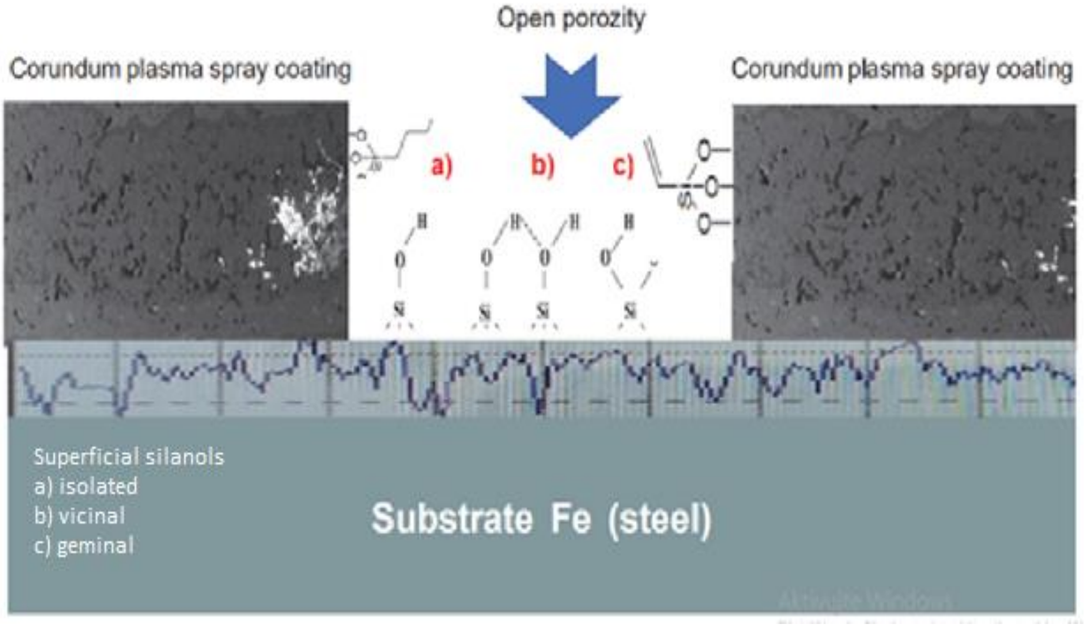
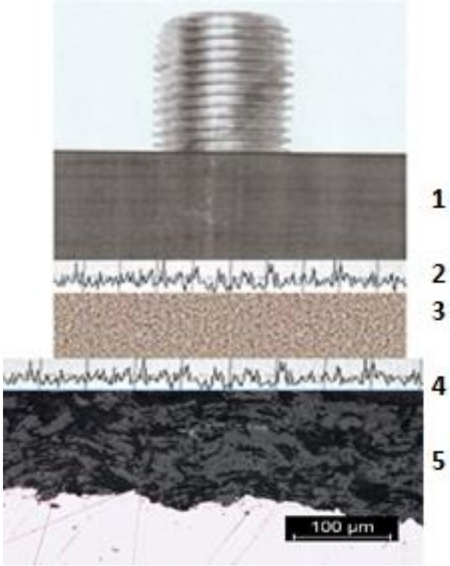


Figure 10. Idealized scheme of anchoring silane in open pores of corundum coating on substrate steel

The tensile (adhesion properties) strength of the coatings before and after impregnation with silane was measured on the COMTEST OP1/2 device according to the standard ČSN EN ISO 4624 673077 together with ČSN EN ISO 2409; see the diagram in Figure 8.



1) Tensile element of the device COMTEST OP1/2 (11kN) for the measuring tear strength (adhesion)
2) Tensile element surface roughness (µm) R_a 3.227, R_q 4.0250, R_z 22.361
3) Glue Loctite EA 9464 – Epoxy Adhesive or cement CEM I-42.5R
4) Sample 5a, 5b, 5c surface roughness R_a R_q R_z (µm)

5a. Steel 10 216 substrate with surface roughness (µm)
R_a 5.445, R_q 7.843, R_z 35.635; Pull of strength 5.08 MPa
5b. Steel with corundum coating with sufrace roughness (µm)
R_a 7.913, R_q 9.837, R_z 44.635; Pull of strength 15.08 MPa
5c. Steel with corundum coating impregnated by GPTES silane
Pull of strength 2.06 MPa

Figure 8. Variant of AH240 corundum coatings on steel 10 216 adhesion measurement

Conclusions

The tensile strength (adhesion properties) of the silane on the steel surface, or on its predominantly oxidized surface, but principally on the corundum porous walls, quantifies the restriction of the ingress of the corrosive medium to the structural steel surface by the porous structure of the corundum coating. Between the organic coating (topcoat) and the steel substrate, organosilane coatings act as adhesion bridges. Here, it is possible to suppose that oxygen bridges are providing vicinal binding[10]. The thermal stability of the samples must be confirmed because the application of various organic coatings is linked to the application of a higher temperature (thermosetting heat properties). Cataphoretic varnishes are guaranteed to be stable up to a temperature of 150°C for practical application. In order to provide useful information, the adhesion strength of this kind, which is determined by the substrate wettability with silane multiplied by its chemical link with inorganic oxides, was observed under heat stress. After 6 hours of heating at 150°C, 3-glycidyloxypropyl-triethoxysilane impregnated corundum coatings with a value of 1.03 Si mg/cm^2 (derived from the XRF analysis of the Si content) did not change the weight within the measurement error. The weight of the adsorbed silane began to gradually decrease only when heated above 150°C (flash point 3-glycidyloxypropyl-triethoxysilane, 144°C)[11], and it wasn't until a temperature of 375°C was reached that the definitive formation of the amorphous SiO_2 modification took place, which helped to firm up and permanently fill pores with another corrosion-resistant material.

Acknowledgement

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References

1. Angst U.M.: Materials and Structures 2018, 51, 1–20.
2. Glass G.K, BuenfeldN.R.: Corrosion Science 1997, 39 (5), 1001–1013.
3. Christodoulou C., Glass G., Webb J., AustinS., Goodier C.: Corrosion Science 2010, 52 (8), 2671–2679.
4. Wilson K., M. Jawed, V. Ngala, Construction and Building Materials 2013, 39, 19–25.
5. Söylev T.A., Richardson M.G.: Construction and Building Materials 2008, 22 (4), 609–622.
6. Manning D.G.: Construction and Building Materials 1996, 10 (5), 349–365.
7. Weishaar A., Carpenter M., Loucks R., Sakulich A., Peterson A.M.: Construction and Building Materials 2018. 191, 125–135.
8. Tittarelli T., Mariconi G.: Cement and Concrete Research 2008, 38 (11), 1354–1357.
9. Moshiri A., Stefaniuk D., Smith S.K., Morshedifard A., Rodrigues D.F., Qomi M.J.A., Krakowiak K.J.: Cement and Concrete Research 2020, 133, 106076.
10. Luštická I., Vyskočilová E., Červený L., Chem. Listy 107, 114–120 (2013). https://cz.vwr.com/store/product/2379083/3-glycidoxypropyl-triethoxysilane-sigma-aldrich

COMPARISON OF INORGANIC BINDERS POROSITY MEASURING METHODS

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Abstract

There are various methods for determining porosity of inorganic binders, but they differ mainly in the extent of determining pore size and connectivity. In this work, a set of samples containing varying content of cement and hydraulic clinker-free binder prepared from FBC ash was prepared. After that, the measurement of porosity was performed using several different methods, among which belong image analysis, mercury intrusion porosimetry and air pressure method, i.e., determination of the size of air pores in fresh unhardened binder. The choice of the method led to different porosity results, which were assessed. It was therefore possible to observe how the results are affected by the measurement ranges of the individual methods. Furthermore, the dependence of the porosity on the water to binder ratio was evaluated.

Introduction

Nowadays, because of the environmental requirements and the CO_2 emissions reduction, there is a tendency to partially replace cement by more environmentally friendly admixtures such as fly ash[1,2]. In order for such materials to be used in practice, it is necessary to test them and ensure their appropriate physical and chemical properties. One such property is the porosity of hardened mixtures containing these materials, which is closely related to strength, frost resistance and resistance in a corrosive environment.

In the past, a number of standardized or non-standardized methods were developed and tested for measuring the porosity of inorganic binders. When choosing a method, it is important to remember which specific parameters need to be obtained or for which types of concrete the measurement will be performed. Furthermore, it is advisable to deal with the range of measurement methods or their appropriate combination[3,4]. In this work, three subsequently described methods were chosen.

The air content pressure method specified in the standard EN 12350-7 Testing fresh concrete — Part 7: Air content — Pressure methods is used for measuring the porosity of fresh mortar[5]. This method is suitable for a quick indicative determination of the total porosity of concrete directly on construction sites. The advantage of this method is measurement simplicity and price. The disadvantage is often the reproducibility of the results and the absence of other information about, for example, the size or distribution of the pores, since the output of the measurement is only one-result values.

Among the most commonly used methods for examining the porosity of hardened mortars or concretes in practice is image analysis (IA), which is governed by the standard EN 480-11 Admixtures for concrete, mortar and grout — Test methods — Part 11: Determination of air void characteristics in hardened concrete[6]. The IA method determines not only the overall porosity, but also the pore size distribution or, for example, the spacing factor. The IA measurement has high reproducibility and can be used to determine pores with a size of 0.15 mm — cm units. The main disadvantage is the small area when scanning the sample.

A different possible non-standard method of measuring porosity is mercury intrusion porosimetry (MIP), which measures the distribution of pores in a wide range of 1.5 nm — 0.1 mm. The question arises whether this method is really suitable for measuring the porosity of concrete, where there is a large number of pores above the upper detection limit of this method. The disadvantage of MIP is mainly the toxicity of Hg, expensive instrumentation and the emergence of the so-called ink-bottle effect[7,8].

Materials and methods

Material characterization

In this experiment, mixed slurries were prepared from two input materials. First material was sulfocalcic binder Sorfix (SFX)[9,10] from Czech Republic, which mainly contains ground FBC ash. Second used material was Portland cement 42.5 R (CEM) Českomoravský cement, cement plant Mokrá, Czech Republic. The basic characteristics of these materials, including particle size distribution (PSD), X-ray fluorescence (XRF) and X-ray diffraction (XRD), are shown in the following Tables I–IV.

Table I.
PSD – frequency quantiles [µm]

Material	D10	D50	D90
SFX	1.60	18.65	140.36
CEM	2.52	14.11	44.19

Table II.
XRF – oxide composition [wt.%], (LOI = loss on ignition)

Material	SiO_2	Al_2O_3	CaO	SO_3	Fe_2O_3	TiO_2	MgO	Others	LOI
SFX	31.6	24.9	20.2	8.4	4.3	2.3	0.7	1.1	6.5
CEM	18.0	4.6	63.7	4.5	3.4	0.0	1.3	1.1	3.4

Table III.
XRD – quantitative SFX phase composition [wt.%], Rietveld method (error Rw <5%)

Material	Amorph. phase	Anhydrite	Quartz	Lime	Portlandite	Calcite	Anatase	Magnetite	Others
SFX	58.0	15.5	8.5	6.0	5.5	1.5	1.5	1.0	2.5

Table IV.
XRD – quantitative CEM phase composition [wt.%], Rietveld method (error Rw <5%)

Material	Amorph. phase	Hatrurite	Larnite	Brownmillerite	Calcium aluminum oxide	Gypsum	Others
CEM	10.0	55.5	17.0	11.0	2.5	2.0	2.0

Preparation of mixtures

In total, 5 mixtures labelled CSK 10 – CSK 70 containing different ratio of CEM and SFX were prepared. All mixtures contained a constant amount of plasticizer based on polycarboxylates, a constant amount of aeration additive and a varying amount of water to binder ratio (*w*), in order to maintain the same workability of the mixtures. The detailed composition of the mixtures is shown in Table IV.

During the preparation of the slurries, the dry ingredients were first weighed on laboratory scale EW 4200-2NM (Kern, Czech Republic). Subsequently, the components were dry homogenized for 1 minute in a standardized ELE mixer. After that, water containing superplasticizer was added. Aeration additive was added for the last minute of mixing. The total mixing time was 17–18 minutes.

Table IV.
Sample preparation

Mixture	CEM [%]	SFX [%]	*w*	Superplasticizer [%]	Aeration additive [%]
CSK 10	90	10	0.20	2	0.025
CSK 20	80	20	0.20	2	0.025
CSK 30	70	30	0.22	2	0.025
CSK 50	50	50	0.23	2	0.025
CSK 70	30	70	0.25	2	0.025

Powder material characterization methods instrumentation

PSD

The laser particle size analyzer Bettersizer ST (Dandong Bettersize Instruments Ltd., China) placed in laboratory Korund Benátky, s.r.o., Czech Republic, was used to determine particle size distribution.

XRF

To measure the elemental composition via X-ray fluorescence, sequential wave-dispersive X-ray spectrometer ARL 9400 XP (Thermo ARL, Switzerland) with the WinXRF software was used. Spectral intensities were measured in vacuum and results were processed using the Uniquant 4 software.

XRD

Using the θ-θ X'Pert3 Powder diffractometer (PANanalytical, Netherlands) with a Bragg-Brentan parafocusing geometry and CuKα radiation wavelength (λ = 1.5418 Å, U = 40 kV, I = 30 mA), the X-ray diffraction was measured. Thanks to HighScore Plus 4.0 software with Rietveld method, qualitative and quantitative analyses were evaluated. Internal standard 10 wt.% ZnO was used to determine the amount of amorphous content of the materials.

Porosity measurement methods instrumentation

Air content – pressure method

The fresh air content – pressure method based on the EN 12350-7 standard was used to measure the aeration of fresh slurries immediately after mixing. The measurement was carried out using a device Air entrainment meter (Testing Bluhm & Feuerherdt GmbH, Germany) with a volume of 1 liter. The slurry compaction time before measurement was chosen to be 2 minutes.

IA

Image analysis was performed according to EN 480-11 standard. Firstly, cylindrical samples with a diameter of 10 cm were prepared from all the mixtures. These were subsequently compacted for 2 minutes and stored in a water-saturated environment at a temperature of 21 °C in the curing cabinet BS VLH-203 (Beton System, Czech Republic) for 28 days. Secondly, the samples were unmolded and cut according to the requirements of the EN 480-11 standard. A confocal laser microscope LEXT OLS5000 (Olympus, Japan) was used for the actual measurement of porosity with a 10x objective magnification. The evaluation was carried out according to the standard in the NIS-Elements Advanced Research 3.10 program (Nikon, Japan).

MIP

Mercury intrusion porosimetry of open pores was measured on 28-day cured samples by AutoPore IV 9500 (Micromeritics, Georgia USA) with the porosity evaluation in the range of 101.325 kPa – 400 MPa with a corresponding range of pore size radius of $6 \times 10^{-6} – 1.5 \times 10^{-9}$ m. The measurement took place in two phases, with the high-pressure analysis measuring the pores in the range of 1.5 nm – 3 µm and the low-pressure analysis measuring the pores in the range of 3 µm – 0.1 mm.

Results and discussion

Since porosity was measured by three different methods, the following Figure 1. shows a comparison of their results including standard deviations.

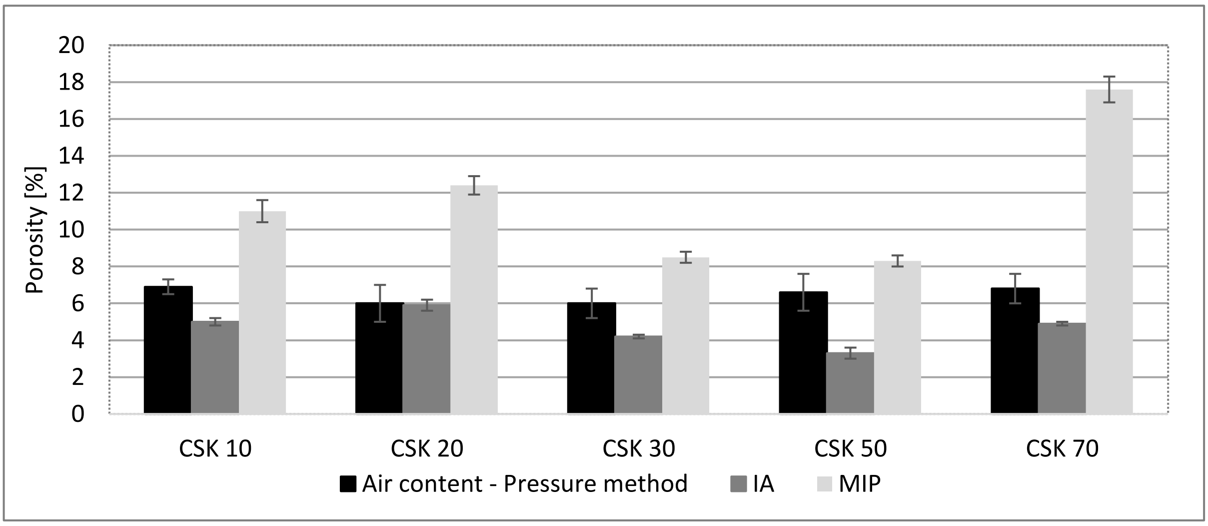

Figure 1. Comparison of total porosity results

Firstly, results of measuring Air content were on average in the range of 6.0–6.9% and no correlation with *w* was found there. Air content – pressure method generally shows a higher degree of variation. This issue probably arises from the fact that the measurement takes place on fresh slurries, where the mixing time, the time of filling the measuring container, the sealing method and even the length of time of the pressure measurement have a great influence. Ley and his team[11] dealt with this issue, for example, as they minimized the error by using two identically calibrated devices at the same time for the same fresh cement mixture.

Secondly, the optical analysis results were in the range of 3.3–5.9%. No correlation with *w* was found; on the contrary, even samples CSK 10 and CSK 20 with the lowest *w* exhibited the highest porosity as a result of IA. An explanation for this can be given using the following detailed MIP results (Figures 2, 3) which show that these two samples contained a higher number of smaller pores that are not detectable with the IA microscope.

Finally, the results of MIP measurements show some degree of variation. Here, the reason is mainly influenced by which part of the sample (center or edge) was selected for measurement. As these were fragments of hardened bodies, different parts of the bodies could be measured each time. The average of the MIP measurement results was in the range of 8.3–17.6% and a direct correlation with *w* was again not found. Only in case of sample CSK 70 possible increase in porosity associated with increasing *w* may be observed. This corresponds to the results of Cook and Hover[12], who confirmed that a lower *w* leads to lower porosity values. However, this information is not completely unambiguous in the case of this work, since the samples were prepared from different mixtures of two binders with different granulometry. The MIP process is illustrated in more detail in the following Figures 2, 3.

Regarding the comparison of methods, the results show that each method measures in a different range and the results cannot be compared with each other. These results are consistent with Gregorová et al.[13] who, among other things, compared the porosity of mullite foam by IA and MIP. The techniques have been shown to contribute different information, but their combination provides a consistent picture of the microstructural properties when suitably modified. Similar conclusions are also contained in works[3,4].

In general, it can be said that the largest porosity values were recorded for MIP, which has the largest measurement range of the aforementioned methods. With the Air content – pressure method, the results from the point of view of concrete preparation are rather indicative, therefore its greater advantage is the simplicity of execution. The IA results proved to be the most consistent.

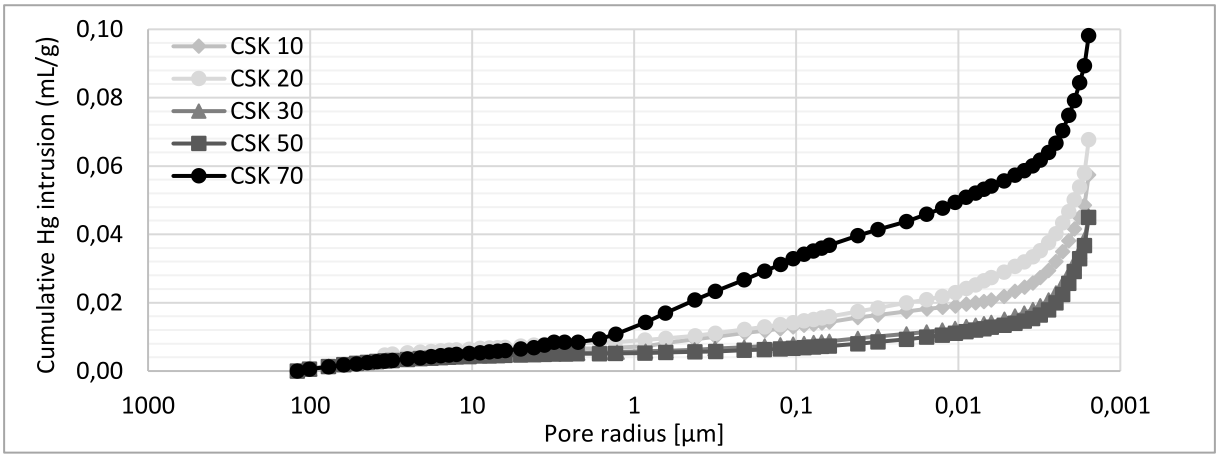

Figure 2. MIP results – cumulative curves

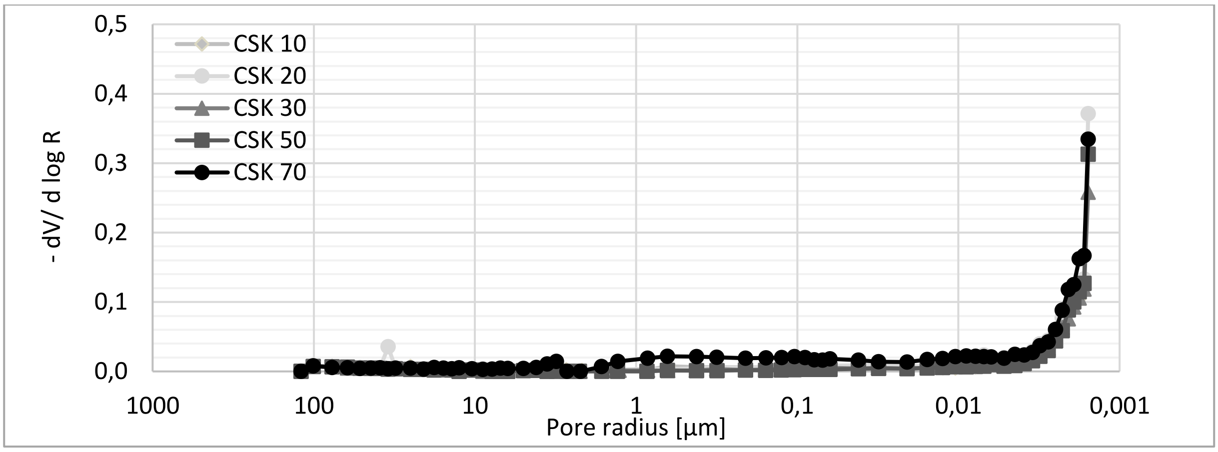

Figure 3. MIP results – distribution curves

For more detailed information regarding the MIP pore distribution of individual slurries, the Figures 2, 3 with cumulative and distribution curves are provided. It is evident from the distribution curves that the highest number of pores measured by MIP for all slurries was below the pore size of 0.01 µm.

Furthermore, it can be seen from the cumulative curves that the highest intrusion volume was recorded for the CSK 70 sample, which contained the biggest amount of SFX binder and also had the highest *w*. The CSK 70 curve shows a change in shape compared to the other samples, which is related to the pore radius, as can be seen for the increased intrusion volume of Hg in the region of 1–0.001 µm. The curves for CSK 10–CSK 50 have a similar shape character, while CSK 30 and CSK 50 have practically identical results. CSK 10 and CSK 20 are almost similar, although CSK 20 has a slightly higher total intrusion volume and thus porosity for the same *w* = 0.20 as CSK 10.

Conclusions

The following results were measured by three porosity measurement methods; air content 6.0–6.9%, MIP porosity 8.3–17.6%, IA porosity 3.3–5.9%. The highest number of pores measured by MIP for all slurries was below the pore size of 0.01 µm. The predicted increase in porosity with increasing *w* was not confirmed. An increasing *w* was observed with an increasing proportion of SFX binder while maintaining the same consistency of the mixtures. No correlation was found between the porosity measurement methods used.

Acknowledgement

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References

1. Siddique, R.; Cachim, P. *Waste and Supplementary Cementitious Materials in Concrete: Characterisation, Properties and Applications*, 1st ed.; Woodhead Publishing, 2018.
2. Lothenbach, B.; Scrivener, K.; Hooton, R. Supplementary cementitious materials. *Cement and Concrete Research* **2011**, *41* (12), 1244–1256. DOI: 10.1016/j.cemconres.2010.12.001.
3. Song, Y.; Zhou, J.; Bian, Z. Pore Structure Characterization of Hardened Cement Paste by Multiple Methods. *Advances in Materials Science and Engineering* **2019**, *2019*, 1–18. DOI: 10.1155/2019/3726953.
4. Jiang, Z.; Pan, Y.; Lu, J.; Wang, Y. Pore structure characterization of cement paste by different experimental methods and its influence on permeability evaluation. *Cement and Concrete Research* **2022**, *159*, 10689. DOI: 10.1016/j.cemconres.2022.106892.
5. EN 12350-7. *Testing fresh concrete – Part 7: Air content – Pressure methods*. CEN, 2019.
6. EN 480-11. *Admixtures for concrete, mortar and grout – Test methods – Part 11: Determination of air void characteristics in hardened concrete*. Cen, 2005.
7. Abell, A. B.; Willis, K. L.; Lange, D. A. Mercury Intrusion Porosimetry and Image Analysis of Cement-Based Materials. *Journal of Colloid and Interface Science* **1999**, *211* (1), 39–44. DOI: 10.1006/jcis.1998.5986.
8. Diamond, S. Mercury porosimetry. An inappropriate method for the measurement of pore size distributions in cement-based materials. *Cement and Concrete Research* **2000**, *30* (10), 1517–1525. DOI: 10.1016/S0008-8846(00)00370-7.

9. Ohenoja, K.; Pesonen, J.; Yliniemi, J.; Illikainen, M. Utilization of Fly Ashes from Fluidized Bed Combustion: A Review. *Sustainability* **2020**, *12*, 2988. DOI: 10.3390/su12072988.
10. Škvára, F.; Šulc, R.; Snop, R.; Peterová, A.; Šídlová, M. Hydraulic clinkerless binder on the fluid sulfocalcic fly ash basis. *Cement and Concrete Composites* **2018**, *93*, 118–126. DOI: 10.1016/j.cemconcomp.2018.06.020.
11. Ley, M. T.; Welchel, D.; Peery, J.; Khatibmasjedi, S.; LeFlore, J. Determining the air-void distribution in fresh concrete with the Sequential Air Method. *Construction and Building Materials* **2017**, *150*, 723–737. DOI: 10.1016/j.conbuildmat.2017.06.037.
12. Cook, R. A. Mercury porosimetry of hardened cement pastes. *Cement and Concrete Research* **1999**, *29*, 933–943.
13. Gregorová, E.; Uhlířová, T.; Pabst, W.; Diblíková, P.; Sedlářová, I. Microstructure characterization of mullite foam by image analysis, mercury porosimetry and X-ray computed microtomography. *Ceramics International* **2018**, *44*, 12315–12328.

RESISTOMETRIC METHOD FOR CORROSION MONITORING

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Abstract

The main objective of this work was to provide information on corrosion monitoring technique – resistometric method. Most metallic materials are exposed to atmospheric conditions, where their corrosion occurs. Corrosion monitoring techniques are used to gather information about corrosion processes which leads to preventing or at least minimizing damages caused by corrosion processes. A principle of resistometric method and development of this technique will be discussed. The development of resistometric method consisted of surface treatments of the sensors. Real metallic materials appear in different states of surface such as: polished, coated, corroded, etc. Therefore, there is an effort to prepare sensors with a surface relatively like a surface of real metallic object. The corrosion response of surface treated sensors was observed.

Introduction

Corrosion monitoring techniques allows us to prevent or at least minimize damages caused by corrosion processes. Resistometric method presents one of the techniques of corrosion monitoring. The main principle of this method consists in measuring the electrical resistance of the resistometric sensor. Resistometric sensors is shown on the Figure 1, on the nonconductive substrate is metallic track, which is divided into two part –reference and measurement. Reference part is covered and is not in contact with environment, thus it doesn´t corrode and a thickness of the reference part remain constant. On the other hand, the measurement part of the sensor communicates with an environment and may corrode, thus the thickness of the measurement part is reducing while it corrodes. The monitoring consists of measuring the electrical resistance of these two parts of sensor, knowing the initial resistances of those parts allows us to calculate corrosion loss in thickness. The electrical resistance depends on the thickness of conductor, therefore when the sensor corrodes, the thickness is reduced and electrical resistance increases. The role of reference is in compensation of temperature changes, because temperature affects electrical resistance. A formula used to calculate the corrosion loss is:

$$\Delta h = h_0 \cdot \left(1 - \frac{R_{\mathrm{ref}}}{R_{\mathrm{sens}}} \cdot \frac{R_{\mathrm{sens},0}}{R_{ref,0}}\right)$$

where h_0 represents initial thickness, R_{ref} represents resistance of reference part and R_{meas} stands for resistance of measurement part, index 0 means initial value. The sensor measures the corrosion rate of itself, not of the metallic object it is placed on, which is quite clear regarding the principle, regarding that the sensor must be from a same material as a monitored object. Sensors may be produced from any metal or alloy. The advantage of resistometric sensors is that it provides real-time data[1,2,3].

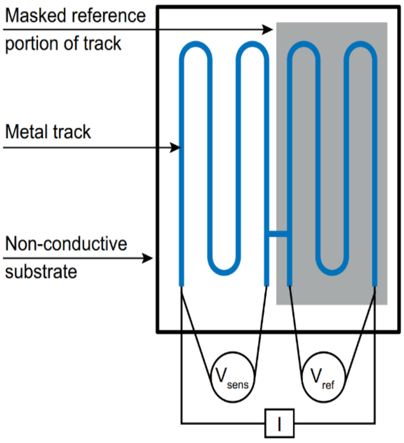

Figure 11. Schematic picture of resistometric sensor[1]

A surface state of sensor plays an important role, it is well known that differently treated surfaces of same metal corrode with different rate. For example, a corroded surface expresses higher corrosion rates in comparison with polished surface. So, a surface of a sensor should be similar to a surface of a monitored object. In this case the resistometric method would provide reliable data. The presence of corrosion products usually doesn´t affect the resistivity, because the corrosion products have much lower conductivity in comparison with metals and thus, we can assume that current flows through the metal track and not through the corrosion products[4,5].

Experiment

Sensor's preparation

Steel resistometric sensors (C1008 steel) were used to monitor corrosion rates for comparison of different surface states – clean surface, corroded surface and protected surface. The thickness of used sensor was 50 µm. The sensors were connected to data logger ACD-03 Metricorr by 10-wire cable. The reference part was covered by the epoxy resin (UHU plus schnellfest). A sensor that represented clean surface was just etched in solution of HCl (1:1 by volume), to get rid of corrosion products, for 30 s and then rinsed by demi-water and dried with ethanol. A sensor representing corroded surface was prepared by exposure of the sensor over the SO_2 vapours for 1 hour, vapours were formed due to the reaction between H_2SO_4 and Na_2SO_3. A sensor representing protected surface was treated by commercial sealing agent (PG Seal Fe), which sealed the surface of steel.

Exposure

Prepared surface treated sensors were put into a climate chamber (Binder KBF 240). Conditions of exposure are shown on the Figure 2 – temperature range was between 20 °C and 30 °C and the relative humidity range was between 30% and 85%.

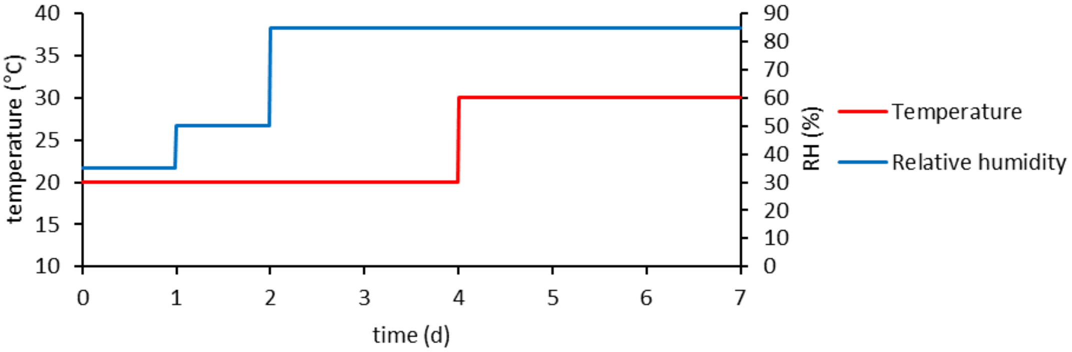

Figure 12. Conditions during exposure – changes in temperature and relative humidity

Discussion and result analysis

The goal was to describe the changes in corrosion rate of different surfaces exposed in climate chamber under changing conditions (Figure 2). The data from steel resistometric sensors with different surface treatments are plotted on the Figure 3. The types of surfaces were: cleaned surface, corroded surface and protected (sealed) surface. The corrosion rate during the first two days of the exposure of all sensors was almost zero. At approximately 48 h, the relative humidity increased from 50% to 85% and this led to increase of the corrosion rate of precorroded and cleaned sensor. The corrosion rate of the sensor representing protected surface remained negligible during whole exposure, it means that the protective sealant was sufficient to the conditions set into climber chamber and the sensor didn´t corrode.

This is not surprising result that the surface which have been already damaged (precorroded) showed higher corrosion rate than clean surface (or even protected surface). The corrosion rate of precorroded surface wasn´t constant during the whole exposure and was changing as the conditions in climate chamber were changing. The response of the sensor on the change of conditions was immediate.

The corrosion rate of cleaned sensor increased slightly when a relative humidity in the chamber reached 85%, it is markable on the Figure 3 that the corrosion rate was changing in time as condition in the climate chamber changed.

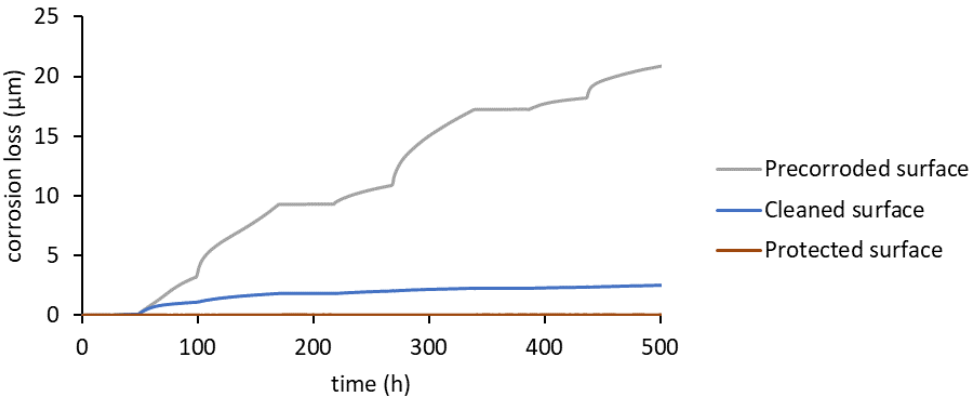

Figure 13. Corrosion loss of resistometric sensors with different surface treatment in climate chamber

The corrosion rate of cleaned and protected sensor remained very low after two weeks of exposure, two complete exposure cycles. Images of resistometric sensors are shown on the Figure 4. The surface of each sensor corresponded to calculated corrosion losses. For example, the sealed surface didn´t show any corrosion loss and the surface appearance remained unchanged. Appearance of the precorroded sensor remained almost same too, only the thickness of corrosion products increased. The thin layer of corrosion products appeared on the surface of the cleaned sensor, as can be seen on the image below.

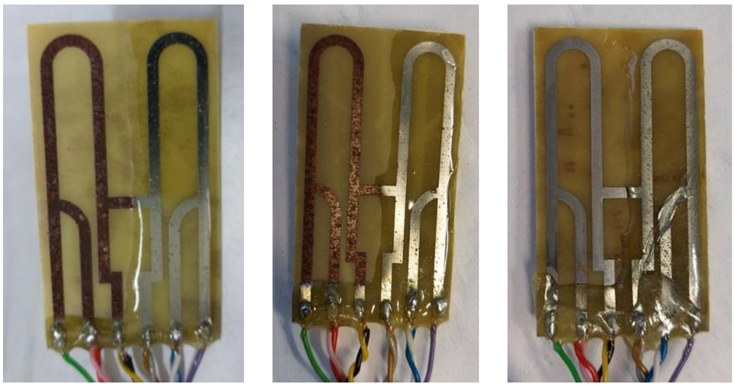

Figure 4. Images of used rezistometric sensors after the exposure test. From left: precorroded sensor, cleaned sensor, protected sensor (sealed)

On the other hand, the laboratory prepared precorroded surface corroded faster than sensors with naturally formed corrosion products (prepared by 1 year long outside exposure) under same condition. But anyway the corosion rate of pre-corroded surface, both naturally and artificially, is higher than the corrosion rate of the cleaned surface. This fact motivates us to find better conditions for preparation of artificialy corrosion products, which would act similairly to naturaly formed corrosion products in atmposhere.

Conclusion

Rezistometric sensors with different surfaces corroded with different corrosion rates. Already pre-corroded sensor showed the highest corrosion rate and the sensor with protected surface (sealed) showed the lowest corrosion rate, which was almost zero. The sensor with surface cleaned from any impurities showed higher corrosion rate only during the time when relative humidity was above 50%. The results from exposure in climate chamber confirm the idea, that for the right corrosion monitoring it is necessary to prepare surface of sensors which is similair to a surface of monitored objects. This work is part of a project focused on development of resistometric sensors. From these results arose other motivation for future research, such as preparation of other types of surfaces which corroectly substitutes real surface or effort to describe limits of the resistometric method.

Acknowledgement

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References

1. M. Kouril, T. Prosek, B. Scheffel, F. Dubois: High sensitivity electrical resistance sensors for indoor corrosion monitoring, Corrosion Engineering, Science and Technology, *48(4)*, 282 (2013).
2. Li S., Kim Y.-G., Jung S., Song H.-S.: Application of steel thin film electrical resistance sensor for in situ corrosion monitoring, Sensors and Actuators B: Chemical, *120,* 368 (2007).
3. Paolinelli L.D., Pérez T., Simison S.N.: The effect of pre-corrosion and steel microstructure on inhibitor performance in CO_2 corrosion, Corrosion Science, *50(9)*, 2456 (2008).
4. Mercier-Bion F., Li J., Lotz H., Tortech L., Neff D., Dillmann P.: Electrical properties of iron corrosion layers formed in anoxic environments at the nanometer scale, Corrosion Science, *137*, 98 (2018).
5. Hao L., Cheng B.R.: Sealing processes of anodic coatings—Past, present, and future, Metal Finishing, *98(12)* 8 (2000).

OIL, PETROCHEMICALS, BIOFUELS

KEY TRENDS AND STRATEGIES IN THE OIL AND PETROCHEMICAL INDUSTRY

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Abstract

The number and capacity of oil refineries in Europe is steadily declining, and refinery equipment is aging. In the last 20 years no new steam cracker unit has been constructed. This is in contrast to the Middle East and Asia, where large investments are commissioned. Most oil refineries in Europe are integrated with petrochemicals, and cooperation in this direction will increase. Past efforts to save energy for economic reasons are now being transformed into nobler decarbonization activities to face the climate change as a fundamental imperative. Some oil refineries are being transformed into biorefineries as part of a transition towards a circular economy. Feedstocks and utilities shift towards recycled plastics and scrap tires, agricultural residues, and municipal waste. State-of-the-art catalysts, new types of equipment, new environmentally friendly technologies, innovative technological schemes, utilities and products with low carbon content are being developed. The drop-in concept will be important in the transition phase towards decarbonized products. E-fuels/e-chemicals represent a way of joining various sources of carbon dioxide and green hydrogen for the methanol or Fischer-Tropsch synthesis and are examples of the increasingly close integration of the refining and petrochemical industries. The role of digitalization is growing for planning, production optimization, predictive maintenance, logistics, efficient use of workforce, safety, and protection of the environment. The change in the mindset of the staff, strong leadership, proper master planning, and new investments will be important in the preparation of successful strategies.

Introduction

The oil refining and petrochemical industries are currently characterized by different trends in developed (Western) and developing (Eastern) countries. While the US and Europe are consolidating and rationalizing this industry, the Middle East, India, China, and Southeast Asia are experiencing rapid growth in oil refining and petrochemical capacities that will last until 2040[1]. Refinery activities in Europe are clearly legislatively driven and will be affected by approval of the new carbon dioxide emissions targets for future cars (EU's Fit for 55 package[2], the EU RED III Directive[3], and the EU-7 standard[4]), the emerging electromobility, the ban on the use of internal combustion engines in new passenger cars in Europe from 2035[5], and the real purchasing power of the population. While the consumption of mogas will gradually decline and the future of diesel is not entirely clear, consumption of jet fuel, marine fuel, and petrochemicals is expected to grow. In 2022, there were 89 refineries in operation in Europe (minus 15 in the last 10 years) with a total crude oil name-plate capacity of 663 Mt·y^{-1} (-65 Mt·y^{-1}). Of these, 74 (-12) were the main stream refineries processing crude oil and 15 (-3) other refineries focused on processing petroleum condensate, asphalt, and lubricants. The average main stream refinery capacity was 8.959 Mt·y^{-1} (+0.494 Mt·y^{-1}), see Figure 1[6].

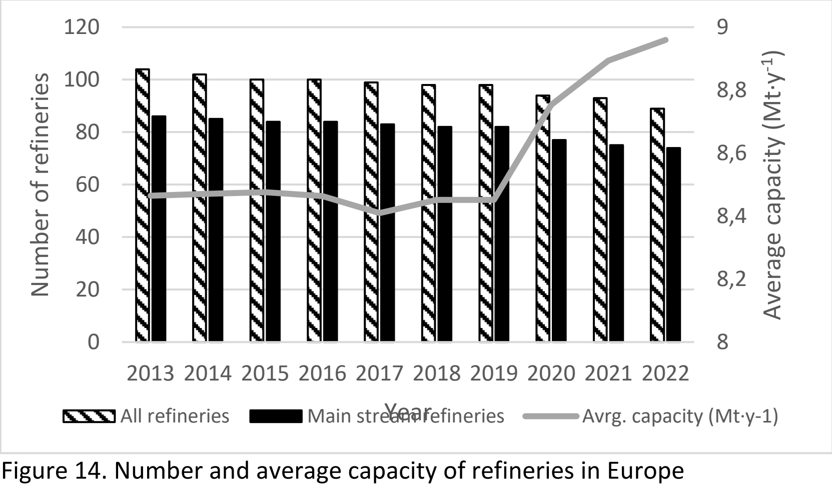

Figure 14. Number and average capacity of refineries in Europe

Three new oil refineries are under construction or planned in Europe in Porto Romano, Albania, Kahramanmaras, Turkey (1.4 $Mt \cdot r^{-1}$), and Aliaga, Turkey[7].

While the refining business in Europe is declining, interest in petrochemicals is growing[1]. In 2021, there were 45 steam crackers in operation in Europe with an ethylene nameplate capacity of 23.5 $Mt \cdot y^{-1}$ and production of 19.3 $Mt \cdot y^{-1}$ (it corresponds to about 60 $Mt \cdot y^{-1}$of feedstocks)[8,9]. A new steam cracker is in construction in Antwerp now (INEOS, 1.54 $Mt \cdot y^{-1}$ ethylene, CAPEX €3.5 bn), the first such investment in Europe in 20 years[10]. An overview of ongoing refinery and petrochemical projects, both conventional and renewable, is available[7,11].

A large number of refineries are integrated with or very close to steam crackers sites, which shows the close link between these two businesses and demonstrates the contribution of refineries to the production of high value-added products. This integration will develop in two directions:

- Optimization of feedstocks for steam crackers, e.g., maximization of n-alkanes in these feedstocks. Significantly higher ethylene yields than 35 wt% can be achieved using naphtha reverse isomerization and adsorption of n-alkanes on molecular sieves.
- Production of basic petrochemicals directly at the refinery, e.g., propene by selective dehydrogenation of propane or from the PetroFCC, and the production of aromatics at the refinery using catalytic reforming technology.

Innovative technological schemes are developed based on matured technologies, e.g., Honeywell Integrated Olefins Suite (IOS)[12-14]. However, the direct use of crude oil to produce olefins, bypassing refinery processing, is also being studied[1,15].

Decarbonization in 20XX plays out as an inevitable goal. The current general baseline is the "Green Deal for Europe"[16]. In the oil refining and petrochemical industry, it takes place is represented by two concepts: the easier "decarbonization of operations" and the more challenging "decarbonization of products"[17]. These concepts are not entirely new[18,19], but are now becoming an absolute priority and are reflected in strategies such as:

- "Zero emissions refinery"[20].
- "Refinery 2050", which focuses on hydrotreatment of lipids, gasification of lignocellulosic biomass, e-fuels based on captured carbon dioxide and green hydrogen (Concawe)[21], and other measures to reduce the carbon footprint (CEIP)[22].
- "Refinery of the future" (Honeywell), based on the following efficiencies – "putting the right molecules in the right place", "doing more with less utilities", "treating water as a scarce source", "providing for a greener tomorrow as concerns emissions", "optimizing the sources", "uses of hydrogen", and "driving for more bankable projects"[23].
- "Zero emissions steam cracker", based on hydrogen as energy source[10].
- "Steam cracker of the future", associated with the idea of electric heating[24].

As concerns decarbonization from operations – refining and petrochemical complexes are among the most energy-intensive industries. They are therefore from the beginning designed as thermally integrated facilities and rationalization of heat consumption, currently interpreted as reducing carbon dioxide emissions, has always been a central operational objective. The following trends occur in this respect[25].

- State-of-the-art catalysts are being implemented, that is, more active and selective golf balls are being developed for tubular reactors of steam methane reformers, catalysts operated in expanded bed to process crude oil residues[26], and ionic liquids[27] are being developed.
- Rationalization and optimization of existing technologies to save energy, reduce emissions, and encourage recycling[21].
- Bottom-of the-barrel processing, to get more valuable products from less oil[28].
- Utilization of new environmentally friendly technologies, focusing on the use of waste process streams, for example the Honeywell nViro concept[29].
- Carbon dioxide capture and storage (CCS)[30].
- Burning of refinery fuels and coke on catalysts with oxygen to obtain carbon dioxide in high concentration to process it chemically (CCU)[31].
- Use of green hydrogen as fuel[32-34]. Oxygen as a by-product of green hydrogen production may be used in line with the previous point.
- Use of new equipment, e.g., revolutionary electric heaters[35-37]. The first demonstration electrically heated steam cracker furnace (duty 6 MW, input 4 $t\ h^{-1}$) will be commissioned at BASF, Ludwigshafen, in 2023, on the basis of a cooperation between BASF, SABIC and Linde[38].
- Integration of oil refineries into local economic value chains related to heat, electricity, green hydrogen, biofuels, CCSU activities, and e-fuels production[22].

As regards decarbonization of products, the RED II Directive on the promotion of the use of energy from renewable sources[39], or the upcoming RED III[2,40] are the governing documents. Refineries accelerate the transition to renewable fuels[41]. Certain mainstream refineries have been partially or fully converted to biorefineries producing low carbon fuels (LFC), for example in Europe these include refineries in Venice[42], Gela[43] (ENI), La Mède[44] (Total), or to terminals for renewables. Particular attention is paid to the treatment of various biofeeds, waste plastics, scrap tires to fuels and chemicals combining petrochemical and refinery processes. Pyrolysis, gasification, methanol synthesis, Fischer-Tropsch synthesis, hydrogenation, and ammonia synthesis are the focus of attention[45-47]. For many reasons, green and blue hydrogen, ammonia, and methanol will be the fastest growing products. E-fuels and e-chemicals represent a new type of products based on green hydrogen and captured carbon dioxide, using matured refinery (Fischer-Tropsch) and petrochemical technologies (methanol synthesis). This issue is discussed in great detail in the Concave reviews and reports[48-50]. E-hydrogen, e-methane, e-methanol, e-OMEx, e-methanol-to-gasoline, e-methanol-to-kerosene, e-ammonia, e-Fischer-Tropsch kerosene and diesel pathways are considered. In 2030, a production of 1 Mt e-fuels and a cost of 2.38 $€\cdot ltr^{-1}$ of diesel eq. are predicted in Central Europe using a high concentration carbon dioxide source. The consumption of 65–160 Mtoe of low carbon fuels is projected in 2050. A reduction in GHG of 92–97% will be achieved compared to standard fossil fuels[51]. E-methanol occupies an exceptional position among all e-products as a platform for the production of various motor fuels, a wide range of chemicals and petrochemicals, and as a final product, e.g., as a marine fuel[52]. Based on different scenarios, electrification of road transport is expected to reduce the consumption of standard petroleum fuels by 1/3 in 2050. The drop-in concept will be important in the transition phase to decarbonize products because it allows to overcome some of the different features of alternative products and to further exploit the existing quality standards and industrial infrastructure. Currently, this concept is most frequently discussed in the context of jet fuel for a wide range of sustainable aviation fuels (SAF)[53].

Digitalization will be important to implement analytical intelligence (production planning and optimization), asset performance management (reduction of downtime), predictive maintenance (development of digital twins, machine learning and artificial intelligence, to save costs), to improve logistics, workforce knowledge and skills of newly implemented technologies (by way of simulators), safety and health, and protection of the environment[9,54,55]. Large software companies (AspenTech, Microsoft, and KBC) are involved in this trend[56].

In a rapidly evolving environment for the refining and petrochemical business, it will be important to properly evaluate project returns, so appropriate methods are being developed[23].

Discussion

It is clear that the capacity of oil refineries in Europe will continue to decline in the face of the declining consumption of motor fuel. Staying in business will require sufficient capacity (economy of scale), the tightest possible integration with petrochemical production, the greatest possible specialization, the most intensive on-site collaboration, and decarbonization of operations and products. However, to what extent the aging assets in Europe will be competitive with the rest of the world will be a serious question.

The concept of "putting the right molecule in the right place" corresponds in reality to the transfer of thinking typical in petrochemistry and organic chemistry to the refining business, to the petroleum continua continuum. Given the huge material flows in oil refineries, such thinking can translate to interesting profit.

Transforming a traditional oil refinery into a biorefinery seems like an interesting idea, but apart from the high costs of such transformation, only pioneering main-stream refineries can be transformed into a biorefinery because unlike in the case of crude oil, there are not enough traditional biofeedstocks available. Importing vegetable oils over long distances makes no sense. In other words, transforming every other oil refinery into a biorefinery will mean inventing new, original solutions, which will be a major challenge.

In terms of decarbonization, refineries offer a wide range of mature technologies for processing alternative feedstocks, from recycled plastics, scrapped tires, agricultural residues, and municipal wastes to LCF. Therefore, current oil refineries can be well incorporated into the recycling economy.

Certainly, for the next two decades, large volumes of petroleum products will make it easy to integrate products from alternative feedstocks. The drop-in concept has been repeatedly and successfully applied in the past, e.g., for the implementation of coal components (aromatics) and biocomponents (bioethanol and FAME) in motor fuels at low concentrations. The current drop-in concept is characterized by the fact that the range of components processed in this way has expanded and that this concept can also be used for the preparation of certain feedstocks, e.g., for steam cracker or FCC. For this reason, it is necessary to continue researching this concept. The drop-in concept is also important in forcing entities that previously had little in common to cooperate.

As concerns e-fuels, extracting carbon dioxide in concentrations of 0.05 wt% from the air when there are many industrial sources of carbon dioxide with concentrations several orders of magnitude higher makes no sense. Chemicals that occur at much higher concentrations in refineries and petrochemical complexes and yet are now being burned should be given priority, e.g., hydrogen or ethylene in FCC gases. Green hydrogen requires green electricity, but in addition to chemical processing it can also be used to store surplus green electricity.

The numerous and serious negative physicochemical properties of the new chemical favourites, e.g., hydrogen, methanol, and ammonia, should not be overlooked and undervalued when new strategies are developed.

The traditionally highly skilled workforce should represent a competitive advantage for the consolidation and rationalization of the refining and petrochemical industry in Europe. A change in staff mindset, strong leadership, proper master planning of future activities, and new investments will be important in preparing and implementing entrepreneurially successful strategies.

Conclusions

The number and total capacity of oil refineries in the developed countries is declining. In Europe, about 15 and 65 MT·y^{-1} of name-plate capacity has been shut down in the last ten years, while the opposite was true in the developing countries. The reasons are related to EU legislation. The strategic milestones in Europe will be 2030, 2035, and 2050. Most oil refineries in Europe are integrated with petrochemical production. This integration, the decarbonization of operations and products, the involvement in the concept of industrial recycling, and the production of e-fuels and e-chemicals will be important for the necessary transformation of the refinery and petrochemical industry. The drop-in concept, digitalization, and skilled workforce should assist this transformation. In the world of energy once dominated by oil, electricity will take over. Realizing a zero-emissions world will require extremely strong and risk-proof investors. Thus, this business will be further integrated and internationalized. At the same time, it will open up the possibility of applying break-through ideas and represent a great challenge for research and development.

Acknowledgement

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References

1. Couch, K.; Funk, G. As global petrochemicals demand increases, how can refiners respond to this opportunity? Blubbry Podcasting, 2023. https://blubrry.com/themaincolumn/93520258/as-global-petrochemicals-demand-increases-how-can-refiners-respond-to-this-opportunity/ (accessed 2023 31 Jan).
2. Store, J. Fit for 55 package: Council reaches general approaches relating to emissions reductions and their social impacts. European Council, 2022. https://www.consilium.europa.eu/en/press/press-releases/2022/06/29/fit-for-55-council-reaches-general-approaches-relating-to-emissions-reductions-and-removals-and-their-social-impacts/ (accessed 2023 16 Apr).
3. EEB. RED III EEB Policy Brief. European Environmental Bureau, 2022. https://eeb.org/wp-content/uploads/2022/02/Policy-Brief-REDIII-and-PAC-Scenario_FINAL-1.pdf (accessed 2023 15 Apr).
4. EU COMMISSION. Commission proposes new Euro 7 standards to reduce pollutant emissions from vehicles and improve air quality. 2022. https://ec.europa.eu/commission/presscorner/detail/en/ip_22_6495 (accessed 2023 14 Apr).
5. Eden, J. EU Approves 2035 Ban on Internal Combustion Engines. Energy Intelligence Group, 2023. https://eeb.org/library/eeb-policy-brief-on-the-renewable-energy-directive-red-iii/ (accessed 2023 31 Apr).
6. CONCAWE. Refinery Sites in Europe. 2023. https://www.concawe.eu/refineries-map/ (accessed 2023 10 Apr).
7. S&P GLOBAL. Refinery news roudup: Plants in Europe focus on renewables projects. S&P Global, 2022. https://www.spglobal.com/commodityinsights/pt/oil/refined-products/jetfuel/031522-refinery-news-roundup-plants-in-europe-focus-on-renewables-projects (accessed 2023 15 Apr).
8. PETROCHEMICALS EUROPE. Cracker Capacity. Petrochemicals Europe, 2021. https://www.petrochemistry.eu/about-petrochemistry/petrochemicals-facts-and-figures/cracker-capacity/ (accessed 2023 14 Apr).
9. Herve, P. From data to optimized performance. Hydrocarbon Engineering 2022, 27 (6), 19–21.

10. HYDROGEN-CENTRAL. INEOS Secures £3.1bn to Build Europe's Greenest 'Cracker' Powered by Hydrogen. 2023. https://hydrogen-central.com/ineos-secures-3-1bn-build-europes-greenest-cracker-powered-hydrogen/ (accessed 2023).
11. Turner, E. Refinery new roudup: Renewables projects in Europe. S&P Global, 2022. https://www.spglobal.com/commodityinsights/en/market-insights/latest-news/petrochemicals/072622-refinery-news-roundup-renewables-projects-in-europe (accessed 2023 11 Apr).
12. HONEYWELL-UOP. Expand your profits: Unleash the potential of your naphtha cracker. Honeywell UOP Integrated Olefin Sutie. HONEYWELL-UOP, 2021. https://uop.honeywell.com/content/dam/uop/en-us/documents/industry-solutions/petrochemicals/olefins/Integrated-Olefin-Suite-Brochure.pdf (accessed 2022 14 Nov).
13. Griffiths, M. A New Look at Integration Opportunities; HONEYWELL UOP, 2020.
14. Cooper, J. E. Statistical Report 2022. FuelsEurope, 2022. https://www.fuelseurope.eu/uploads/files/modules/documents/file/1665047024_zrE38MrGrfYYXK6mcGb47mnq0S3KhbFC8iAq6YP3.pdf (accessed 2023 24 Apr).
15. Biswas, G.; Maesen, T.; Sundaram, K. M. Unlocking Permian valuen. Hydrocarbon Engineering 2022, 27 (4), 29–32.
16. EU COMMISSION. COMMUNICATION 2019/ 640 FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE EUROPEAN COUNCIL, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS from 11 Dec. 2019; The European Green Deal. The European Commission: Brussels, 2019.
17. Gelder, A. Crisis? What Crisis? Hydrocarbon Engineering 2022, 27 (6), 9–14.
18. Wright, T. L. Carbon storage and the zero emissions refinery. Hydrocarbon Process. 2005, 84 (10).
19. Stockle, M. Towards a zero (net) carbon refinery. Petroleum technology quarterly 2013, 18 (1), 95–99.
20. Sunny, N.; Bernardi, A.; Danaci, D.; Bui, M.; Gonzalez-Garay, A.; Chachuat, B. A Pathway Towards Net-Zero Emissions in Oil Refineries. Frontiers in Chemical Engineering 2022, 4, 4. DOI: https://doi.org/10.3389/fceng.2022.804163
21. Gudde, N.; Larivé, J. F.; Yugo, M. Refinery 2050: Conceptual Assessment. Exploring opportunities and challenges for the EU refining industry to transition towards a low-CO2 intensive economy. 2019. https://www.concawe.eu/wp-content/uploads/Rpt_19-9-1.pdf (accessed 2023 15 Mar).
22. Kreijkes, M.; van der Linde, C.; Nivard, M. Refinery 2050 - Refining the clean molecule. 2018. https://www.clingendaelenergy.com/inc/upload/files/CIEP_Paper_2018-_01_Web_beveiligd.pdf (accessed 2023 2 Apr).
23. Couch, K.; Griffiths, M.; Ritchie, J. The journey to sustained profitability — How to benchmark the efficiency of your investment. Digital Refining, 2020. https://cdn.digitalrefining.com/data/articles/file/1523037660.pdf (accessed 2023 3 Apr).
24. Voermans, L. Accelerating electrification with the "Cracker of the Future" Consortium. Brightlands Chemelot Campus. Sittard-Geleen, 2021. https://www.borealisgroup.com/news/accelerating-electrification-with-the-cracker-of-the-future-consortium (accessed 2023; 20 Apr).
25. Toledano, I. Embracing change. Hydrocarbon Engineering 2022, 27 (3), 53–55.
26. Kapustin, V.; Chernysheva, E.; Khakimov, R. Comparison of moving-bed catalytic tar hydrocracking processes. Processes 2021, 9 (3), 500. DOI: https://doi.org/10.3390/pr9030500
27. Timken, H. K.; Luo, H.; Chang, B.-K.; Carter, E.; Cole, M. ISOALKY™ Technology: Next-Generation Alkylate Gasoline Manufacturing Process Technology Using Ionic Liquid Catalyst. In Commercial Applications of Ionic Liquids, Shiflett, M. B. Ed.; Springer International Publishing, 2020; pp 33–47.
28. Elshout, R.; Bailey, J.; Brown, L.; Nick, P. Upgrading the Bottom of the Barrel. Hydrocarbon Processing 2018, 97 (3).
29. HONEYWELL-UOP. Today´s the best time to build for tomorrow´s regulations. nViro Waste Management Solutions. HONEYWELL-UOP, 2022. https://pmt.honeywell.com/content/dam/pmt/en/documents/gated/nViro-brochure.pdf (accessed 2023 5 Apr).
30. Gargallo, K. Carbon capture (and the role of gas analysis). Hydrocarbon Engineering 2022, 27 (5), 45–48.
31. Marquez, M. T., X. The role of oxygen and hydrogen in refining. LINDE, 2016. https://www.linde-gas.com/en/images/The%20role%20of%20oxygen%20and%20hydrogen%20in%20refining_tcm17-416854.pdf (accessed 2013 16 Apr).
32. Glashan, L.; Thirunavukkarasu, K. Decarbonizing your fired heaters with hydrogen fuel. Hydrocarbon Processing 2022, 101 (11), 51–54.

33. Ditaranto, M.; Anantharaman, R.; Weydahl, T. Performance and NOx Emissions of Refinery Fired Heaters Retrofitted to Hydrogen Combustion. Energy Procedia 2013, 37, 7214–7220. DOI: https://doi.org/10.1016/j.egypro.2013.06.659
34. Rehfeldt, M.; Worrell, E.; Eichhammer, W.; Fleiter, T. A review of the emission reduction potential of fuel switch towards biomass and electricity in European basic materials industry until 2030. Renewable and Sustainable Energy Reviews 2020, 120, 109672. DOI: https://doi.org/10.1016/j.rser.2019.109672
35. Long, D. Breaking down the barriers. Hydrocarbon Engineering 2023, 28 (03), 73–77.
36. Long, D.; Juliano, R. Can electric pullit weight? Hydrocarbon Engineering 2022, 27 (3), 49–51.
37. Hawkins, G. Process Engineering Guide: Electric Process Heaters. 2007. https://www.academia.edu/3642004/Electric_Process_Heaters (accessed 2023 15 Mar).
38. Nonnast, T.; Spengler, U.; Kron, M. BASF, SABIC and Linde start construction of the world’s first demonstration plant for large-scale electrically heated steam cracker furnaces. BASF, 2022. https://www.basf.com/global/en/who-we-are/sustainability/whats-new/sustainability-news/2022/basf-sabic-and-linde-start-construction-of-the-worlds-first-demonstration-plant-for-large-scale-electrically-heated-steam-cracker-furnaces.html (accessed 2023 14 Apr).
39. EU PARLIAMENT. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources (RED II). European Parliament and Council: Brussels, 2018.
40. EU COMMISSION. IN-DEPTH ANALYSIS IN SUPPORT OF THE COMMISSION COMMUNICATION COM(2018) 773-A Clean Planet for all. A European long-term strategic vision for a prosperous, modern, competitive and climate neutral economy. EU COMMISSION: 2018.
41. Carugo, M. Valentine., J. Accelerating the transition to renewable fuels. Hydrocarbon Processing 2022, 101 (10), 41–43.
42. ENI. The Venice biorefinery. ENI Italy, 2020. https://www.eni.com/en-IT/operations/italy-venice-biorefinery.html (accessed 2020 2 Dec).
43. ENI. Eni opens its bio-refinery in Gela. ENI, Italy, 2019. https://www.eni.com/en-IT/media/press-release/2019/09/eni-opens-its-bio-refinery-in-gela.html (accessed 2020 1 Dec).
44. Total. La Méde: A Facility for the energies of tomorrow. Toal, France, 2020. https://www.total.com/energy-expertise/projects/bioenergies/la-mede-a-forward-looking-facility (accessed 2020 5 Dec).
45. Reynolds, A.; Tardy, A.; Allemand, C. Renewable carbon for chemicals. Hydrocarbon Engineering 2022, 27 (4), 14–20.
46. Olszynski, P. Plastic´s potential. Hydrocarbon Engineering 2022, 27 (7), 23–26.
47. Owens, B. Working towards a circular economy. Hydrocarbon Engineering 2022, 27 (4), 21–24.
48. Yugo, M.; Soler, A. A look into the role of e-fuels in the transport system in Europe (2030–2050). Concawe review 2019, 28 (1), 22.
49. Soler, A.; Yugo, M. Role of e-fuels in the European transport system. Literature review. 2020. https://www.concawe.eu/wp-content/uploads/Rpt_19-14.pdf (accessed 2023 31 Mar).
50. Soler, A.; Gordillo, V.; Lilley, W.; Schmidt, P.; Werner, W.; Houghton, T.; Dell´Orco, S. E-fuels: A techno-economic assessment of European domestic production and imports towards 2050. 2022. https://www.concawe.eu/wp-content/uploads/Rpt_22-17.pdf (accessed 2022 15 Dec).
51. Soler, A. E-fuels: future markets and challenges. Hydrogen Europe, 2022. https://hydrogeneurope.eu/wp-content/uploads/2022/12/112_S11.pdf (accessed 2023 1 Jan).
52. Rispoli, G.; Borgogna, A. Shipping´s new scene. Hydrocarbon Engineering 2022, 27 (8), 51–54.
53. van Dyk, S.; Si, J.; McMillan, J. D.; Saddler, J. Drop-in: The key role that co-processing will play in its production. The IEA Bioenergy, 2019. ttps://www.ieabioenergy.com/wp-content/uploads/2019/09/Task-39-Drop-in-Biofuels-Full-Report-January-2019.pdf (accessed 2023 28 Feb).
54. Stuckye, M. A step change in catalyst development. Hydrocarbon Engineering 2023, 28 (3), 36–40.
55. Bergman, S. The value of digital assistance. Hydrocarbon Engineering 2022, 27 (3), 66–70.
56. Pietri, A. Digitalization Strategies to Gain Leadership in Sustainability. Aspen Technology, Inc., 2023. https://www.aspentech.com/en/resources/executive-brief/digitalization-strategies-to-gain-leadership-in-sustainability (accessed 2023 14 Apr).

SLUDGE FORMATION DURING LONG-TERM STORAGE OF VARIOUS TYPES OF CRUDE OIL

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Abstract

Long-term storage of crude oil in large-capacity aboveground floating roof tanks requires preserving not only its quantity but also quality, which changes over time due to processes such as evaporative losses or sedimentation of solids leading to the formation of tank bottom sludges, which can be either prevented by regular mixing or removed after its extensive accumulation. Both methods are costly due to energy consumption, loss of the stored medium, operation of cleaning technologies, as well as blocking capacity during tank outages. The right choice of crude oil types for long-term storage can minimize the risk of sludging. The aim of this work was to model crude oil sedimentation in a laboratory model to evaluate the sedimentation tendency. Obtained results were related to basic properties of the crude oil samples in order to assess the possibility of predicting sludging tendency for the purpose of long-term storage.

Introduction

Sediments formed at the bottom of the storage tanks contain various types of insoluble fractions, e.g., equipment corrosion products and mineral substances, but the main part of the sludges consists of organic substances such as waxes and asphaltenes. The main components of waxes are high molecular weight n-alkanes, whose precipitation is caused by their low solubility especially at low temperatures. As the temperature of the crude oil drops below its cloud point or wax appearance temperature (WAT), the waxes begin to form solid crystals. The shape and morphology of the crystals depend on the composition, temperature, cooling rate, and mechanical stress at which the solid phase is formed. If the crude oil is stirred during cooling, smaller particles are formed than during cooling at quiescent conditions[1].

The size of the crystals formed affects the rate of settling and the formation of deposits at the bottom of storage tanks[2]. The motion of a settling particle can be described by scalar equations according to Newton's law taking into account the gravitational, buoyant, and environmental drag force. During settling, the forces acting on the particle reach equilibrium very quickly and their sum is zero, so that the particle moves at a constant velocity in a straight (vertical) line according to the equation:

$$V_p g(\rho_p - \rho) = \varsigma_u S_p \rho \frac{v_u^2}{2}$$

Where – V_p is the particle volume, g gravity constant, ρ_p – particle density, ρ – environment density, ς_u- drag coefficient, S_p – particle cross-section area, v_u – velocity.

Based on the above equation, the settling velocity can be calculated, but for actual waxy particles in oil, some parameters remain unknown, such as particle density, because in most cases the particles are inhomogeneous because they are a mixture of paraffins and the liquid part of the oil. In addition, the particle size and shape factor vary over a wide range. Therefore, experimental data on settling in model reservoirs are necessary to predict the settling behaviour of oil and to assess its suitability for long-term storage in storage tanks.

Experimental

In order to monitor changes in the composition of stored oil and the formation of bottom sediments, experiments of long-term storage of oils in scaled-down model tanks were carried out. Based on previous studies[3], a laboratory model scale was 1:20, with a container height of 0.8 m. Due to the sensitivity of the crude oil to the temperature history, the samples were transported and stored in temperature-controlled containers at the temperature of the sampling after they were taken. According to the model scale, sedimentation tests were carried out in model tanks at constant temperature for 1/20 of the actual storage time.

The sampling of bottom layers of accumulated deposits was carried out carefully by gradual vacuum suction of the content of sedimentation cylinders[4]. The formation of the deposits was further evaluated based on the content and distribution of n-alkanes in the deposit layers. First, the concentrate of saturated hydrocarbons was prepared using liquid adsorption chromatography[5]. Subsequently, saturates were dissolved in carbon disulphide and analysed by gas chromatography to obtain the content of individual n-alkanes in the range of ca

16 to 60 carbon atoms in the molecule[6]. Finally, the total content of n-alkanes having 20 or more carbon atoms (C_{20}^+) was calculated.

Since waxy sludges are mainly composed of crystallized paraffinic particles, the technique of polarized light microscopy was be used for their direct observation with subsequent image analysis to obtain information on the particle size distribution[7]. The microscopic evaluation of samples was carried out at constant temperature equal to that of sampling and storage tests. The image analysis resulted in a data set consisting of the area of each particle in the image, which was then used to calculate the overall particle size distribution and their total content in the samples.

Results and discussion

A correlation between oil properties and sediment formation was the main goal of the experiments. Table I. shows the properties of tested samples (viscosity, content of saturated hydrocarbons, content of C_{20}^+ n-alkanes, pour point, maximum and average particle diameter obtained from image analysis) in relation with the results of model storage (number of 5 mm deposit layers and the total increase of C_{20}^+ in the deposits) each equivalent year of deposition.

Table I.

Crude oil properties and sedimentation results 15 °C

Sample number	Viscosity [mPa.s]	Sat. [% w/w]	C_{20}^+ [% w/w]	Pour point [°C]	Max. particle diameter [µm]	Weight average diameter [µm]	Numbers of sediment layers			Total C_{20}^+ in sediments [% w/w]		
							1 year	2 years	3 years	1 year	2 years	3 years
1	3.58	15.56	2.59	0	145	56	4	5	5	12.9	20.3	15.9
2	4.39	20.76	1.81	-9	50	16	2	3	3	2.1	3.7	3.8
3	6.43	22.25	2.31	-6	175	66	3	3	4	11.1	10.2	15.2
4	8.50	24.84	3.56	2	135	44	2	2	3	5.3	8.4	10.5
5	6.21	21.39	1.95	-5	90	27	2	2	2	3.5	3.5	2.8
6	25.55	19.66	1.33	-6	95	21	3	3	3	1.2	1.2	1.6

Conclusions

The amount of C_{20}^+ n-alkanes in crude oil and waxy particle size can be used to predict long-term storage behaviour of the crude oil. As there are obviously more parameters that could affect the sedimentation rate and total amount of tank bottom sludge, greater data set would help to clarify their effect on the bottom sludge formation. Despite the difficulty of predicting the intensity of deposition, the findings have contributed to explaining the long-term storage behaviour of crude oils, which is also relevant for the selection of oil types selected for the storage in strategic reserves.

References

1. Kané M., Djabourov M., Volle J. L., Lecharine J. P., Frebourg G.: Morphology of paraffin crystals in waxy crude oils cooled in quiescent conditions and under flow. *Fuel 82*, 127 (2003).
2. Šnita D.: *Chemické inženýrství*. VŠCHT v Praze, ISBN 80-7080-589-7, Praha 2006.
3. Straka P., Maxa D, Šebor G.: Dlouhodobé skladování ropy. *Aprochem,* Praha 2011.
4. Straka P., Maxa D., Šebor G., Šimáček P.: Metodika hodnocení rop při jejich dlouhodobém skladování. *Sborník 14. konference Aprochem*, 339 (2005).
5. Petr Straka, Daniel Maxa, Martin Staš: A novel method for the separation of high-molecular-weight saturates from paraffinic petroleum based samples. *Organic Geochemistry 128*, 63 (2019).
6. Šimáček P., Procháska F., Straka P., Vysokoteplotní plynová chromatografie v analýze ropných produktů. *Paliva 2*, 55 (2010).
7. Němcová K., Maxa D., Straka P., Šebor G.: *Vliv teploty na strukturu parafinických částic v ropách*. *Paliva 4,* 100 (2012).

ZERO EMISSION REFINERY: REALITY OR DREAM?

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Abstract

Oil refining is a carbon dioxide emissions-intensive industry. Addressing 20XX zero emissions will be a major challenge considering further needs of hydrocarbons (crude refining derivatives) for part of transport and petrochemical industry. There are various pathways to reduce these emissions, including electric heating. The use of 'green' electric heating will be advantageous due to zero emissions and the ability to substitute different energy sources in the refinery. Relevant technologies are already available. Therefore, a case study of electric heating utilization on decarbonization of the operation of a 6 $Mt \cdot y^{-1}$ FCC conversion refinery that emits 1139 kt $CO_2 \cdot y^{-1}$ was modeled. In case 1, emissions were reduced by 55.9 kt $CO_2 \cdot y^{-1}$ ending the purchase of steam, in case 2, emissions were reduced by 361 kt $CO_2 \cdot y^{-1}$ selling fuel and natural gas to a local electricity and heat producer as a natural gas substitute. Case 3 targeted zero carbon dioxide emissions by producing 550 kt y^{-1} methanol using the carbon dioxide produced by the combustion of coke during the regeneration of the FCC catalyst and introducing the production of green hydrogen. Hence, a zero-emission refinery will not be a dream assuming the technological use of coke from the FCC.

Introduction

Oil refining is an energy-intensive industry[1]. Distillation (atmospheric and vacuum distillation of crude oil, redistillation of gasoline, and gas separation) and endothermic technologies (thermal cracking, catalytic cracking, and catalytic reforming) are important consumers of heat in refineries. Tube furnaces are the most important heat source in refinery processes. They are facilities with a wide range and flexibility of performance and high thermal efficiency of up to 90%. They burn some of the by-products and less valuable products of crude oil processing, mainly fuel oils and desulfurized refinery gases. The energy balance of a refinery is supplemented with natural gas also for safety reasons (for stabilization burners of heaters and flares). The furnaces are used to warm and evaporate the process streams in the range of 100 to 750 °C, to produce steam, and to preheat the combustion air. Another important source of heat is the combustion of coke in processes with continuous catalyst regeneration, mainly on FCC, or fuel gas from fluid coking. The hydrocarbon fuels consumed, and the coke burned are a direct source of carbon dioxide emissions from refineries. To reduce energy consumption, oil refineries have always been designed and constructed as integrated systems with high heat recovery from exothermic processes (hydrocracking and hydrotreating) and hot output streams (FCC, catalytic reformer) by exchanging heat with input streams and generating water steam at different pressures and temperatures. This steam is then used to strip the products, as a heat source in various reboilers, to drive pump and compressor turbines, and for heating of piping and tanks. It depends on the type of refinery and the operating conditions whether it purchases or sells fuel gas and water steam.

Decarbonization of a refinery operation or finally zero-emission refinery in 20XX will be a major challenge. Global refining carbon intensity was reported at the country and crude level of 0.105–0.466 t CO_2 eq. t^{-1} of the crude oil processed, with an average value of 0.305 t CO_2 eq.$\cdot t^{-1}$ of crude oil[2]. In 2015, European refineries processed 723.3 Mt of oil and emitted 128 Mt CO_2 eq, that is, 0.177 t CO_2 eq$\cdot t^{-1}$ of the crude oil[1]. These are the following general pathways to reduce emissions from oil refineries: digitalization; capture and storage of carbon dioxide (CCS); oxygen enrichment of combustion air; use of carbon dioxide for chemical syntheses (CCU); upgrading refinery technologies to less energy intensive ones; use of hydrogen injecting instead of carbon rejection technologies; burning low-carbon fuels, biofuels, or green hydrogen directly as fuel in refinery furnaces[3,4]; or replacing fuel consumption and external steam with green electricity. These pathways can be used in parallel[5,6].

Electricity already contributes to the energy consumption in refineries, mainly to drive rotating machines. In today's refineries, electric heating is also used for some specific operations, e.g., to regenerate various sorbents, for pipeline tracing, and tank heating. The use of green electricity to heat the process streams will be advantageous due to zero emissions and the ability to substitute different energy sources in the refinery, such as external steam of various pressures and temperatures and fuel gas of various compositions. The appropriate electric heating technology is already available. From a design and technological point of view, the substitution of steam for electric heating is relatively simple, because the construction of the steam reboilers and electric heaters is similar (it is a heat exchanger), the required temperatures are moderate (<300 °C), and the heat duty is small or medium (<20 MW). However, replacing tubular furnaces with electric heating is much more complicated due to higher temperatures of heated streams (up to 750 °C) and heat output (up to 200 MW). The pros of electric heating include higher watt densities, less thermal lag, safer operation, and less fouling. The cons include the high costs of equipment itself (CAPEX), the cost of electricity (OPEX), the necessary integration into the electricity grid, and the storage of energy from renewable sources (battery storage)[1,7,8]. References for a more extensive replacement of standard refinery furnaces and reboilers by electric equipment in refinery practice are not yet available.

This paper focuses on the balance of energy and carbon dioxide emissions of a FCC conversion oil refinery that replaces purchased steam, fuel, and natural gas with green electricity and deals with carbon dioxide emissions from the burning of FCC coke on the catalyst.

Method

The conversion oil refinery with a capacity of 6 Mt y^{-1} of a crude oil (it contains 85 wt% of carbon) was modeled, consisting of a standard hydroskimming section and a residual FCC unit, processing atmospheric residue from light low sulfur crude oil, with a capacity of 2.8 Mt y^{-1} as central technologies. For simplified scheme of energies see Figure 1.

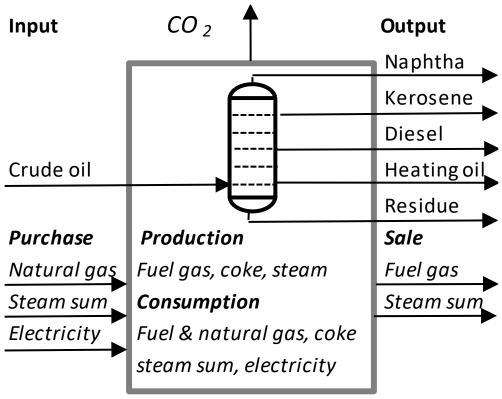

Figure 15. Simplified scheme of energies at the refinery balance boundary

FCC coke and fuel gas originate from the input crude oil. As FCC represents carbon rejection technology, coke formation is a natural consequence of this technology. It cannot be eliminated and can be controlled to a limited extent only. The problem is that this carbon is deposited on the surface of the catalyst and the only way to separate it is by oxidation to carbon monoxide or carbon dioxide. The modeled refinery has two internal sources of fuel gas – from the hydroskimming section and from the FCC unit. The yield of this gas is related to the portfolio of technologies, the technological regime, and can only be controlled to a limited extent, similarly as for FCC coke. The modeled refinery also burns excess hydrogen from the catalytic reforming unit as part of the fuel gas. Therefore, refinery fuel gas is a type of low-carbon fuel. Unlike coke, fuel gas can be sold as a natural gas substitute and replaced with a green, emission-free energy source. The refinery uses steam of different pressures and temperatures and can purchase steam of a certain quality and sell steam of different quality at the same time because steam throttling is not economically beneficial. In the modeled refinery, the main fuel consumers are atmospheric crude oil distillation, straight-run gasoline redistillation, catalytic reforming, gas oil hydrotreater, FCC unit, and FCC gasoline redistillation.

In line with the difficulty of substituting different types of energy for green electricity, as discussed in the Introduction, three cases of carbon dioxide elimination were analyzed.

1. Replacement of external steam by electric heating.
2. Additionally to case 1, replacement of refinery gas by electric heating and export of refinery gas to an external consumer, replacing its natural gas import.
3. In addition to case 2, capture of FCC off-gas carbon dioxide and its use together with green hydrogen for the synthesis of methanol.

For the electrolysis of water, to obtain green hydrogen, an efficiency of 0.7 was considered. The oxygen produced as a by-product of the electrolysis can be used to enrich the air used to burn the FCC coke, i.e., it is mostly recirculated locally. The synthesis of methanol from carbon dioxide and water, i.e., substances in their maximum oxidation state, is very energy intensive. As recommended in the Introduction, the considered cases combine multiple alternatives to possible decarbonization of refinery operations, i.e., replacing external steam and consumed refinery gas with green electricity, oxygen burning, and the capture, purification, and utilization of carbon dioxide produced during the regeneration of the FCC catalyst and the synthesis of methanol. Only a small consumption of natural gas was kept to stabilize the operation of the flare necessary to burn the refinery off-gases.

The following basic assumptions were considered: 1,000 Nm^3 natural gas heat content equal to 10.3 MWh, electric heater efficiency equal to 90%.

Results and discussion

The basic numeric results of the model for the considered cases are given in Table I.

Table I.
Total energy, electricity, and carbon dioxide balance for analyzed cases

Case description	Total energy consumption ($GWh \cdot y^{-1}$)	Consumption of electricity ($GWh \cdot y^{-1}$)	Export of energies ($GWh \cdot y^{-1}$)	CO_2 refinery emissions ($kt \cdot y^{-1}$)
Base case – Current configuration	4540.1	338.8	-800.6	1138.7
Case 1 + Replacement of external steam by electric heating (zero purchase of steam)	4540.1	589.3	-800.6	1138.7
Case: Case 1 + Replacement of refinery gas by electric heating (export of refinery gas)	4540.1	2494.0	-2705.4	756.4
Case 3: Case 2 + use of FCC off-gas CO_2 for methanol production, utilizing green H_2	10393.4	8347.4	-2705.4	0* (11)

* Note: approx. 11 $kt \cdot y^{-1}$ carbon dioxide will be emitted for security reason: off-gases flare

In the base case, the refinery purchased steam and sold fuel gas. The total energy consumption of the refinery corresponded to 6.5% of the energy contained in the processed oil and a power input of 518.3 MW. The energy intensity was 0.757 MWh t^{-1}or 2.725 $GJ \cdot t^{-1}$ of the crude oil processed and the carbon dioxide intensity was 0.189 t t^{-1} of the crude oil processed. These emissions were only slightly higher than the average emissions of European refineries in 2015[1]. The share of electricity in the energy pool of the refinery was only 7.5%. The structure of energy consumption in the considered refinery model is fundamentally influenced by the operation of the FCC because coke combustion, as such, provided 45.1% of the refinery's energy. If the fuel gas produced from the FCC is also considered, it can be stated that the operation of the FCC unit was essential for the refinery's energy balance (Figure 2).

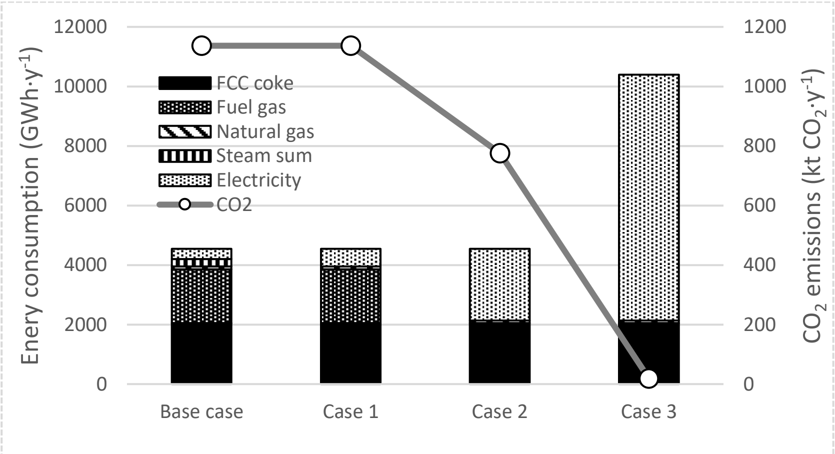

Figure 16. Contribution of individual energies to refinery's energy balance

In case 1, purchased steam from an external supplier contributed to the energy balance of the 250 GWh y^{-1}. Therefore, its replacement by electric heating increased the share of electricity in the refinery's energy balance to 13%. There was no direct reduction in emissions from the refinery, but from the external steam supplier of 55.9 kt y^{-1}. Ending the purchase of steam does not mean the end of its use at the refinery. Steam produced by heat recovery from furnace flue gases, from the heat of exothermic reactions, and from hot hydrocarbon streams, i.e., inside the balance boundaries (Figure 1), continued to be used. This case would require the replacement of a limited amount of reboilers at the refinery and is therefore feasible already today.

In case 2, the fuel gas and natural gas were replaced by electric heating, including the heat of the flue gases used to generate steam. The share of electricity in the refinery's energy balance increased significantly to 52.3%. The surplus of fuel gas w supplied to a local electricity and heat producer that substitutes for the import of natural gas, with a reduction in carbon dioxide emissions at the refinery gate of approximately 34% (Table I.). This case would require the replacement of a large amount of key heat-transfer equipment in the refinery, especially the tube furnaces, and would be an investment (CAPEX)-intensive reconstruction. Such reconstruction can be carried out step by step. However, the FCC units remained the main emitter of CO2.

Case 3 targeted zero carbon dioxide emissions. The case dealt with the utilization of emissions from the combustion of FCC coke, which contributed significantly to the refinery's emissions from operations (45.1%). Compared to previous cases, the use of heat from FCC coke combustion to perform endothermic cracking reactions and generate steam remained unchanged. Thus, the refinery had sufficient process steam available (fluidization and stripping of the FCC catalyst and stripping of the hydrocarbon streams). The coke yield in the FCC catalyst was relatively substantial at 224.8 kt y^{-1} (8.1 wt% of the FCC feed), which is nevertheless typical for this process. Carbon dioxide from the FCC regenerator was used to produce 550.1 kt y^{-1} of methanol, which represents an important platform for a number of chemical syntheses and the production of synthetic motor fuels (E-fuels). Due to the need for 'green hydrogen', the electricity consumption increased significantly to 181.8% and the total energy consumption to 228.9% of the total original energy consumption of the refinery in the base case. However, this hydrogen does not have to be provided directly by the refinery but rather from a central source. Therefore, this increase in energy consumption at the refinery would not occur. Construction of a new methanol unit will require significant CAPEX and will be a strategic project.

Conclusions

The reduction of carbon dioxide emissions from a crude oil conversion refinery with a capacity of 6 Mt y^{-1} and with 2.8 Mt y^{-1} FCC unit was modeled. This refinery (base case) is an energy demanding facility (4540 GWh y^{-1}, 0.757 MWh t^{-1} of crude oil, share of electricity in energy consumption 7.5%) with high carbon dioxide emissions intensity from operation (1139 Mt CO_2 y^{-1}, 0.189 t CO_2 t^{-1} of crude oil). Three cases of carbon dioxide emission reduction using green electricity have been modeled. Case 1, substitution of purchased steam resulting in a share of electricity increase of 13% (total electricity consumption increased by 1.7 times) and savings of 56 kt CO_2 y^{-1} emissions by the external supplier of the steam. Case 2, substitution of fuel and natural gas resulting in an increase in the share of electricity to 52.3% (total electricity consumption increased by 7.4 times) and 382 kt CO_2 y^{-1} savings. Case 3, the use of carbon dioxide from FCC coke and green hydrogen for methanol synthesis, resulting in a share of electricity increase to 181.8% of the total energy consumption in the base case (total electricity consumption increased by 24,6 times), additional savings of 756.4 kt CO_2 y^{-1}, and the production of 550 kt of methanol·y^{-1}. Hence, zero emissions from an FCC conversion refinery will not be a dream, but reality assuming the technological capture and utilization of the coke from the FCC unit. Of course, this would require replacement of heaters and reboilers and investment in a new methanol production unit and possibly a green water-producing unit. The available information shows that all considered cases are currently technologically possible; however, individual steps will require a proper economic justification and their sustainability confirmation upon given energy prices and environmental requirements.

Nomenclature

CAPEX	Capital Expenditures
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
FCC	Fluid Catalytic Cracking
OPEX	Operating Costs

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References

1. Rehfeldt, M.; Worrell, E.; Eichhammer, W.; Fleiter, T. A review of the emission reduction potential of fuel switch towards biomass and electricity in European basic materials industry until 2030. *Renewable and Sustainable Energy Reviews* **2020**, *120*, 109672. DOI: https://doi.org/10.1016/j.rser.2019.109672.
2. Jing, L.; El-Houjeiri, H. M.; Mofort, J.-C.; Brandt, A. R.; Masnadi, M. S.; Gordon, D.; Bergerson, J. A. Carbon Intensity of Global Crude Oil Refining and Mitigation Potential. *Nature Climate Change 10* (6) **2020**, 526–532. DOI: https://doi.org/10.1038/s41558-020-0775-3.
3. Glashan, L.; Thirunavukkarasu, K. Decarbonizing your fired heaters with hydrogen fuel. *Hydrocarbon Processing* **2022**, *101* (11), 51–54.
4. Ditaranto, M.; Anantharaman, R.; Weydahl, T. Performance and NOx Emissions of Refinery Fired Heaters Retrofitted to Hydrogen Combustion. *Energy Procedia* **2013**, *37*, 7214–7220. DOI: https://doi.org/10.1016/j.egypro.2013.06.659.
5. Toledano, I. Embracing change. *Hydrocarbon Engineering* **2022**, *27* (3), 53–55.
6. Long, D.; Juliano, R. Can electric pullit weight? *Hydrocarbon Engineering* **2022**, *27* (3), 49–51.
7. Long, D. Breaking down the barriers. *Hydrocarbon Engineering* **2023**, *28* (03), 73–77.
8. Hawkins, G. *Process Engineering Guide: Electric Process Heaters*. **2007**. https://www.academia.edu/3642004/Electric_Process_Heaters (accessed 2023 15 Mar).

POTENTIAL FOR USE OF SIDE STREAMS IN THE PRODUCTION OF DICYCLOPENTADIENE

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Abstract

During the trial run of the unit for dicyclopentadiene (DCPD) production based on light pyrolysis gasoline (LPyGas) technology, initial experience were obtained. The process data verified the previous research assumptions accompanying the development of the technology and also show the potential for various process optimization. The maximum effectiveness of the DCPD isolation from LPyGas should be achieved by optimizing the operating conditions with the aim of minimizing direct losses of DCPD to backflow gasoline and at the same time by efficient use of side streams with a high content of DCPD. Finding the commercial use of methyldicyclopentadiene (MeDCPD) which is produced as a by-product of DCPD production represents the example of evaluation of one from a group of hydrocarbons originating from the Steam cracker and apparently also the potential for expanding the DCPD unit to include a part of MeDCPD stream processing. The main goal of optimization is primarily to find key operating conditions for precise control of purity and other parameters of the produced DCPD and MeDCPD – especially the color and impurities.

Introduction

Cyclopentadiene – cyclopenta-1,3-diene (CPD) C5H6 and its more stable dimer dicyclopentadiene – 3a,4,7,7a-tetrahydro-4,7-methanoindene (DCPD) C10H12, are produced as by-products of ethylene pyrolysis of petroleum fractions. If isolated, they can be very profitable monomers for a number of different chemical applications. Dicyclopentadiene (DCPD) is formed very easily by the dimerization of cyclopenta-1,3-diene (CPD) by the Diels-Alder mechanism. The reaction of CPD to DCPD is reversible and takes place spontaneously even at low temperatures. At higher temperatures, DCPD decomposes back to monomer. This is used in a number of chemical reactions and industrial technologies where DCPD is said to by the starting material, although in reality the reactant is monomeric cyclopentadiene. DCPD exists in two stereoisomeric forms: exo and endo. The endo isomer is the majority, practically only endo DCPD occurs in commercial DCPD. Chemically pure DCPD is a colorless crystalline substance with a melting point of 34 °C and a boiling point of 172 °C. DCPD in lower purity is a colorless to yellowish liquid with a characteristic fruity-camphor odor. Due to its chemical reactivity, DCPD is a widely used chemical compound in many branches of the chemical industry and materials engineering, from specialty chemicals to composites, from simple adducts to polymeric materials. Cyclopentadiene and dicyclopentadiene are some of the main components of hydrocarbon resins, cyclohydrocarbon polymers and many other specialty chemicals[1].

ORLEN Unipetrol, in cooperation with the Institute of Chemical Technology in Prague, developed a technology for the production of technical DCPD of intermediate to high purity. In 2022, the construction of the ORLEN Unipetrol unit for the production of DCPD was completed and production started. This technology of DCPD production, as shown in the simplified process scheme in Figure 1, uses a stream of light pyrolysis gasoline (LPyGas) as a feedstock, in which DCPD and CPD are represented as ones of the main components[2]. Light pyrolysis gasoline is the bottom product of the debutanizer in the steam cracking unit[3]. The principle is that light pyrolysis gasoline is first dimerized in a cascade of dimerization reactors (R) to increase the DCPD content in LPyGas by conversion CPD to DCPD and then LPyGas is processed in a four-stage rectification line to the final DCPD product[4]. These four stages include the depentanizer (C1), which is used for the separation of C5 and partially C6 hydrocarbons from LPyGas, the BTX column (C2) for the separation of C6–C9 hydrocarbons and partially C10 co-dimers, the DCPD column (C3) for DCPD quality control by separating C11 and heavier fraction, and finally the purification column (C4) for the purification of DCPD to the final product.

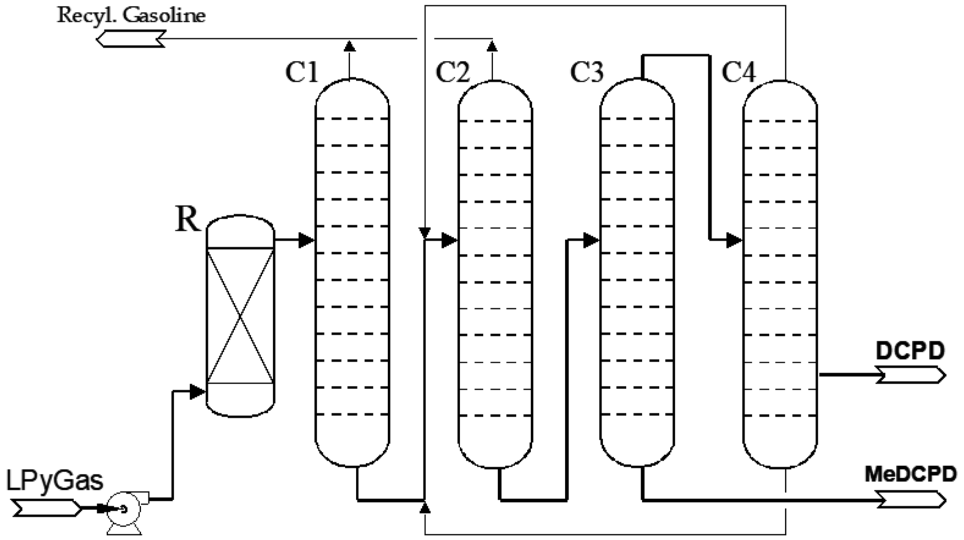

Figure 1 Simplified process scheme for DCPD production from light pyrolysis gasoline (LPyGas)[4]

In the upstream dimerization reactors, in addition to the conversion reaction of CPD to DCPD, other reactions of dienes also take place, as a result of which light pyrolysis gasoline also contains CPD and methylcyclopentadiene (MeCPD) dimers and the corresponding co-dimers of these cyclic dienes with acyclic dienes as isoprene – 2-methylbuta-1,3-diene and piperylene - penta-1,3-diene. These C10 and C11 co-dimers are the major accompanying components or impurities in the final DCPD product. The DCPD production unit is capable of producing DCPD with a quality of 80 to 94% in campaigns. The capacity of this DCPD unit is expected to be up to 26 thousand tonnes per year depending on derivative product portfolio and purity of the DCPD[4]. The change in the required quality of the produced DCPD during production takes place by gradually adjusting the process conditions during the distillation process. The final DCPD product is specified by the content of DCPD (endo+exo) and other quality parameters such as the content of lower-boiling and higher-boiling co-dimers C10 and C11, color, water and peroxide content, etc. Table I. shows the limits of these parameters for the individual DCPD grades produced by ORLEN Unipetrol according to the commercial specification.

Table I.
Dicyclopentadiene (DCPD) product specification[5]

Quality parameter	DCPD grades			
	DCPD 80	DCPD 85	DCPD 92	DCPD 94
DCPD (endo+exo), % wt.	**min. 80**	**min. 85**	**min. 92**	**min. 94**
CPD, % wt.	max. 0.05	max. 0.05	max. 0.05	max. 0.05
Benzene, ppm wt.	max. 300	max. 300	max. 100	max. 100
Toluene, ppm wt.	max. 300	max. 300	max. 100	max. 100
Lower boiling C10 co-dimers, % wt.	max. 7	max. 7	max. 7	max. 5
Trimers, % wt.	max. 0.1	max. 0.1	max. 0.1	max. 0.1
Inhibitor BHT or p-TBC	100–200	100–200	100–200	100–200
Peroxides, ppm wt.	max. 15	max. 15	max. 15	max. 15
Water, ppm wt.	max. 300	max. 200	max. 200	max. 200
Sulphur, ppm wt.	max. 20	max. 20	max. 20	max. 20
Colour APHA, HAZEN units	max. 120	max. 120	max. 100	max. 100

Discussion

Trial run experience

With the completion of construction and the performing of comprehensive tests in the second half of 2022, a trial run of the DCPD production unit has begun. The purpose of the trial run was mainly to verify the performance and various operating options and limits of the production equipment, therefore different production modes were tested. First, the unit was put into non-production mode, meaning all process streams including DCPD flowed back to the stream cracker unit.

The aim of this operating mode was mainly to verify the technological functionality of the device as a whole. This operating mode was short-lived, as stable product parameters were successfully achieved in a relatively short time in values corresponding to the required specification for sale, and based on this, production was redirected to warehouses and subsequently to shipping to customers. The next step was the introduction of by-streams from the purification column (C4) as recycle to the injection of the BTX column (C2) as shown in Figure 1. This results in the recycling of streams with a high DCPD content, which increases the total production capacity and also the overall efficiency of the production plant.

One of the complications during the trial run was a risk of DCPD freezing during the winter season. The freezing point temperature of DCPD product depends on the DCPD content. Especially high-purity DCPD and ultra-pure DCPD have a relatively high freezing point temperature, see the results of the measured values in Table II. The higher freezing point temperature of DCPD is problematic for the product transport, especially before unloading. In generally, insulated tank containers are used for transporting the product without heating the product during the transport. If there is a risk of freezing, the tank containers are heated before unloading. However, this means a transport delay, and in addition, it can have an undesirable effect on some DCPD product parameters and thus affect its overall quality. Therefore, it was necessary to provide measures to reduce the risk of DCPD freezing during the transport and thus eliminate the need for subsequent heating of the tank containers. As a measure, a new DCPD quality production plan has been set up taking into account the weather conditions of the current season. This means that in the winter the quality of the produced product has been reduced from DCPD 94 to DCPD 92, and as a second measure the temperature in the storage tanks has been increased so that the DCPD product has been loaded into the tank containers at a higher temperature. During the short-term transport of a few days, the temperature of the product has not dropped to a critical level.

Table II.
Typical cloud point and freezing point values of Dicyclopentadiene (DCPD) product

Parameter	DCPD grades			
	DCPD 80	DCPD 85	DCPD 92	DCPD 94
DCPD (endo+exo), % wt.	83.1	86.7	92.6	94.9
Cloud Point, °C	-12	2	9	13
Freezing Point, °C	-22	-5	3	7

During the trial run, there was also a change in the inhibitor used, which is added to the DCPD product as an oxidation inhibitor. DCPD is a material easily subject to autoxidation, especially in the presence of atmospheric oxygen and elevated temperature[6,7]. Auto-oxidation is a radical chain reaction which leads to the formation of various peroxide compounds, which are initially manifested by a loss of spark, gradual clouding of the product, and the formation of yellow gels – polymer resins. Peroxides can be formed during production, storage and transport, the formation of peroxides occurs faster or slower depending on the conditions. In the subsequent processing of DCPD, peroxides represent a problem especially during polymerization processes and are therefore kept at the lowest possible level. This is helped by the addition of an inhibitor, which is already added during the production of DCPD. Sterically hindered phenols are used as the oxidation inhibitor – a typical representative of which is the commonly used butylated hydroxytoluene (BHT). In recent years, the discussion regarding the safety of BHT has intensified. The European Commission is also concerned about BHT's effects on human health and its impact on the environment. Therefore, it issued Commission Regulation (EU) 2022/2195 of 10 November 2022 restricting the use of BHT in cosmetic products. Manufacturers producing in other sectors are also reacting to this and are already replacing BHT with other alternatives. BHT was considered as an inhibitor in the proposed DCPD production technology, and finally, due to customer requirements, it was decided to replace it with 4-tert-butylcatechol (p-TBC).

One of the important parameters of the DCPD product for some downstream applications is color. APHA color also referred to as the Hazen scale, and more appropriately as the Platinum Cobalt (Pt/Co) scale is used for DCPD color evaluation. What substances cause the color of DCPD or what conditions have a significant effect on the color of DCPD has not yet been fully revealed[4,8]. In general, the color of the DCPD product can be affected by process conditions, residence time in equipment, and feedstock. The DCPD color is caused by presence of colored organic compounds with a boiling point close to DCPD. For yellow substances that come with the feedstock and cannot be completely separated from the product by distillation, the name primary yellow substances. Secondary yellow substances, which are formed by new formation during the distillation process, and yellow-brown substances, which are formed during the process due to the residence time and thermal load of the material in the device[8].

Further optimization of the process during the trial run focused primarily on monitoring utility consumption and increasing the efficiency of DCPD isolation from LPyGas by adjusting operating conditions and minimizing DCPD losses. The total DCPD losses in the process can be defined as the DCPD content of a recycled gasoline that flows from the DCPD unit back to the stream cracking unit. The recycled gasoline is a stream in which, in this operating mode described above, are mixed the streams of the overhead products of columns C1 and C2 and the bottom product of column C3. The DCPD content in the column C1 overhead product is practically negligible but the losses of DCPD through the overhead product of column C2 represent up to 5% of the flow amount of this stream and thus the effort is to minimize the DCPD content in this stream. However, the most significant are the DCPD losses by the bottom product of the C3 column, where the DCPD content can be up to 20% of the flow amount of this stream. On the DCPD column (C3) almost final quality of DCPD product is achieved. Thus, the DCPD content in the bottom product of the C3 column cannot be significantly reduced, as it is a side effect of the quality control of the DCPD concentrate, which is the overhead product of the column C3. The most advantageous way to use this stream is to find a commercial use for this by-product, as the proposed technology assumes.

Utilization of MeDCPD as a side stream in DCPD production

Any streams not processed into the DCPD during the test run are fed back from the DCPD unit to the ethylene unit for further processing. MeDCPD appears in the DCPD product as one of the its main components and also is present as a major component in the exiting stream as in the bottom product of the DCPD column (C3) at a concentration of approximately 55–65%[9], depending on the required quality of the DCPD product (see Figure 1). The developed technology of DCPD production involves the release of the main by-product methyldicyclopentadiene concentrate, and its production should start in 2024 at the latest[4]. The MeDCPD concentrate from the DCPD unit is going to be produced in campaigns in three technical grades A/B/C according to the ratio of DCPD and MeDCPD content in the expected amount up to 10 thousand tonnes per year.

MeDCPD is a very valuable hydrocarbon similar to DCPD properties and prices. Unlike DCPD, this later molecule has received only a little attention. Methyldicyclopentadiene (MeDCPD) $C_{11}H_{14}$ is a methylated derivative of DCPD. It is a co-dimer, formed by the dimerization reaction of CPD with methylcyclopentadiene (MeCPD). There are three stereoisomeric forms of MeCPD, which is why dimerization is resulting to several isomers of MeDCPD, of which there are five main isomers[10]. Due to its similarity to DCPD, MeDCPD could be applied in some of the numerous areas where DCPD has already been implanted, particularly in UPR. MeDCPD is so far only a superficially studied material. Especially, its influence on UPRs compared to standard UPRs or DCPD resins have not been extensively studied so far. In comparison with other dimers observed in DCPD mixtures[11], MeDCPD could have an interesting added value in the UPR. As a confirming the commercial use of MeDCPD in the UPR, an effort to replace standard grade DCPD in UPR has been made. This implementation would increase the efficiency of the DCPD distillation line and reduce the cost of final polyester resins. Unsaturated polyester resins (UPR) are a solution of linear or weakly branched UPs in reactive solvents, predominantly styrene[12]. UPRs are an important class of thermoset resins.

DCPD modified polyesters have some advantages compared to classic orthophthalic UP types: the main stated advantage is the price, also lower consumption of styrene for dilution (lower viscosity of the produced resin) and due to lower styrene emissions[13]. Compared to unmodified UP, these materials show lower shrinkage, exothermic and rapid curing in thin layers. In contrast, the disadvantage is higher brittleness, lower glass temperatures and lower chemical resistance due their lower network density.

In the first study[9], we studied the influence of MeDCPD in a standard UPR formulation. The properties of neat resins were assessed for different compositions with increasing amounts of MeDCPD. Two DCPD formulations were tested: higher quality monomers up to 90% to evaluate the influence of MeDCPD in commonly used UPR feedstock, and a technical by-product containing approximately 65% MeDCPD to determine the potential reuse of this substance. In the second study[14], a “water process” method based on a patent[15] was used to prepare unsaturated polyesters with the aim to achieve a smaller proportion of gel particles in the resin. Two UPRs based on two different DCPD/MeDCPD blends were compared to clearly assess the influence of MeDCPD content on a readily useable DCPD polyester resin. In parallel, the reaction occurring between maleic anhydride, DCPD (or MeDCPD) and water during the first stage of the modified polyesters synthesis was engaged. It enriched the interpretation of observed phenomena at the polymeric scale. The result of these studies[9,14] was that MeDCPD can be successfully implanted into the UPR formulation. The UPR modified with

MeDCPD could probably be adequately used in composites in less demanding applications. Another interesting perspective of technical MeDCPD could be its use in alkyd resins, a polycondensation material that can be also modified by DCPD. To better control the properties of the final product and use the full potential of this compound, further optimization of the synthesis technology and a deeper understanding of the reaction between MeDCPD should be performed. Also, a deeper focus on MeDCPD isomers and the use of purer monomers could open a new direction for further applications. Based on next studies, the optimal ratio of individual MeDCPD isomers would be defined, which is a significant potential for the expansion of the DCPD production plant. The production of MeDCPD concentrate with adjusted isomer ratio can be advantageously linked to the implemented dicyclopentadiene technology[9]. The part intended for the processing of technical MeDCPD into MeDCPD of medium to high purity would technologically be included downstream the bottom of the DCPD column (C3), where the MeDCPD concentrate flows as a bottom product. In principle, this would be a one-stage or two-stage rectification process that would remove the higher-boiling component and at the same time adjust the ratio between the individual MeDCPD isomers. In the case of the production of high-purity MeDCPD, some more DCPD would be separated as a by-product, which would be flowed as recycle to the DCPD plant. The product could be colorless to yellow MeDCPD with a quality of 75–90%.

Conclusion

ORLEN Unipetrol's unit for the production of dicyclopentadiene (DCPD) was designed to meet high requirements for operation and process control and to enable the deployment of modern tools for process optimization, including digitization tools. The trial run verified the full functionality and variability of the production unit. It has been confirmed that the DCPD unit is capable of producing DCPD of exactly the required parameters. In addition, the DCPD unit allows two different streams to be used as the DCPD product, which meet the commercial specification for DCPD intermediate and DCPD high purity. The produced DCPD is shipped from the unit all over Europe to almost two dozen customers. At the same time, it should be pointed out that not all of these customers have the same requirements for the quality of DCPD product, the quality requirements often differ significantly in some parameters. The operation of the unit is therefore basically a constant search for a compromise and optimum in terms of DCPD production in the required quantities and parameters, so that the needs of customers are fulfilled and the possibilities of the production unit are also effectively used. To further optimize and increase the yield of DCPD from light pyrolysis gasoline, the process conditions should be adjusted to minimize DCPD losses during the recycling of light pyrolysis gasoline to the steam cracker unit. It is also necessary to focus on the energy balance of the unit.

Based on the tests performed, it appears that the by-product methyldicyclopentadiene (MeDCPD) concentrate could find advantageous commercial use in applications such as modified unsaturated polyester resins and alkyd resins. There is also the possibility of further processing of the MeDCPD concentrate as an extension of the DCPD production unit, which would adjust its properties to suit a specific selected application.

References

1. Cheung P.T.T., 16-Cyclopentadiene and dicyclopentadiene, in: Encycl. Polym. Sci. Technol, 759 (2001).
2. Karaba A., Zámostný P., Bělohlav Z., Lederer J., Herink T.: Application of a Semi-Mechanistic Model for Cracking Unit Balance. Chem. Eng. Technol., *38*, 609 (2015). https://onlinelibrary.wiley.com/doi/10.1002/ceat.201400628
3. Doskočil J., Bělohlav Z., Herink T., Zámostný P.: Improvement of pyrolysis reactors in Chemopetrol Litvinov. Chem. Listy, *97*, 1176 (2003).
4. Herink T., Fulín P., Krupka J., Pašek J.: New technology for production of Dicyclopentadiene and methyl-dicyklopentadiene. Polymers 14, 667 (2022). https://doi.org/10.3390/polym14040667.
5. Dicyclopentadiene (DCPD) Sales specification. ORLEN Unipetrol RPA s.r.o., Edition 3/2023 [available online] https://www.orlenunipetrolrpa.cz/.
6. Hamielec A. E., Tobita H.: Polymerization processes, VCH Weinheim (2000).
7. Vana P., Barner-Kowollik C., Davis. T., Matyjaszewski K., Radical polymerization: Encyclopedia of Polymer Science and Technology, *11* (2003).
8. Krupka J., Herink T., Pašek J., Kačer P.: Characterization of yellow compounds at isolation of dicyclopentadiene from Light Pyrolysis Gasoline. Ropa, uhlie, plyn o petrochémia *47*, 55 (2005).
9. Perrot A., Hyršl J, Bandžuch J., Waňousová S., Hájek J., Jenčík J., Herink T.: Use of dicyclopentadiene and methyl dicyclopentadiene for the synthesis of unsaturated polyester resins. Polymers, *13* (2021). https://doi.org/10.3390/ polym13183135.
10. Lauer J.C., Laurens T., Schmit-Quiles F., Nikole D., Matlengiewicz M., Henzel N.: Analusis, *21*, 239 (1993).

11. Xu R., Jocz J.N., Wiest L.K., Sarngadharan S.C., Milina M., Coleman J.S., Iaccino L.L., Pollet P., Sievers C., Liotta C.L.: Cyclopentadiene Dimerization Kinetics in the Presence of C5 Alkenes and Alkadienes. Ind. Eng. Chem. Res., *58*, 22516 (2019). http://doi.org/10.1021/acs.iecr.9b04018.
12. Mleziva J.: Polyesters, Their Production and Processing; SNTL-Technical Literature Publishing House: Prague, Czech Republic (1978).
13. Perrot Y., Baley C., Grohens Y., Davies P.: Damage resistance of composites based on glass fibre reinforced low styrene emission resins for marine applications. Appl. Compos. Mater. *14*, 67 (2007). https://doi.org/10.1007/s10443-006-9033-8.
14. Perrot A., Hyršl J, Bandžuch J., Waňousová S., Hájek J., Jenčík J., Herink T.: A comparative study of a modified unsaturated polyester resin with dicyclopentadiene and methyl dicyclopentadiene blends. Polymer, *267* (2023). https://doi.org/10.1016/j.polymer.2022.125639.
15. Riley D. J., Loza R.: Process for the Preparation of Dicyclopentadiene Modified Polyester Resins. US Patent US10/152,714, February 04, 2003.

ORGANIC TECHNOLOGY

PRODUCTION OF 4-AMINO-4H-1,2,4-TRIAZOLE AND ITS APPLICATION AS THE NITRIFICATION INHIBITOR

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Abstract

The cost-effective technology of the 4-amino-4H-1,2,4-triazole preparation has been developed to supply the nitrification inhibitor for the mineral fertilizers.

The inhibitors of the nitrogen nitrification are incorporated into the modern mineral fertilizers to enhance the efficiency of the utilization of this nutrient by plants, reduce the NOx formation and decrease the nitrate leaks into the groundwater. The nitrification inhibitor has therefore favourable economic and ecological effects.

4-amino-4H-1,2,4-triazole is known and efficient nitrification inhibitor. However, its poor availability and high market price present serious obstructions of its utilization in the role of the fertilizer additive. The preparation procedure has been simplified in the laboratories of VUCHT to overcome these drawbacks. Three production steps have been reduced to two. The existing parts of the shut production lines in Duslo have been used to scale up the process. The investment and operating costs are decreased by this way and the product price becomes acceptable for the production of the fertilizers. The cost cuts result in the higher fraction of impurities in the product. It has been necessary to verify that the impurities have no negative impact on the process safety. The fertilizers containing 4-amino-4H-1,2,4-triazole have been subsequently produced and evaluated in the agricultural field tests.

Introduction

The ASN fertilizer is important source of the ammonium nitrogen for the plants. However, the undesired conversion of the NH_4^+ nutrient into NO_x, N_2O or NO_3^- decreases efficiency of the fertilization. This process is called nitrification and it is mediated by one sort of the soil bacteria. The nitrification represents also the source of the environmental pollution. NO_x and N_2O are the greenhouse gasses and NO_3^- is easily leached into the ground water.

Nitrification inhibitors are added into the new generation of fertilizers in order to suppress the nitrification and increase the utilization of the nitrogen by crops. The fertilizers containing the nitrification inhibitors can be applied in lower doses with the same positive effect on the harvest.

4-amino-4H-1,2,4-triazole is the promising nitrification inhibitor. However, it availability on the market is poor. The compound is mainly sold as the pharmaceutical intermediate and it is offered for 18–23 $/kg. The price is not acceptable for the application in fertilizers.

Our project aimed the production of 4-amino-4H-1,2,4-triazole for the application in the ASN fertilizer in the production scale. The development was determined with two requirements:

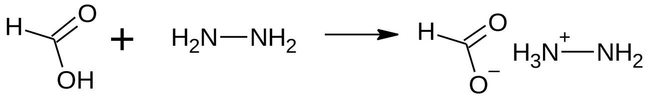
1. Prepare the inhibitor with the quality satisfactory for fertilizer production.
2. Minimize the production costs to achieve the economic viability of the fertilizer containing the inhibitor.

Experimental

Synthesis of the 4-amino-4H-1,2,4-triazole in the laboratory conditions

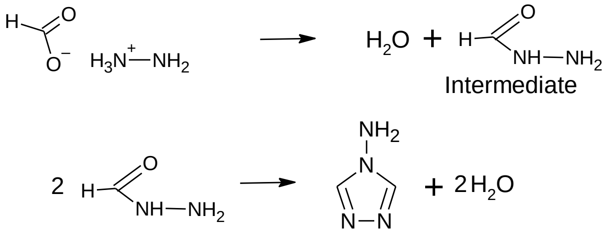
The preparation of the 4-amino-4H-1,2,4-triazole consists of three steps:

1st step: Reaction of hydrazine with formic acid to form hydrazinium format:



Hydrazine hydrate (201 g, 4 mols) is placed into the flask equipped with stirrer and formic acid (183 g, 3.9 mols) is added dropwise. The cooling of reaction mixture and rate of the acid addition are set to keep the maximum temperature of 40 °C.

2nd step: Condensation into the intermediate formylhydrazine and subsequent 4-amino-4H-1,2,4-triazole:



The condenser is added to the flask containing the product of the 1st step. The mixture is heated slowly to the maximum desired temperature. The maximum temperature is achieved after 7.5–8 hours. The water is collected behind the condenser. The reaction is completed when the water condensation ceased. The reaction mixture is cooled to 80°C.

3rd step: Purification of product by recrystallization from isopropanole:

Isopropanole (230 g) is added into the flask and the mixture is homogenized. It is cooled to 5 °C and left to crystallize for 16 hours. The crystals of 4-amino-4H-1,2,4-triazole are collected and washed with 50 g of cold isopropanole for twice.

The process of 4-amino-4H-1,2,4-triazole is described by the following block diagram (Figure 1):

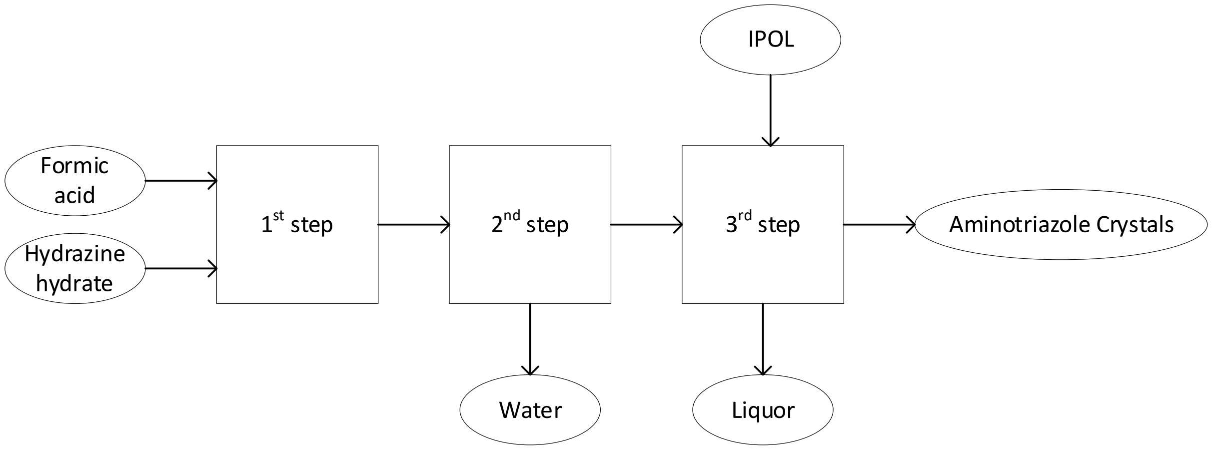


Figure 1. Block diagram of 4-amino-4H-1,2,4-triazole preparation

Discussion of results

Synthesis of the 4-amino-4H-1,2,4-triazole in the laboratory conditions

The conditions of the synthesis were optimized in order to achieve the maximum yield of the 4-amino-4H-1,2,4-triazole. The first set of trials has been focused on the reaction temperature during the second stage of the synthesis. Our trials begun with the reaction temperature 170 °C according to Bourdauducq[1]. However, we have soon found, that the products prepared in these conditions had poor quality, their melting points did not exceed 60 °C. The decrease of the reaction temperature to 150 °C led to the significant improvement of the product purity. Its melting point increased to the desired value of 79 °C.

Increase of the yield was the objective of another set of trials. First trials gave yields in the range 61–65% after the purification step, the product purity was 99,8%. We have determined the fraction of the 4-amino-4H-1,2,4-triazole in the reaction mixture during the second and third step of the synthesis. Known quantities of the raw materials, intermediates, products and side products enabled to calculate the material balance of these reaction steps. Table I. shows, that the main product is formed with the yield 98,7% in the 2nd step of the reaction. The crystallization from isopropanole in the third step is not complete and ca 27% of the main product remains dissolved in the liquor. The most efficient way to the yield increase would involve either isolation of the product from the liquor or omitting the crystallization at all and utilize the product of the 2nd step. The former way will provide the product of high purity, later one is more cost efficient.

Table I.
Material balance of the 4-amino-4H-1,2,4-triazole preparation

Raw materials (mols)	1st step	Aminotriazole		
		2nd step	3rd step – crystals	3rd step – liquor
Formic acid	3.73			
Hydrazine hydrate	4.08			
Product in mols		1.84	1.34	0.50
Product in % of theory		98.7%	71.8%	26.8%

The product of the second step was analysed with the following result (Table II.):

Table II.
Composition of the product before the crystallization

Component	**Fraction**
4-amino-4H-1,2,4-triazole:	92.5%
Intermediate Formylhydrazine	0.9%
Diformylhydrazine and Triazole:	<0.01%
Water	7.8%

The result of analysis showed, that the 4-amino-4H-1,2,4-triazole was obtained with the purity 92.5%. The inhibitor would be applied in the form of the water solution, so the 7.8% of water did not present any problem. Formylhydrazine is the reducing agent. The fertilizers produced in Duslo contain ammonium nitrate – strong oxidizing agent. It was necessary to verify, that the formylhydrazine fraction would not initiate the explosive decomposition of the fertilizer during it production, manipulation, transport or storage. The details of the safety tests are not subject of this paper, however, their results have shown that the safety is not violated after the application of the inhibitor. The positive result of the safety tests confirmed that it was possible to produce the 4-amino-4H-1,2,4-triazole by simplified way for the application in the fertilizers.
This result encouraged the scale up of the preparation procedure to the production apparatus.

Scale up of the 4-amino-4H-1,2,4-triazole preparation
The cost efficiency was the main priority of our project. The minimization of the capital expenditures motivated searching for the existing apparatus in Duslo, which enables the synthesis of 4-amino-4H-1,2,4-triazole in the production scale. The stirred tank reactor equipped with the heating/cooling jacked and condenser was selected for this purpose. Its parameters were as follows:

Table III.
Size of the production apparatus

Inner diameter	2 m
Stirrer diameter	0.66 m, paddle
Height of the cooled / heated space	1.32 m
Heat exchange medium	Oil (Marlotherm), 33 mPa.s at 30°C
Heating medium:	Steam (12 bar)
Cooling medium	Water, 25°C

Heating / cooling of Marlotherm proceeded in the separate heat exchanger.
The size of the heated / cooled space in the reactor has volume $4.14 m^3$. It enables the reaction of 2,350 kg (49.94 kmol) hydrazinehydrate with 2,103 kg (45.69 kmol) formic acid.

First reaction step: Cooling capacity and reaction time:

The laboratory development showed that the maintaining of the maximum reaction temperature is crucial for the product the quality and yield. The heat transfer in both reaction steps was therefore the determining process in the production conditions.
The exothermic neutralization reaction between the hydrazine and formic acid is the first reaction step. The measured reaction heat was -43.7 kJ per mol of formic acid. The total quantity of reaction heat formed during the production in the 1st step will be 43.7×45.69 mol, e. g. 1,996 MJ. This heat must be removed from the

reaction mixture continuously during the dosing of formic acid, so the reaction temperature would not exceed 40 °C. The rate of the heat evolution is determined by the rate of the dosing and the dosing rate would determine the reaction time during the 1st step. The correct estimation of the reaction time required the knowledge of the cooling capacity of the reactor. The capacity was estimated as follows:

Table IV.
Estimation of the cooling capacity of the production apparatus:
Jacket: Stirred vessel:

Inlet temperature of the heat exchange medium	30°C	Temperature of the reaction mixture	40°C
Heat exchange area in jacked	5.53 m^2	Heat transfer coefficient from reaction mixture	681 W/m^2/K
Flow rate of heat exchange medium (oil)	2 m/s	Aggregate heat transfer coefficient:	195 W/m^2/K
Heat transfer coefficient into the oil	297 W/m^2/K	Medium temperature difference	9.28°C
Outlet temperature of heat exchange medium	31.4°C	**Rate of the heat removal**	**10.1 kW or 36MJ/h**

The known rate of the heat removal enabled to calculate the reaction time of the first step to be 1996/36 = 55.4 hours. The estimated dosing rate of formic acid would be 38 kg/hour.

Second reaction step: the heat balance and reaction time.
Second reaction step includes two endothermic processes:

1. Heating of the reaction mixture from 40 °C to 150 °C
2. Distillation of the water formed in the reaction

The heat consumption is calculated as follows:

Table V.
Estimation of the heating capacity of the production apparatus:

Heating from 40 to 150°C		**Evaporation of water**	
cp [kJ/kg/K]	3.18	dh evaporation [kJ/kg]	2,114
m [kg]	4,544	m [kg]	2,457
dt [°C]	110	**Q evaporation [kJ]**	**5,194,579**
Q heating [kJ]	**1,589,514**		

Total heat consumed in the 2nd step:	Q = Q evap. + Q heating [MJ]	6,784

The calculations of the heat transfer parameters gave following results:

	Heating	Evaporation of water
Heat exchange area (m^2)	5.53	5.53
Temperature of heat transfer medium (°C)	161 < t < 180	171 < t <180
Mean temperature difference (K)	75.1	25.2
Aggregate heat transfer coefficient (W/m^2/K)	402	600
Rate of heat transfer (MJ/h)	**600**	**300**

Using the information about the heat consumption and about the heat transfer rate in the conditions of the second step, the reaction time can be estimated. The heating from 40 to 150 °C will require about 3 hours and evaporation of water about 17 hours.

Comparison of calculated values with the run of the production trial

The calculated estimation of the reaction time was applied in the design of the production trial conditions. The dosing of formic acid begun with the estimated rate 38 kg/h in during the 1st step. It was soon found, that the rate can be increased. The initial temperature of the reaction mixture was 24 °C. The content of the reactor was heated to 36 °C with the reaction heat during the first 5 hours. The dosing rate was increased to 50 kg/h and later to 70 kg/h. The reaction temperature was kept at 38 °C with the safe difference 2 °C from the maximum 40 °C. The result shows, that the rate of heat transfer was higher than the estimated one. The explanation follows from the fact, that the level of the liquid present in the vessel was not horizontal but formed the vortex due to the stirring. The heat transfer area was then larger than 5.53 m^2 and the heat was removed more efficiently. This effect was enhanced as the volume of the reaction mixture increased due to the addition of formic acid. The real reaction time was 44 hours. The evolution of the reaction temperature and dosing rate of formic acid describes Figure 2.

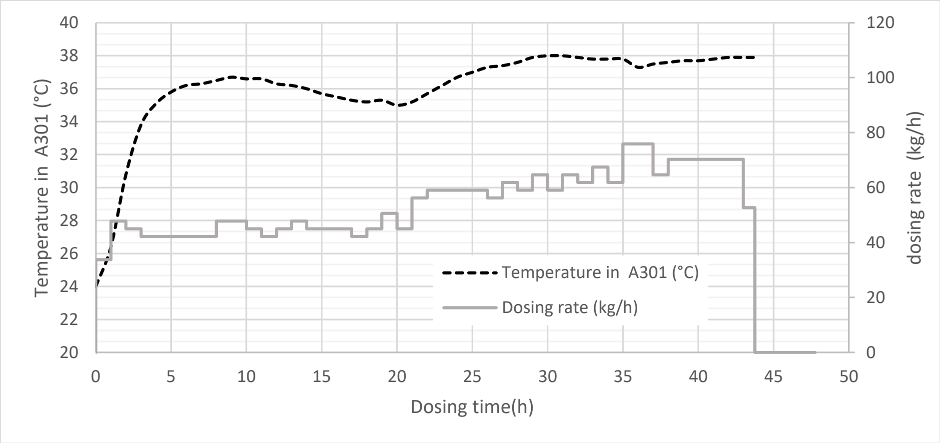


Figure 2. Production trial of 4-amino-4H-1,2,4-triazole preparation: Reaction temperature and dosing rate of formic acid during the 1st reaction step.

The heating of the reaction mixture during the 2nd reaction step was initially complicated by the problems with the clogged condenser, the distillation was postponed by 4 hours until the problem was fixed. The distillation then proceeded faster than the calculations estimated. The Figure 3 shows that the 80% of the total water amount distilled at reaction temperature 110–120 °C. The real temperature difference between the heating oil and reaction mixture was then 50–60 °C instead of estimated 25 °C. This fact increased the reaction rate and distillation was completed 13 hours after its beginning instead of 17 hours as was estimated by calculations.

The comparison of real reaction times with the calculated ones have shown, that the safe scale up of the 4-amino-4H-1,2,4-triazole preparation was possible. The calculations underestimated the rate of the heat transfer. They provided the first estimation of the reaction time and dosing rate for each step and enabled to run the first production batch in the way, that required temperature profiles were fulfilled. There is still the space for the process optimization based on the experience obtained in the real production conditions.

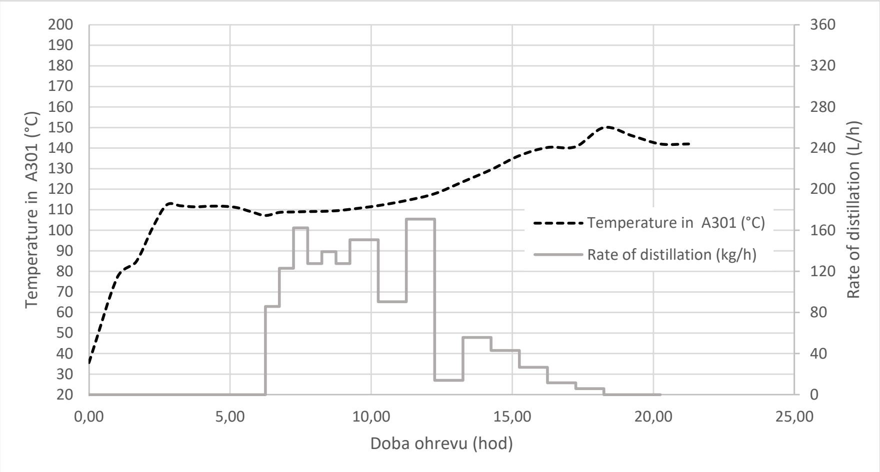


Figure 3 Production trial of 4-amino-4H-1,2,4-triazole preparation: Reaction temperature and distillation rate of water during the 2nd reaction step.

Conclusions

The preparation procedure of the nitrification inhibitor 4-amino-4H-1,2,4-triazole was developed in the laboratory and scaled up in the production apparatus. The product purity of 90% was satisfactory for its application in fertilizers. This fact enabled to decrease the number of production steps from three to two and simplify the process by this way. The laboratory preparation was optimized by the modification of the reaction temperature limits. It was necessary to keep maximum 40 °C in the first and maximum 150 °C in the second step. The yield higher than 98% was obtained in these conditions. Maintaining of the reaction temperature limits was the main condition to achieve such good result in the production scale. The exothermic nature of the first step of production and endothermic nature of the second one caused that the heat transfer was the crucial phenomenon in the production apparatus. Calculations of the heat transfer parameters provided the first estimation of the dosing rates and reaction times. The results of the following production test showed that the real reaction times can be shorter than the calculated ones. The duration of the first reaction step is 44 hours instead of calculated 55 hours and the reaction time of the second step is 13 hours instead of calculated 17 hours. These results are achieved in the existing apparatus, so the capital expenditures are spared.

The simplification of process, achievement of satisfactory yield and use of existing apparatus enabled to produce 4-amino-4H-1,2,4-triazole with the costs acceptable in the fertilizer industry. The inhibitor was successfully applied into the ASN fertilizer and the field tests of the modified fertilizer gave desired result.

Acknowledgement

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References

1. Bourdauducq P.: Process for the preparation of 4-amino-1,2,4-triazole; US6040456A; 21.3. 2000; Elf Atochem.

INFLUENCE OF THE REACTION CONDITIONS ON 3-CARENE EPOXIDATION

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Abstract

3-Carene, a representative of monoterpenes, is found in conifers (for example cypress, spruce, pine). It could be used as a renewable source for many fine chemicals production. Monoterpenes generally can be oxidized to form monoterpene oxides (epoxides). 3-Carene oxide is an important intermediate, which has utilization in production of pharmaceuticals and fragrances. Conversion of 3-carene and the selectivity to the desired oxide can be affected by oxidant, solvent, catalyst and additives. In this work, the synergy of the oxidizer with the solvent was investigated. From used oxidants, *m*-chloroperoxybenzoic acid was the only applicable. We ascertained that solubility of *m*-chloroperoxybenzoic acid and *m*-chlorobenzoic acid (by-product) influenced the rate and the selectivity to the desired 3-carene oxide. 3,4-Carane diol and 4-caranone detected in the reaction mixture were produced by following isomerization or hydration of 3-carene oxide as undesired products. The best selectivity was obtained under reaction conditions: 1 ml 3-carene, 1.5 eq. *m*-chloroperoxybenzoic acid, 15 ml cyclohexane, first hour at 0 °C then room temperature. The selectivity was 88% at > 99% conversion.

Introduction

Currently, an effort exists to choose a raw material base from renewable resources. One of the many options is the use of essential oils from plants that are rich on monoterpenes. These compounds compose of two isoprene units (2-methyl-1,3-diene), and are usually fragrant with a characteristic scent. Their names are typically derived from the Latin name of plants in which a high content was found in their essential oil, e. g. *α*-pinene in pine (*Pinus sp.*), menthol in mint (*Mentha sp.*), etc. Monoterpenes can be oxidized to form monoterpene oxides (epoxides) that is a simple and selective way to include oxygen atom into the structure. It is possible to carry out various reactions on epoxides, therefore monoterpene oxides are interesting intermediates for isomerizations, reductions, ring openings with a nucleophile, etc.

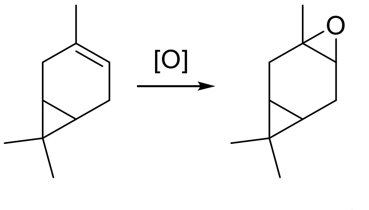


Figure 1. Epoxidation of 3-carene

3-Carene is contained in conifers, e. g. cypress, spruce, pine[1-3]. Its epoxidation gives 3-carene oxide (Figure 1.), an important intermediate for the production of pharmaceuticals (e. g., the reaction of 3-carene oxide with morpholine followed by two steps producing the second-generation nonnucleoside, reverse transcriptase inhibitor)[4], and fragrances[5]. Conversion of 3-carene and the selectivity to the desired oxide can be affected by oxidant, solvent, catalyst, and additives[6,7].

Experimental

Materials

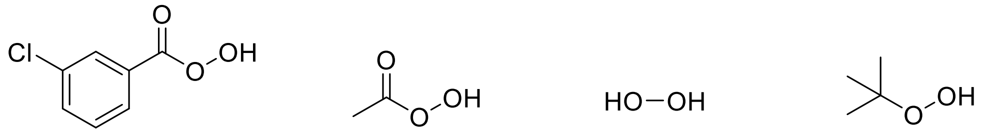
Reactant. 3-Carene (90%) was purchased from Sigma Aldrich.
Oxidant. *m*-Chloroperoxybenzoic acid (3-chloroperbenzoic acid, 77%) and *tert*-butyl hydroperoxide (70% water solution) as Luperox were purchased from Sigma Aldrich. Peroxyacetic acid (36% water solution) as Persteril was purchased from Conlac. Hydrogen peroxide (30% water solution) was purchased from Penta.
Solvent. Hexane (99%, p.a.), dichloromethane (p.a.), and acetonitrile (p.a.) were purchased from Penta. Cyclohexane (99%, p.a.), ethyl acetate (99%, p.a.) were purchased from Lachner. Methyl propionate (≥ 98%) was purchased from SAFC. Dimethyl carbonate (≥ 99.8%) was purchased from Roth.

Typical experiment

1 ml of 3-carene in 1 ml of solvent was cooled in ice bath. Mixture of oxidant with solvent at room temperature was prepared from 1.5 eq. of oxidant and 14 ml of the same solvent. Into cold mixture of 3-carene solution of oxidant was added. The reaction mixture was vigorously stirred and cooled in ice bath on a magnetic stirrer. After 1 hour of cooling, ice bath was removed and the reaction mixture was freely kept heat up to the room temperature. Samples were taken at 1, 1.5, 2, 3, and 6 hours. The, they were centrifuged and the organic layer was analysed. Structures were identified on GC-MS. Quantity was determined using GC-FID.

Results and discussion

Structures of used oxidants are depicted in Figure 2. Two peracids (MCPBA, PAA), one peroxide (H_2O_2) and one hydroperoxide (TBHP) were used. The reaction conditions for epoxidation were slightly adjusted by Cimarelli et al.[6]. They used only MCPBA and chloroform as a solvent.



m-chloroperoxybenzoic acid MCPBA | peroxyacetic acid PAA | hydrogen peroxide H_2O_2 | *tert*-butyl hydroperoxide TBHP

Figure 2. Structures of oxidants

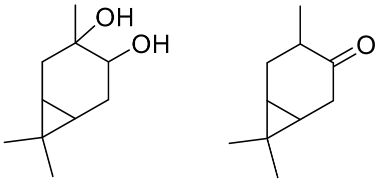
MCPBA was proven as an efficient oxidant (Table I.). The average conversion over all used solvents (list of solvent below, Table II.) using MCPBA was 91% at 1 hour, i.e., during under low temperature. The other oxidants provided significantly lower conversions than MCPBA. Low conversion can be caused by the existence of phase interface of organic-water layer.

Table I.

Average conversion in % over all used solvents using specific oxidant at different reaction time (1 ml 3-carene, 1.5 eq. oxidant, 15 ml solvent, 1 hour at 0 °C then RT)

reaction time [h]	MCPBA	PAA	H_2O_2	TBHP
1.0	91.0	2.8	0.3	0.1
1.5	96.5	4.4	0.5	0.2
2.0	99.3	5.0	0.7	0.4
3.0	99.7	5.3	1.0	0.5
6.0	99.8	5.8	1.2	0.6

Moreover, 3,4-carane diol and 4-caranone (Figure 3) were produced by following isomerization or hydration of 3-carene oxide. These reactions could take place under acidic conditions. The used peracids are less acidic than corresponding acids, which are the by-product of epoxidation (e.g., from MCPBA *m*-chlorobenzoic acid (MCBA) is formed).



3,4-carane diol | 4-caranone

Figure 3. Structures of the undesired by-products

The solvent had an effect on the selectivity. Influence of the solvent was studied using hexane (H), cyclohexane (CH), dichloromethane (DCM), methyl propionate (MeOPr), ethyl acetate (EtOAc), acetonitrile (AcN), and dimethyl carbonate (DMC). These were two hydrocarbons with same number of carbons, one chloro derivate, two esters with same number of carbons (3 + 1, 2 + 2), one nitrile and dimethyl carbonate as a green solvent. Usually in epoxidations, chlorinated solvents and acetonitrile are used. Values of the selected properties are depicted in Table II.

Table II.
Properties of all used solvents[8-11]

solvent property	H	CH	DCM	MeOPr	EtOAc	AcN	DMC
dipole moment [D]	0	0.3	1.14	1.67	1.88	3.2	4.5
polarity [1 = water]	0.006	0.009	0.309	0.23	0.23	0.46	0.25
donor number [kcal/mol]	0	0	1	11	17.1	14.1	17.2
relative permittivity [-]	1.9	2.01	9.1	6.23	6.02	37.5	3.17
boiling point [°C]	69	80.1	39.6	79.8	77	82	90

Both MCPBA and its product after epoxidation (MCBA) are white crystalline substances. Their solubility probably affected the reaction. The rate of the reaction was influenced by the solubility of MCPBA, while the solubility of both had an effect on the selectivity. The solubility was observed visually. Solubility of MCPBA was observed before adding into cold mixture of 3-carene with solvent. The solubility of both substances is described in Table III. If MCPBA was soluble, but MCBA was poorly soluble (insoluble), the generating of MCBA in cold reaction mixture was observed in a few minutes after adding of MCPBA.

Table III.
Solubility of oxidant MCPBA and its product MCBA in used solvents

soluble	MCPBA	MCBA
H	poorly	poorly
CH	poorly	poorly
DCM	well	poorly
MeOPr	well	well
EtOAc	well	well
AcN	well	poorly
DMC	well	well

From the results in Table IV., we can see that the solubility had an influence on the rate of reaction. MCPBA was poorly soluble or insoluble only in H and CH. 99+% conversion of 3-carene was observed in H at 1.5 hours and in CH at 3 hours, while in other solvents it was up to 1 hour. The insolubility of MCPBA relates with low values of polarity, relative permittivity, and dipole moment, which are typical for non-polar solvents.

Table IV.
Conversion of 3-carene for all used solvents at different reaction time (1 ml 3-carene, 1.5 eq. MCPBA, 15 ml solvent, 1 hour at 0 °C then RT)

Reaction time [h]	H	CH	DCM	MeOPr	EtOAc	AcN	DMC
1.0	69.2	69.6	99.5	99.5	99.5	99.6	99.8
1.5	99.7	77.6	99.6	99.6	99.5	99.7	99.8
2.0	99.8	96.7	99.8	99.7	99.6	99.7	99.8
3.0	99.8	99.2	99.8	99.8	99.7	99.8	99.8
6.0	99.8	99.8	99.8	99.7	99.8	99.9	99.8

Because over 99% conversion was obtained in all of used solvents at 3 hours, the results of selectivity in Figure 4 are featured for this time. We can observe, how solubility of MCPBA and MCBA influenced of the selectivity. Under condition when both substances were soluble, the selectivity for 3-carene oxide was around 50%. In this case, the solvent has the middle value of polarity about 0.25 (1 = water). If MCPBA was soluble but MCBA was insoluble, the selectivity was higher (around 60%) and it was characteristic for the solvent with a higher polarity. The highest selectivity was achieved, if MCPBA and MCBA were both insoluble in reaction mixture. In this case, the selectivity was over 85% for hydrocarbons as solvents.

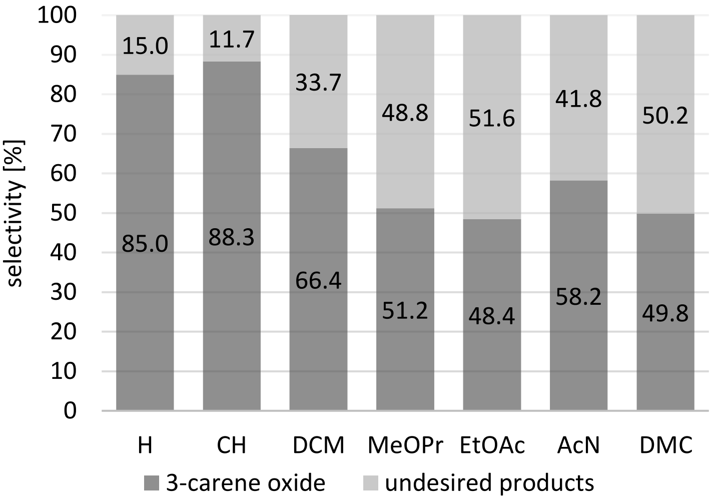


Figure 4. Selectivity at > 99% conversion (3 hours): 1 ml 3-carene, 1.5 eq. MCPBA, 15 ml solvent, 1 hour at 0 °C then RT

Very important information was about the change selectivity with the conversion. Results in Figure 5 show that the selectivity practically didn't change.

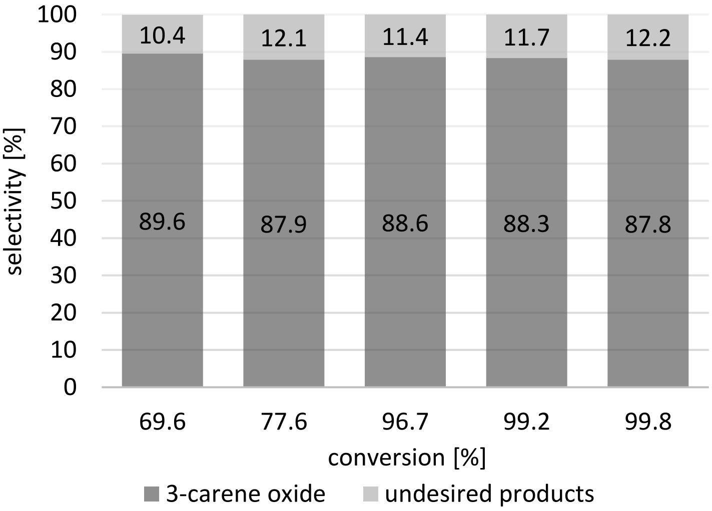


Figure 5. Dependence of selectivity on conversion: 1 ml 3-carene, 1.5 eq. MCPBA, total 15 ml CH, 1 hour at 0 °C then RT

In Figure 4, it was shown that the selectivity for 3-carene oxide was the lowest using EtOAc after 3 hours. Using EtOAc, the conversion of 3-carene was over 99% at 1 hour already. Trend of the selectivity at the time is described in Figure 6. We can see, the selectivity very slightly decreases at the time.

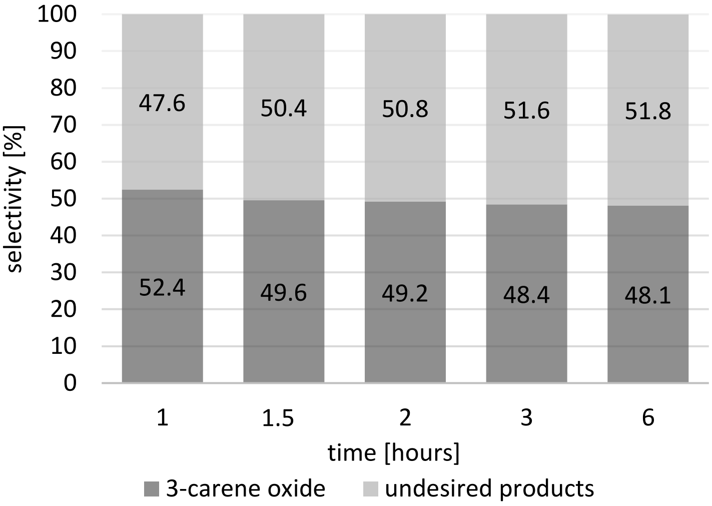


Figure 6. Selectivity at time: 1 ml 3-carene, 1.5 eq. MCPBA, 15 ml EtOAc, 1 hour at 0 °C then RT

Conclusion

3-Carene oxide was successfully prepared; undesired products (3,4-carane diol, 4-caranone) were detected. The strength of oxidant (MCPBA >> PAA > H_2O_2 ≈ TBHP) was established with influence of solvents (H, CH, DCM, MeOPr, EtOAc, AcN, DMC). Almost total conversion was achieved using all solvents. The solvent affected the rate of reaction by solubility of MCPBA and the selectivity of production of 3-carene oxide by solubility of MCBA. Very good results provided solvents with low values of polarity, relative permittivity and dipole moment, because both substances were insoluble in such solvents. The highest selectivity was obtained at reaction conditions 1 ml 3-carene, 1.5 eq. *m*-chloroperoxybenzoic acid, 15 ml cyclohexane, first hour at 0 °C then room temperature. The selectivity was 88% at > 99% conversion. Cimarelli et al.[6] achieved the similar results. However, cyclohexane, which was chosen in this work is more ecologically friendly comparing chloroform used in their work.

Acknowledgement

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References

1. Pierre-Leandri C., Fernandez X., Lizzani-Cuvelier L., Loiseau A.-M., Fellous R., Garnero J.: J. Essent. Oil Res. *15*, 242 (2003).
2. Persson M., Sjödin K., Borg-Karlson A.-K., Norin T., Ekberg I.: Phytochem. *42*, 1289 (1996).
3. Piechowiak T., Balawejder M., Grzelak-Błaszczyk K., Oracz J., Matłok N.: LWT – Food Science and Technology. *173*, 114262 (2023).
4. Kauffman G. S., Harris G. D., Dorow R. L., Stone B. R. P., Parsons Jr. R. L., Pesti J. A., Magnus N. A., Fortunak J. M., Confalone P. N., Nuget W. A.: Org. Lett. *2*, 3119 (2000).
5. Surburg H., Panten J.: *Common Fragrance and Flavour Materials*. *Preparation, Properties and Uses*. Wiley. Weinheim 2006.
6. Cimarelli C., Fratoni D., Palmieri G.: Tetrahedron: Asymmetry. 22, 603 (2011).
7. Cunningham W. B., Tibbetts J. D., Hutchby M., Maltby K. A., Davidson M. G., Hintermair U., Plucinski P., Bull S. D.: Green Chem. 22, 513 (2020).
8. Smallwood I. M.: Handbook of Organic Solvent Properties. Available online: https://app.knovel.com/kn/resources/kpHOSP0005/toc (accessed on 15 June 2023).
9. Cataldo F.: Eur. Chem. Bull. *4*, 92 (2015).
10. Gill A. H., Dexter F. P.: Ind. Eng. Chem. *26*, 881 (1934).
11. Gutmann Acceptor and Donor number. Available online: http://www.stenutz.eu/chem/solv21.php (accessed on 15 June 2023).

STUDY OF UNCATALYZED LOW TEMPERATURE OXIDATION OF CYCLOHEXYLAMINE WITH AIR IN LIQUID PHASE – EFFECT OF REACTION TEMPERATURE AND CONCENTRATION OF WATER

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Abstract

In the presented work, we study the kinetics of uncatalyzed oxidation of cyclohexylamine with air in the liquid phase. The effect of reaction temperature 80–110 °C and concentration of water 0.17–1.17 wt. % on the reaction rate was studied. From the experimental data, the value of activation energy of oxidation of cyclohexylamine towards imine *N*-cyclohexylidenecyclohexanamine was calculated, 139.4 kJ mol^{-1}. The kinetic model consists of other reactions that accompany the title reaction and their kinetic parameters were calculated. Hydrolysis of imine to cyclohexanone and cyclohexylamine, 89.3 kJ mol^{-1}, condensation of cyclohexanone and cyclohexylamine to imine, 36.9 kJ mol^{-1} and oxidation of cyclohexylamine to cyclohexanone oxime, 58.5 kJ mol^{-1}. Moreover, it was discovered that the added amount of water in cyclohexylamine has practically no effect on the reaction rate of its oxidation.

Introduction

Cyclohexylamine (CHA) is mostly produced by the hydrogenation of aniline in the gaseous phase over a nickel or more selective cobalt catalysts[1-3]. Czech Republic (chemical plant BorsodChem MCHZ, s.r.o.) is one of the largest world producers of CHA[4]. CHA is an important raw material and fine chemical intermediate for the production of metal corrosion inhibitors, rubber vulcanization accelerators, plasticizers, agricultural chemicals, surfactants, dyestuffs and artificial sweeteners[5-7]. In all these applications of CHA its purity is crucial. During the storage and transport of this cycloaliphatic amine, its quality can be decreased due to its contact with air, which leads to a rise in the concentration of imine *N*-cyclohexylidenecyclohexanamine (NCCHA) and a change in the colour of CHA from colourless to yellow to faint red. The most published works deal with the catalytic oxidation of CHA to cyclohexanone oxime (CHOX) as a desired product[8-10]. However, there are no works with an aim at uncatalyzed oxidation of CHA with air towards NCCHA in a liquid phase. In our previous work[11] we focused on the kinetics of uncatalyzed oxidation of dicyclohexylamine (DCHA) with air in the liquid phase alongside the study of the promotional effect of water on the reaction rate of DCHA oxidation. This contribution follows the scope of our previous work[11], but now from the view of oxidation of CHA.

Experimental

Chemicals and gases

The CHA was acquired from BorsodChem MCHZ, s.r.o. (99.9%) and the solvent methanol was purchased from Penta, s.r.o. (99.9%). Both chemicals were used without further purification. For the experiments of oxidations of CHA was used technical air purchased from SIAD, Czech Republic. For the gas chromatography, used helium (5.5) was purchased from LindeGas, a.s.

Experimental apparatus

The experiments of oxidation of CHA in the liquid phase were carried out in apparatus described as follows (**Figure 1**): The air from gas cylinder **1** was fed through regulators **2** and **3** and distributed by aerator **4** into liquid CHA (reaction mixture). By syringe **5** the samples of the reaction mixture were collected from the reactor (250 ml three-neck round-bottom flask) **6** placed in the bath of glycerol. Temperature of the glycerol bath was regulated by the thermostat **7**. On the side arm of the reactor was placed a Dimroth condenser (cooled by water to *ca.* 15 °C) **8**.

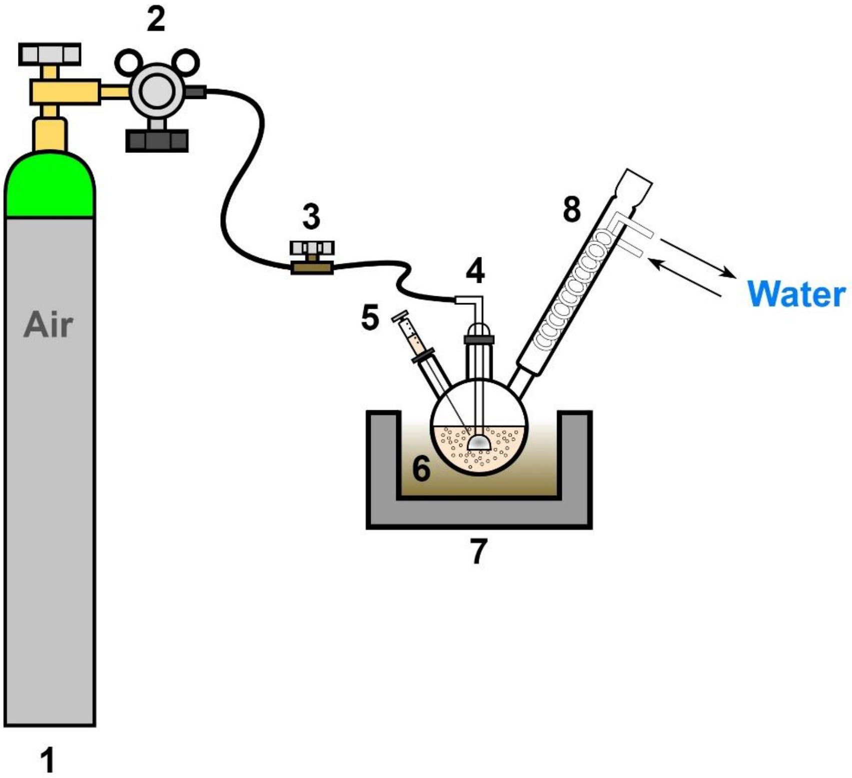

Figure 1. Schematic diagram of the experimental apparatus for the CHA oxidation.

Reaction procedure

The experiments were carried out with 93±0.1 g of CHA at reaction temperature 80–110 °C, atmospheric pressure and concentration of water 0.17-1.17 wt. % and flow of air 1±0.3 l h^{-1}.

Analytical

Quantitative chromatographic analyses were performed using a Shimadzu GC-2010 chromatograph with a flame ionization detector using Rxi®-624Sil MS capillary column (30 m x 0.25 mm x 1.40 μm) and He as a support gas. The column temperature regime was set as follows: Initial temperature 80 °C for 2 min, heating with the temperature ramp of 15 °C per min up to the temperature of 210 °C. The injector and detector temperatures were set to 250 °C.

Data processing

The reaction system of oxidation of CHA to *N*-cyclohexylidenecyclohexanamine (NCCHA) for the purpose of this work was simplified and includes only these chemical reactions (**Figure 2**):

- oxidative dehydrogenation (ODH) of CHA to cyclohexanamine (CHI) and its sequential condensation with another molecule of CHA leading to the formation of imine NCCHA (for the purpose of kinetic modelling, this reaction was summarized as a reaction of 2 molecules of CHA with oxygen leading directly to NCCHA),
- consecutive reversible reaction of NCCHA, its hydrolysis to cyclohexanone (CHON) and CHA,
- parallel reaction of CHA, its oxidation towards cyclohexanone oxime (CHOX).

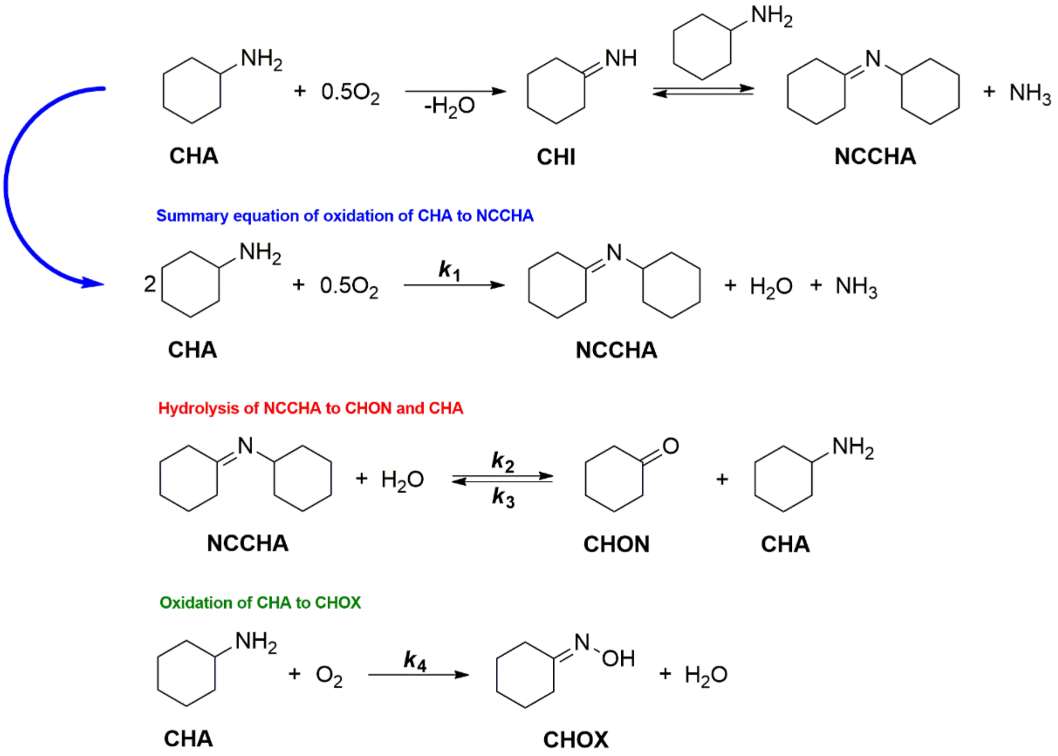

Figure 2. Reaction scheme of ODH of CHA alongside side reactions.

The regression analyses of the experimental data were performed by the Easy Regression Analysis (ERA) software[12]. The dependence of concentrations (mmol l^{-1}) of components of the reaction mixture on the time were input parameters for the estimation of values of activation energy E_{ai} and rate constant (at reference temperature 100 °C) $k_{i,\mathrm{ref}}$ for above presented chemical reactions. The dependence of the rate constant k_i on temperature for the reaction i was expressed by the Arrhenius relation as follows:

$$k_i = k_{i,\mathrm{ref}} \cdot \exp\left[\frac{E_{\mathrm{a}i} \cdot (T - T_{\mathrm{ref}})}{\mathrm{R} \cdot T \cdot T_{\mathrm{ref}}}\right] \qquad (1)$$

where $k_{i,\mathrm{ref}}$ is a rate constant at reference temperature T_{ref}, T is the reaction temperature, E_{ai} is the activation energy of reaction i and R is the universal gas constant. The reference temperature was used in order to eliminate the strong correlation between the activation energy E_{ai} and the pre-exponential factor A in the Arrhenius relation[11,13]. The studied reaction system of ODH of CHA presented in **Figure 2** was described by power-law kinetics. The model is simplified by the assumption that CHA is saturated by oxygen at a given reaction temperature, thus a concentration of O_2 is constant, hence not taken into account in the kinetic model. The regression model used in ERA software consists of the following equations:

$$r_1 = k_1 \cdot c_{\mathrm{CHA}}{}^2 \qquad (2)$$

$$r_2 = k_2 \cdot c_{\mathrm{NCCHA}} \cdot c_{\mathrm{H_2O}} \qquad (3)$$

$$r_3 = k_3 \cdot c_{\mathrm{CHON}} \cdot c_{\mathrm{CHA}} \qquad (4)$$

$$r_4 = k_4 \cdot c_{\mathrm{CHA}} \qquad (5)$$

$$\frac{\mathrm{d}c_{\mathrm{CHA}}}{\mathrm{d}t} = -\, 2 \cdot r_1 + r_2 - r_3 - r_4 \qquad (6)$$

$$\frac{\mathrm{d}c_{\mathrm{NCCHA}}}{\mathrm{d}t} = r_1 - r_2 + r_3 \qquad (7)$$

$$\frac{\mathrm{d}c_{\mathrm{CHON}}}{\mathrm{d}t} = r_2 - r_3 \qquad (8)$$

$$\frac{\mathrm{d}c_{\mathrm{CHOX}}}{\mathrm{d}t} = r_4 \qquad (9)$$

$$\frac{\mathrm{d}c_{\mathrm{H2O}}}{\mathrm{d}t} = r_1 - r_2 + r_3 + r_4 \qquad (10)$$

$$\frac{\mathrm{d}c_{\mathrm{NH3}}}{\mathrm{d}t} = r_1 \qquad (11)$$

The concentrations of water and ammonia formed by the reactions during the process of ODH of CHA were obtained by mass balance.

Results and discussion

The effect of temperature on the reaction rate of ODH of CHA

The experiments were carried out at the temperature range of 80–110 °C. There was no recognized arise of concentration of the main product, *i.e.,* NCCHA at 80–90 °C at the time range of 7 hours. The concentration changes of NCCHA were observed in the case of ODH of CHA at 100–110 °C (**Figure 3**). From the experimental data of concentrations of reactant CHA, main product NCCHA and other products (CHON, CHOX etc.) and their dependence on time and temperature were obtained the values activation energy and rate constant (at reference temperature) for each reaction (**Table I.**). Values of activation energy of side reactions are compared with the results of our previous work[11].

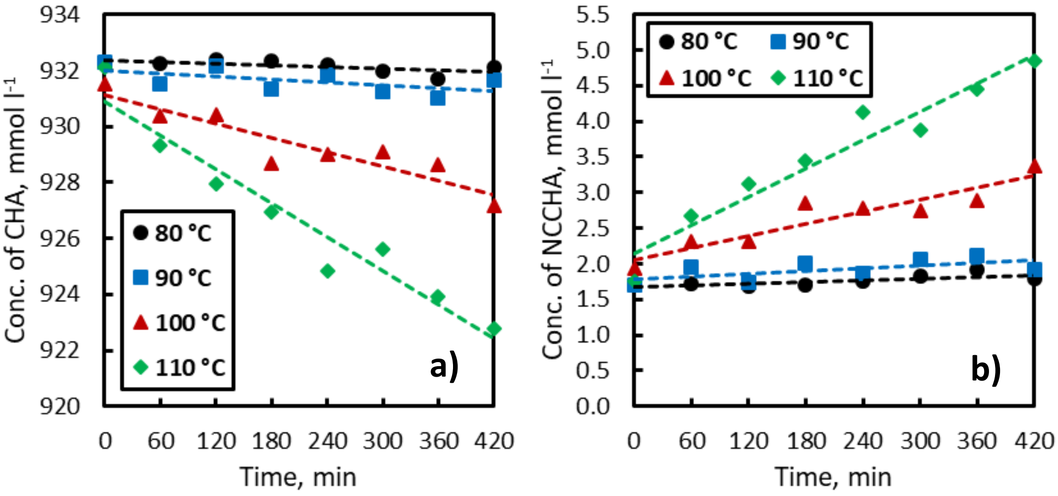

Figure 3. Time and temperature dependence of concentration of **a)** reactant CHA, **b)** main product NCCHA.

Table I.
Results of the regression analysis of the kinetic model of ODH of CHA

Reaction *i*	$k_{i(100\,°\mathrm{C})} \times 10^8$	E_{ai}	E_{ai}*
	[mol l^{-1} min^{-1}]	[kJ mol^{-1}]	[kJ mol^{-1}]
2 CHA + 0.5 O_2 → NCCHA + H_2O + NH_3	0.08	139.4	-
NCCHA + H_2O → CHON + CHA	0.42	89.3	356.0
CHON + CHA → NCCHA + H_2O	0.14	36.9	44.7
CHA + O_2 → CHOX + H_2O	0.14	58.8	53.6

*Data from our previous work[11].

The value of activation energy of ODH of CHA to NCCHA, 139.4 kJ mol^{-1} is higher than that of the ODH of DCHA to NCCHA[11], 52.7 kJ mol^{-1}. This could be an outcome of that that the transformation of CHA to NCCHA proceeds first through to the formation of CHI and subsequent condensation of CHI and CHA to DCHA. ODH of DCHA proceeds directly to the NCCHA. The values of activation energy of others reactions are in close similarity, with the exception of hydrolysis of NCCHA to CHON and CHA. The 89.3 kJ mol^{-1} is a more presumable value of activation energy compared to 356.0 kJ mol^{-1}. It cannot be ruled out that the former high value of activation energy of NCCHA hydrolysis is an outcome of error during data processing. Further, the rate of the formation of NCCHA during ODH of CHA and DCHA is compared at temperatures 80 and 100 °C (**Figure 4**). The concentration of NCCHA resulting from ODH of DCHA[11] is corrected to the initial concentration of NCCHA in CHA (ODH of CHA). There is a double rate of formation of NCCHA in the case of ODH of DCHA. It is due to the significant difference in values of activation energy of both ODH reactions. There is also visible stagnation of the concentration of NCCHA due to its consecutive hydrolysis to CHON and CHA.

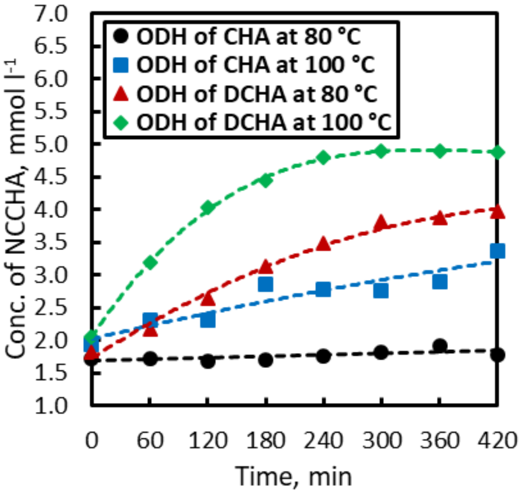

Figure 4. Time and temperature dependence of concentration of NCCHA from ODH of CHA and DCHA.

The effect of concentration of water on the reaction rate of ODH of CHA

The experiments were carried out at the reaction temperature of 100 °C and concentration of water 0.17–1.17 wt.% in CHA. The water does not accelerate the ODH of CHA to NCCHA, the effect of water on the reaction rate is $r(0.57\%\ H_2O)/r(0.17\%\ H_2O) = 0.99$ and $r(1.17\%\ H_2O)/r(0.17\%\ H_2O) = 0.90$. Compared to that water has a promotional effect on the reaction rate of ODH of DCHA[11]. It is possible that the reaction rate of ODH of CHA is not affected by water due to better solubility of water in CHA[14, 15]. The concentration of water has a promotional effect on the hydrolysis of NCCHA as follows: $r(0.57\%\ H_2O)/r(0.17\%\ H_2O) = 1.28$ and $r(1.17\%\ H_2O)/r(0.17\ \%\ H_2O) = 3.08$. The stagnation of the concentration of NCCHA (**Figure 5a**) is connected to its hydrolysis demonstrated by the concentration profile of one of the hydrolysis products, CHON, in **Figure 5b**.

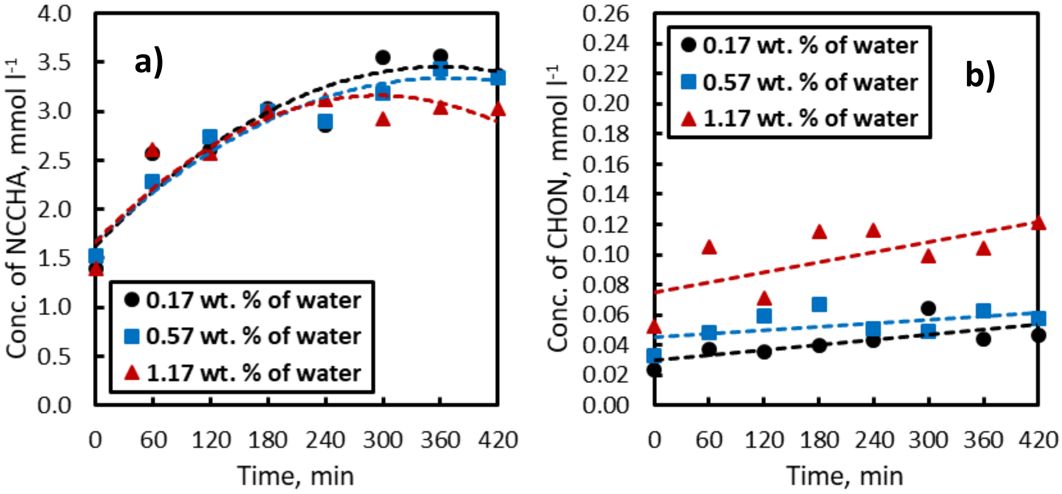

Figure 5. Time dependence of the concentration of **a)** main product NCCHA, **b)** hydrolysis product CHON.

Conclusion

In this contribution, it was studied the effect of temperature 80–110 °C and the concentration of water 0.17–1.17 wt.% in cyclohexylamine on the reaction rate of its uncatalyzed oxidative dehydrogenation towards imine *N*-cyclohexylidenecyclohexanamine with air in a liquid phase. The value of activation energy of the title reaction is 139.4 kJ mol^{-1}. Conjointly, it was estimated values of activation energy of other reactions, which accompany the oxidative dehydrogenation of cyclohexylamine. It was found that the water has no significant effect on the reaction rate of the oxidative dehydrogenation of cyclohexylamine but greatly affects the hydrolysis of imine to cyclohexanone. This work is part of the complex problem of the production of cyclohexylamine and dicyclohexylamine. Is it appropriate to store and transport cyclohexylamine in an inert atmosphere to suppress the formation of undesirable imine. In addition, the cyclohexylamine should have as low concentration of water as possible in purpose to eliminate arise in concentration of other undesirable species such as cyclohexanone.

Acknowledgement

This work was supported from the grant of Specific university research – grant No A1_FCHT_2023_001.

List of abbreviations

CHA	Cyclohexylamine
CHI	Cyclohexanimine
CHON	Cyclohexanone
CHOX	Cyclohexanone oxime
DCHA	Dicyclohexylamine
ERA	Easy Regression Analysis (software)
NCCHA	*N*-Cyclohexylidenecyclohexanamine
ODH	Oxidative dehydrogenation

References

1. Valeš R., Dvořák B., Krupka J.: Pol. J. Chem. Tech. *23*, 43 (2021).
2. Roose P., Eller K., Henkes E., Rossbacher R., Hartmut H.: Amines, Aliphatic in Ullmann’s Encyclopedia of Industrial Chemistry (2015).
3. Valeš R., Zapletal M., Krupka J.: Pol. J. Chem. Tech. *25*, 1 (2023).
4. Valeš R., Krupka J.: Study of specific properties of cobalt catalyst for applying in a new large-scale capacity unit for the cyclohexylamine production, in: *Proceedings of the 9th International Conference on Chemical Technology*, Czech Society of Industrial Chemistry, Prague 158–163 (2022).
5. Chaudhari Ch., Sato K., Ikeda Y., Terada K., Abe N., Nagaoka K.: New. J. Chem. *45*, 9743 (2021).
6. Wei Y., Ni W., Zhang Ch., You K., Zhao F., Chen Z., Ai Q., Lou H.: ACS Sustain. Chem. Eng. *10*, 13367 (2022).
7. Araki S., Nakanishi K., Tanaka A., Kominami H.: J. Catal. *389*, 212 (2020).
8. Ding W., Peng H., Zhong W., Mao L., Yin D.: Catal. Sci. Technol. *10*, 3409 (2020).
9. Zhao F., Yi L., Deng R., You K., Song J., Jian J., Liu P., Ai Q., Lou H.: Mol. Catal. *475*, 110494 (2019).
10. Ni W., You K., Yi L., Zhao F., Ai Q., Liu P., Lou H.: Ind. Eng. Chem. Res. *60*, 3907 (2021).
11. Valeš R., Kukučková A., Dvořák B., Krupka J.: The effect of temperature and concentration of water on oxidation of dicyclohexylamine with air, in: *Proceedings of the 8th International Conference on Chemical Technology*, Czech Society of Industrial Chemistry, Prague 115–119 (2021).
12. Zámostný P., Bělohlav Z.: Comput. Chem. *23*, 479 (1999).
13. Krupka J.: Reac. Kinet. Mech. Cat. *116*, 315 (2015).
14. Cyclohexylamine, Chemtex. [Online] 2022. [Cited: May 25, 2023]. https://www.chemtexltd.com/products-and-solutions/water-treatment-chemicals/boiler-water-treatment/cyclohexylamine/.
15. Dicyclohexylamine, Chemical Book. [Online] 2022. [Cited: May 25, 2023]. https://www.chemicalbook.com/ChemicalProductProperty_EN_CB6852609.htm.

POLYMERS COMPOSITES

MODELING OF GAS-PHASE POLYMERIZATION PROCESS OF PROPYLENE – REACTION KINETICS

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Abstract

This paper presents an experimental kinetics study of the propylene polymerization in gas phase with a conventional heterogeneous Ziegler-Natta catalyst. The gas phase kinetics is described using a kinetic model of the first order decay, where the reaction rate is proportional to the hydrogen concentration and polymerization temperature using equal concentration of the active centers in the catalyst. This model was based on the deconvolution of GPC curves[1], considering and using a 4-active site catalytic model, which describes the overall production of polypropylene well both in semi-batch and in industrial polymerization reactors. It can be finally used as a gas-phase kinetic polymerization model of propylene applicable for the modeling of polypropylene production in the industrial polymerization reactors.

Introduction

The industrial production of polypropylene is a relatively complex manufacturing process, which is rather demanding from the process control point of view. To successfully study and model this process from the catalytic polymerization kinetics point of view, it is essential to take into account:

- the presence of different active sites in the catalyst
- the activity decay during a polymerization reaction (polymerization time)

and the principal process variables, which significantly affect the polymerization kinetics:

- the polymerization temperature
- the hydrogen concentration

having other process variables, such as catalyst, cocatalyst and external donor type and concentration, constant.

Concerning the temperature effect, it is ordinarily observed in conventional Ziegler-Natta catalysts that the polymerization rate shows a distinct maximum in the range of 60 °C to 70 °C and then decreases with increasing temperature[2,3].

Concerning the hydrogen effect, there is a remarkable activating effect of hydrogen observed for almost all Ziegler-Natta catalysts in propylene polymerization at lower concentrations, but on the contrary, at higher concentrations the rate of polymerization decreases as the monomer concentration at the active catalytic site goes down[2,4,5,6].

Concerning the activity decay during the polymerization reaction, we considered, according to common knowledge, that the rate profile starts at a maximum or rises very rapidly to a maximum value and then the polymerization rate decreases with time in a first order decay profile.

Experiment

The polymerization conditions and corresponding polymer yields create the data set, which is essential for the parametrization of the kinetic model.

Polymerization experiments comprising the necessary range of polymerization conditions were performed using the high-yield Ziegler-Natta catalyst system in a 2-Litre reactor in gas-phase at a polymerization pressure of 2.2 MPa and the following conditions:

- polymerization temperature (4 temperatures: T = 65, 75, 85 and 95 °C) and
- hydrogen concentration (8 hydrogen concentrations in the range: H_2/propylene = 0.120–120 mmol/mol).

The complete model thus comprises 4 x 8 combinations of these polymerization parameters and 32 final polypropylene materials intended for GPC deconvolution and the calculation of kinetic parameters.

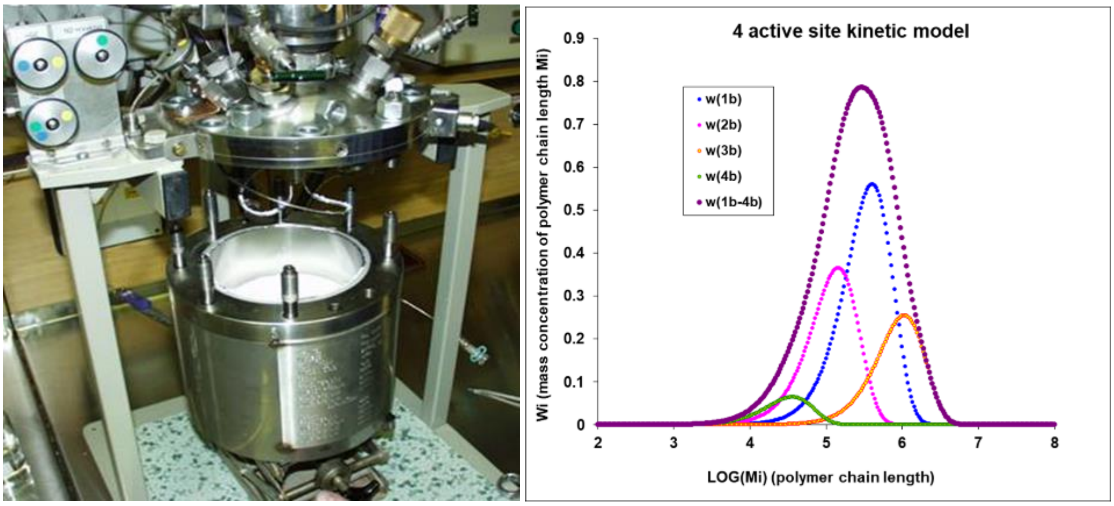


Figure 1. The polymer materials necessary for kinetic homopolymerization model parametrization were synthesized under specified polymerization conditions in a 2-Litre reactor – left side. The resulting polymer materials were analyzed by GPC and described via a 4-center model (summative curve of 4 deconvoluted curves) – right side.

Results and discussion

Heterogeneous Ziegler-Natta catalysts consist of several types of active sites, which produce a different amount of polymer of different qualities (molecular weight). The distribution curve of molecular weights can be considered to be the expression of their activities and performance.

These particular parameters of the polymerization process itself can be derived via a deconvolution of the original GPC MWD curve (polymer MWD is a sum of Schulz-Flory distribution curves with PD = M_w/M_n = 2). A 4-center model is sufficient for this description, considering that the correspondence of the deconvoluted model (summative curve of 4 deconvoluted curves) and GPC experimental curve is fully satisfactory (Figure 1). The 4-center model thus describes the reality of the produced PP with high accuracy.

The particular active sites produce polymers at different propagation rates and at different H_2 chain-transfer abilities. This way each active site generates a different amount of the polymer with a different molecular weight. As a result, the variable polymerization yields and the variable average molecular weights of the final polymer are created according to the related polymerization conditions (polymerization temperature, hydrogen concentration, polymerization time).

The character of the particular deconvoluted curves (1–4) is described by deconvoluting parameters *h* and *a*, according to the Schulz-Flory equation 1:

$$h_i(n) = a_i^2 n \, exp(-a_i n) \qquad (1)$$

where $h_i(n)$ is the weight fraction of the polymer of chain length *n* produced at site type *i*, and a_i is a fitting parameter for site type *i*. a_i represents the inverse of the polymer M_n produced at site type *i* ($a_i = 1/M_n$). The parameter *a* is also related to parameter *q*, the probability of propagation at the particular active catalyst site ($q = 1 - a$).

The chain length distribution of PP is the sum of these distributions weighted by the mass fractions of polymer produced at each site type, according to equation 2:

$$W(n) = \sum_{i=1}^{j} m_i h_i(n) \qquad (2)$$

where $W(n)$ is the total weight fraction of the polymer of chain length *n*, m_i is the mass fraction of the polymer produced at site type *i*, and *j* is the total number of site types.

It was found that the parameters *h* and *a* are dependent on the concentration of hydrogen, but not on the polymerization temperature (Figure 2). Further, it was found that these parameters don´t change with the polymerization time.

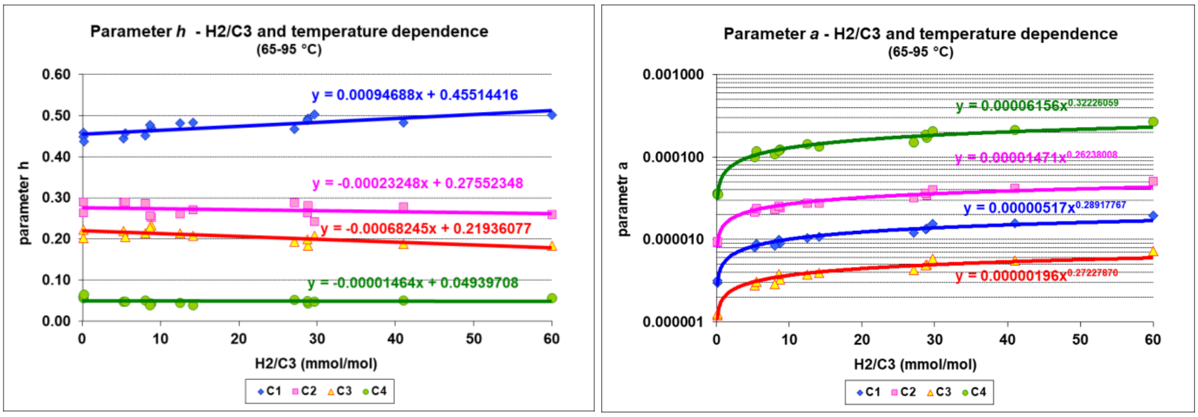


Figure 2. The deconvolution parameter h represents the portion of the polymer formed on the particular active site AC1–AC4 and the character of the formed polymer (*$M_n = 1/a$*). They both are dependent on the hydrogen concentration ($H_2/C3$), but not on the polymerization temperature (T).

The function, which describes the one-hour PP yield as a dependence on the polymerization temperature and the hydrogen concentration has the character of a three-dimensional surface. At the area $H_2/C3$ = 0–11 mmol/mol, the yield has the character of a logarithmic increase with growth of the $H_2/C3$ concentration, but at the area $H_2/C3$ = 11–125 mmol/mol, it turns to a linear decrease (Figure 3). It is evident that the description of the polymerization yield on the polymerization temperature and hydrogen concentration is realizable. To enlarge it to the time-dependent kinetic model, the aforementioned deconvolution parameters were utilized for the evaluation of the polymerization kinetics constants.

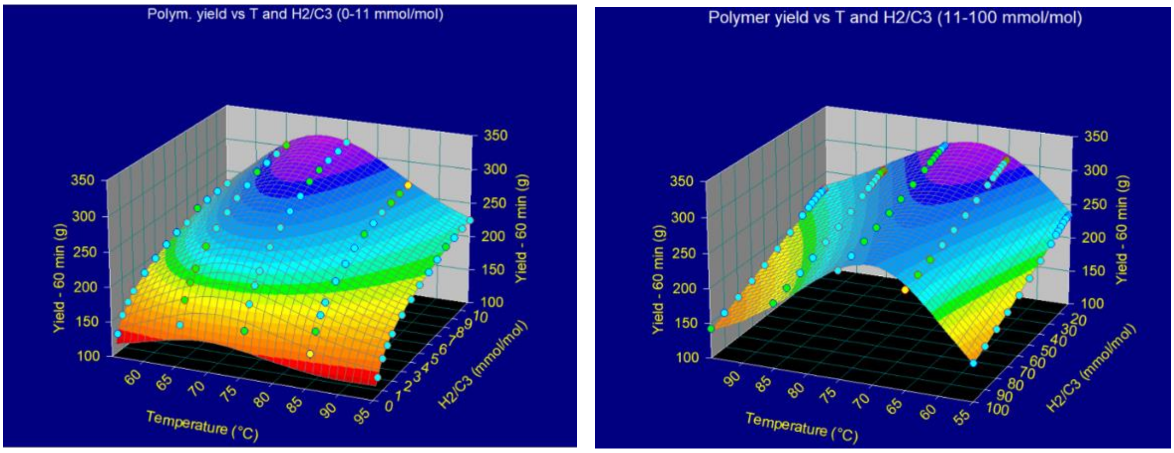


Figure 3. One-hour PP yield as a dependence on the polymerization temperature and hydrogen concentration. At $H_2/C3$ = 0–11 mmol/mol, the yield has the character of a logarithmic increase, at $H_2/C3$ = 11–125 mmol/mol, it turns to a linear decrease.

When we consider the exponential decrease of the polymerization rate according to common knowledge, it also decreases in an exponential way with time the number of growing polymer chains. The number of these chains at the beginning of the polymerization is described by equation 3:

$$P_0 = \frac{P_{60}}{\exp(-k_d.t).(1-q)} \qquad (3)$$

where P_{60} is the number of growing polymer chains in 60 min of polymerization, P_0 is the number of growing polymer chains at the beginning of polymerization (extrapolation to the maximum catalyst activity at time = 0 min), k_d is the deactivation constant, t is the polymerization time, q is the probability of propagation at a particular active catalyst site ($q = 1 - a$).

The number of growing polymer chains at an arbitrary polymerization time is described by equation 4:

$$P_i = \frac{P_0}{\exp(-k_d.t).(1-q)} \qquad (4)$$

where P_i is the number of growing polymer chains at an arbitrary polymerization time, P_0 is the number of growing polymer chains at the beginning of polymerization (extrapolation to the maximum catalyst activity at time = 0 min), k_d is the deactivation constant, t is the polymerization time, q is the probability of propagation at a particular active catalyst site ($q = 1 - a$).

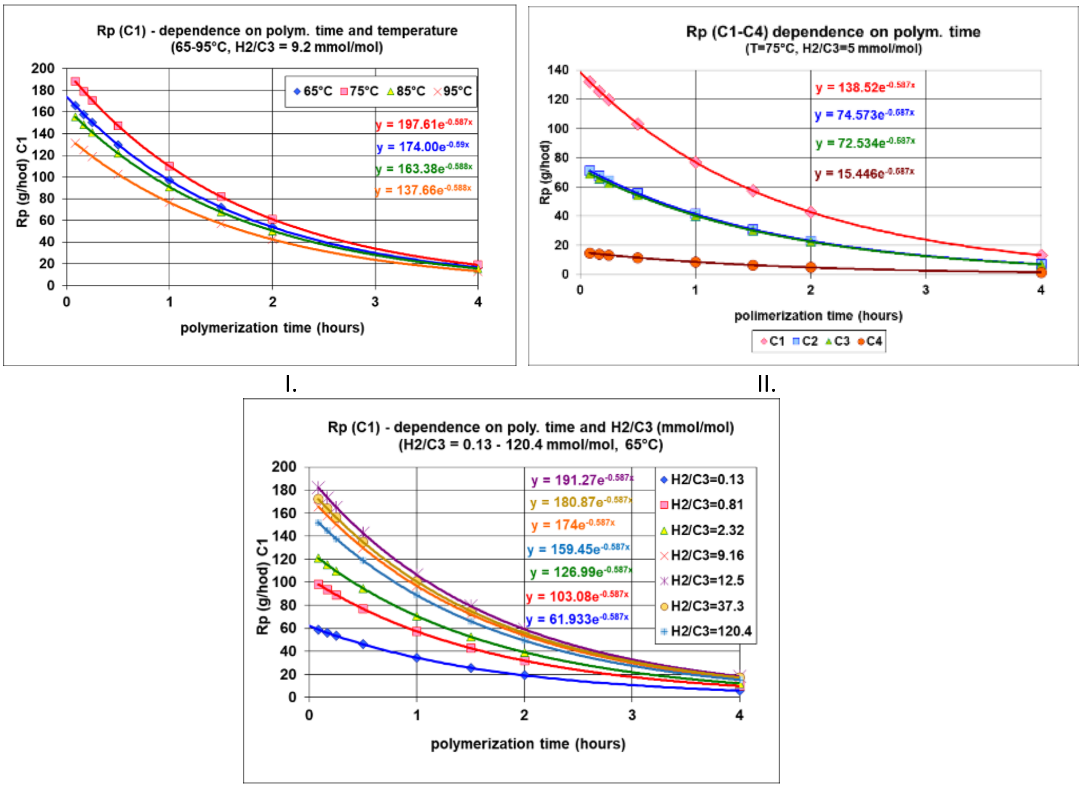
The polymerization rate at an arbitrary polymerization time is characterized by equations 5 and 6:

$$Rp_i = P_i.M_n \qquad (5)$$

$$Rp_i = k.\exp(c.i) \qquad (6)$$

where Rp_i is the polymerization rate at the arbitrary polymerization time i, P_i is the number of growing polymer chains at the arbitrary polymerization time i and M_n is the numerical molecular weight of the polymer chains ($M_n = 1/a$), k is the pre-exponential factor (initial polymerization rate), c is the exponential factor (deactivation constant) and i is the polymerization time.

For the description of both the effects of the polymerization temperature and the hydrogen concentration on the polymerization kinetics and thus also on the polymerization yield for the particular active sites AC1, AC2, AC3 and AC4, it is good to note that the exponential kinetic dependencies (Figure 4) are differing only in the pre-exponential factor, the exponent is always the same.



I.

II.

III.

Figure 4. I.: Simulation of the influence of the polymerization temperature on the polymerization rate at active site AC1, II.: Simulation of the polymerization rate at the selected H_2/C3 and T combination for the particular active sites AC1, AC2, AC3, AC4, III.: Simulation of the influence of the hydrogen concentration on the polymerization rate at active site AC1.

This reality enables the modeling of the impact of both the polymerization temperature and the hydrogen concentration on polymerization kinetics (pre-exponential factor k) for particular active sites (AC1, AC2, AC3, AC4). For the description of any combination of the polymerization temperature and the hydrogen concentration on the kinetics of polymerization it is convenient to express this dependence in the form of a 3-dimensional surface (Figure 5).

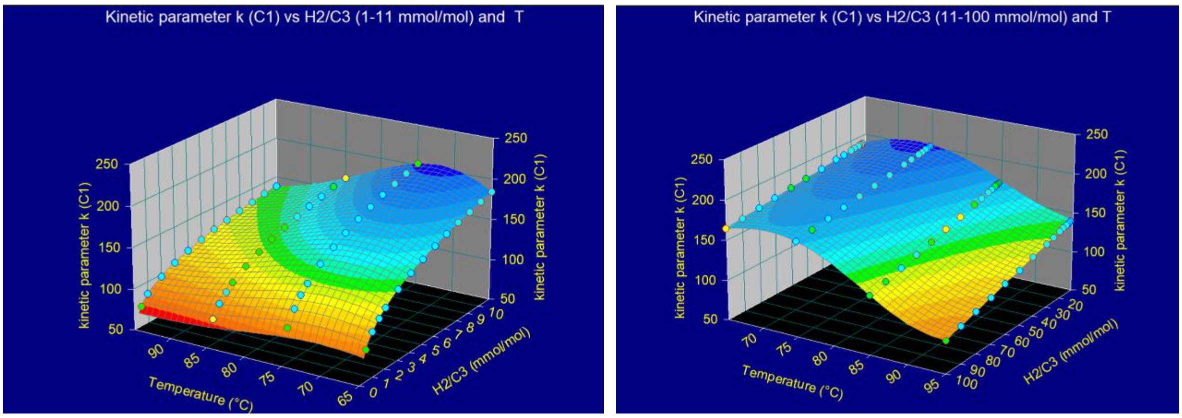


Figure 5. Left side – exponential increase of exponential factor *k (Rp₀)* of active site AC1 in H_2/C3 range: 0–11 mmol/mol. Right side – linear decrease of exponential factor *k (Rp₀)* of active site AC1 in H_2/C3 range: 11–100 mmol/mol.

Considering the fact that the yields at particular active sites (AC1, AC2, AC3, AC4) differ, it is evident that each active site has itself a 3-dimensional dependence of the pre-exponential factor (k1, k2, k3, k4) on both parameters (T and H_2/C3). The aforementioned 3-dimensional dependences of the pre-exponential factor (considering the knowledge that the exponential factor is invariable) are sufficient for the kinetic modeling of particular active sites (AC1, AC2, AC3, AC4) at an arbitrary combination of the polymerization temperature and the hydrogen concentration and the calculation of the yield at any polymerization time is possible according to equation 7:

$$Y = \int_{a}^{b} k.\exp(c.i) = k.\frac{1}{c}.\exp(c.b) - k.\frac{1}{c}.\exp(c.a) \quad (7)$$

where *Y* is the PP yield at a particular active site, *a* and *b* are defining the time interval in the polymerization time i. The sum of these yields of the particular active sites (AC1, AC2, AC3 and AC4), considering their particular kinetic parameters (k-AC1, k-AC2, k-AC3, k-AC4) at specified conditions and polymerization intervals, represents the total polymerization yield (Figure 6)

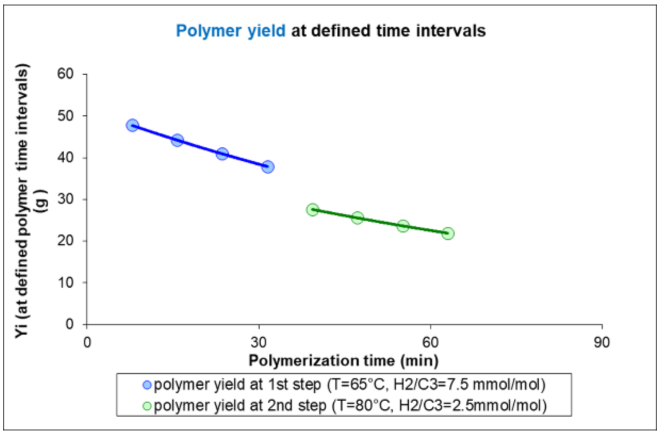


Figure 6. 4-centre homopolymerization model: calculation of yield at any examined T and H_2/C3 combination at defined polymerization time intervals.

Conclusion

A 4-centre homopolymerization model is able to calculate the yield based on the knowledge of 4 kinetic parameters k-AC1, k-AC2, k-AC3, k-AC4 as a sum of particular PP yields produced at AC1, AC2, AC3 and AC4 active sites at any examined temperature and H2 concentration combination at any defined polymerization time intervals.

This kinetic polymerization model can be used in the following ways:

- For the on-line prediction of polymerization yield and activity.
- For the optimization of reactor productivity.
- Later as a part of a more complex model for the calculation of the M_w and MWD distribution of produced homopolymer PP materials.

As the modeling conditions correspond to the industrial reality, it can also be used as a gas-phase kinetic polymerization model of propylene polymerization applicable for the modeling of polypropylene production in the industrial polymerization reactors.

Abbreviations

AC1, AC2, AC3, AC4 – active catalyst sites
GPC – gel permeation chromatography
C3 – propylene
H_2/C3 – hydrogen / propylene ratio in polymerization, mmol/mol
M_n – number average molecular weight
M_w – weight average molecular weight
MWD – molecular weight distribution
PD – polydispersity
PP – polypropylene
T – polymerization temperature, °C
ZN – Ziegler-Natta

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References

1. Kissin Y. V.: Makromolekulare Chemie. Macromolecular Symposia, *66(1)*, 83 (1993).
2. Guastala G., Gianinni U.: Makromolekulare Chemie-Rapid Communications, *4*, 519 (1983).
3. Spitz R., Masson P., Bobichon C., Guyot A.: Macromolecular Chemistry and Physics, *190(4)*, 717 (1989).
4. Keii T., Suzuki E., Tamura M., Murata M., Doi Y.: Macromolecular Chemistry and Physics, *183(10)*, 2285 (1982).
5. Samson J. J. C., van Middelkoop B., Weickert G., Westerterp K. R.: AIChE Journal, *44*, 1424 (1998).
6. Pater J. T. M., Weickert G., van Swaaij W. P. M.: Chemical Engineering Science, *57(16)*, 3461 (2002).

PRODUCTION AND APPLICATION OF GROUND TYRE RUBBER: A WAY TO INCREASE THE CIRCULARITY OF RUBBER MATERIALS

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Abstract

The increasing amount of rubber waste, the most of it being constituted by scrapped tyres, is one of the biggest global issues of today. Therefore, the portion of recycled rubber needs to be increased. Several recycling methods are used widely, e.g., reclaiming, pyrolysis and grinding. First step of rubber powder production consists of collecting, sorting and milling of waste tyres to produce ground tyre rubber (GTR), without being devulcanized. Various milling methods can be applied, resulting in particles of different sizes and shapes. Some amount of GTR finds application out of rubber industry, e.g., as infill of artificial turf, in construction of roads, playgrounds and buildings, etc. However, the amount of rubber waste utilized in these applications is limited. Therefore, to increase the circularity of rubber material, it is desirable to apply GTR in the production of new tyres. This is not easy: As the compatibility of GTR and rubber matrix is poor, higher dosages of GTR can lead to insufficient mechanical properties of the new material. This drawback can be improved by activation of the GTR prior to mixing and by alteration of mixing procedure. The paper brings an overview of GTR production and some ideas of its application.

Introduction

The worldwide consumption of natural and synthetic rubber in 2021 was 27 million metric tons[1]. 65–70% of rubber is consumed for production of tyres[2]. The global annual production of tyres is 2,300 million units[3]. Development in countries like China is still sharp and socioeconomical changes are accompanied by increasing number of tyres. As the consumption of rubber increases, the production of rubber waste increases as well. The major part of rubber waste is consisted of scraped tyres, the amount of which is estimated to be 20 million metric tons, i.e., more than 1,000 million pieces[4]. Rubber waste presents a significant ecological problem. During vulcanization, the rubber chains are crosslinked with covalent bonds to form a three-dimensional structure. The material becomes insoluble and infusible, and its natural decomposition takes around 400 years. Tyres are composed of cured rubber, together with reinforcing materials (steel and textile cords and wires, Table I.).

Table I.
Composition of tyres (% w/w)[5]

		passenger	truck
Rubber compound	rubber	41–48	41–45
	filler	22–28	20–28
	other additives	10–12	7–10
Reinforcing materials	metal	13–16	20–27
	textile	4–6	0–10

Utilization of end of life tyres (ELT)

Waste tyres can be utilized in various ways (Figure 1). Some worn tyres are regrooved, rethreaded or exported to non developed countries. End of life tyres are a challenge for new ways of use. Landfilling of waste tires is a problem both for the environment and for human health due to the proliferation of rodents, insects and snakes and above all due to the significant risk of fire, which is very difficult to extinguish[6-10]. For these reasons, the legislation of many developed economies prohibits or at least limits the disposal of tyres in landfills. For instance, In European Union, Directive 1999/31/EC prohibits the landfilling of whole tires in the European Union since 2003 and shredded tires since 2006. Furthermore, according to Directive 2000/53/EC on end-of-life vehicles, tyres must be removed before the vehicle is disposed of. Similar measures have been applied in other developed countries[6-8,11]. Collecting of ELT tyres is not regulated on EU level; member states have introduced legal requirements. EU member states apply one of three ways of handling waste tires[8,12,13].

1. Extended responsibility of producers and importers who place tyres on the market (EPR). They have the obligation to ensure the collection of waste tyres and dispose of them in accordance with legislation, i.e., to achieve a certain proportion of recycling. The leading manufacturers usually establish and finance non-profit organizations that ensure take-back and recycling or recovery of tires.
2. Tax system where manufacturers pay recycling fees to the government budget, which are reflected in the price of a new tyre. The authorities are responsible for the collection and recycling of waste tyres and for this purpose it establishes and finances relevant organizations.
3. Liberal market system that assumes the profitability of the tyre recycling process. The system does not establish any obligation to collect waste tyres, it only defines the basic rules. Companies that transform waste tyres into a valuable secondary raw material are expected to make a profit from this activity.

Figure 1. Utilization of end of life tyres

Combustion of waste tyres has been done mostly in cement kilns and heat production plants, utilizing high calorific value of rubber; currently it is being inhibited gradually mostly for ecological reasons. This form of rubber recycling is not preferred, because of real wasting of sources.

The main approach include following procedures: reclaiming, pyrolysis and rubber grinding.

Reclaiming and *devulcanization* consist in splitting the chemical bonds in the rubber mass to restore the thermoplasticity and thus the workability of this material. During reclaiming (also called regeneration), both the crosslinks between the rubber chains and the bonds of the main rubber chains are split. Conversely, during devulcanization, only the crosslinks between the rubber chains are split. In real technologies, it can be hardly distinguished which of the two processes prevails. Both processes can be induced by applying heat, chemicals, or high shear forces to ground rubber. However, the utilization of the reclaimed rubber is limited while the devulcanization methods need to be further investigated and scaled-up[5,7,9-11,14-15].

Pyrolysis consists in the thermal decomposition of waste rubber in a limited air (oxygen) presence. The products are gas and oil, steel and powder composed of carbon, silica and zinc compounds.

Considering the purchase and operating costs of pyrolysis units, their profitability strongly depends on the current market situation and energy price development[5-11].

Grinding, milling, granulation or *pulverization* of waste rubber can be conducted on various devices. The main procedures can be classified into ambient, cryogenic, wet, Berstorff`s and water jet method[5-11,16]. Ultrasound-assisted milling is a special process[17]. The products of milling are steel, textile and rubber grit or powder, often called *ground tyre rubber* (GTR), *crumb tyre rubber* (CTR), *ground rubber powder* (GRP), *powder rubber* (PR), *pulverized rubber* (PR), etc. During the milling of rubber, no chemical change is intended, although degradation reactions may occur which can lead to devulcanization or reclaiming of GTR[4-5,7-11,16]. About 74% of waste tyres generated in EU, United Kingdom, Norway, Serbia, Switzerland and Turkey is recycled by granulation[4].

Grinding and milling of waste rubber

Grinding or milling of waste rubber is a complex process that requires special equipment capable of exerting high force and crushing this stiff and at the same time elastic material into particles of the required size.

Ambient milling involves the crushing and grinding of waste rubber in shredders, mills, knife granulators, or calendars with ribbed rolls. The product is rubber powder with particles of an irregular shape and a very rough surface. Although the method is called "ambient", a significant amount of heat is released during this process; therefore, the material needs to be cooled, otherwise the temperature can rise up to 130 °C, which leads to thermal degradation of the rubber[5,7-11].

In *cryogenic milling*, pre-chipped rubber is cooled with liquid nitrogen below the glass transition temperature of the rubber and then ground in hammer mills or other processing machines. This is less energy intensive than grinding at normal temperatures. Nitrogen also serves as an inert gas preventing rubber oxidation. The process produces very fine particles with a smooth surface and sharp edges. Cryogenic rubber powder is cleaner than the one from ambient milling but contains a significant amount of moisture that must be removed by drying. The main disadvantage of this method is the additional cost of liquid nitrogen. Therefore, sometimes this method of cooling is replaced by cheaper but less effective cooling with subcooled air[5,7-11].

Wet process consists in milling an aqueous suspension of pre-crushed rubber particles in a special device between stable and moving discs. The water cools the rubber and the discs. The product is a very fine powder with a high specific surface area. The disadvantage is the need to dry the product[5,7-9,11].

The *Berstorff`s method* is an improved ambient milling. It consists in the connection of a calendar with ribbed cylinders with a twin-screw extruder. The product is characterized by small particles with a high specific surface area and low moisture content[8].

In a *water jet* process, the only grinding tool is high-pressure water (typically around 170–230 MPa). Advantage of this technology is that the strips of rubber peel away from the steel cord, which remains intact. In this way, rubber powder of high purity is produced, with fine particles of a convex-concave microstructure and a large surface area. It is thus possible to obtain powder from individual parts of the tyre, e.g., separately from the tread. The process is energy-saving, relatively silent and ecological[5,8,10-11].

Applications of ground tyre rubber

Rubber powder has many potential applications. It can be used alone without further modifications, e.g., as a sorbent of an oil leakage or as a infill for artificial grass[6]. Coarser particles and pieces of rubber are used as filler materials in landscaping and construction[6,8,11]. The finer fractions of rubber crumb can bet combined even without additives simply by the effect of increased pressure and temperatures. This concept was introduced in 2002 by Morin, Williams and Farris and called *high-pressure high-temperature sintering.* The authors assume that intense reactions occur during this process, i.e., both splitting and re-emergence of mainly S-S crosslinks, whereby new bonds are created not only inside the rubber powder particles, but also across the interface between the particles, which leads to the disappearance of these interface and sintering of the original rubber crumb particles into a single unit. The properties of the products predetermine them as less demanding applications[18,19].

Another group of applications is based on the connection of rubber powder with a suitable binder, e.g., polyurethanes, epoxies or liquid rubbers. The products of this method include, for example, the surfaces of children's playgrounds and sports fields, elastic interlocking pavements and mats in exteriors, components of anti-noise elements for roads and railways, protective elements, etc. Currently, increased attention is paid to the hygienic safety of such materials, especially the content of polycyclic aromatic hydrocarbons (PAH), especially where the recycled material is used in interiors or as backfill for artificial turf on football pitches[5-7,9-11,16].

Rubber crumb is also added to asphalt (bitumen) in the production of "rubber-asphalt" road surfaces, which are more elastic, more resistant to frost cracks and permanent deformation, and thus more durable and safer than traditional surfaces[5-6,8-11,14,16,20]. The use of rubber powder in the production of concrete is also described, which improves its flexural strength, acoustic and thermal insulation properties and resistance to dynamic stress and cracking[8-10,16].

Another application of fine fractions of rubber powder is mixing with thermoplastic melt to form elastic, but still thermoplastic materials, such as thermoplastic elastomers (TPE) or tough plastics. The elastic component here is a secondary raw material (based on waste) and thus may contribute to the reduction of the price of such material. The thermoplastic component is usually new or waste plastic, mainly non-polar (PE-LD, PE-HD, PE-LLD or PP), because most waste rubber comes from discarded tyres and is also practically non-polar in nature (NR, SBR, BR, IIR) and substances with similar polarity show good tolerance[5,7,9,10,16].

The principle of the circular economy is the closing of the real recycling loop, i.e., the use of waste to produce a new product with as little use of virgin raw materials as possible. Thus, it would be desirable to make new tires from waste tires. For the reasons stated above, such a procedure is impossible; a new tire can only contain a limited amount of recycled material. The powder obtained by milling rubber waste is often mixed with common rubbers (NR, SBR, BR, EPDM), as these substances are non-polar in nature and therefore show good compatibility[7,8,10,16,21,22]. Karger-Kocsis et al.[7] reported a rule of thumb stating that each 1% of GTR results in a 1% deterioration of mechanical properties; therefore, the concentration of GTR in rubber compounds usually did not exceed 10% (w/w). Nevertheless, much higher concentrations are reported in other papers, although mostly for less demanding products than tyres[10,21-25].

Influence of GTR on the properties of rubber compounds

In most cases, due to the addition of GTR to the rubber compound, there is an increase in Mooney viscosity, a reduction in die-swelling during extrusion, and an improvement in the surface and dimensional stability of the extruded profile. During vulcanization, the presence of GTR increases the minimum torque on the curve (ML), which is attributed to an increase in the compound viscosity. On the contrary, the maximum torque (MH), scorch time (TS2) and optimum cure time (T90) decrease. The decrease in MH is attributed to the migration of sulphur from the rubber matrix to the GTR, while the decrease in TS2 and T90 is likely due to the migration of accelerator fragments from the crumb to the matrix[8,10,23].

The presence of GTR mainly affects the mechanical properties of the vulcanizate. Tensile strength usually decreases with increasing GTR content. Elongation at break, modulus, hardness and tear strength show different trends depending on the nature of the GTR and the formulation of the rubber compound. In most cases, elongation at break decreases while modulus and hardness increase. Abrasion resistance generally worsens with increasing GTR content, although the opposite trend has also been noted[5,7,10,16,21,24,25].

Parameters of GTR affecting the performance of rubber

The properties of rubber compounds and cured rubber containing GTR depend on many factors, in particular:

- feed stock – origin and composition of waste rubber (type of tyre, formulation of original compound),
- type and technological parameters of the milling process,
- GTR particle size and distribution,
- concentration of GTR in the rubber compound,
- treatment of GTR before mixing,
- compatibilization of the blend during mixing,
- mixing protocol (type of device, technological parameters, order of components addition).

The type of milling process used to produce GTR influences the properties of the rubber with GTR. The compound containing ambient GTR may have higher viscosity than the one with cryogenic GTR. This is attributed to occlusion of continuum rubber with sponge-like ambient GTR, whereas such occlusion is not possible with the smooth cryo-ground particles[26]. In another study, the influence of cryogenic and ambient GTR from truck tyres on the properties of NR and NR/BR compounds was analysed. Despite the fact that the cryogenic powder had much smaller particles, the tear strengths of the rubbers containing cryogenic GTR were inferior to the ones containing the ambient GTR. This was attributed to the less convoluted surface of cryogenic powder with sharp edges and hence lower interfacial adhesion between the GTR and rubber matrix. On the contrary, in BR-based compounds, the tear strength was higher with the cryogenic powder because of its reinforcing effect[23].

The particle size of GTR influences the properties of GTR-containing rubbers as well. As the particle size of GTR increases, the tensile strength, hardness, abrasion resistance, and crosslink density deteriorate whereas the swelling degree increases[22,27-29]. The deterioration of properties is attributed to phase separation of the GTR and matrix, which is more pronounced with bigger GTR particles[27]. Conversely, the particle size hardly influences the viscosity[26] and curing properties[27] at all. Smaller GTR particles contain less rubber and carbon black and more silica and transition metals (except zinc), which results in poorer aging characteristics of GTR-containing rubber, probably because the metals catalyse its thermal degradation[22].

The properties of the final rubber product can be improved by treatment of ground tyre rubber prior to mixing. According to the conditions applied, the treatment can lead to devulcanization or reclaiming of the entire volume of GTR, or to partial activation of the GTR surface, which is favourable as it increases the compatibility of GTR with rubber matrix. The treatment can involve various physical and chemical procedures[4,5,10,11,16,30-33].

- mechanical or thermomechanical treatment, e.g., in a two-roll mill, inner mixer, extruder or special mechanochemical reactor[31,34,35],
- chemical or thermochemical treatment, e.g., with mixture of oil and peptizers or common curing accelerators, oxidizing agents (HNO_3, $KMnO_4$, H_2O_2), devulcanization agents (mainly diphenyl disulphide and its derivatives), supercritical fluids, ozone, ionic liquids, deep eutectic solvents and other chemicals[30,31,36-41],
- ultrasound treatment[42],

- microbiological treatment with fungi or bacteria[43-52],
- irradiation treatment, namely by microwaves[25,53-62], less frequently by ultraviolet radiation[56], accelerated electrons or gamma rays[31],
- treatment with plasma[16],
- combination of the above mentioned methods[63-71].

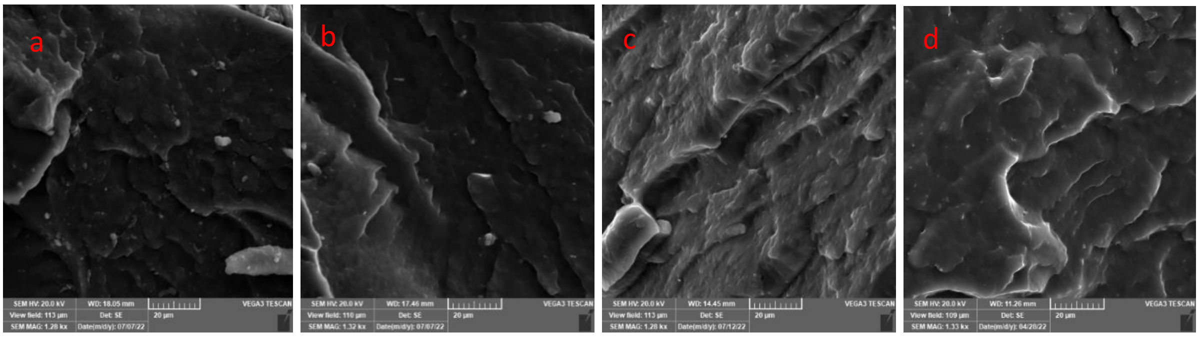

Figure 2. SEM images of the cryo-fractured surfaces of cured tyre rubber: (a) reference without GTR, (b) with 7% untreated GTR, (c) with 7% microwave-treated GTR, (d) with 7% bacteria-treated GTR.

References

1. Consumption of natural and synthetic rubber worldwide from 1990 to 2020. https://www.statista.com/statistics/275399/world-consumption-of-natural-and-synthetic-caoutchouc/, access date 19.4.2023.
2. ETRMA Statistic booklet 2021. https://www.etrma.org/wp-content/uploads/2021/12/20211215-Statistics-booklet-2021VF.pdf, access date 19.4.2023.
3. Global tire market. www.imarcgroup.com/global-tire-market, access date 19.4.2023.
4. Formela K., Kuranska M., Barczewski M.: Polymers 14, 42 (2022).
5. Ramarad S., Khalid M., Ratnam C. T., Chuah A. L., Rashmi W.: Prog. Mater. Sci. 72, 100–140 (2015).
6. Sibeko M. A., Adeniji A. O., Okoh O. O., Hlangothi S. P.: Environ. Sci. Pollut. Res. 27, 43553–43568 (2020).
7. Karger-Kocsis J., Meszaros L., Barany T.: J. Mater. Sci. 48, 1–38 (2013).
8. Sienkiewicz M., Kucinska-Lipka J., Janik H., Balas A.: Waste Manage. 32, 1742-1751 (2012).
9. Isayev A. I.: Recycling of Rubbers. In: The Science and Technology of Rubber, Elsevier Academic Press (2005), p. 663–695.
10. Fazli A., Rodrigue D.: J. Compos. Sci. 4, 43 (2020).
11. Myhre M., Saiwari S., Dierkes W., Noordermeer J.: Rubber Chem. Technol. 85, 408–449 (2012).
12. Circular Economy. https://www.etrma.org/key-topics/circular-economy/, access date 19.4.2023.
13. eltma. https://www.eltma.cz/, access date 14.4.2023.
14. Barlow F. W.: Waste Disposal. In: Rubber Products Manufacturing Technology, New York: Marcel Dekker (1994), p. 889–902.
15. Edwards D. W., Danon B., van der Gryp P., Gorgens J. F.: J. Appl. Polym. Sci. 133, 10 (2016).
16. Sienkiewicz M., Janik H., Borzedowska-Labuda K., Kucinska-Lipka J.: J. Clean Prod. 147, 560–571 (2017).
17. Dobrota D., Dobrota G.: J. Clean Prod. 172, 3591–3599 (2018).
18. Morin J. E., Williams D. E., Farris R. J.: Rubber Chem. Technol. 75, 955–968 (2002).
19. Tripathy A. R., Morin J. E., Williams D. E., Eyles S. J., Farris R. J.: Macromolecules 35, 4616–4627 (2002).
20. Alfayez S. A., Suleiman A. R., Nehdi M. L.: Sustainability 12, 15 (2020).
21. Myhre M., MacKillop D. A.: Rubber Chem. Technol. 75, 429–474 (2002).
22. Naskar A. K., De S. K., Bhowmick A. K., Pramanik P. K., Mukhopadhyay R.: Rubber Chem. Technol. 73, 902–911 (2000).
23. Hassim D., Abraham F., Summerscales J., Brown P.: Express Polym. Lett. 13, 248–260 (2019).
24. Zhao X. P., Hu H., Zhang D. K., Zhang Z., Peng S. X., Sun Y. M.: e-Polymers 19, 482–488 (2019).
25. Simon D. A., Pirityi D., Tamas-Benyei P., Barany T.: J. Appl. Polym. Sci. 137, 8 (2020).
26. Gibala D., Laohapisitpanich K., Thomas D., Hamed G. R.: Rubber Chem. Technol. 69, 115–119 (1996).
27. Li S. Y., Lamminmaki J., Hanhi K.: Macromol. Symp. 216, 209–216 (2004).
28. Han S. C., Han M. H.: J. Appl. Polym. Sci. 85, 2491–2500 (2002).
29. Gibala D., Hamed G. R., Zhao J.: Rubber Chem. Technol. 71, 861–865 (1998).
30. Saputra R., Walvekar R., Khalid M., Mubarak N. M., Sillanpaa M.: Chemosphere 265, 32 (2021).
31. Kenawy S. H., Khalil A. M.: Biointerface Res. Appl. Chem. 11, 8413–8423 (2021).

32. Bockstal L., Berchem T., Schmetz Q., Richel A.: J. Clean Prod. 236, 16 (2019).
33. Asaro L., Gratton M., Seghar S., Hocine N. A.: Resour. Conserv. Recycl. 133, 250–262 (2018).
34. Zhang X. X., Lu C. H., Liang M.: J. Polym. Res. 16, 411–419 (2009).
35. Cavalieri F., Padella F., Cataldo F.: J. Appl. Polym. Sci. 90, 1631–1638 (2003).
36. Phiri M. M., Phiri M. J., Formela K., Hlangothi S. P.: Compos. Pt. B-Eng. 204, 18 (2021).
37. Li X., Deng X. Q., Dong C.: J. Braz. Chem. Soc. 29, 2169–2179 (2018).
38. Liu Z. J., Li X., Xu X. F., Wang X. J., Dong C., Liu F. X., Wei W.: Polym. Degrad. Stabil. 119, 198–207 (2015).
39. Dubkov K. A., Semikolenov S. V., Ivanov D. P., Babushkin D. E., Panov G. I., Parmon V. N.: Polym. Degrad. Stabil. 97, 1123–1130 (2012).
40. Fan P., Lu C. H.: J. Polym. Environ. 19, 943–949 (2011).
41. Kojima M., Ogawa K., Mizoshima H., Tosaka M., Kohjiya S., Ikeda Y.: Rubber Chem. Technol. 76, 957–968 (2003).
42. Isayev A. I., Yushanov S. P., Kim S. H., Levin V. Y.: Rheol. Acta 35, 616–630 (1996).
43. Joseph A., Gupta P., De G., Lal M., Meena M. K., Singh L. P., Rattan J.: Nature Environment and Pollution Technology 21, 1039–1048 (2022).
44. Andler R.: Biotechnol. Adv. 44, 14 (2020).
45. Kaewpetch B., Prasongsuk S., Poompradub S.: Express Polym. Lett. 13, 877–888 (2019).
46. Aboelkheir M. G., Bedor P. B., Leite S. G., Pal K., Toledo R. D., de Souza F. G.: Sci Rep 9, 12 (2019).
47. Ghavipanjeh F., Rad Z. Z., Pazouki M.: J. Polym. Environ. 26, 3168–3175 (2018).
48. Tatangelo V., Mangili I., Caracino P., Anzano M., Najmi Z., Bestetti G., Collina E., Franzetti A., Lasagni M.: Appl. Microbiol. Biotechnol. 100, 8931–8942 (2016).
49. Li Y. H., Zhao S. H., Wang Y. Q.: J. Polym. Environ. 20, 372–380 (2012).
50. Li Y. H., Zhao S. H., Wang Y. Q.: Polym. Degrad. Stabil. 96, 1662–1668 (2011).
51. Jiang G. M., Zhao S. H., Li W. J., Luo J. Y., Wang Y. Q., Zhou Q. S., Zhang C. R.: Polym. Adv. Technol. 22, 2344–2351 (2011).
52. Jiang G. M., Zhao S. H., Luo J. Y., Wang Y. Q., Yu W. Y., Zhang C. R.: J. Appl. Polym. Sci. 116, 2768–2774 (2010).
53. Formela K., Hejna A., Zedler L., Colom X., Canavate J.: Express Polym. Lett. 13, 565–588 (2019).
54. de Sousa F. D. B., Scuracchio C. H., Hu G. H., Hoppe S.: Polym. Degrad. Stabil. 138, 169–181 (2017).
55. Scuracchio C. H., Waki D. A., da Silva M.: J. Therm. Anal. Calorim. 87, 893–897 (2007).
56. Aboelkheir M. G., Lima J. G., Toledo R. D., Souza F. G., Siqueira C. Y. D.: J. Polym. Res. 28, 11 (2021).
57. Canavate J., Colom X., Saeb M. R., Przybysz M., Zedler L., Formela K.: Afinidad 76, 171–179 (2019).
58. Zhang Y. Z., Hwang J. Y., Peng Z. W., Andriese M., Li B. W., Huang X. D., Wang X. L., Li L. K.: Microwave Heating of Waste Tires. 7th International Symposium on High-Temperature Metallurgical Processing, Nashville, TN, USA, 14. –18.2.2016.
59. Colom X., Faliq A., Formela K., Canavate J.: Polym. Test 52, 200–208 (2016).
60. Karabork F., Akdemir A.: J. Appl. Polym. Sci. 132, 9 (2015).
61. de Sousa F. D., Scuracchio C. H.: Mater. Res.-Ibero-am. J. Mater. 18, 791–797 (2015).
62. Zanchet A., Carli L. N., Giovanela M., Brandalise R. N., Crespo J. S.: Mater. Des. 39, 437–443 (2012).
63. Vahdatbin M., Jamshidi M.: Resour. Conserv. Recycl. 179, 13 (2022).
64. Saputra R., Walvekar R., Khalid M., Ratnam C. T., Mubarak N. M., Dharaskar S.: J. Mol. Liq. 306, 12 (2020).
65. Walvekar R., Kunju K., Saputra R., Siddiqui K., Ramarad S.: Parametric Study for Devulcanization of Waste Tire Rubber Utilizing Deep Eutectic Solvent (DES). 9th International Engineering Research Conference (Eureca), Taylors Univ, Subang Jaya, MALAYSIA, 6.12.2017.
66. Molanorouzi M., Mohaved S. O.: Polym. Degrad. Stabil. 128, 115–125 (2016).
67. Seghar S., Hocine N. A., Mittal V., Azem S., Al-Zohbi F., Schmaltz B., Poirot N.: Express Polym. Lett. 9, 1076–1086 (2015).
68. van Hoek J. W., Heideman G., Noordermeer J. W. M., Dierkes W. K., Blume A.: Materials 12, 19 (2019).
69. Saiwari S., van Hoek J. W., Dierkes W. K., Reuvekamp L., Heideman G., Blume A., Noordermeer J. W. M.: Materials 9, 17 (2016).
70. Wang X. J., Shi C. P., Zhang L., Zhang Y. C.: J. Appl. Polym. Sci. 130, 1845–1854 (2013).
71. Saiwari S., Dierkes W. K., Noordermeer J. W. M.: KGK-Kautsch. Gummi Kunstst. 66, 20–25 (2013).

EFFECT OF CATALYTIC SYSTEM ON THE STRUCTURE OF ETHYLENE/PROPYLENE COPOLYMERS

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Abstract

The research is focused on the structural study of ethylene-propylene copolymers (E/P copolymers) produced by gas phase polymerization in a stainless-steel batch reactor. The aim of the work was to determine the effect of different catalysts on the distribution of ethylene units in the resulting material. Three E/P copolymers with the same content of ethylene were prepared on commercial Ziegler-Natta (ZN) catalysts, which differed in the structure of the internal donor (ID). One ZN catalyst contained diether ID and the second phthalate ID.

The E/P copolymers were fractionated using the Temperature Rising Elution Fractionation (TREF) method, which separated the original samples into fractions according to their crystallisation ability. The TREF analysis revealed that the incorporation of ethylene into a growing polypropylene chain is dependent on the catalytic system. Using structural analysis methods, the difference between the copolymers structure was described and it was found that the catalyst with the phthalate internal donor combined with alkoxysilane external donor (ED) supports the creation of ethylene blocks capable of crystallising, while the catalyst with diether ID does not have this ability.

Introduction

Among other things, the properties of the resulting polymer or copolymer are influenced by the type of catalyst used[1]. This determines, for example, the comonomer incorporation, the final length of the chains, their structure and polydispersity[2]. The kinetic profiles expressing the dependence of the rate of homopolymerization on time for ethylene and propylene are very different. In the case of propylene, the rate increases very sharply, reaching its maximum value almost immediately and then decreasing. It is different with ethylene. The rate of polymerization slowly increases until it reaches a constant value and this rate is then stable for several hours[3]. However, it should be noted that the overall isospecificity of the catalyst is also influenced by the combination of internal (ID) and external (ED)donor and the amount of external donor applied into polymerization[4]. In order to know and subsequently predict the properties, it is necessary to understand the structure of the polymer, which the catalyst also modifies.

This article presents the results of research focused into the effect of selected catalysts on the structure of commonly produced E/P copolymers with an ethylene content of around 2 mol. %. All samples were synthesised on Ziegler-Natta catalysts with diether or phthalate internal donors. For a more detailed structure determination, the original samples were fractionated by temperature rising elution fractionation (TREF), which separated the original samples according to their crystallisation ability[5]. The structure of the samples and individual fractions were investigated and described using selected structural analytical methods[6].

Experimental part

Samples

Three samples of E/P copolymers designated R1806, R1877 and R2930 were evaluated in this research. They were produced by a gas-phase process in a 50-litre stainless steel batch reactor. All catalysts were activated by a triethylaluminium cocatalyst. Copolymer R1806 was produced using a phthalate-based internal donor catalyst combined with an alkoxysilane external donor, while the copolymers R1877 and R2930 were produced with a diether-based internal donor. Each internal donor has a different chemical composition. Sample R1877 was prepared on a prepolymerized catalyst. All copolymer samples were selected to contain similar amount of incorporated ethylene (C2 = 1.9–2.2 mol.%, determined by a ^{13}C-NMR analysis) and to have the MFI 0.30 $g \cdot 10\ min^{-1}$.

TREF Method

For more detailed information about structural properties, the E/P samples were fractionated into fractions according to the crystallisation ability by using the preparative TREF method[7,8]. TREF fractionation was performed with a Polymer Char PREP mc^2 instrument.

One gram of the polymer sample was dissolved in 200 ml of o-dichlorobenzene (ODCB) stabilised with 0.1% BHT (butyl hydroxytoluene) at 160 °C and stabilised at this temperature for 90 min. It was then cooled to a temperature of 95 °C, at which the solution was stabilised for another 45 min. Subsequently, crystallisation occurred at a rate of 0.10 °C·min^{-1} at a temperature of 30 °C. Again, the solution was stabilised for 30 min and the first fraction F30 was taken. The temperature was then increased to the value at which the next fraction was collected, a 30-minute stabilisation took place, and the procedure was repeated up to 160 °C, at which the last fifth fraction, F5, was collected.

Each copolymer sample was divided into five fractions according to the elution temperature. The first fraction was eluted at 30 °C (labeled F30), the second at 90 °C (labelled F90), the third at 100 °C (labeled F100), the fourth at 110 °C (labeled F110) and the fifth at 160 °C (labeled F160).

Analytical Method

The ^{13}C-NMR measurement to determine the content of incorporated ethylene was carried out on a Bruker DRX 500 spectrometer. A Nicolet iS50 FTIR spectrometer with a resolution of 2 cm^{-1} was used for the measurements of the FTIR spectra, which were normalised to the same sample thickness as the 1897 cm^{-1} propylene reference peak. The melt flow index (MFI) was determined by using Dynisco LMI 5000 plastometer (ISO 1133 standard). The DSC analysis was performed on a DSC Q100 calorimeter supplied by TA according to the ISO 11357-3 standard.

Results and discussions

Evaluation of Original Samples

As is known from literature, in the case of phthalate-based catalysts, the effect of an alkoxysilane external donor on the incorporation of ethylene units into a growing polypropylene chain must be included because ED replaces the phthalate internal donor, which is extracted from the catalyst by reaction with a triethylaluminium (TEA) cocatalyst[9,10]. In the case of diether-based catalysts, the external donor does not play such an important role, because ID extraction from the catalyst by the reaction with TEA is limited.

By comparing the EEP and EEE triads, it can be seen that the R1806 sample with phthalate ID contains, a small number of sequential ethylene units in addition to the isolated ethylene unit (Table I.). In contrast, neither EEE nor EEP sequences were measured in the samples R1877 and R2930, which contain a diether ID. This ascertainment does not correlate with values from a study by Song[11], which also compared E/P copolymers with an internal donor of phthalate and diether. The presence of the EEE triad sequence in that study was significantly higher for the diether ID copolymer (1.0 mol. % in the case of diether versus 0.3 mol. % for phthalate ID). The fact may be that the mass fractions of ethylene of the examined samples from the study[11] were around 4.5 mol. %.

Table I.
Characterization of original samples:

Original samples	**R1806 phthalate ID + alkoxysilane ED**	**R1877 diether ID, prepol.**	**R2930 diether ID**
MFI [g·10 min^{-1}]	0.30	0.30	0.29
Triad distribution	mol. %	mol. %	mol. %
PPP	94.1	94.4	94.0
PPE	3.8	3.7	3.7
EPE	0.0	0.0	0.0
PEP	1.9	1.9	2.2
EEP	0.2	0.0	0.0
EEE	0.1	0.0	0.0
P in RC	97.8	98.1	97.8
E in RC	2.2	1.9	2.2
Medium length of sequence E	1.1	1.0	1.1
Medium length of sequence P	51.1	52.5	47.4

TREF Fractionation

All three samples were fractionated by TREF into 5 fractions at elution temperatures of 30, 90, 100, 110 and 160 °C. The aim was to achieve fractions based on the ability of the material to crystallise and to compare the properties of the resulting fractions. Because the mass fraction of ethylene of all three original samples is around 2.0 mol. % with similar MFI, it is also possible to compare the same fractions of different original samples. The mass distribution of the fractions is in Figure 2.

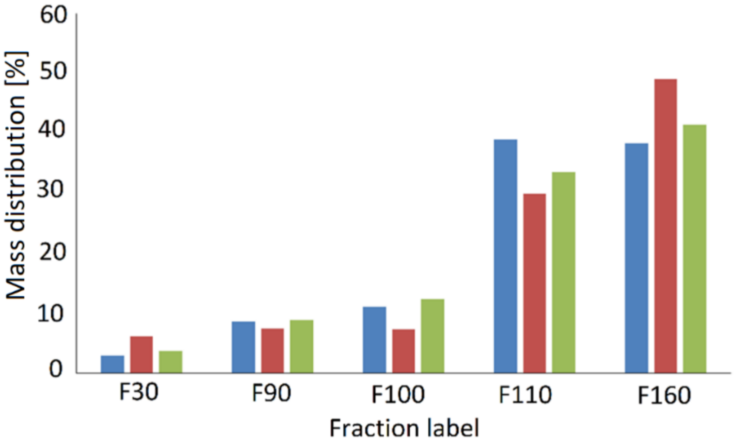

Figure 2: Mass distribution of F30–F160 TREF fractions [wt. %]. ●R1806 (phthalate ID + alkoxysilane ED), ●R1877 (diether ID, prepol.), ●R2930 (diether ID).

From the fractionation results of the samples, it is obvious that the largest part of the copolymer samples consists of highly crystalline fractions F110 and F160. The total amount of the highly crystalline phase (sum of F110 and F160) is the lowest in R1877 (71.8 wt. %), then in sample R2930 (75.0 wt. %) and the highest in R1806 (77.3 wt. %). Thus, the phthalate-based ID catalyst provides a larger amount of the highly crystalline phase, which has also the highest enthalpy of second heating ΔH_{m2} (Table II.). In Table II. for sample R1806 at fraction 100, two values can be seen for the melting temperature (T_{m2}) and enthalpy of second heating (ΔH_{m2}), which are described in chapter 3.1.2.2.

Table II.

Mass distribution (M. D.), Melting temperature (T_{m2}), enthalpy of second heating (ΔH_{m2}) and ethylene content of samples and TREF fractions. R1806 (phthalate ID+ alkoxysilane ED), R1877 (diether ID, prepol.), R2930 (diether ID).

	R1806 phthalate ID + alkoxysilane ED			**R1877 diether ID, prepol.**			**R2930 diether ID**		
	M. D. [wt. %]	T_{m2} [°C]	ΔH_{m2} [J·g^{-1}]	M. D. [wt. %]	T_{m2} [°C]	ΔH_{m2} [J·g^{-1}]	M. D. [wt. %]	T_{m2} [°C]	ΔH_{m2} [J·g^{-1}]
Orig.	-	152.8	94.8	-	153.2	89.5	-	149.6	77.6
F30	2.9	151.1	2.7	6.9	150.0	1.7	3.7	150.9	19.9
F90	8.7	131.5	50.3	9.8	129.3	41.8	8.9	150.9	45.1
F100	11.1	124.0; 146.0	30.2; 55.5	11.4	146.4	83.6	12.4	145.9	84.9
F110	38.9	154.4	88.2	37.0	155.4	87.4	33.4	153.2	93.4
F160	38.4	154.4	96.9	34.7	154.2	95.6	41.5	153.8	95.7

The mass yields of medium crystalline fractions F90 and F100 are approximately the same for all samples, only F100 of sample R1877 is lower. However, this sample R1877 has the largest yield of the low crystalline to amorphous fraction F30, which was 6.9 wt. %, compared to 2.9 wt. % (R1806) and 3.7 wt. % (R2930).

When comparing data (Table II: and III.) with a higher fraction crystallinity, the ethylene content decreases, however melting enthalpy increases. This fact supports the claim that the ethylene units cause a chain disorder and thus reduce the ability of the polymer chain to crystallise[12].

Table III.
Ethylene content in original samples and its fractions [mol. %]. R1806 (phthalate ID + alkoxysilane ED), R1877 (diether ID, prepol.), R2930 (diether ID).

Sample	Orig.	F30	F90	F100	F110	F160
R1806	2.2	18.3	8.5	4.5	1.4	1.2
R1877	1.9	15.4	4.1	2.1	1.3	1.1
R2930	2.2	14.2	4.6	2.6	1.4	1.4

Individual fractions and original samples were measured by FTIR, where the ethylene content of the individual fractions was confirmed by a rising peak at 733 cm^{-1} (Figure 3). A noticeable difference in the spectra, and thus also in the structure, can be seen when comparing the F100 fractions, where this difference is explained in chapter 3.1.2.2.

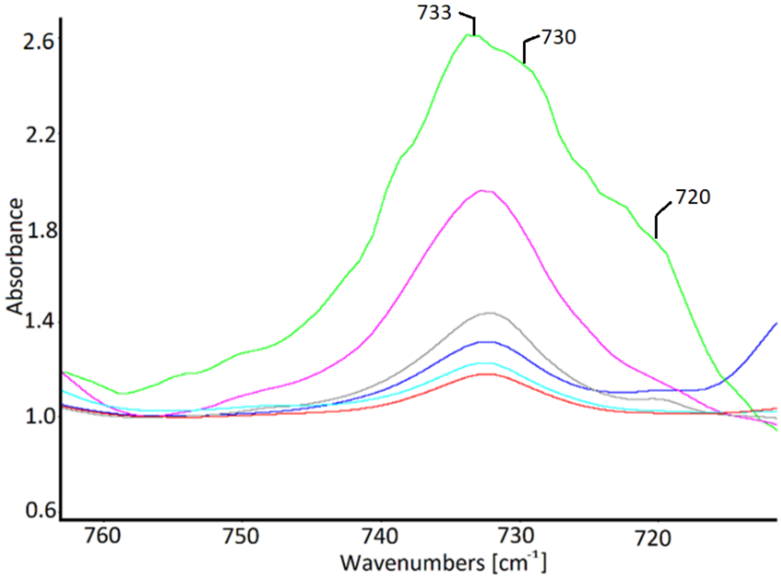

Figure 3: FTIR spectrum of sample R1877 (diether ID, prepol.) and its fractions after TREF fractionation: ●F30; ●F90; ●F100; ●original; ●F110; ●F160.

Evaluation of the Low Crystalline Fraction F30

Fraction F30, which dissolve and elutes at the lowest temperature, is assumed to have the lowest crystalline phase i.e., a predominantly amorphous structure. The suppression of crystal formation in the structure is mainly due to the presence of ethylene. Compared to the other fractions, the F30 of the phthalate ID sample has a higher ethylene content (R1806, 18.3 mol. %) than the F30 fractions of the diether ID copolymers (R1877 15.4 mol. % and R2930 14.2 mol. %).

The FTIR spectra of the F30 fractions also show a different character and confirm the ^{13}C-NMR results. All F30 fractions show a very broad band corresponding to the presence of ethylene (Figure 3). In addition to the peak at 733 cm^{-1} corresponding to isolated ethylene units and the peak at 730 cm^{-1} which present crystalline domains of ethylene, the presence of a band at 720 cm^{-1} belonging to long ethylene sequences can also be observed in samples R1806 and R1877. However, all peaks overlap.

Evaluation of Medium Crystalline Fractions F90 and F100

The mass fractions of medium crystalline fractions F90 and F100 of all samples are similar, but their structure is very different. The obtained ^{13}C-NMR and FTIR data show the main difference between the two types of internal donors.

Fraction F100 of sample R1806 contains long ethylene sequences and these blocks are able to crystallise according to the FTIR spectrum (Figure 4). It is specifically a peak at 730 cm^{-1}, which is typical for the crystalline sequence of ethylene. This also leads to a rapid increase in the peak at 719 cm^{-1}, which corresponds to the sum of amorphous and crystalline ethylene chains. These peaks are not present in the F100 fractions in both diether ID samples, and therefore ethylene occurs here mainly in isolated units.

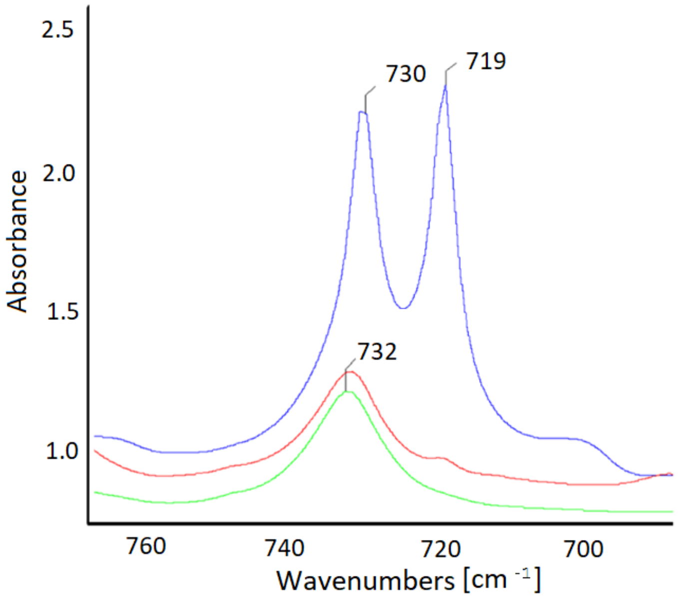

Figure 4: Detail of FTIR spectrum F100 TREF fraction •R1806 (phthalate ID + alkoxysilane ED), •R1877 (diether ID, prepol.), •R2930 (diether ID)

The ability of the ethylene blocks of fraction F100 of sample R1806 to crystallise was also confirmed by DSC. The curve of dependence of the heat flow on the temperature of this fraction showed two maximum values, at 124 and 146 °C (Figure 5). It can be concluded that the first maximum corresponds to segments of crystalline ethylene, the second to segments of propylene. This phenomenon was measured only in the 100 fraction of sample R1806 (i.e., a catalyst with phthalate ID combined with alkoxysilane ED).

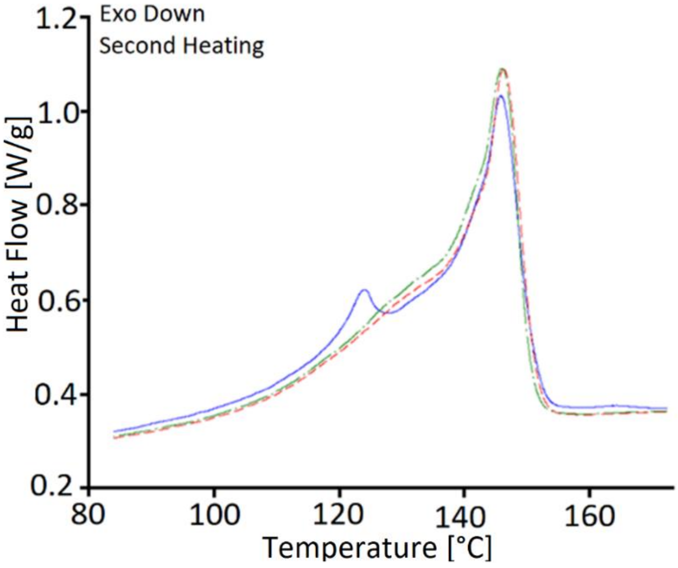

Figure 5: Dependence of heat flux change on temperature at DSC fraction F100 during the second melting. •R1806 (phthalate ID + alkoxysilane ED), •R1877 (diether ID, prepol.), •R2930 (diether ID)

Evaluation of Highly Crystalline Fractions F110 and F160

The highly crystalline fractions F110 and F160 have the most significant mass representation in all the original samples. It is evident from the measured ^{13}C-NMR data that these fractions contain the smallest amount of ethylene of all fractions.

As expected, both melting points and enthalpy of fusion will have the highest values comparing all fractions. The melting temperatures are close to the values of pure polypropylene, which is also confirmed by its majority weight content.

Conclusions

For detailed information about the influence of internal donors on the structure of E/P copolymers, three samples with the same melt flow index and ethylene content were selected. Samples were synthesised on catalysts with diether- or phthalate-based internal donors. Subsequently, the samples were fractionated using TREF into five fractions. These fractions were further analysed using structural analysis methods and the results were compared.

Each original sample was divided into fractions according to the crystallisation ability, and the efficiency of the fractionation was verified by DSC by measuring the melting enthalpy of the fractions. All samples contain a low crystalline to amorphous part (fraction F30), in which a high proportion of ethylene, about 16 mol. %, was measured.

The greatest influence of the used ID on the polymer structure was observed for intermediate crystalline fractions that eluted at 90 and 100 °C. ^{13}C-NMR measurements showed that the F100 fraction of sample R1806 (phthalate-based ID) formed chains where ethylene was incorporated into the blocks, while this was not observed with the diether-based catalyst. Using DSC and FTIR, it was further established for this fraction that, in addition to the propylene segments, these ethylene blocks are also capable of crystallising. Thus, beside the PP crystal structures some of the material synthesised with phthalate ID can crystallise also in crystal structure corresponding to PE.

The smallest amount of ethylene was found in the highly crystalline fractions, which constituted approximately 70 wt. % of the sample and where ethylene was present in an amount of 1.2 mol. %. Ethylene was present in the form of isolated units, which had no significant effect on the ability of long propylene sequences to crystallise. Therefore, the temperature and enthalpy of melting of these fractions were the highest.

The results show that internal donors influence the structure of the E/P copolymers and the way ethylene is incorporated into chains. Short blocks of ethylene capable of crystallisation occur with phthalate-based catalyst, not observed in samples produced with diether-based catalysts. We assume that the alkoxysilane compound in the case of the phthalate-based catalyst and the diether compound in the case of the diether-based catalyst are the main reason of the different incorporation of ethylene units into the growing polypropylene chain.

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References

1. Mori, H., Yamahiro, M., Terano, M., Takahashi, M., & Matsukawa, T. (2000). *Macromolecular Chemistry and Physics*, *201*(3), 289–295.
2. Soares, J. B. P., & McKenna, T. F. L. (2012). *Polyolefin reaction engineering*. Wiley-VCH.
3. Kissin, Y. V. (2003). *Journal of Polymer Science Part A: Polymer Chemistry*, *41*(12), 1745–1758.
4. Moore, E. P. (Ed.). (1996). *Polypropylene handbook: Polymerization, characterization, properties, processing, applications*.
5. Gahleitner, M., Jääskeläinen, P., Ratajski, E., Paulik, C., Reussner, J., Wolfschwenger, J., & Neißl, W. (2005). *Journal of Applied Polymer Science*, *95*(5), 1073–1081.
6. Paukkeri, R., & Lehtinen, A. (1993). *Polymer*, *34*(19), 4075–4082.
7. Lee, J. W., & Jo, W. H. (2009). *Journal of Organometallic Chemistry*, *694*(19), 3076–3083.
8. Song, B. G., & Ihm, S.-K. (2014). *Journal of Applied Polymer Science*, *131*(15),
9. Borrajo, J., Cordon, C., Carella, J. M., Toso, S., & Goizueta, G. (1995). *Journal of Polymer Science Part B: Polymer Physics*, *33*(11), 1627–1632.
10. Siriwongsarn, E., Anantawaraskul, S., Chokputtanawuttilerd, N., Alghyamah, A. A., & Soares, J. B. P. (2012). *Macromolecular Chemistry and Physics*, *213*(18), 1892–1906.
11. Song, B. G., Choi, Y. H., & Ihm, S.-K. (2013). *Journal of Applied Polymer Science*, *130*(2), 851–859.
12. Botha, L., & Van Reenen, A. J. (2013). *European Polymer Journal*, *49*(8), 2202–2213.

POLYOLEFIN STRUCTURE MODIFICATION: FROM BASIC MATERIALS TO POLYMER SPECIALITIES

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Abstract

A method for polyolefin rubber synthesis is described for branched polyethylene obtained by ethylene polymerization initiated by nickel α-diimine chain-walking catalyst. The principal of the method is to support chain-walking isomerisation to obtain hyperbranched polyethylene structures with suppressed crystallinity. Prepared polyethylene contained from 62 to 110 branches per 1000 carbon atoms which led to crystallinity between 6.1% and 0.0%. Elastomeric material was vulcanized by dicumyl peroxide to prepare polyethylene rubber. Mechanical properties of the rubber were measured to estimate application potential.

Introduction

Polyethylene (PE) is the most produced plastic material nowadays[1]. Properties and easy processability in combination with low price of monomer makes polyethylene ideal polymer for a wide range of applications[2]. Nevertheless, due to crystalline character of polyethylene homopolymer, application in rubbery industry is limited to copolymers of ethylene[3,4]. This natural crystallinity can be suppressed by introduction of branches into a polymer chain[5]. Hyper-branching can lead to elastomeric hyper-branched polyethylene (HBPE)[6] and followed by vulcanization pure polyethylene rubber can be prepared. This approach can even broaden the application possibilities of polyethylene.

Topology of polyethylene structure (Figure 1) plays the main role in product properties and final application. Radical polymerization of ethylene at high temperatures and pressures produce low-density polyethylene (LDPE) with crystallinity between 30% and 50% containing long-chain and short-chain branches[7,8]. Since invention of Phillips and Ziegler-Natta catalysts, ethylene can be polymerized at mild conditions by coordination polymerization to get high-density polyethylene (HDPE) with crystallinity from 80% to 90% with mostly linear structure[7,9]. Ziegler-Natta catalysts can be also used for ethylene copolymerization with longer-chain olefins such as butene, hexene or octene to obtain linear low-density polyethylene (LLDPE) with 30 % – 45% crystalline phase containing only short-chain branches[10]. It is obvious that branching and/or substituents incorporation along the chain is the key to suppress crystallinity[2,11-13]

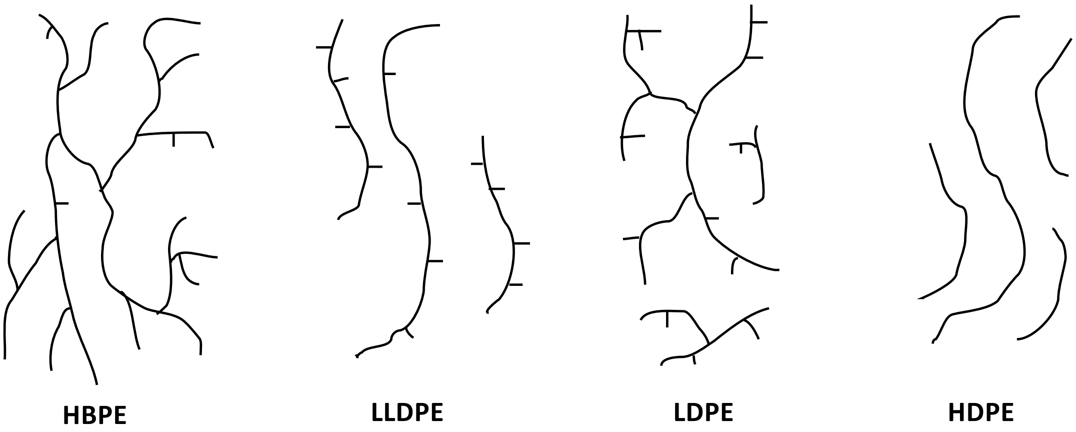

Figure 1: Different topology of polyethylene: hyper-branched polyethylene (HBPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE) and high-density polyethylene (HDPE)

Among a lot of well-known catalysts used in ethylene polymerizations, α-diimine complexes are one of the most intensively studied systems. The group of α-diimine nickel and palladium catalysts hold a unique position in ethylene polymerization because due to combination of living polymerization and chain-walking isomerisation they allow to control polymer branching and topology[14-17]. Most works on ethylene-based elastomers and/or thermoplastic elastomers prepared using α-diimine complexes are focused on ethylene copolymerization with longer-chain α-olefins[12,18-21]. Thermoplastic elastomers based on pure polyethylene are high molecular weight polymers with hyperbranched structure prepared by modified unsymmetrical α-diimine catalysts[19,22,23].

Although α-diimine complexes of nickel (Figure 2) are well-established catalysts for preparation of highly-branched polyethylene, to the best of our knowledge, they have not been investigated for the preparation of polyethylene rubber and characterization of its vulcanization behaviour. This work describes an efficient method of polyethylene rubber synthesis using nickel α-diimine complex for ethylene polymerization followed by dicumyl peroxide vulcanization of hyperbranched polyethylene.

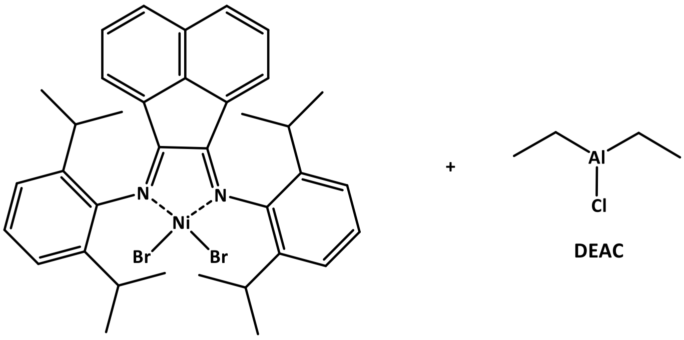

Figure 2: Nickel (II) α-diimine complex used in this study, complex was in-situ activated by diethylaluminium chloride (DEAC)

Experimental part

Materials

Synthesis of nickel (II) α-diimine complexes, manipulations with all air-sensitive compounds and polymerizations were performed under a protective atmosphere of a dry nitrogen (SIAD, 99.999%) using standard Schlenk techniques. Nitrogen (SIAD, 99.999%) and ethene (SIAD, 99.9%) were passed through the columns with molecular sieves and deoxygenation Cu catalyst to remove traces of water and oxygen. Toluene (p.a., Penta) was dried over sodium and distilled under nitrogen. Chlorobenzene (CLB, p.a., Penta) was dried over CaH_2 and distilled under nitrogen. Diethylaluminium chloride (DEAC, 0.9 M solution in toluene, Acros) was used as received. Nickel complex was prepared according to reported procedure[14]. Catalyst was dosed in dichloromethane solution prepared freshly before the polymerization. Dicumyl peroxide (98%, Aldrich) was used as received.

Preparation of hyperbranched polyethylene

Polymerizations of ethylene were performed in magnetically stirred 300 mL pressure ampoules under protective atmosphere of a dry nitrogen. The pressure vessel with solvent (CLB/toluene) and cocatalyst (DEAC) was placed in circulation thermostat and left for 10 minutes to saturate by monomer. The polymerization was initiated by addition of catalyst solution (CH_2Cl_2, 10 µmol/mL). After defined time the reaction was terminated to 1500 mL of ethanol with 10% HCl. Product was separated, cut to small pieces and dried under vacuum at 50 °C for 48 hours.

Polymer characterization

^1H NMR spectra of were measured at 500 MHz in $C_2D_2Cl_4$ at 120 °C on Bruker Avance DRX 500 spectrometer. Degree of branching from ^1H NMR spectra was determined by integrating methyl proton signals belonging to CH_3 groups with respect to signals of all protons in 1H NMR spectrum and calculated using the formula:

$$(1)\quad N = \frac{2\cdot I[CH_3]}{3\cdot[I(CH+CH_2+CH_3)]}\cdot 1000$$

Molar masses of poly(ethylene)s were determined using high temperature GPC-IR® (Polymer Char) chromatograph equipped with infra-red and viscometric detector (HT SEC-IR-η). Separations were performed on two columns (PSS Polefin, linear XL, 10 µm) at 150 °C in 1,2,4-trichlorobenzene at an elution rate of 1 ml min^{-1}.

DSC analyses of PE were performed on TA Instruments (Q100) calorimeter. Temperature range was from -90 °C to 160 °C, temperature rate 10 °C/min and N_2 flow 50 mL/min. Glass transition temperatures and enthalpies of fusion were obtained from the second heating run. Enthalpy of fusion of theoretically 100% crystalline polyethylene ΔH_m^* = 293 J/g was taken from literature.[24] Crystallinity of HBPE (α) was determined using the formula:

$$(2)\quad \alpha = \frac{\Delta H_m}{\Delta H_m^*} \times 100$$

ΔH_m is enthalpy of fusion of the sample and ΔH_m^* is the enthalpy of fusion for the hypothetical 100% crystalline polyethylene.

The Mooney viscosity of the HBPE at 100°C was determined with a V-MV 3000 Variable Mooney Viscometer (MonTech) in mode preheat 1 min + measurement 4 min at 2 rev min^{-1} + 30 s relaxation test after the rotor stop. The final viscosity and relaxation decay indexes were evaluated.

The course of the vulcanisation was measured with the rubber process analyser RPA 2000 (Alpha Technologies) at a temperature of 160°C, an oscillation amplitude of 0.5 degrees of arc, and a frequency of 100 cpm (cycles per minute) for a period of 1 hour.

The specimens for mechanical testing were pre-pared by compression moulding using the laboratory hydraulic press LabEcon 300 (Fontijne Presses). Sheets (150 mm × 150 mm ×2.5 mm) were moulded in a flat mould for (t_{90} + 2 min), where t_{90} is the optimum cure time as derived from the vulcanisation data obtained from RPA test. The temperature was 160 °C; the moulding force was 250 kN.

Tensile tests were performed on dumb-bell specimens which were cut out from moulded sheet. Then, the specimens were placed to a tensile test on an Instron 3365 tensile tester equipped with a long travel extensometer. The tensile strength, elongation at break, 100% and 300% moduli (if possible) of PE rubber were evaluated.

The Shore A hardness of PE rubber was measured with a manual durometer (Mitutoyo) using residual parts of the sheets layered on top of each other to reach a 6 mm thickness. The hardness value was registered 15 s after the start of the test.

Results and discussion

Ethylene polymerization using α-diimine nickel complexes activated by diethylaluminum chloride

To prepare hyperbranched polyethylene with suppressed crystallinity and elastic behaviour we used method based on maximum support of chain-chalking isomerisation provided by nickel α-diimine complex (Figure 2) activated by DEAC. Chain-walking can be supported by increasing of polymerization temperature, lowering a monomer concentration and rigidity/bulkiness of catalytic complex structure. Ethylene polymerization conditions were settled to reach maximum conversion of monomer and obtain high molar mass product: ethylene pressure 7 bar (abs.), time 3 hours.

Table I.
Branched poly(ethylene)s prepared by polymerization of ethylene initiated by nickel (II) α-diimine complex activated by DEAC at different temperatures for 3 hours in toluene

Exp.	*T* [°C]	Yield [g]	M_n[a] [kg/mol]	$Đ_n$[a]	Branching[b]	T_g[c] [°C]	Crystallinity [%]
1	40	10.4	47	4.2	62	-46	6.1
2	50	10.1	55	3.1	74	-51	5.7
3	60	8.3	39	3.1	82	-54	1.6
4	70	7.0	36	3.0	87	-55	0.6

DEAC, n_{cat} = 9 µmol, [Al]/[Ni] = 200, V_{total} = 300 ml, 3 h, toluene, [a] M_n and $Đ_n$ determined by HT-SEC in 1, 2, 4-trichlorbenzenu at 150 °C (universal calibration on PE), [b] number of branches per 1000 C atoms obtained from ^{1}H NMR, [c] T_g and crystallinity obtained from DSC

First, we tried ethylene polymerizations in toluene and changed reaction temperature in the range between 40 and 70 °C (Table I.). Changing of temperature had significant impact on final structure of PE. Yield of PE was descending from 10.4 g down to 7.0 g with increasing of temperature which indicates that stability of Ni growth centres is lower when temperature is over 60 °C. Branching increased with temperature from 62 up to 87 branches per 1,000 C atoms which led to decrease in crystallinity from 6.1% down to 0.6% together with glass transition temperature from -46 °C down to -55°C. Considering that maximum molar mass was 55 kg/mol at 50 °C together with yield and branching parameters, temperature for further experiments was settled to 50 °C.

Table II.
Branched poly(ethylene)s prepared by polymerization of ethylene initiated by nickel (II) α-diimine complex activated by DEAC at 50 °C for 3 hours with different solvents and amounts of Ni complex

Exp.	Solvent	n_{cat} [µmol]	Yield [g]	TOF^a [h-1]	M_n^b [kg/mol]	$Đ_n^b$	Branching[c]	T_g^d [°C]	Crystallinity[d] [%]
2	toluene	9.0	10.1	13 334	55	3.1	74	-51	5.7
5	CLB	9.0	24.3	32 081	43	2.8	110	-67	0.0
6	CLB	4.5	17.6	46 471	68	2.5	105	-59	0.0
7	CLB	1.0	13.5	160 404	83	2.5	86	-54	0.0

DEAC, [Al]/[Ni] = 200, V_{total} = 300 ml, 3 h, [a]TOF = turnoverfrequency, $TOF = m_p / (M_{mon} \cdot n_{cat} \cdot t)$, [b] M_n and $Đ_n$ determined by HT-SEC in 1, 2, 4-trichlorbenzenu at 150 °C (universal calibration on PE), [c] number of branches per 1000 C atoms obtained from ^1H NMR, [d] T_g and crystallinity obtained from DSC

Further we focused on the influence of a solvent and the amount of dosed Ni complex on ethylene polymerization (Table II.). In CLB (Table II., Exp. 2) the yield of PE was more than doubled compared with reaction in toluene (Table II., Exp. 5). Obtained PE branching also increased in CLB from 74 (toluene, Table II., Exp. 2) to 110 (CLB, Table II., Exp. 5) branches per 1000 C atoms which lowered crystallinity from 5.7% (toluene) to 0.0% (CLB) together with glass transition temperature from -51 °C (toluene) down to -67 °C (CLB). Molar mass of PE was slightly reduced in CLB from 55 kg/mol (toluene) to 43 kg/mol. In CLB it was possible to prepare amorphous product with high yield, that is why only reactions in CLB was further investigated.

Mooney viscosity of HBPE obtained from experiment 5 (Table II., Figure 3) with molar mass 43 kg/mol was measured. Mooney viscosity was 21 MU which is low value but indicates elastic behaviour[25]. No relaxation time indicated lack of physical bonds in polymer. This results clearly showed that increasing of molar mass is necessary. To reach higher molar mass HBPE the amount of dosed Ni complex was lowered (Table II.) from 9 µmol (Table II., Exp. 5) to 4.5 µmol (Table II., Exp. 6) resulting in molar mass increase to 68 kg/mol, further lowering to 1 µmol od Ni complex (Table II., Exp. 7) provided HBPE with 83 kg/mol. Mooney viscosity of HBPE obtained from experiment 7 (Table II., Figure 3) was 79 MU which is similar to prevulcanized natural rubber[26] but no relaxation time indicated lack of physical bonds so vulcanization was necessary for gaining better mechanical properties and permanent elasticity.

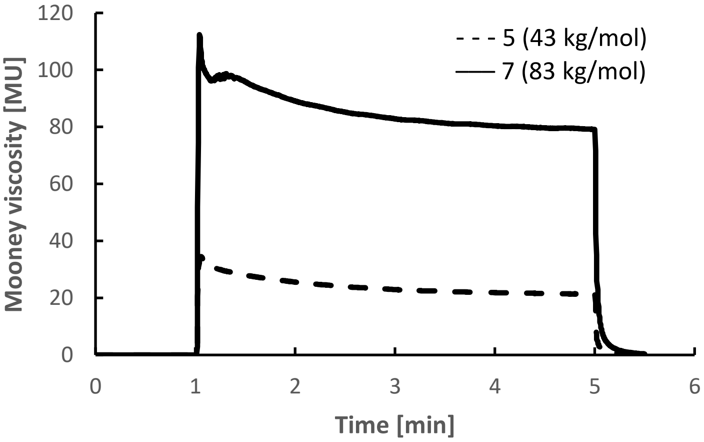

Figure 3: Mooney viscosity of 43 kg/mol sample (Exp. 5, dashed line) and 83 kg/mol sample (Exp. 7, full line)

Vulcanization of prepared hyper-branched polyethylene using dicumyl peroxide

Experiment 5 and 7 (Tab.2) were repeated several times to synthetize sufficient amount HBPE for vulcanization and following material tests. Mixture 40k (mix 40k) is blend of HBPE prepared at conditions for experiment 5 and mixture 80k (mix 80k) is blend of HBPE prepared at conditions for experiment 7. Since pure HBPE does not contain double bonds, which would allow for sulphur vulcanization, radical vulcanization using peroxides was used. In this work we used dicumyl peroxide as vulcanization agent in the amount of 2 phr and vulcanization temperature was settled to 160 °C. Vulcanization time was settled according to RPA measurements. For mix 40k t_{90} was 18.6 min (optimum cure time) and t_{S2} = 2.3 min (induction time), for mix 80k t_{90} was 15.2 min and t_{S2} = 2.1 min. Both courses of the vulcanisation were plateau (Figure 4).

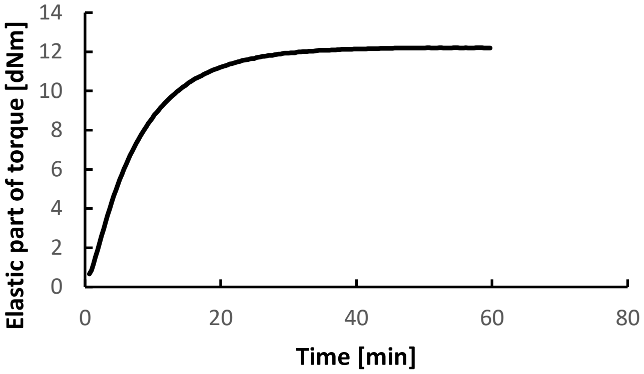

Figure 4: Plateau course of vulcanization of mix 40k

Mechanical properties of polyethylene rubber

Tensile tests and Shore A measurements (Table III.) were performed on vulcanized HBPE rubber 40k and 80k. Tensile strength, modulus 100 and Shore A hardness had higher values for rubber 80k whereas elongations at break were almost the same. Neither of samples accomplished modulus 300. Tensile strength of rubber 80k is comparable with silicone rubber[27] but has lower elongation at break value.

Table. III.
Mechanical properties of vulcanized HBPE using 2 phr of dicumyl peroxide at 160°C

Rubber	σ [MPa]	ε [%]	*M100* [MPa]	Shore A
40k	0.82	202	0.62	35
80k	1.27	204	1.03	48

Conclusions

Method for synthesis of ethylene homopolymer rubber was successfully tested. Ideal conditions for preparation of amorphous hyper-branched polyethylene using α -diimine Ni complex were found (p_{PE} = 7 bar (abs.), n_{cat} = 1 µmol, DEAC, [Al]/[Ni] = 200, CLB, V = 300 ml, T = 50 °C, t = 3h). Prepared HBPE was vulcanized by dicumyl peroxide (2 phr) to obtain PE rubber. Mechanical properties (σ = 1.27 MPa, ε = 204%, *M100* = 1.03 MPa) and absence of free double bonds in the rubber main chain indicates possibility to apply the PE rubber in chemically aggressive environment.

Acknowledgement

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References

1. *Statista Research Department, Global market volume of polyethylene 2015–2029*. 2022.
2. Jeremic, D., *Polyethylene*, in *Ullmann's Encyclopedia of Industrial Chemistry*. p. 1–42.
3. Amberg, L.O. and A.E. Robinson, *Ethylene—Propylene Rubber.* Industrial & Engineering Chemistry, 1961. **53**(5): p. 368–370.

4. Easterbrook, E.K. and R.D. Allen, *Ethylene-Propylene Rubber*, in *Rubber Technology*, M. Morton, Editor. 1987, Springer US: Boston, MA. p. 260–283.
5. Shirayama, K., S.-I. Kita, and H. Watabe, *Effects of branching on some properties of ethylene/α-olefin copolymers.* Die Makromolekulare Chemie, 1972. **151**(1): p. 97–120.
6. Guan, Z., et al., *Chain Walking: A New Strategy to Control Polymer Topology.* Science, 1999. **283**(5410): p. 2059–2062.
7. Andrady, A.L., *The plastic in microplastics: A review.* Marine Pollution Bulletin, 2017. **119**(1): p. 12–22.
8. Maraschin, N., *Ethylene Polymers, LDPE*, in *Encyclopedia of Polymer Science and Technology*.
9. Benham, E. and M. McDaniel, *Ethylene Polymers, HDPE*, in *Encyclopedia of Polymer Science and Technology*.
10. Simpson, D.M. and G.A. Vaughan, *Ethylene Polymers, LLDPE*, in *Encyclopedia of Polymer Science and Technology*.
11. Noordermeer, J.W.M., *Ethylene–Propylene Elastomers*, in *Encyclopedia of Polymer Science and Technology*.
12. O'Connor, K.S., et al., *Controlled Chain Walking for the Synthesis of Thermoplastic Polyolefin Elastomers: Synthesis, Structure, and Properties.* Macromolecules, 2016. **49**(18): p. 6743–6751.
13. Amberg, L. and A. Robinson, *Ethylene—propylene rubber.* Industrial & Engineering Chemistry, 1961. **53**(5): p. 368–370.
14. Johnson, L.K., C.M. Killian, and M. Brookhart, *New Pd(Ii)-Based and Ni(Ii)-Based Catalysts for Polymerization of Ethylene and Alpha-Olefins.* Journal of the American Chemical Society, 1995. **117**(23): p. 6414–6415.
15. Killian, C.M., et al., *Living Polymerization of α-Olefins Using NiII−α-Diimine Catalysts. Synthesis of New Block Polymers Based on α-Olefins.* Journal of the American Chemical Society, 1996. **118**(46): p. 11664–11665.
16. Wang, F. and C. Chen, *A continuing legend: the Brookhart-type α-diimine nickel and palladium catalysts.* Polymer Chemistry, 2019. **10**(19): p. 2354–2369.
17. Gottfried, A.C. and M. Brookhart, *Living Polymerization of Ethylene Using Pd(II) α-Diimine Catalysts.* Macromolecules, 2001. **34**(5): p. 1140–1142.
18. Leone, G., et al., *Ni(II) α-Diimine-Catalyzed α-Olefins Polymerization: Thermoplastic Elastomers of Block Copolymers.* Macromolecules, 2015. **48**(5): p. 1304–1312.
19. Mahmood, Q. and W.-H. Sun, *N,N-chelated nickel catalysts for highly branched polyolefin elastomers: a survey.* Royal Society Open Science, 2018. **5**(7): p. 180367.
20. Leone, G., et al., *Polyolefin thermoplastic elastomers from 1-octene chain-walking polymerization.* Polymer, 2016. **100**: p. 37–44.
21. Hotta, A., et al., *Semicrystalline thermoplastic elastomeric polyolefins: Advances through catalyst development and macromolecular design.* Proceedings of the National Academy of Sciences, 2006. **103**(42): p. 15327–15332.
22. Mahmood, Q., et al., *Ultra-high molecular weight elastomeric polyethylene using an electronically and sterically enhanced nickel catalyst.* Polymer Chemistry, 2017. **8**(41): p. 6416–6430.
23. He, Z., et al., *Random hyperbranched linear polyethylene: One step production of thermoplastic elastomer.* Polymer, 2015. **56**: p. 119–122.
24. Wunderlich, B. and G. Czornyj, *A study of equilibrium melting of polyethylene.* Macromolecules, 1977. **10**(5): p. 906–913.
25. Zhang, C., et al., *A study on mechanical and thermal properties of silicone rubber/EPDM damping materials.* Journal of Applied Polymer Science, 2011. **119**(5): p. 2737–2741.
26. Pasquini, C., F.C. Figueiredo, and B. Prince, *Evaluation of the Mooney Viscosity of Natural Rubber by Near-Infrared Spectroscopy.* Spectroscopy Letters, 2005. **38**(6): p. 741–748.
27. Butts, M., et al., *Silicones*, in *Encyclopedia of Polymer Science and Technology*.

VOLATILE COMPOUNDS RELEASED FROM PVC WIRE COATING

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Abstract

Poly(vinyl chloride) is widely used in the field of electrical engineering as an insulating material. Its properties are significantly dependent on the content of the plasticisers. In this work we identify plasticisers in commercially available insulated electrical wire. We quantify and qualify released hydrogen chloride and qualify volatile organic compounds at enhanced temperatures by thermogravimetric analysis, potentiometric titration, and gas chromatography-mass spectrometry system. Changes in glass transition temperatures and mechanical properties caused by enhanced temperatures are measured by dynamic mechanical analysis. The data show a significant release of hydrogen chloride above 180 °C, which has a significant effect on the mechanical properties.

Introduction

Understanding the composition and behaviour of poly(vinyl chloride) (PVC) insulation during operation is a vital part of hardware development[1,2]. Plasticised polyvinyl chloride (PVC) is a flexible, durable, lightweight insulator resistant to weather, but prone to thermal degradation[3,4]. The plasticiser content[5] significantly affects its mechanical, dielectric and insulation properties[6].

Thermal degradation of PVC wire insulation can be observed using a wide range of techniques, including the determination of thermal stability, glass transition temperature, storage modulus, and decrease in plasticiser content[7]. PVC releases corrosive HCl during thermal degradation, which can be quantified by continual potentiometric titration[8].

Here, we report methodology for complex analysis of PVC wire insulation, quantification of HCl and qualification of volatile organic compounds (VOCs) released after short-time exposure to enhanced temperatures. Changes in mechanical properties are studied in detail in the final part of this work.

Materials and methods

Commercially available PVC coated copper wire, cross section 0.2 mm^2, diameter 0.5 mm, was obtained vacuum-packed and stored in a closed ZIP bag. Wire was used for analyses without separating the phases. Tetrahydrofuran (THF) (p.a., Lach-Ner), diethyl ether (DEE) (p.a., Lach-Ner), and toluene (TOL) (p.a., Lach-Ner) were used without further purification.

To determine copper content in the sample, three times ≈ 0.1 g of wire was put into 25 ml of THF. The samples were left for three days to completely dissolve the polymer phase. Subsequently, the copper was washed with pure solvent and dried in a vacuum oven at 35 °C.

The quantification of released hydrochloride (HCl) at enhanced temperatures (180, 190, and 200 °C) was conducted by continuous potentiometric titration. Due to thermal degradation, the sample (≈ 0.2 mg) released HCl which was absorbed by the water solution containing $AgNO_3$. The chemical reaction between the released HCl and $AgNO_3$ caused a potential change, which was measured through standard electrodes. The amount of liberated HCl was calculated using the Nernst equation. The thermal stability (*TS*) values were read from the kinetics and represent the time interval (in minutes) from the start of the heat treatment to the moment of a rapid increase in the amount of liberated HCl.

Thermogravimetric analyses were performed on Discovery TGA550 Auto Advanced, sample mass ≈ 8 mg, gas flow (air, Linde Gas) 60 ml/min. The heating rate 50 °C/min was used up to 80; 100; 120; 140; 180; 190 and 200 °C followed by an isothermal step of 150 min for static measurements.

The plasticiser content was determined by repeated extraction with DEE and TOL. The samples (1 g, three samples for each solvent) were refluxed three times for 30 min in 50 ml of solvent. Subsequently, the samples were dried in a vacuum oven at 35 °C. The used solvent was collected and quantitatively moved into 500 ml volumetric flask that was filled to this volume with DEE and TOL, respectively.

Obtained plasticiser solutions were further analysed via GC/MS: gas chromatograph Thermo TRACE 1310 with a semi-standard nonpolar TraceGOLD TG-5SilMS column connected to a single-quadrupole mass spectrometer ISQ7000. The system was equipped with a TriPlus RSH autosampler. 1 µl of the prepared solution was injected into the inlet preheated to 300 °C with a split ratio of 360, a column flow of 1.2 ml/min (He 6.0, Linde Gas a.s.). The temperature programme was 40 °C isothermal for 1 min, followed by a ramp of 5 °C/min to 300 °C and then 5 min isothermal.

Infrared spectra were scanned on a NICOLET 6 700 FTIR spectrometer (Thermo-Nicolet, USA) in connection with GladiATR with diamond ATR attachment (PIKE, USA); reflectance measurement, DTGS KBr detector; measurement parameters: spectral range of 4000–400 cm^{-1}, resolution 4 cm^{-1}, number spectral accumulation 64, Happ-Genzel apodization. The spectra were mathematically processed using OMNIC 9 software (Thermo-Nicolet Instruments Co., USA). ATR correction and air humidity readings were performed.

The molar mass was determined by size exclusion chromatography using a Waters Breeze system (autosampler Waters 717+, pump Waters 1515, Waters 2410 detector) with a miniDawn TREOS (Wyatt) MALLS detector. THF was used as a solvent; measured values are equivalent to the molar mass of polystyrene due to calibration on polystyrene standards.

Volatile organic compounds (VOCs) were studied using the same GC/MS system. The sample (5 cm) was enclosed in a 25 ml headspace vial. The sample was incubated at 100 °C for 30 min. This temperature was chosen to be low enough so that no HCl release should be observed and high enough for the evaporation of VOCs. Incubation was followed by extraction at 100 °C for 30 min onto the CWR-DVB-PDMS SPME arrow. This step was followed by injection into the preheated inlet at 280 °C with a split ratio of 10. The desorption time was 5 min. The temperature programme was 40 °C isothermal for 5 min, followed by a ramp of 5 °C/min to 280 °C and then 5 min isothermal.

Cable samples were pretreated at various temperatures in an environmental chamber (80; 100; 120; 140; 180; 190, and 200 °C for two hours) and subsequently analysed by the Q400 thermomechanical analyser (TA Instruments, USA) in dynamic mode (DMA) to determine the glass transition temperature (*Tg*) and storage modulus. For this purpose, three 1 cm long cable samples were tested per each annealing temperature. The cable sample was placed onto a 3-point bend quartz fixture with a 5.08 mm spacing. The static force (0.1 N) and the modulated force (0.05 N) with a frequency of 1 Hz were applied to the centre of the sample using a flexural probe. During the test, the sample was heated in an inert nitrogen atmosphere from room temperature (22 °C) to 100 °C with a heating ramp of 2 °C/min. From the analysis, storage modulus curves are obtained. The determination of *Tg* was in accordance with the ASTM E1640-13 international standard; the resulting values of the storage modulus listed below are determined at 30 °C.

Results and discussion

The copper content in the sample was determined as 55.0±0.8 wt% (Table I.). The remaining part is the polymer insulation, and the value is used for further calculations.

Table I.
Determination of the copper content

Wire mass [g]	Copper residue mass [g]	Copper content [wt%]
0.09010	0.05018	55.7
0.08939	0.04941	55.3
0.09709	0.05257	54.1
		55.0±0.8

The hydrochloride quantification process is presented in Figure 1. Data show that the thermal stability of PVC insulation decreases sharply as the degradation temperature increases (TS_{180}>200 min, TS_{190}~120 min, TS_{200}~60 min). After the thermal stabiliser is consumed, HCl leaks faster, in other words, the resulting chlorides act as prodegradants.

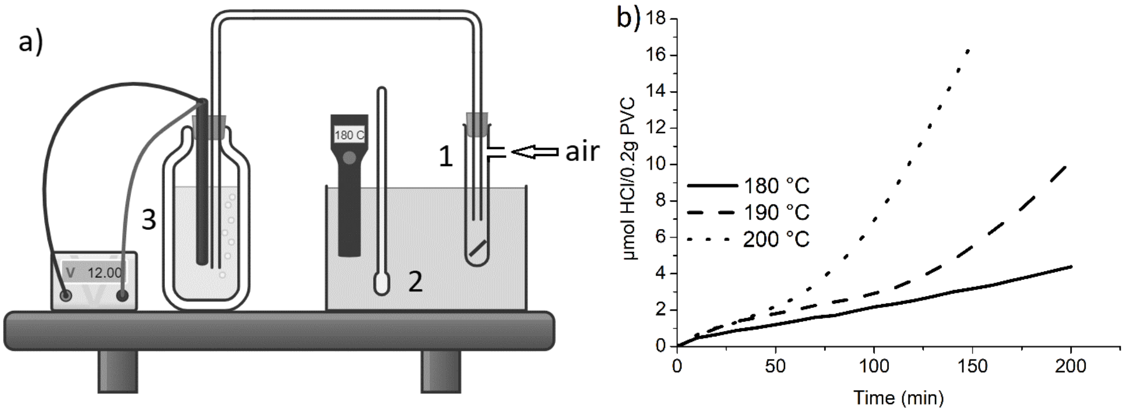

Figure 1. a) apparatus for HCl quantification, 1-sample, 2-salt bath, 3-potetiomettic titration; b) quantification of HCl released during exposure to enhanced temperatures

The TGA analysis (Figure 2.) shows weight loss during static measurement. Lower temperatures (up to 140 °C) cause plasticiser evaporation. No equilibrium was reached; therefore, longer exposures should lead to further weight loss. Losses at 180, 190, and 200 °C are caused both by released HCl and plasticisers. Because of these results, changes in mechanical properties caused by short-time exposure to enhanced temperatures are studied further in this work.

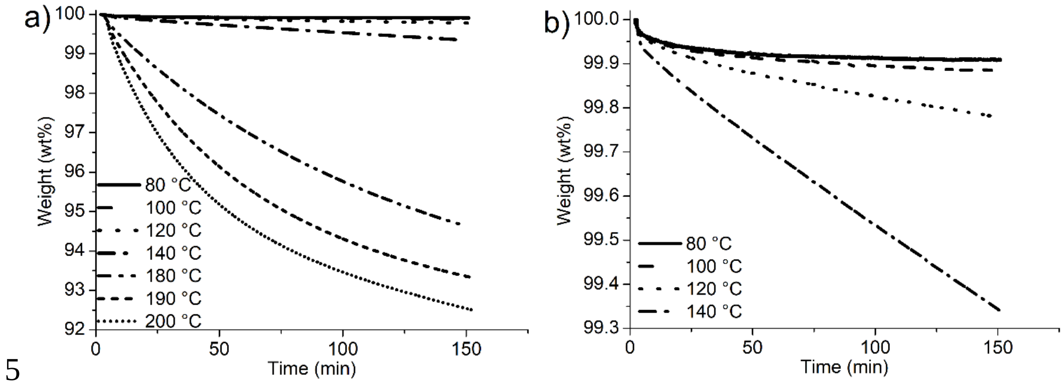

Figure 2. a) TGA curves from isothermal measurement; b) zoomed in a)

Table II. presents data from the quantification of plasticisers by extraction to TOL and DEE. Surprisingly, the extractable content of TOL (24%) is significantly higher than the DEE (17%).

Table II.
Plasticizers content

Wire mass [g]	Extractable content DEE [wt%]	Wire mass [g]	Extractable content TOL [wt%]
1.0524	17.1	1.03780	26.1
1.0608	17.2	1.03572	22.2
1.0456	17.6	1.03582	24.1
	17.3±0.3		**24.1±2.0**

The TOL and DEE extracts were measured by the GC/MS system. Both samples showed only one main peak corresponding to **Benzenedicarboxylic acid, bis(2-ethylhexyl) ester** plasticiser. This data was very surprising due to the variations in the quantitative analysis.

However, a white powder spontaneously precipitated from the TOL solution after a rest period of 2 weeks. This powder was characterised by FTIR (Figure 3.), and it was determined that it is low molecular weight PVC without plasticisers. No precipitant was observed in the DEE solution. Therefore, the difference in measured values between DEE and TOL is caused by the TOL solubility of PVC from the samples.

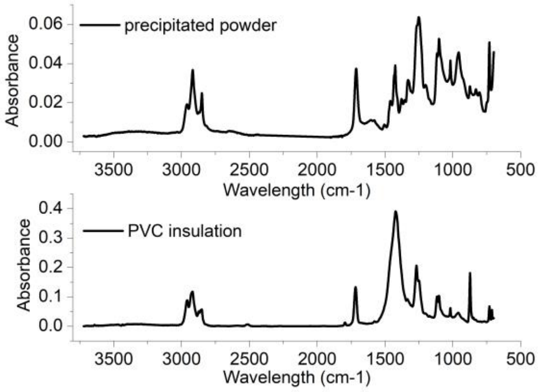

Figure 3. FTIR spectra of PVC insulation and powder precipitated from TOL

The number-average polystyrene equivalent molar mass of PVC insulation was determined to be 112,000 g/mol. A similar value was observed for PVC after extraction with DEE (111,000 g/mol). However, the value for the sample after TOL extraction was significantly higher (148,000 g/mol). This is caused by the removal of lower molecular weight chains into the TOL (see Table II.). The powder, which precipitated from TOL solution was also measured and showed a molar mass of 57,000 g/mol. This experiment confirmed that DEE is suitable for the quantification of plasticisers as it does not remove lower molecular weight PVC from the sample.

The chromatogram from the VOCs analysis is presented in Figure 4. Fifteen main compounds were qualified (Table III.). The first peak corresponds to the common PVC solvent cyclohexanone. Most of the compounds released are hydrocarbons, probably from lubricants; peak number 15 corresponds to the plasticiser.

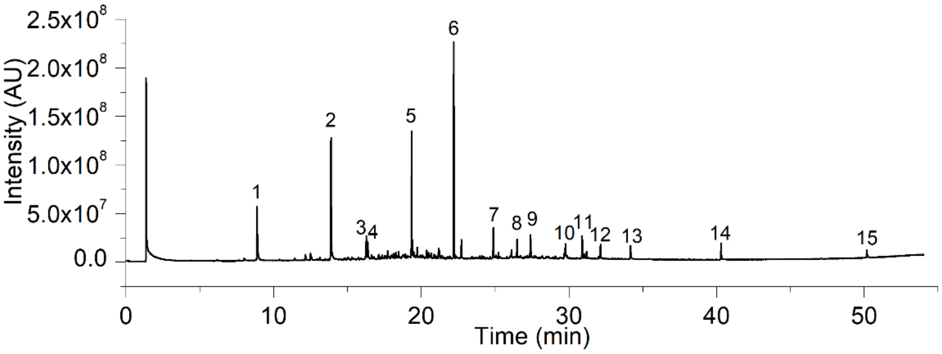

Figure 4. Chromatogram of VOCs released from PVC-coated wire

Table III.
Main VOCs

Peak number	Retention time [min]	Compound	CAS
1	8.87	Cyclohexanone	108-94-1
2	13.88	1-Hexanol, 2-ethyl-	104-76-7
3	16.27	Undecane	1120-21-4
4	16.37	Nonanal	124-19-6
5	19.35	Dodecane	112-40-3
6	22.2	Pentadecane	629-62-9
7	24.86	Alkane	
8	26.47	Alkane	
9	27.38	Alkane	
10	29.75	Alkane	
11	30.88	Hexanoic acid, 3,5,5-trimethyl-, 2-ethylhexyl ester	

12	32.12	Benzoic acid, 2-ethylhexyl ester	5444-75-7
13	34.15	Benzene, 1,1'-[1,2-ethanediylbis(oxy)]bis-	104-66-5
14	40.29	2-Ethylhexyl methyl isophthalate	
15	50.17	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (or 1,4-)	6422-86-2, 137-89-3

Figure 5. presents glass transition temperatures (*Tg*) and storage modulus for the untreated sample and after a short-time exposure to enhanced temperatures measured by DMA. Both *Tg* and the storage modulus are not significantly affected by temperatures up to 140 °C; higher temperatures lead to increasing values. This trend is caused by a decrease in plasticiser content and mainly by changes in molecular structure caused by the release of hydrogen chloride.

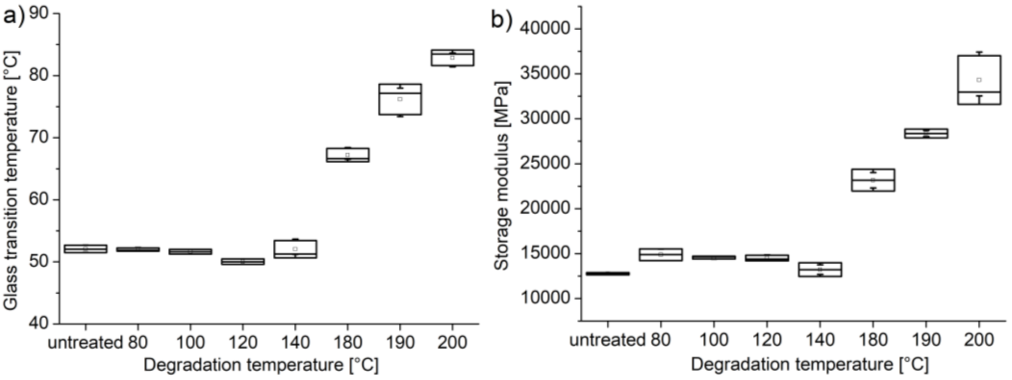

Figure 5. Glass transition temperatures and storage modulus

Conclusions

PVC wire insulation releases VOCs during short-time exposure to enhanced temperatures. Higher temperatures (above 180 °C) are necessary for the degradation and release of HCl. The general quantification of evaporated and released compounds was performed by TGA, and the quantification of HCl by potentiometric titration. The plasticiser was qualified and quantified by combination of extraction and GC/MS as benzenedicarboxylic acid, bis(2-ethylhexyl) ester; diethyl ether was found to be selective solvent for extraction of this plasticiser. The VOCs were qualified using the SPME GC/MS system. The sample released mainly hydrocarbons and plasticiser. Mechanical properties are not significantly affected by short-term exposure to temperatures up to 140 °C. Temperature of 180 °C and above led to an increase in both glass transition temperature and storage modulus. This was probably caused mainly by changes in the chemical structure of PVC during the release of HCl.

Longer exposure times at lower temperatures (up to 140 °C) might cause changes in mechanical properties due to evaporation of the plasticiser used. This is supported by the fact that no equilibrium was reached during the TGA analysis.

Acknowledgement

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References

1. Kapitány, D.; Csányi, G. M.; Tamus, Z. Á., 2014 IEEE Electrical Insulation Conference (EIC), 24–28 (2014).
2. Packa, J.; Váry, M.; Lelák, J.; Šály, V., 2017 18th International Scientific Conference on Electric Power Engineering (EPE), 1–4 (2017).
3. Beneš, M.; Plaček, V.; Matuschek, G.; Kettrup, A. A.; Györyová, K.; Emmerich, W. D.; Balek, V., *J. Therm. Anal. Calorim., 82* (3), 761–768 (2005).
4. Beneš, M.; Milanov, N.; Matuschek, G.; Kettrup, A.; Plaček, V.; Balek, V., *J. Therm. Anal. Calorim., 78* (2), 621–630 (2004).
5. Beneš, M.; Plaček, V.; Matuschek, G.; Kettrup, A.; Györyová, K.; Balek, V., *J. Appl. Polym. Sci., 99* (3), 788–795 (2006).
6. Nagy, A.; Tamus, Z. Á., 2016 Conference on Diagnostics in Electrical Engineering (Diagnostika), 1–4 (2016)
7. Linde, E.; Gedde, U. W., *Polym. Degrad. Stabil., 101*, 24–31 (2014).

SYNTHESIS AND PRODUCTION OF DRUGS

DETERMINATION OF CYTOTOXIC EFFECTS OF DERIVATIVES OF BETULONIC AND PLATANIC ACID ON CELL LINES HepG2 AND HEK 293T

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Abstract

Our aim was to determine the cytotoxic activity of triterpenoid acid derivatives. This work was mainly focused on oxime and oximester derivatives of platanic and betulonic acid. The cytotoxic effects were tested *in vitro* on the human tumor cell line HepG2 using two different methods. The work also included testing the degree of selectivity, for these purposes the non-tumor cell line HEK 293T was chosen.

Introduction

Triterpenoids are a group of bioactive natural products (secondary metabolites) with a great diversity of structure, originating from squalene or oxidosqualene[1]. The best-known representatives belonging to the class of pentacyclic triterpenoids of the lupane type are betulin, betulinic, betulonic and platanic acids[1,2].

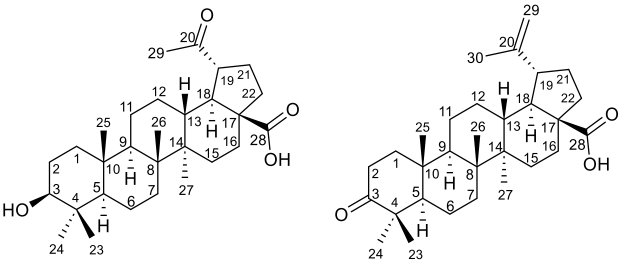

Figure 1. Pentacyclic triterpenoid acids: platanic acid (**I**; **PA**) on the left and betulonic acid (**II**; **BA**) on the right.

Their main natural source is birch or platan bark[2]. Betulin constitutes up to 90% of the total isolated products from the bark of *Betula* spp. (family *Betulaceae*) and represents the starting point for the production of the mentioned acids[1,3,4]. A number of pharmacologically beneficial activities have been described: antimicrobial, antitumor, anti-inflammatory, antiviral activity or cardio- and hepatoprotective effects. Approximately 80% of the anticancer drugs in use are derived from natural compounds[1]. The first data on the antitumor properties of lupane were investigated more than 40 years ago in an *in vivo* cancer model[2]. Liver cancer is the third leading cause of cancer death worldwide, according to 2021 data from the article by Arzumanian et al. The HepG2 cell line was isolated in 1975 from the liver tissue of a 15-year-old boy and was described as hepatocellular carcinoma (hepatoma, HCC), later reclassified as hepatoblastoma (HB). One of the characteristic molecular features is a mutation in the third exon of the CTNNB1 gene encoding *β*-catenin leading to damage to the Wnt/*β*-catenin signaling pathway, which is involved in the development, regeneration and metabolism of the liver. HepG2 cells (10–20 μm) have three to seven nuclei and have half the number of mitochondria and a poorly developed endoplasmic reticulum. The number of chromosomes in HepG2 cells corresponds to a hyperdiploid karyotype (50–60 chromosomes). They have translocations between the short arms of chromosomes 1, 21; trisomy 2, 16, 17 and tetrasomy 20. It is also characterized by a mutation in the promoter of the TERT gene contributing to the immortalization and protection of telomeres in tumor cells, or a mutation of the wild-type tumor suppressor gene TP53 (lit.[5]). HEK 293 cells were isolated in 1973 from the kidney tissue of a human aborted embryo of unknown origin by transfection of spliced adenovirus 5 DNA fragments to form a stable line. A 4-kbp adenoviral genomic fragment has integrated into chromosome 19 and encodes E1A/E1B proteins, which affect cell cycle control and at the same time act against apoptosis[6]. The HEK 293T cell line is derived from HEK 293 cells expressing the SV40 large T antigen[7]. Compared to human RefSeq, 293 lines have rearranged the telomeric end of chromosome 1q causing the loss of four out of five copies of the locus containing the fumarate hydratase gene[6]. In an article by Kommera et al., betulinic and betulonic acid derivatives showed antiproliferative activity is depended on concentration and antitumor properties were influenced by minor modifications in the structure of. Derivatives dissolved in DMSO (lower 0.5%) was found to be non-toxic to cells[3]. Modifications of the lupane skeleton are commonly carried out at the C-1, C-2, C-18, C-20, C-22, C-29 and C-30 positions and especially at the C-3 hydroxyl group and the C-28 carboxyl group[1]. Hoenke et al reported the presence of a carboxyl functional group as necessary to achieve positive cytotoxicity results. Therefore, betulinic acid derivatives are in most cases more cytotoxic than betulin derivatives[8]. Derivatives of these acids have been found to cause a cytotoxic effect by inducing apoptosis and cell cycle disturbances, mediated mainly by direct effects on the mitochondrial signaling apoptotic pathway. Caspase-dependent apoptosis was observed. Caspase 9 is activated, leading to caspase 3 activation and PARP DNA fragmentation[1,2,4]. The selective cytotoxicity of betulinic acid against melanoma cell lines (MEL-2) was discovered by the NCI in 1995[1,3]. The results of Šarek et al., who tested selected betulinic acid derivatives on a panel of cell lines of different histogenetic origin, including HepG2 cells, speak of proven selectivity towards malignant cells and a favorable therapeutic index. Meanwhile, non-malignant cells (NIH3T3 fibroblasts and healthy human lymphocytes) tolerated higher doses of the tested derivatives than malignant cells. Furthermore, some of these derivatives have been shown to have activity against cell lines carrying mutations in cell cycle proteins and cytotoxicity independent of the hormonal status of the cells[2]. Betulonic acid was shown to be more cytotoxic than betulinic acid[1,8]. Similar to betulinic acid, betulonic acid was found to have antimelanoma properties[4]. Amide derivatives of betulonic acid were able to reduce tumor growth and the number of metastases in a mouse model with lung tumor cells[1]. Research group Yang et al. evaluated that betulonic acid is able to inhibit the growth of various types of human tumor cell lines, including HepG2 or PC3, etc. Inhibition of cell proliferation was observed for amide derivatives of betuolonic acid with amino acid esters and with aliphatic and heterocyclic amines, especially for amino groups in the C-28 position[4]. In the research of Hoenke et al., acetylated derivatives of betulonic and platanic acid were modified at C-28 amide derivatives formed from benzylamine, 4-aminoisoquinoline or 5-aminoquinoline. It was found that unmodified platanic and betulinic acids did not show cytotoxicity at a concentration of 30 µM. A significant increase in cytotoxicity occurred as soon as the amide was obtained[8]. The EC_{50} cytotoxic activity ranged from 7.8–14.0 µM for derivatives formed by the reaction of hydroxylamine hydrochloride in pyridine with platanic acid C-3,28 diacetates to form C-20 oxime derivatives. Greater cytotoxicity is indicated by derivatives in which the oxime group has been reduced to form C-20 amine derivatives. The most active compound was (3*β*, 20 *R*)-3,28-diacetyloxy-20-amino-30-norlupane with an EC_{50} of 2.1 µM tested on MCF-7 (breast adenocarcinoma) tumor cells. By converting the keto group of platanic acid at the C-20 position, the cytotoxic effects are improved[9].

Experiment

Samples of tested substances

Test substances were dissolved in 1 ml of 100% DMSO to form 10 mM storage solutions, which were stored in a freezer at -28°C. For the experiment, 1 mM, 200 µM and 20 µM solutions were used, created by diluting the storage solutions with RPMI medium.

Phosphate buffer (PBS)

8 g of NaCl, 0.2 g of KCl, 1.81 g of $Na_2HPO4·2H_2O$ and 0.24 g of KH_2PO_4 were mixed in 1 l of distilled water. The resulting solution was adjusted to pH 7.4 with HCl solution. It was subsequently filtered and sterilized in an autoclave.

RPMI cultivation medium

500 ml of RPMI 1640 (R24025) medium (Sigma-Aldrich, USA) was mixed with 55 ml of bovine serum FBS (Gibco, UK) and 5 ml of MEM vitamin mixture (Gibco, UK)

Resazurin

For the experiment, a resazurin solution was used, prepared from a storage solution with a concentration of 0.3 mg·ml-1 and diluted in a ratio of 9 ml of PBS to 1 ml of resazurin solution.

Table I.
Overview of used tissue cultures

Cell lines	Strain	Cultivation conditions
HepG2 (human tumor liver cells)	ATCC ® CCL-2™, USA	RPMI, 37 °C, 5% CO_2, 95% humidity
HEK 293T (human embryonic kidney cells)	ATCC ® CRL-11268™, USA	RPMI, 37 °C, 5% CO_2, 95% humidity

Preservation of tissue cultures

Cell lines were stored in cryotubes at -150 °C in 7.5% DMSO for a long time.

Passage and cultivation of tissue cultures

After thawing, the tissue culture storage suspension was centrifuged. The old medium was then aspirated and the cells were resuspended in 1 ml of new medium and transferred to a Petri dish containing 10 ml of RPMI. The dish was placed in the incubator. The tissue culture was passaged after approximately 72 h, after reaching 80% cell confluence. The old medium was first aspirated from the Petri dish with grown cells. In the next step, the cells were washed with 10 ml of PBS solution. After aspirating the PBS, 1 ml of trypsin solution (0.25%, EDTA solution, Sigma-Aldrich, USA) was pipetted to the cells to detach the cells from the surface, and the dish was left in the incubator for 5-10 minutes. 4 mL of RPMI was added to the dish. 1 ml was transferred to a second dish with 10 ml of fresh RPMI, (The remaining 3 ml was used for the experiment). This was mixed and put into the incubator for the next passage. Before the first experiment, the culture was passaged at least 4 times.

Determination of cytotoxic activity RTCA DP Analyzer (xCELLigence®)

The system enables monitoring of cytotoxicity, viability and proliferation of cells in real time. For the measurement was used 16-well plate contains gold electrodes on the bottom, with which the device detects the degree of cell adherence to the substrate. Cell proliferation is monitored, its decrease indicates a cytotoxic effect. The interaction between cells and microelectrodes is recorded as an impedance, expressed in dimensionless units, the so-called "cell index" as a function of time. 90 µl of RPMI was first pipetted into the wells and the background was measured. Subsequently, 100 µl of diluted cell suspension ($5\cdot10^5$ cells·ml^{-1}) was added to all wells (except A1) and the cells were incubated for 24 h, during which their proliferation curve was recorded at hourly intervals. After 24 h, 10 µl solutions of the test substances were added with a final concentration of 50 µM, 10 µM and 1 µM, including a negative control of 0.5% DMSO; 0.1% DMSO and 0.01% DMSO. The plate was put back into the device and the measurement was continued for another 72 h. The result of the measurement is the cell proliferation curves affected by the test substance. The proliferation inhibition coefficient I (%) at 72 h was also calculated from the values of the proliferation curves.

Determination of cytotoxic activity by resazurin test

This test enables the determination of the metabolic activity (viability) of cells that have the ability of mitochondrial enzyme reduction of the dye resazurin. A 96-well plate was used for the measurements. 90 µl of RPMI and 100 µl of diluted cell suspension ($5\cdot10^5$ cells·ml^{-1}) were pipetted into the wells. The corner effect was taken into account, therefore only RPMI was pipetted into the outer wells of the plate. After 24 hours of cultivation, 10 µl of the solution of individual samples including the DMSO solution (negative control) was added to the grown cells. The resulting concentration of substances and DMSO was the same as measured with the RTCA DP Analyzer (xCELLigence®). Samples were always tested in triplicate. The plate was put back into the incubator for another 24 h. Then the old medium was aspirated from all the wells and 100 µl of resazurin solution (0.03 mg·ml^{-1}) was pipetted. After approximately 1–2 hours, a color transformation of the blue color of resazurin with low fluorescence to the pink color of resorufin with high fluorescence was observed. Finally, the fluorescence value was measured on a Synergy H1 spectrophotometer with two wave filters λexcitation = 560 nm, λemission = 590 nm. Percentage inhibition was calculated from the measured fluorescence values. In parallel, the samples were tested after 72 h of exposure.

Structures of the tested substances

The substances were synthesized in a previous work under the direction of prof. Ing. Zdeněk Wimmer, DrSc.

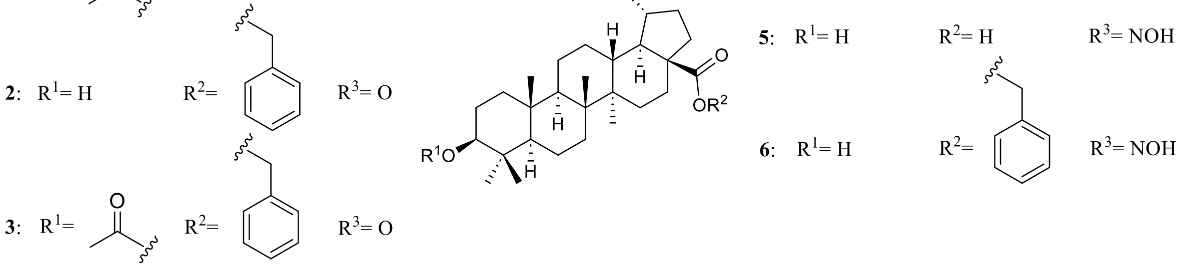

Figure 2. Platanic acid derivatives

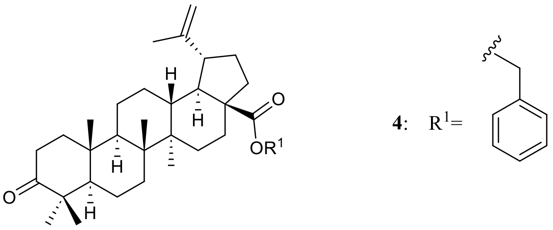

Figure 3. Benzylester derivative of betulonic acid

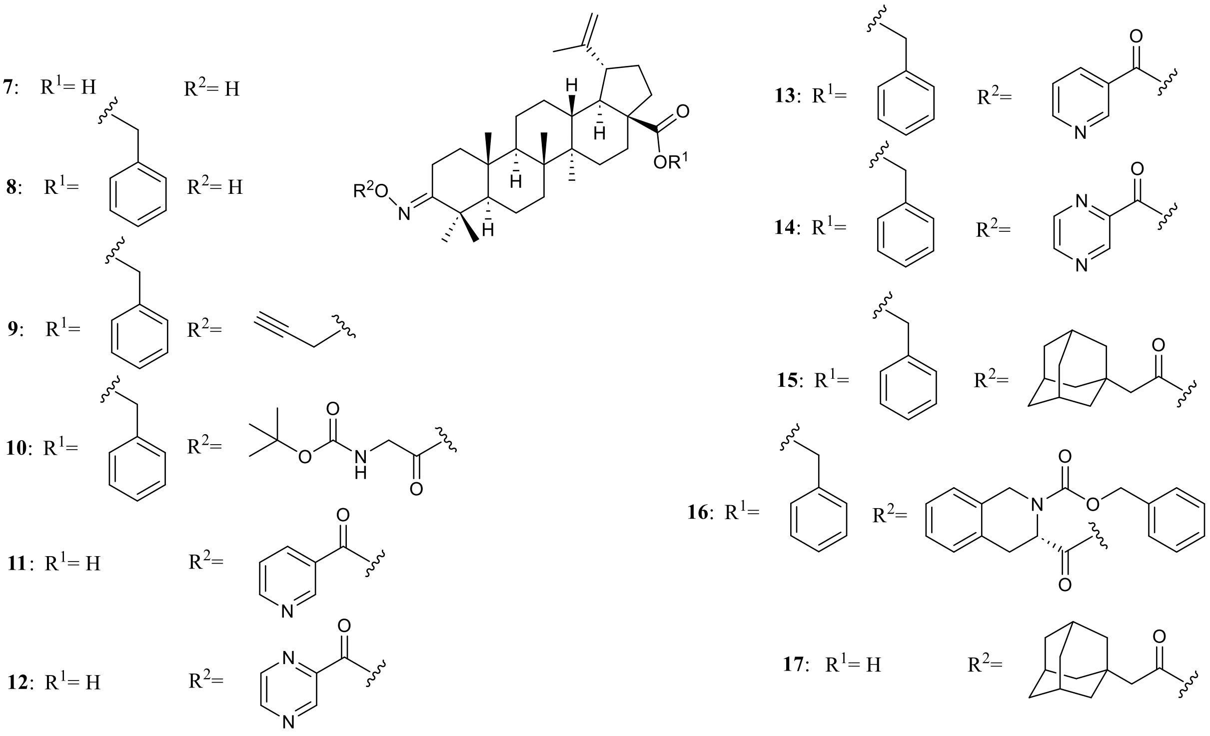

Figure 4. Oxime, oximether and oximester derivatives of betulonic acid

Discussion and result analysis

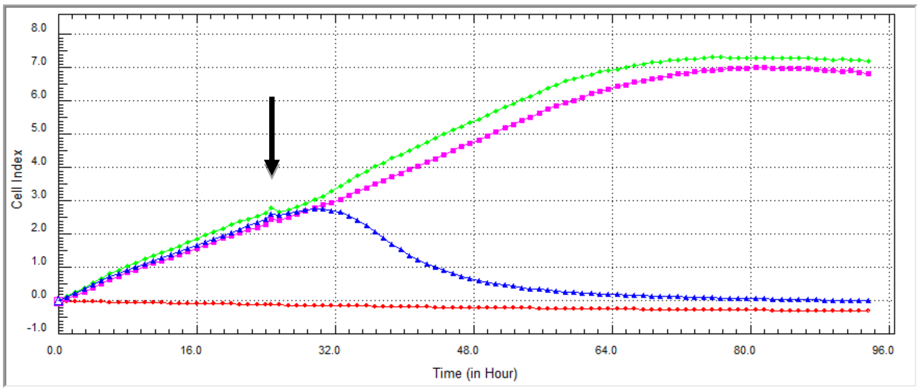

Figure 5. Proliferation of HepG2 cells in the presence of sample 12 (50 µM). Green – 0.5% DMSO (negative control), red – RPMI without cell line (background), pink – unaffected cell line, blue – cell line affected by sample **12**, black arrow – time point addition of the test substance.

Table II.
Resulting values of % inhibition of viability (resazurin test) and proliferation (RTCA DP Analyzer (xCELLigence®) of HEK 293T and HepG2 cell lines by the action of the tested substances at a concentration of 50 µM and 10 µM after 72 hours of incubation.

% Inhibition72 h								
Cells	**HEK 293T**				**HepG2**			
Method	**Resazurin test**		**RTCA DP Analyzer**		**Resazurin test**		**RTCA DP Analyzer**	
c [µM]	50	10	50	10	50	10	50	10
I (PA)	83 ± 12	-	46 ± 7	-	55 ± 8	-	50 ± 8	-
II (BA)	98 ± 15	73 ± 11	99 ± 15	20 ± 3	65 ± 10	39 ± 6	99 ± 15	-
1	98 ± 15	1 ± 0	98 ± 15	-	7 ± 1	-	99 ± 15	-
2	88 ± 13	11 ± 2	-	25 ± 4	43 ± 6	87 ± 13	29 ± 4	4 ± 1
3	84 ± 13	47 ± 7	26 ± 4	-	56 ± 8	80 ± 12	49 ± 7	-
4	34 ± 5	-	-	-	-	74 ± 11	15 ± 2	-
5	54 ± 8	-	-	-	-	83 ± 12	64 ± 10	17 ± 3
6	73 ± 11	4 ± 1	98 ± 15	-	-	-	58 ± 9	-
7	96 ± 14	16 ± 2	98 ± 15	-	68 ± 10	10 ± 2	72 ± 11	-
8	88 ± 13	-	-	17 ± 3	65 ± 10	49 ± 7	4 ± 1	8 ± 1
9	95 ± 14	-	-	41 ± 6	30 ± 5	67 ± 10	24 ± 4	10 ±2
10	52 ± 8	4 ± 1	-	-	-	-	-	3 ± 0
11	100 ± 15	82 ± 12	99 ± 15	50 ± 8	99 ± 15	99 ± 15	85 ± 13	5 ± 1
12	96 ± 14	16 ± 2	99 ± 15	-	97 ± 15	-	97 ± 15	-
13	47 ± 7	-	-	-	-	59 ± 9	2 ± 0	-
14	59 ± 9	-	-	-	20 ± 3	55 ± 8	9 ± 1	-
15	54 ± 8	-	-	-	5 ± 1	51 ± 8	18 ± 3	-
16	40 ± 6	-	-	74 ± 11	-	15 ± 2	2 ± 0	-
17	91 ± 14	56 ± 8	99 ± 15	47 ± 7	75 ± 11	29 ± 4	72 ± 11	-
DMSO	7 ± 1	-	-	-	-	1 ± 0	-	-
DMSO (w %)	0,5	0,1	0,5	0,1	0,5	0,1	0,5	0,1

The results contain a calculated ± 15% deviation. (- Maintenance of proliferation or metabolic activity)

Considering that the treatment of oncological diseases including hepatocellular carcinoma or hepatoblastoma of the liver is still a current topic[5], our work was focused on finding antitumor agents against Hep G2 cells. Article Salvador et al. describes lupane-derived triterpenoids as valuable substances with a variety of activities including antitumor properties. Therefore, a total of 17 betulonic and platanic acid derivatives were selected for the tests. The experiment also included tests on unmodified acids and determination of cytotoxic effects on healthy HEK293T cells. The results of the cytotoxic activity are shown in Table II. In their work, Kommera et al.

talk about antiproliferative effects depending on the concentration and the type of modification made to the structure. This was also observed in our work. However, for some derivatives (e.g., **2**, **3**; Table II.) tested by the resazurin assay, higher cytotoxic activity against Hep G2 was observed at the lower concentration of 10 µM compared to the higher concentration of 50 µM. This may be due to the supramolecular self-assembly of substances. The substances were dissolved in DMSO and the concentration used in the tests (0.5% and 0.1%) was non-toxic to both cell lines, which agrees with Kommera et al. The results of the testing of betulinic acid derivatives by Šarek et al. showed selectivity towards tumor cells without affecting healthy cells. In the case of the tested derivatives of betulonic and platanoic acid at a concentration of 50 µM,a significant inhibition of proliferation and metabolic activity was observed against cancerous Hep G2 cells, but also against non-cancerous HEK293T cells. From the results of the resazurin test after 72 hours of exposure to 10 µM substances, a higher selectivity towards tumor cells was achieved without affecting healthy ones. For example, samples **2**, **3**, **4**, **5**, **8**, **9**, **11**, **13**, **14**, **15** inhibited Hep G2 by 49–99%. However, the RTCA DP Analyzer (xCELLigence®) detected a significant inhibition of HepG2 proliferation especially at a concentration of 50 µM derivatives and was not significant at a concentration of 10 µM. Betulonic acid is more cytotoxic than betulinic acid[1,8]. From our results comparing betulonic and platanoic acid, betulonic acid also showed higher cytotoxicity. As part of increasing the cytotoxic effect, amide derivatives or derivatives with an attached amine heterocycle were described in publications[4,8]. We focused mainly on oxime and oximesters derivatives, and in the case of the tested substances **11** and **12**, an increase in cytotoxic activity was observed compared to the unmodified acid, which corresponds to the results of work Kahnt et al. The result of the inhibition of the proliferation of HepG2 cells after 72 h of exposure to samples **12** is shown in Figure 5.

Conclusion

The cytotoxic activity of 17 derivatives derived from platanic and betulonic acids including unmodified acids was determined, specifically on two cell lines HepG2 and HEK 293T. It was demonstrated that 50 µM derivatives: platanoic acid acetate **1**, oxime derivatives of platanic and betulonic acid **5**, **6**, **7** and C-3 oximester derivative of betulonic acid formed by synthesis with nicotinic acid **11**, pyrazin-2carboxylate acid **12** and 1-adamantylacetic acid **17** are able to inhibit cell proliferation of HepG2 cells by more than 50% after 72 h of exposure. In the case of derivatives: acetate of benzylester of platanic acid **3**, C-3 oxime derivatives of betulonic acid **7**, **8** and C-3 oximester derivatives of betulonic acid **11**, **12**, **17** the metabolic activity of HepG2 cells was suppressed by more than 50%. A significant inhibition of HepG2 viability also occurred at a concentration of 10 µM, and in most samples a higher activity than at 50 µM was even measured. At a concentration of 50 µM, the substances lose selectivity and healthy HEK 293T cells are inhibited. At a concentration of 10 and 1 µM, a decrease in cytotoxicity to HEK 293T and an increase in selectivity to HepG2 were observed. The most cytotoxic substances from this series were betulonic acid **II**, its C-3 derivatives (3*E*)-3-{[(pyridine-3-ylcarbonyl)oxy]imino}lup-20(29)-ene-28-oic acid **11** and (3*E*)-3-{[(pyrazin-2-ylcarbonyl)oxy]imino}lup-20(29)-ene-28-oic acid **12**.

Acknowledgement

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References

1. Salvador J. A. R., Leal A. S., Alho D. P. S., Gonçalves B. M. F., Valdeira A. S., Mendes V. I. S., Jing Y.: Stud. in Nat. Prod. Chem., *41*, 332014 (2014).
2. Šarek J., Klinot J., Džubák P., Klinotová E., Nosková V., Křeček V., Kořínková G., Thomson J. O., Janošťáková A., Wang S., Parsons S., Fischer P. M., Zhelev N. Z., Hajdúch M.: J. Med. Chem. *46*, 5402 (2003).
3. Kommera H., Kaluderovic G. N., Kalbitz J., Drager B., Paschke R.: Eur. J. Med. Chem. *45*, 3346 (2010).
4. Yang S. J., Liu M. C., Zhao Q., Hu D. Y., Xue W., Yang S.: Eur. J. Med. Chem. *96*, 58 (2015).
5. Arzumanian V. A., Kiseleva O. I., Poverennaya E. V.: Int. J. Mol. Sci. *22*, 13135 (2021).
6. Lin Y. C., Boone M., Meuris L., Lemmens, I., Van Roy N., Soete A., Reumers J., Moisse M., Plaisance S., Drmanac R., Chen J., Speleman F., Lambrechts D., Van de Peer Y., Tavernier J., Callewaert N.: Nat. Commun. *5*, 4767 (2014).
7. Iuchi K., Oya K., Hosoya K., Sasaki K., Sakurada Y., Nakano T., Hisatomi H.: Cytotechnol. *72*, 131 (2020).
8. Hoenke S., Heise N. V., Kahnt M., Deigner H. P., Csuk R.: Eur. J. Med. Chem. *207*, 112815 (2020).
9. Kahnt M., Heller L., Al-Harrasi A., Schäfer R., Kluge R., Wagner C., Otgonbayar C., Csuk R.: Med. Chem. Res. *27*, 1757 (2018).

COMBINING DIFFERENT POWDER UNIAXIAL COMPRESSION ARRANGEMENTS TO BETTER PREDICT POWDER COMPRESSIBILITY BEHAVIOUR DURING THE ROLLER COMPACTION PROCESS

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Abstract

Dry granulation processes are most commonly performed with roller compaction. To find the most suitable process parameters on roller compactors involves to perform many screening and verification batches to obtain the most suitable batch of granulate for further processing (such as tableting). Most commonly, the most suitable granulate prepared this way is characterized by the unmilled intermediate called the ribbon (roller compacted compact). When such pilot studies are conducted on lab scale roller compactors the information about the intermediates of preferable batches can be characterized by their ribbon density. This ribbon density can then be used in mathematical modelling if scale-up or technology transfer is desired. The work presented minimizes the scale of pharmaceutical material processing even further as it utilizes an instrumented tablet press Gamlen D1000 with three different die sizes. The aim of this work was to show that when multiple arrangements for powder compaction simulation are utilized the compressibility of the powder (material property that is transferable to roller compaction to predict process parameters on different compactors via mathematical modelling) can be adequately utilized since the proposed experiment design helps elucidate powder densification behaviour from feeding stage (at very low pre-compaction pressures) to the compression zone where the gap between rollers is the most narrow.

Introduction

Roller compaction (RC) is a dry granulation method used in the pharmaceutical industry to prepare granulates from powders with poor flow properties. The resulting granulates are more suitable for further processing, such as tableting or encapsulation. RC is becoming more widespread for granulating pharmaceutical mixtures due to its advantages in scalability and manufacturing cost compared to other significantly more complex granulation processes [1-5]. To control the RC process the quality of the intermediate product, which is the ribbon, must be maintained identically. Therefore, preliminary experiments are performed to identify the optimal batch. Such pilot studies aim to produce many granulate batches that differ in their specific ribbon physical properties due to the process parameters that are set on the roller compactors. The three most important process parameters that affect ribbon properties and are usually subjected to monitoring of their influence are compaction pressure, gap size (between rolls), and roll speed[4, 6]. The most important quality of the intermediate that is monitored to maintain process reproducibility is the ribbon envelope density. To determine the envelope density of a sampled ribbon batch, individual samples of ribbons are subjected to measurement of envelope volume most commonly via volume displacement methods such as mercury porosimetry or solid displacement. If one mixture undergoes a pilot study that produces multiple batches of ribbons with rising compaction pressure, the data can be used to create a compressibility profile and to determine compressibility constant of this powder[7-10]. Because compressibility constant is important for mathematical modelling of this process, the aim of this work was to compare which arrangement of simulated compaction done on the instrumented tablet press is the closest or if a combination of data is comparable to solid medium volume displacement method (utilized on ribbons of the same powder) for use in mathematical modelling.

Materials and methods

Ribbon batches

Ribbon batches of the X1 mixture (composition of the powder mixture is known to the authors but cannot be disclosed, due to industrial partner Zentiva k.s.) were prepared on the Gerteis Mini-pactor®. Four batches were prepared with fixed gap size between the rolls and roll speed. The difference between prepared batches was in increasing compaction pressure. The specific process parameters are listed in results and discussion in Table II.

Simulated compaction via instrumented tablet press

Preparation of compacts was simulated with uniaxial compression in Gamlen D1 instrumented tablet press (Gamlen tableting Ltd., United Kingdom). The compacts were prepared with a flat face punch travelling at 60 mm/min up to load of 1000 kg. The hold time of the material in the die was set to zero in order for the punch to retract immediately when the target load was reached; this was done to better mimic roller compaction. The three different arrangements utilized are listed in Table I. The design of experiments was done in the specified pressure range. Each pressure range was divided into 5 intervals and 5 tablets were prepared at each pressure point. The dimensions and weight of these tablets was measured to calculate average tablet density to construct the compressibility profile.

Table I.
Experiment setup of simulated compaction

Die size	Average sample weight	Pressure range
15 mm	1000 mg	10–50 MPa
10 mm	400 mg	25–125 MPa
5 mm	80 mg	50–250 MPa

Solid displacement method

The solid displacement method utilizes glass microspheres (Glass Sphere s.r.o, Czech Republic) with sphere diameter distribution of 100 – 200 µm. The experiments are done in a glass cylinder on a tap density analyzer JV1000 (Pharmatron AG, Switzerland). Firstly, a sample of glass microspheres (large enough to cover the ribbons) is weighed and then calibrated to measure their exact volume without samples. The volume is calculated from geometric measurements of dimensions using a digital caliper after the vibrational consolidation. Afterwards, the glass microspheres with approximately 2 g of ribbon samples is vibrated to determine the extent of the microsphere column displacement. The displaced volume of the glass microspheres (from the calibrated value) corresponds to the envelope volume of the tested ribbon samples which is then used to calculate their envelope density. The envelope density for each ribbon batch is then calculated as an average from individual measurements (which included reproducibility tests) of a sample set of randomly selected ribbon samples for each batch. All prepared ribbon batches of the X1 mixture were analysed with this method and the results are also listed in Table II.

Mathematical modelling roller compaction

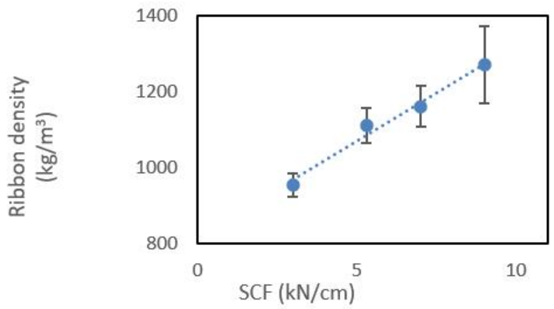
Mathematical modelling was done in the gProms Formulated products 2.2 software (PSE, Siemens UK) using the Reynolds model (2010)[11]. Ribbon and tablet density data was fed to software to calculate compressibility and validate the model for future use.

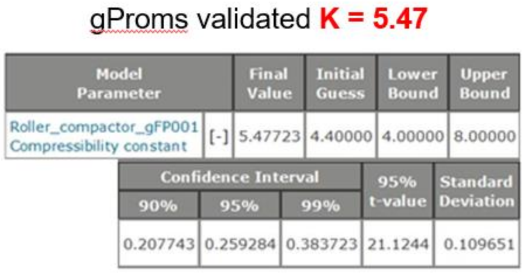
Results and discussion

The results of the ribbon batches for the X1 mixture measured for their ribbon density by solid displacement method are listed in Table II. These data allowed to calculate the compressibility of the mixture with linear regression (Figure 1) via gProms formulated products software and was evaluated.

Table II.
Process parameters for ribbon batches

		Solid displacement method		
Batch	Specific Compaction Force (kN/cm)	Ribbon density (kg/m^3)	Gap (mm)	Roll speed (RPM)
1	3	954 ± 30	2	5
2	5	1,110 ± 45	2	5
3	7	1,160 ± 54	2	5
4	9	1,270 ± 102	2	5



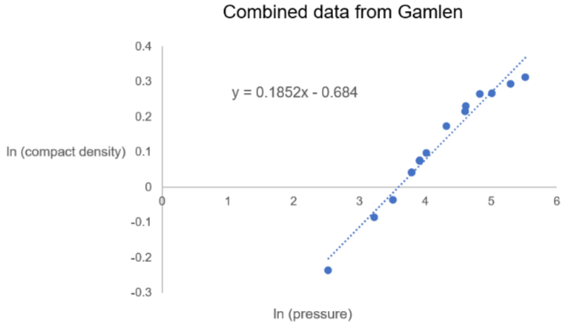

gProms validated **K = 5.47**

Model Parameter		Final Value	Initial Guess	Lower Bound	Upper Bound
Roller_compactor_gFP001 Compressibility constant	[-]	5.47723	4.40000	4.00000	8.00000

Confidence Interval			95% t-value	Standard Deviation
90%	95%	99%		
0.207743	0.259284	0.383723	21.1244	0.109651

Figure 17: Compressibility calculation **K** for the X1 ribbon density data (evaluated with gProms software)

Using the three arrangements on the instrumented tablet press has yielded data that were all combined to evaluate compressibility as it demonstrated better fit to the solid displacement compressibility as shown in Figure 2. At the same time it was possible to confirm that the predicted bulk density is very close to reality as, which was evaluated to be 491 kg/m^3 (measured with method suggested by pharmacopeia).



Compressibility K = 1/0.1852 **= 5.39**

Feed bulk density (predicted)
= exp(-0.684) **= 497 kg/m^3**

Figure 18: Compressibility of the X1 mixture evaluated from simulated compaction experiments

Conclusion

The research shows that the scale-down tactic to instrumented tablet press with the triple die arrangement can provide almost identical compressibility data which was attainable in previous work where only 5 mm die was utilized. This is probably because utilizing the increasing size of dies simulates more material volume throughput and therefore gap size variability in the roller compaction process. It is important to note that as mass in the experiment with increasing die size also increases the effect of wall friction would decrease and inter-particle friction would increase. This means such arrangement of experiment allows to examine broader scope of particle behaviour which adds to closer data fit to the ribbon density evaluated compressibility.

Acknowledgement

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References

1. Wilms, A.; Kleinebudde, P., Towards better understanding of the influence of process parameters in roll compaction/dry granulation on throughput, ribbon microhardness and granule failure load. *Int J Pharm X* **2020,** *2*, 100059.
2. Kalaria, D. R.; Parker, K.; Reynolds, G. K.; Laru, J., An industrial approach towards solid dosage development for first-in-human studies: Application of predictive science and lean principles. *Drug Discovery Today* **2020,** *25* (3), 505–518.
3. Muliadi, A. R.; Banda, A.; Mao, C., Recent Progress in Roll Compaction Process Development for Pharmaceutical Solid Dosage Form Manufacture. In *Continuous Pharmaceutical Processing*, Nagy, Z. K.; El Hagrasy, A.; Litster, J., Eds. Springer International Publishing: Cham, 2020; pp 227–267.
4. Reynolds, G., Model-based development of roller compaction processes. 2019; pp 119–145.
5. Toson, P.; Lopes, D. G.; Paus, R.; Kumar, A.; Geens, J.; Stibale, S.; Quodbach, J.; Kleinebudde, P.; Hsiao, W.-K.; Khinast, J., Model-based approach to the design of pharmaceutical roller-compaction processes. *Int J Pharm X* **2019,** *1*, 100005–100005.
6. Amini, H.; Akseli, I., A first principle model for simulating the ribbon solid fraction during pharmaceutical roller compaction process. *Powder Technology* **2020,** *368*, 32–44.
7. Riepma, K. A.; Vromans, H.; Zuurman, K.; Lerk, C. F., The effect of dry granulation on the consolidation and compaction of crystalline lactose. *International Journal of Pharmaceutics* **1993,** *97* (1), 29–38.
8. Matji, A.; Donato, N.; Gagol, A.; Morales, E.; Carvajal, L.; Serrano, D. R.; Worku, Z. A.; Healy, A. M.; Torrado, J. J., Predicting the critical quality attributes of ibuprofen tablets via modelling of process parameters for roller compaction and tabletting. *International Journal of Pharmaceutics* **2019,** *565*, 209–218.
9. Perez Gandarillas, L.; Perez-Gago, A.; Mazor, A.; Kleinebudde, P.; Lecoq, O.; Michrafy, A., Effect of roll-compaction and milling conditions on granules and tablet properties. *European Journal of Pharmaceutics and Biopharmaceutics* **2016,** *106*.
10. Johanson, J. R., A Rolling Theory for Granular Solids. *Journal of Applied Mechanics* **1965,** *32* (4), 842–848.
11. Reynolds, G.; Ingale, R.; Roberts, R.; Kothari, S.; Gururajan, B., Practical application of roller compaction process modeling. *Computers & Chemical Engineering* **2010,** *34* (7), 1049–1057.

TECHNOLOGY FOR ENVIRONMENTAL PROTECTION

DIESEL EXHAUST FLUID QUALITY IMPEDANCE MEASUREMENT SYSTEM

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Abstract

The possibility of measuring the quality of the diesel engine exhaust fluid (DEF, AdBlue®) used in selective catalytic reduction (SCR) systems to reduce nitrogen oxide (NO_x) emissions is discussed in this paper. There are two key motivations for quality measurement. Firstly, the quality of AdBlue® significantly influences the efficiency of SCR. Secondly, there are attempts to tamper DEF systems with water. DEF quality measurement is therefore required by regulations such as California Air Resources Board (CARB) or European emission standards (EURO 1–6). The quality of AdBlue® is affected by factors such as storage conditions, contamination and degradation. The results of AdBlue® quality measurements can be used to ensure optimal engine performance and minimize environmental impact. Several types of systems based on acoustic wave-based sensors, optical sensors, and others are used for measuring AdBlue® quality in vehicles. Impedance spectroscopy is a non-destructive technique used to study the electrical properties of materials over a wide range of frequencies. The technique has a high sensitivity and can provide valuable information about the properties of the varied materials. The paper explores the impedance spectroscopy for measuring AdBlue® quality and the results demonstrate the possibility of using this method.

Introduction

Due to the increasing industrial activity of recent decades, air pollutants are constantly increasing, posing a significant threat to the environment and health. Air pollution control, especially in industrialized countries, is a crucial factor in regulating and reducing emissions. Emission standards such as EURO, EPA or China VI have become part of the legislation of many countries over the world. The car traffic, which is one of the main sources of pollution, produces high levels of carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NO_x) and unburnt hydrocarbons (HC). A high content of NO_x in the air is dangerous to human health and causes irritation of the respiratory tract and reduces blood oxygenation. To combat this problem, tightening legislation has been introduced and several technologies including catalytic approaches have been developed. For comparison purposes, the car producers are grouped (for example, the Volkswagen Group includes VW, Audi, SEAT, Škoda and Porsche) by fuel type, the Euro standard and engine placement. The grouping is based on the approach used by the International Council on Clean Transport (ICCT). There is no correlation between vehicles with the highest total NO_x emissions and higher and lower NO_2 emissions [1]. Some of the lowest emitters of NO_X emitters also emit low proportions of NO_2, demonstrating the potential for manufacturers to produce diesel passenger cars that have performance good for NO_x and NO_2 [1].

The selective catalytic reduction (SCR) method is one of the most efficient technologies for removing NO_x emissions. In addition to SCR, other systems are also used to reduce exhaust oxide (NO_x) emissions from diesel vehicles. Exhaust Gas Recirculation (EGR) returns part of the exhaust gases back to the engine and reduces the combustion temperature and thus NO_X emissions. The next method is reducing overall exhaust emissions and uses Diesel Oxidation Catalyst (DOC) to oxidize carbon monoxide (CO) and organic compounds. Other system – Diesel Particulate Filter (DPF) captures particulate matter (PM) of exhaust gases and thus reduces the total emission of particulate matter. The last one mentioned method is Lean NO_x Trap (LNT), which uses a catalyst to capture nitrogen oxides (NO_x) and then reduce them to nitrogen (N_2).

The chemical reaction in SCR can be represented by the following equation [2]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

In this reaction, NO_x and ammonia (NH_3) react in the presence of oxygen (O_2) over a catalyst, typically made of a material such as titanium dioxide. The reaction produces nitrogen (N_2) and water (H_2O) as the primary products. The Denoxtronic system is based on this principle (Figure 1). As can be seen from Figure 1, DOC and DPF methods are used before catalytic reduction (SCR) in the exhaust system.

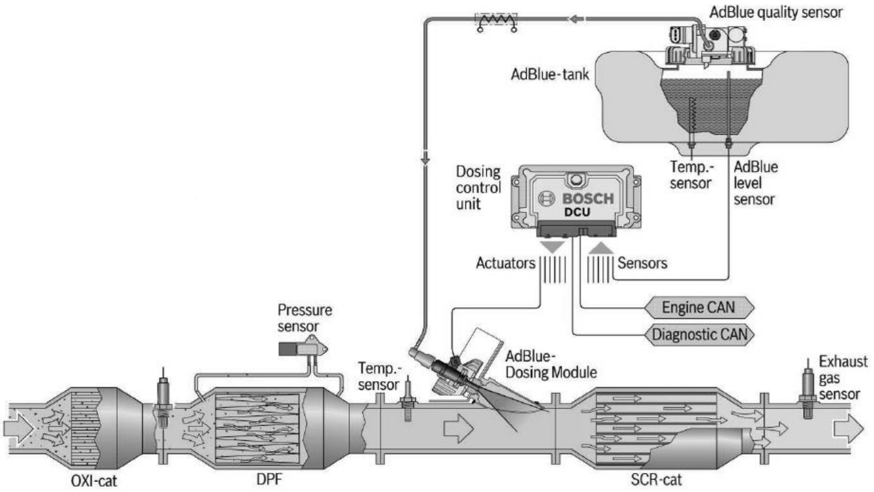

Figure 1. Denoxtronic (Bosch) system with AdBlue® quality sensor [3].

Among the primary factors influencing the quality of a DEF liquid, storage conditions, degradation contamination, and the replacement of the DEF with water (tampering) are considered significant. Therefore, an effect of AdBlue® dilution is studied in the paper.

Materials and Methods

Urea 32.5 wt. % in H_2O [$(NH_2)2CO + H_2O$] (OMV AdBlue®) (Austrian Mineral Oil Administration Stock Company, Austria) was used as received.

Experiment

The five samples diluted in deionized water in the range of 0.05−0.25 vol. were prepared. A sample with pure deionized water to control the effects of dilution was also measured. Each sample was placed in a cylindrical cell made from cooper with a volume of 20 mL. An impedance using Vector Network Analyzer – Bode 100 (OMICRON-LAB) with frequency range from 100 Hz to 50 MHz was measured. Network Analyzer was calibrated to zero, infinite and to dedicated resistance of 50.4 Ohms before the measurement. All measurement were performed at the constant temperature 24.4 °C

Discussion and result analysis

As can be seen from Figures 2–4, the impedance response exhibits capacitive behavior.

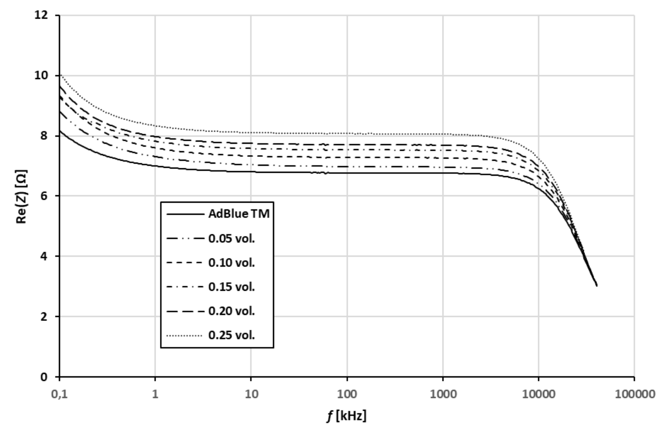

Figure 2. Real part of impedance vs frequency.

The double layer effect is applied here, and the equivalent circuit contains a Warburg diffusion element [4]. Figure 2 reveals that within the frequency range of 10 –1000 kHz, the real part of impedance remains constant.

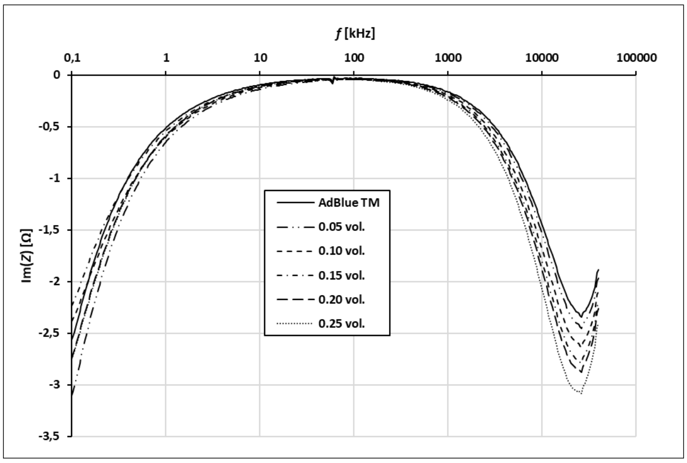

Figure 3. Imaginary part of impedance vs frequency.

As can be seen from Figure 3, there is a zero imaginary part of the impedance for a frequency of about 100 kHz, which would correspond to the physical effects of resonance (if we understand resonance as a state where the imaginary component is zero), and which occurs around a frequency of 106 kHz (Figure 3).

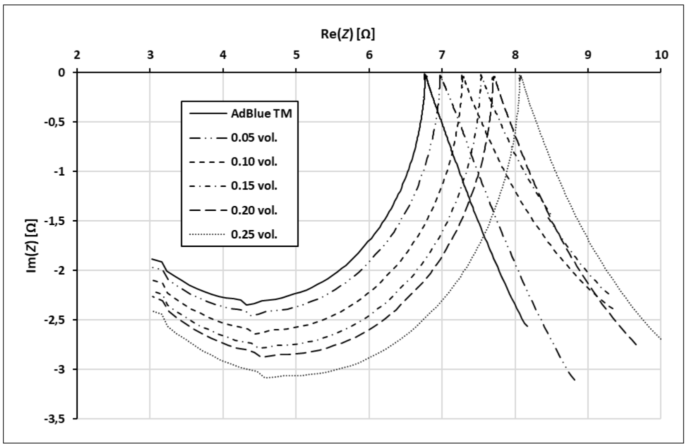

Figure 4. Nyquist plot.

Furthermore, the zero imaginary part is also shown in Figure 4.

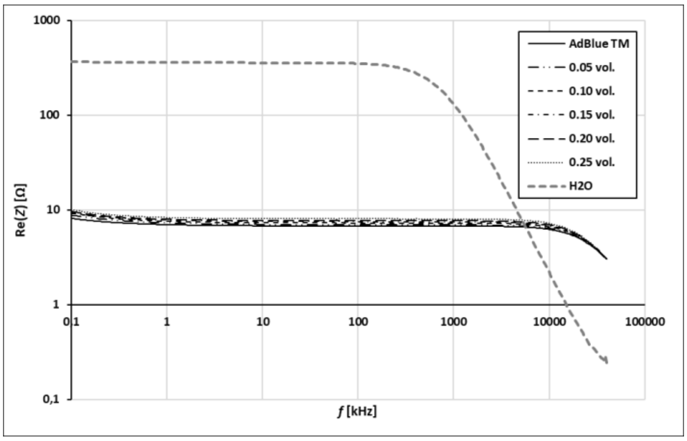

Figure 5. Effect of presence of water in impedance chart.

A sample of pure deionized water was prepared to investigate the effect of water presence on impedance. As can see from Figure 5, water has a significant effect on the change of impedance (dashed line) compared to samples with a small dilution (0.05–0.25 vol.).

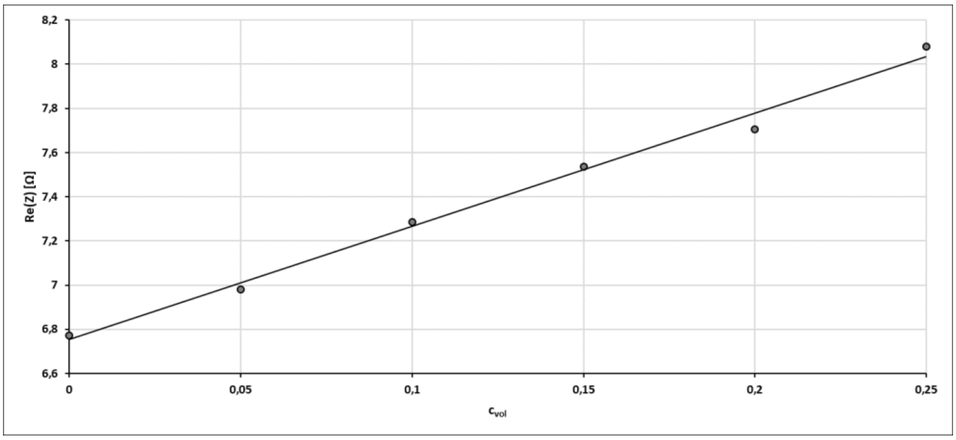

Figure 6. Impedance at zeroes imaginary part (*f* = 106 kHz) vs volumetric dilution with deionized water.

The real part is constant at frequencies close to 100 kHz, where the imaginary part tends to zero. Here it is appropriate to evaluate the real component. As evident from Figure 6, the real part of impedance at *f* = 106 kHz exhibits a linear dependence on sample concentration, with a correlation coefficient of $\mathrm{R}^2 = 0.992$.

Conclusion

The possibility of measuring the quality of the diesel engine exhaust fluid (DEF, AdBlue®) used in selective catalytic reduction (SCR) systems to reduce nitrogen oxide (NOx) emissions was discussed. The replacement of the DEF with water (tampering) is one of the important quality factors. The samples diluted in deionized water in the range of 0.05−0.25 vol. were prepared. Each sample was placed into a cylindrical cell made from cooper with volume of 20 mL. An impedance using Vector Network Analyzer – Bode 100 (OMICRON-LAB) with frequency range from 100 Hz to 50 MHz was measured. Water has a significant effect on the change of impedance compared to samples with a small dilution. The real part of impedance at resonance exhibits a linear dependence on sample concentration, with a correlation coefficient $\mathrm{R}^2 = 0.992$.

References

1. Carslaw D., Farren N., Vaughan A., Drysdale W., Young S., Lee J.: Atmos. Environ., *1*, 100002 (2019).
2. Koebel M., Madia G., Elsener M.: Catal. Today, *73*, 239 (2002).
3. Classen T., Sahner K.: D3. 1-Trends in Automotive Exhaust Gas Sensing. Proceedings SENSOR 2011, 554 (2011).
4 Fendri A., Büschel P., Abelkafi A, Kanoun O.: P7 – Spectroscopy. Proceedings SENSOR 2015, 830 (2015).

ECONOMICS OF CHEMICAL INDUSTRY

POSSIBILITIES OF IMPLEMENTATION OF CIRCULAR ECONOMY PRINCIPLES IN MEDIUM-SIZED ENTERPRISES OF THE CHEMICAL INDUSTRY IN THE CZECH REPUBLIC

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Abstract

In connection with the introduction of sustainable procedures and solutions into corporate practice, new topics are coming to the fore, including the circular economy. Its goal is to reduce the consumption of natural resources in the economy, it is based on the principle of closing or circulating flows within product and material systems, even taking into account other aspects of sustainable development. To achieve the goals of the circular economy, so-called R-strategies were developed. Among the most common are the 3Rs: Reduce, Re-use, Recycle, these were gradually supplemented by strategies such as Refuse, Rethink, Repair, Refurbish, Remanufacture, Repurpose, or Recover. The transition to a circular economy thus requires innovations, new business models or social-institutional changes, focusing already on the product design phase and evaluating all phases of the product life cycle. This contribution summarizes the results of the research, the main goal of which was to find out how small and medium-sized enterprises are affected by this new direction, what activities they implement in this area, what obstacles they face, and how they perceive threats, as well as opportunities. What are the reasons for introducing the principles of the circular economy. Specifically, companies from the chemical industry were selected. The research was carried out using qualitative research methods including personal interviews and discussions with representatives of selected companies.

Introduction

The circular economy has become a key issue in sustainable development as the traditional linear model of production and consumption causes environmental degradation and threatens the availability of resources needed for economic growth. The concept of circular economy cannot be considered as a novel idea, but it has received more attention in the last 10 years, both among academics and practitioners. It focuses on the circularisation of material flows and the efficient use of resources to minimise waste and reduce consumption and dependence on primary raw materials. In the circular economy, resources are re-used, and products are designed to be recyclable and reusable, upgradable, etc. As interest in the circular economy grows, different definitions of the concept are emerging across the literature[1]. According to the Ellen MacArthur foundation, the most common definition of the circular economy is as an industrial economy that is restoring and regenerative, based on the principles of eliminating waste and pollution, including the release of greenhouse gases and hazardous substances, as well as the circulation of products and materials with the highest possible value, and on the regeneration of nature[2]. An analysis of 114 definitions of circular economy across scholarly publications showed that recycling is most frequently mentioned term, followed by re-use and resources reduction, with the least mentioned term recovery; the most frequent definitions focus on the environmental and economic domains of sustainability, and the least on the social part[2]. According to the European Union, the circular economy aims to preserve the long-term value of products, materials, and resources by returning them to the product cycle in the post-use phase, it is also a model in which waste is minimised; it is a model of production and consumption that involves sharing, leasing, reusing, repairing, refurbishing and recycling existing materials and products for as long as possible[3].

The principles of circular economy are often associated with the so-called R-strategies, with the 3Rs: Reduce, Reuse, Recycle being the most widely used framework for circular strategies, however, R strategies were further extended from R0 up to R9[4] and also elaborated to implementation of circular strategies at the corporate level[5]. The lower the circular strategy number, the less materials and energy are required to implement it, thus reducing the pressure on the environment. Stahel and MacArthur[6] recognizes a "high-value route" after the end-of-life of products, which preserves as much value as possible from used products and waste for as long as possible using R-strategies. The other route is then to try to extract atoms and molecules from them in their highest possible quality and purity for reuse, the so-called "low-value route", where various D-strategies find their application, such as: de-polymerise, de-alloy, de-laminate, de-vulcanise, de-coat, etc[6].

The circular economy can be built on macro, meso and micro levels[2]. At the macro level, two approaches can be used to transition to a circular economy[7]:

- Top down – legislation and policy, supporting infrastructure, social awareness,
- Bottom up – collaborative business models, product design, supply chain.

It is important to address the transition to the circular economy at all levels of the economy, including the level of manufacturing companies. The literature offers various tools to implement the circular economy in corporate business models. However, so far little attention has been paid to the design of a structured approach for the implementation of the circular economy in small and middle enterprises[8]. Chemical manufacturing companies have a specific position, which is associated with both possible the negative and positive aspects of their activities for society and the environment, as they can contribute to the transition to the circular economy of other subject actors, for example in recycling and separation processes. With the operation of sustainable chemical production, the term Green Chemistry has become established. This framework has been further elaborated into 12 or 15 principles of circular green chemistry[9]. The need is to optimize design of the process to enable efficient separation, purification, reuse, and recycling of waste products in an environmentally friendly manner, while at the same time, through the efforts of distribution links to reformulate formulations, rethink material inputs and strengthen their commitment to sustainability, chemical companies will be in an ideal position to drive their own growth while gaining a better competitive position. Active collaboration on common goals across the distribution chain will be key. For example, chemical companies can provide important advice and technical skills.

Implementing circular strategies can be a challenge for companies due to financial, technological, or organisational barriers. There is also the problem of a lack of company awareness, which can hinder the full potential of the circular economy. Obstacles of Barriers to the transition to the circular economy can be seen in various areas: cultural, legislative, market and technological barriers. They stem, for example, from the habits, consumption patterns and behaviour of the links in the distribution chain and end-users; they are related to the lack of interest and awareness of customers and the habit of operating in a linear system, with a hesitant corporate culture[10]. Legislative barriers are related to the lack of action, especially in the areas of ownership, finance, and transport of waste across borders[11]. Kumar et al.[12] points to the lack of a standardized system to measure performance, ineffective recycling rules, and poor enforcement and support for legislation. Kirchherr et al.[10] adds the high cost of recycled materials and the high economic cost of CE investment, etc.

Research methodology

The aim of the research was to find out how companies are affected by the onset of the circular economy, what activities they implement in this area, what obstacles they face and what opportunities the circular economy offers to these companies. The research was carried out using a qualitative analysis of two companies of the chemical industry. Both companies belong to traditional Czech manufacturing companies, producing consumer chemicals, sold both on the Czech market and in other countries of the European Union. Both companies implement both serial production and custom production with development and adjustment according to the customer's wishes. Primary data was obtained using a controlled interview with representatives of both companies, and secondary data from websites and annual reports. To evaluate the degree of implementation of circular measures in these companies, the frameworks 0-9R and Scanner of circular strategies were used.

Discussion and result analysis

Profile of the companies

The two companies have different approaches to managing their activities with an awareness of their contribution to sustainable development and the implementation of circular economy principles, and similarly have different attitudes towards the introduction of environmentally friendly products, where one only complies with legislative regulations and considers environmental products uncompetitive, while the other sees them as an opportunity and introduces practices towards sustainable development out of the owners' and management's own conviction. Only the second company has both an environmental management system and an eco-label for some products. Both enterprises, however, have a certified quality management system and food safety standards, and also pay attention to the social pillar of sustainable development, for example in the ratio of men and women in management positions or the employment of people with disabilities. None of the companies publish an annual non-financial report on sustainable development.

Use of circular strategies

The R0-R9 strategy framework[4] and the Circular Strategy Scanner framework of Blomsma et al.[5] was used to describe and categorize specific circular strategies in the analysed companies.

Framework R0-R9

The results of the analysis show what strategies companies are choosing for the transition to the circular economy and what specific activities they are implementing in this area.

R0 – Refuse

- The use of Refuse strategy is often not obvious in corporate practice.
- For both companies it can be identified in the form of a refusal to purchase a new line that would only produce a certain type of product, as both companies use modular lines that can produce several types of products. This results in a reduction in a certain product amount (line) that is actually needed. In the case of these companies, there is a type of internal sharing, which extends this activity to the following strategy R1 – Rethink.

R1 – Rethink

- Sharing is an important activity within the Rethink strategy. The results of the research showed that one of the companies' shares its production capacity, specifically providing custom product packaging services to other companies, with the company standing on both sides, offering the service for some products and buying it for others.
- Packaging design is an important activity of this strategy to ensure that products are completely emptied from their packaging.
- The research showed that neither company uses chemical leasing. This is due to the cost of implementation, lack of capacity, and the impossibility of regenerating chemicals due to their consumable nature.

R2 – Reduce

- Both companies achieve raw material savings through optimization and regular maintenance of production facilities.
- Furthermore, in the case of precision packaging, both companies have confirmed the production of concentrated product variants mainly for the B2B market and professional use, thereby reducing the consumption of packaging materials, using the product more efficiently and reducing the number of shipments and the quantities transported.
- One of the companies further reduces the amount of material used by using the minimum possible thickness of the packaging.
- Both companies place emphasis on the possibility of precise dosing of the product, particularly through the use of measuring cups integrated in the product caps.
- A clear trend in companies is also to reduce energy and water consumption, thanks to efficient production planning so that processes with the same production technology build on each other and there is no need for frequent system flushing. A steam generation plan is used to heat the steam so that it is maximally used in as many processes as possible. The planned activity is also to save energy by changing the state of the feedstock. One of the enterprises has reduced energy consumption mainly through the installation of a photovoltaic power plant, furthermore, it uses waste heat for heating and hot water, or the enterprises replace lighting with energy saving LED bulbs.

R3 – Reuse

- Both companies apply Reuse principle in production, for example by returning products that do not meet the output control back into the production process.
- The use of take-back programmes is a common company practice, companies have packaging accounts with their suppliers – mainly Euro pallets, IBC tanks and drums are circulated.
- Reuse principles can also be applied to the use of non-standardised pallets for handling in your own warehouse or for non-standard goods. Discarded pallets and tanks are also sold to employees for personal use (the circular Repurpose strategy is also applicable here).
- The use of discarded lines for the production of smaller batches of products where production on new lines with higher production volumes would be uneconomical was also identified.

R4 – Repair

- Companies have implemented preventive maintenance plans for equipment and buildings. As such, the companies' products cannot be repaired.
- Repair activities include repairs of euro pallets, either by external or internal forces.

R5 – Refurbish

- The use of this strategy's activities can be found in the modernisation and upgrade of product transport pipelines, such as the replacement of manual shunts with modern electric ones and includes the upgrading of buildings and equipment recently carried out by both companies.

R6 – Remanufacture

- An identified activity of this strategy is, for example, the use of parts of decommissioned production facilities in the construction of new ones. However, enterprises are finding that the decommissioned equipment and lines are no longer compatible with the new ones.

R7 – Repurpose

- Companies use this circular strategy mainly through the modification of discarded lines for the production of new products.

R8 – Recycle

- The products of both companies cannot be recycled as such, due to their consumer nature, so the focus of the companies' recycling efforts is on packaging materials. Both companies aim to use packaging for their products that contains as much recycled plastic as possible and is reasonably priced. The proportion of recycled plastic is normally 30% of the total weight of the packaging, and in selected cases, according to the requirements of the foreign customer, the packaging is made of 100% recycled PET. This is due to the country's tax on imports of non-recycled plastic packaging.
- Of course, the separation of waste and packaging material within the company is a matter of course for both companies.
- Most of the packaging for both companies' products is recyclable, with the exception of the caps.

R9 – Recover

- Both companies use waste-to-energy principles. Installed waste pits have been identified, which, once filled, are taken away and incinerated in an energy recovery plant. Or the use of sludge from the wastewater treatment plant itself.

A framework based on the Circular Strategy Scanner of Blomsma et al.[5]

The research results were further organized according to the Circular Strategies Scanner by Blomsma et al.[5], see the following Table I.

Table I.
Scanner of circular strategies used by enterprises

Circular Strategies Scanner			
Reinvent		**Recirculate - products/equipment and their use**	
Efforts to reduce resource consumption	1/1	Upgradability	1/0
Rethink and reconfigure		Reuse (for packaging)	1/1
Extending product lifetime	0/1	Repair	1/1
Access and availability (sharing)	1/0	Refurbish	1/1
Result and performance (of the service)	0/0	Remanufacture	0/1
Restore, reduce and avoid		Repurpose	1/1
Raw materials for products and packaging		**Recirculate – materials**	
Renewable resources (packaging)	1/1	Recycle (for packaging)	1/1
Recyclable materials	1/1	Recover	1/1
Secondary sources	1/1	**Logistics**	
Restorative resourcing	0/0	Reduction in quantity/weight of products	1/1
Non-toxic and benign materials	1/1	Reduction in packaging quantity	0/1
Lowest suitable grade	0/1	**Energy**	
Production		Energy saving	1/1
Lean manufacturing and cleaner production	0/1	Energy recovery	0/1
Pre-employability	1/0	Renewable resources	0/1
Recycling in production	1/1		
Recover	1/1		
Use and operation of the product			
Low consumption of resources by a product	1/1		

This framework is designed for manufacturing companies and can be adapted to companies with chemical production, specifically packaging materials were included in the Raw Materials group and activities related to production facilities were included in the Recirculation group. This framework doesn´t consider the circular strategies that cannot be implemented in enterprises due to the nature of the production and the products produced. These are circular strategies: long technological life of the product, long moral life of the product, cascading for final products, cascading by-products from production, offering multiple products from one source (production), use of unused product capacity, renewable resources (products). Due to the similar focus of the two enterprises, the use of circular strategies is similar, yet it is possible to find strategies that are not used by either or only one of the enterprises: 1 represents the first/second company that implements the given activity, 0 represents the first/second company that doesn´t implement the given activity.

Assessment of perceived benefits and barriers

Benefits

Both companies perceive the benefits of implementing circular strategies primarily in the economic sphere. The most frequently cited are cost reductions associated with savings from production optimisation, reduction of raw material costs, energy costs and transport of packaging to the plant. Revenues are mainly generated from the sale of certain waste (discarded equipment, paper or packaging film). Similarly, these benefits have been reported in the literature[13,14,4]. Both companies perceive a better reputation and competitive advantage associated with a better environmental profile, also mentioned by Yin et al.[13].

Another benefit is better readiness for tightening legislation. One of the companies also expects increasing pressure from end-customers and customers, to which it can be prepared to respond by implementing circularity measures.

Barriers

Among the barriers perceived by both companies is the too rapidly changing legislation, which forces them to allocate part of their resources to changes in recipes and production processes, thus not focusing on environmental protection in other areas. Legislation burdens the costs of companies, both in terms of waste and packaging payments and in terms of innovation costs, where inputs have to be replaced by new ones, and it also triggers interventions in production processes, or the costs of monitoring the preparation of changes and the changes themselves. Another barrier that emerged from the research is the lack of positive motivation and legislative support from the state. For example, the charges for produced plastic packaging are constantly increasing, while the benefits for recycled packaging are minimal, similarly see Kumar et al.[12].

Another barrier common to both companies is the current lack of interest of end customers in organic products, due to the higher purchase price, which was also pointed out by Kirchherr et al.[10]. The research also revealed a barrier in the form of end customers' lack of trust in the functionality of these products. The companies then disagree on whether this is a temporary phenomenon or a long-term trend. The positive perception of this situation may stem from the fact that they have already successfully introduced a green range of cleaning products.

The market barriers for recycled materials are common to both companies. The higher price of recycled plastic packaging is significantly reflected in the final price of the product. The different properties of materials with different recycled content are associated with higher scrap rates and slower production when blowing out the packaging.

Conclusion

Although circular strategies are more visible in enterprises of the mechanical industry, it is also possible to identify circular activities in the chemical sector, at all levels of R strategies from R0 to R9. Measures can be observed in all the areas from production, logistics, energy, and raw materials. Most of the implemented measures comes from normal business practice, but it is also possible to identify activities that are based on the company's innovative approach, reflecting new trends and new technologies. The COVID-19 pandemic probably also had an impact on the measures. Businesses were forced to save material due to its unavailability and look for other ways to replace it. New measures were implemented that are in line with the principles of the circular economy. A number of activities also result from valid legislation and customer requirements, or the implementation of environmental quality control systems or critical points.

In both companies, you can find certain activities that the companies do not implement, or only one does, even though their implementation would be beneficial. The reason for their non-acceptance may be a hesitant corporate culture and the habit of operating in a linear system[10]. These are mostly strategies where consumption habits or business models change and product design innovations or high investments are introduced. Examples of these circular strategies include:

- Offering a product as a service, which is based on close cooperation between the supplier and the customer.
- Establishing partnerships and developing circular solutions with customers (packaging-free partnership).
- Redesign of packaging towards lower material demand and sharing of free capacities, which, according to the results, was always used by only one of the companies.
- Using digital platforms for buying and selling waste, causing small changes in consumption behaviour. Waste can be purchased and used by other companies as raw material for their production.
- Use of restorative resources.

The study shows that both companies are already implementing some circular strategies and measures but are still facing some obstacles to full implementation. The main obstacles include, for example, a lack of financial resources, insufficient legislative support of circular activities, the difficulty of changing internal processes and corporate culture, and insufficient availability of technology. Although these obstacles are significant, the results also showed many opportunities, including maintaining competitiveness in the future. Research in this area can further help businesses develop sustainable and circular business models.

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References

1. Grafström J., Aasmas S.: J. Clean. Prod. 292, 2 (2021)
2. Kirchherr J., Reike D., Hekkert M.: Resour. Conserv. Recy. 127 (2017)
3. Eurostat: Circular economy – Overview. Brusel (2023)
4. Potting J., Hekkert M., Worrell E.: Circular economy: Measuring innovation in the product chain. The Hague. (2017)
5. Blomsma F., Pieroni M., Kravchenko M., Pigosso D.C.A., Hildenbrand J., Kristinsdottir A.R., Kristoffersen E., Shahbazi S., Nielsen K.D., Jönbrink A.K., Li J., Wiik C, McAloone T.C.: J. Clean. Prod. 241, 20 (2019)
6. Stahel W.R., MacArthur E.: The Circular Economy, New York: Routledge (2019)
7. Lieder M., Rashid A.: J. Clean. Prod. 115 (2016)
8. Prieto-Sandoval V., Torres-Guevara L.E., Ormazabal M., Jaca C.: J. Ind. Engineering Manage. 14(3) (2021)
9. Keijer T., Bakker V., Slootweg J.C.: Nat Chem 11(3) (2019)
10. Kirchherr J., Piscicelli L., Bour R., Kostense-Smit E., Muller J., Huibrechtse-Truijens A., Hekkert M.: Ecol. Econ. 150(150) (2018)
11. Badhotiya, G.K., Avikal, S., Soni, G. and Sengar, N.: Int. J. Productiv. Perform. Manage. 71(3) (2021)
12. Kumar V., Sezersan I., Garza-Reyes J.A., Gonzalez E.D.R.S., Al-Shboul M.A.: Manage. Decis. 57(4) (2019)
13. Yin, S., Jia, F., Chen, L., Wang, Q.: Resour. Conserv. Recy. 190 (2023)
14. Linder M., Williander M.: Bus. Strateg. Environ. 26(2) (2017)

SUSTAINABLE HUMAN RESOURCES MANAGEMENT

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Abstract

Sustainable development is a concept that has been worked with for many years. However, sustainable human resource management has only appeared in the literature in the last 15 years and the content of this concept is not yet fully unified. Whatever the view, in what is still a very global and highly competitive world, the issue of sustainable human resource management will also have to be faced by chemical companies relatively soon.

This article presents selected Czech results of a major international survey on sustainable development issues. It focuses on comparing the differences found between industrial and service enterprises and suggests basic ways to introduce sustainable human resource management in chemical enterprises. The expected significant difference between industry and services was found to be the offering of remote work (p-value = .00035). Surprisingly, industrial enterprises were found to be significantly more likely than services (p-value = .00057) to tie a portion of employee compensation to compliance with CSR objectives. The research also confirmed high employee job satisfaction.

Introduction

In the history of management, there have been several phases when people were seen more as working tools or accessories to machines and then approaches that gave them back their dignity. After scientific management came to the school of interpersonal relations, the leaning towards management by quantitative methods was followed by empirical approaches[1]. There was also a period of increased interest in HRM as an activity. In the 1980s it was rewards and their link to performance, with very little interest in wellbeing or social responsibility; in the 1990s, harder to measure social indicators such as wellbeing began to be added to easily measurable financial indicators, and by the end of the 20th century strategic HR management[2] emerged along with human capital theory. In the 21st century, equal opportunities, employee well-being and corporate social responsibility began to be discussed. Strategic HR management had relatively little interest in employee well-being[2], but about fifteen years ago the concept of sustainable HR management emerged and could grow into one of the main concepts of HRM.

Sustainable HRM is based on the idea of (sustainable) development, i.e. development that preserves resources and conditions for development for future generations. This idea is already well known and generally accepted, although its concrete application in everyday life is not easy and not welcomed by all. Nevertheless, many companies are building not only on the economic but also on the environmental and social pillars. In general terms, sustainability is mostly understood as environmental protection, but until the Covid pandemic, global thinking and long-term planning were also quite successful, with resources or products often being transported over very long distances. The drastic reduction of transport in times of crisis, but also the environmental demands and scarcity of resources are again pushing for more self-sufficiency and more local thinking. The benefits of sustainable development include energy efficiency, social stability, and environmental improvements. In this context, it is also possible to encounter the term Green Human Resource Management, i.e. sustainable human resource management with a primary focus on environmental protection[3].

Even though the number of papers about sustainable HRM and organizational sustainability is growing, based on the literature review from 1990-2020, it seems needs to be clarified which HR practices characterize the core concept for sustainable leading and managing people. It can build on organizational fairness, the quality of relations between supervisors and subordinates, performance appraisal, pay-for-performance, and work-life balance[4].

Ehnert et al. (2014) in Kumar[5] defined sustainability as a concept for providing new solutions and making economic systems and organisations more viable over the long term with less harm to society and the world's well-being. According to him, Human resource management has a great role in its practical assimilation. Jílková[6] highlights the crucial role of human capital in driving sustainable corporate strategies and their correlation with Corporate Social Responsibility. The research emphasizes the necessity of supporting flexible working arrangements during the COVID-19 crisis and advocates for increased investment in employee education to achieve long-term sustainability. Additionally, the study shows the significance of a well-structured benefit system in fostering employee satisfaction and loyalty, ultimately contributing to the overall success of the organization's sustainability efforts.

Foreign sources provide several possible interpretations of the term sustainable human resource management. Almost always, they pursue sustainability in its pillars (environmental, economic and social). Sometimes the focus is on managing people so that the organisation can achieve its goals in a sustainable way, sometimes it is on engaging people in volunteer activities, thereby enhancing the company's image as a socially responsible organisation, and still other times the focus is on actually having sustainable employees[7]. This includes socially responsible recruitment, placement and dismissal of employees. Practices are put in place that look at fairness, equality and employee well-being.

Kumar[5] also defined barriers to SHRM implementation. These include a lack of resources, time, support from management or technical support, high costs and staff reluctance.

A closer examination of the area of sustainable human resource management reveals yet another pattern. According to it, sustainable HRM means managing people to be employable throughout their working life. It is not entirely clear whether this employability is to be made possible by the company developing all its employees and offering them motivating work throughout their working careers, or rather by offering, in addition to training, a work environment suitable for entry-level workers, those in their 'prime' and even for employees at the end of their working lives. We prefer the latter interpretation, which is more about the employability of anyone, although age management issues are most often considered.

The characteristics of sustainable human resource management are therefore long-term orientation, employee care and development, employee participation in management, fairness and equality[8] and take diversity[9]. Individual aspects are of course also present in the previously mentioned concepts of sustainable HR. In addition to a more individualised approach, such people management also requires investment in adapting the working environment to the requirements of individual (groups of) employees. However, this is a model that we consider to be very necessary. The world is changing, a new generation is coming along and it is no longer enough to be able to compete with your direct competitors, but it is also necessary to identify conditions in seemingly unrelated areas. Even in chemical companies, many professions can accept an offer from a completely different field. These are mainly service and managerial positions, those that can relatively easily apply their skills elsewhere - security, catering, IT, accounting, HR, partly maintenance, purchasing, marketing, law and others.

Employability needs to adjust working conditions and develop employees, often offering them retraining in completely different areas. Especially the youngest generations (Y and Z) want, among other things, interesting work and are willing to leave their current jobs for it. Retraining them allows them to work in a different position without the company losing the investment it has made in them. Using a sample of 391 employees across sectors and generations, Vraňáková[8] found that in Slovakia, three of the eight pillars offered for job retention are generally considered the most important, namely: “Satisfied life”, “Ensuring good workability and motivation” and “High level of competencies”.

Ensuring good workability and, in particular, a high level of competence directly requires employee development. However, due to its diversity, it is difficult to provide it within the organisation at a sufficient level for all the required areas of training. Online courses are often the solution. We anticipate that this is a trend that will become even more pronounced over time and that micro-courses will be created to update or acquire specific competencies. Similar courses already exist today and include, for example, the digiDozent project, developed under the Erasmus+ programme, aimed at increasing competencies in digital learning. It is an e-learning course that is very suitable for professionals who have to start delivering training themselves. Implementing training in the company by oneself is another common solution to the need to increase the competencies of employees and at the same time strengthen the motivation of employees selected as trainers. Practice shows that while in industrial enterprises, specific competencies are often needed in particular, which are relatively easy to acquire through in-house training, in the service sector external training is more widely used. The differences in the understanding and implementation of sustainable human resource management between industrial and service enterprises are the focus of this paper, which draws on Czech data for an international comparative study. It aims to find out whether industrial enterprises are sufficiently prepared to implement sustainable HRM.

Methodology and research

The data for this article was collected as part of an international study of sustainable human resource management involving a total of 46 countries. For this article, only data from the Czech Republic are used, for which the take question was integrated, asking from which area of the economy the respondent's company originates. Only industrial enterprises as a whole were included, no distinction was made between industry types. Other areas were services, education, health care and others.

205 respondents participated in the survey, 111 of whom were from industrial enterprises. The total number of questions was 75 and covered the following areas:

- SHRM practices
- Green HRM
- Job satisfaction
- Wellbeing
- Work engagement
- Personal values

Each question was answered by a five-point Likert scale with 1 as the worst and 5 as the best result. For this article, only the answers to the selected questions were selected. The survey was conducted in the fall of 2022, the questionnaires were placed on a google doc platform, and respondents were sent a link and asked to share it with their network of contacts.

Given the preferred view of sustainable management as keeping people employed throughout their working lives, we focused on job satisfaction issues and then compared industrial and non-industrial companies.

Testing was carried out with Student's t-test and chi-square test in contingency tables.

Job satisfaction

Job satisfaction was directly examined by the question "All in all I am satisfied with my job". Surprisingly, respondents were extremely satisfied (average was 4.21), both in industrial companies (average 4.22) and in other companies (average 4.09). Only six respondents answered that they disagree with the claim “All in all I am satisfied in my job”. Also, only 6 of them agreed (none of them strongly agreed) with the claim “In general, I do not like my job” and only 9 of them disagreed with the claim “In general, I like working here”. Since in further investigation, we wanted to assess the dependence of satisfaction on various factors, we decided to look for another item that should correlate with satisfaction, but whose answers would not be as strongly positive. We chose the item "When someone criticizes my company, it feels like a personal insult", which we believe reflects loyalty to the company, which is also a very important characteristic for employee sustainability. The average rating for this item was 3.55, for industrial companies it was 3.67 with a standard deviation of 0.971 and for other companies, it was 3.48 (st. deviation 0.976).

Comparison of industrial and other companies

Across all questions, except for work engagement and personal values, we identified only three items where the responses of respondents from industrial enterprises were significantly different from those of other respondents. These are shown in Table 1, together with a statistical analysis of the item "We have skill training programmes and continuous learning that support workers' employability", which we consider important given the assumed need for training to maintain employability.

Table I

Basic comparison of Industry and Services companies

Items	Industry		Services		Analyses
	Average	Standard deviation	Average	Standard deviation	p-Value
We promote working at home	2.49	1.138	3.67	1.262	0.00035
We provide adequate compensation to employees if leaving a company or retiring	3.35	1.336	2.74	1.430	0.01720
We link part of the compensation to employees' compliance with corporate social responsibility goals	2.47	1.130	1.83	1.067	0.00057
We have skill training programmes and continuous learning that support workers' employability	3.16	1.270	2.96	1.440	0.16814

Evaluation of the dependence of job satisfaction on selected factors

As already mentioned, we consider competence development through training to be a very important factor for sustainable human resource management. Therefore, statements related to training were correlated with job satisfaction. Job satisfaction presented in basic claims was extremely high. In the case of using job satisfaction, we would have to integrate intervals of answers so much that we lose too much information. We decided to use the claim "When someone criticizes my company, it feels like a personal insult". We believe, that a loyal employee is usually satisfied, but not all satisfied employees are also loyal.
We also performed correlations with factors in which the responses of respondents from industrial enterprises were significantly different from those of other respondents. Table 2 and Table 3 summarize the results.

Table 2
Contingency tables tests

Value 1: When someone criticizes my company, it feels like a personal insult	p-Value
Value 2a: We have skill training programmes and continuous learning that support workers' employability	0.856
Value 2b: We implement specific programmes to facilitate the adaptation and integration of new candidates	0.226
Value 2c: We promote working at home	0.229

Table 3
Contingency tables tests (Industry only)

Value 1: When someone criticizes my company, it feels like a personal insult	p-Value
Value 2a: We have skill training programmes and continuous learning that support workers' employability	0.851
Value 2b: We link part of the compensation to employees' compliance with corporate social responsibility (CSR) goals	0.965
Value 2c: We promote working at home	0.464

Discussion and result analysis

Comparison of industrial and other companies

Unsurprisingly, the results showed that respondents from industrial enterprises were significantly less satisfied with the support for working from home. This may be because working from home is less feasible in the industry in general. It is probably also less supported, as the main focus is on production, on machinery. Even employees in managerial positions usually need to be in close contact with production, so it is better for the company if they work in situ. Since working from home is already seen as a basic benefit, it would be advisable to offer and promote it also in industrial enterprises. Of course, for positions where this is possible - economic, marketing, some managerial positions, etc., in accordance with results remote work is more evaluated by lower-level managers[10].
Another significant difference can be seen in the care of employees when they leave their jobs. Employees from industrial enterprises are significantly more satisfied with the support. This may be related to the persistent shortage of technically educated professionals, who are then generally better looked after by industrial enterprises.
Unsurprisingly, rewards in the industry are also significantly more closely linked to social responsibility goals. Given that industrial and especially chemical companies are under more scrutiny than utilities in terms of environmental protection, it is logical that they work more with social responsibility issues. On the other hand, many service companies also proclaim social responsibility in their PR. From this perspective, the average values achieved (2.47 and 1.83 respectively) are rather low.
Considering the focus of this paper, the degree of respondents' agreement with the existence of training programs to maintain employability was also assessed. The difference was non-significant and the responses showed that such programs are probably not sufficiently offered or promoted by enterprises (3.16 resp. 2.96).

Evaluation of the dependence of job satisfaction on selected factors

As already mentioned, the global job satisfaction was extremely high. This result is better than the results of a cross-sectional survey in the Czech Republic provided in the year 2019 on a sample of 1,271 respondents from different fields. Its average total satisfaction was between three and four on a six-point scale[11].

Using the claim “When someone criticizes my company, it feels like a personal insult” as a satisfaction indicator we could test the significance of training programs as a part of loyalty, but the results were not significant. Neither in the whole sample nor in industrial companies only. Interestingly, promoting the home office was not a significant factor for loyalty. Maybe it is already so frequently used benefit, that employees do not consider it important for their loyalty.

Conclusion

Sustainable Human Resources Management (SHRM) seems to be a new trend in the area of Human resources. It could be focused both on the sustainability of the company and the employability of employees. The study realized in the Czech Republic showed that there are only small non-significant differences in the implementation of SHRM between industry and service companies. One important difference is offering remote work, so also the industry should offer more remote work possibilities to improve employees' satisfaction.

Research has not shown that the training provided is important for job satisfaction. However, the increasing demands on employees imply a continuous improvement of competencies and it is likely that, given the popularity and prevalence of online activities, also training will be increasingly online. And since Generation Z entering the labour market, and Generation Y, which will gradually dominate it, are strongly oriented towards multitasking and concise, preferably pictorial information[12], the courses offered should take this into account. Short, narrowly focused e-learning courses using multiple media might be appropriate.

Further research would be useful to assess the extent to which staff can be trained and what types of courses they prefer to verify the previous conclusions.

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References

1. E Muldoon, J., Bendickson, J. S., Gur, F. A., Murphy, P. J.: Management's knowledge filter: entrepreneurship theory and the historic conceptual evolution of opportunism in management studies. J. Small. Bus. Ent. Dev. *3*, 402 (2022).
2. F Beer, M., Boselie, P., Brewster, C.: Back to the Future: Implications for the Field of HRM of the Multistakeholder Perspective Proposed 30 Years Ago. Hum. Resour. Manage. *54*, 427 (2015).
3. Bednaříková, M., Košťálová, J.: Green Human Resource Management in Companies of Czech Chemical Industry. In: 8th International Conference on Chemical Technology (ICCT 2021), on-line, 3-5. 5., 175, (2021).
4. Dvorakova, Z. Sustainable human resource management in the time of global uncertainty. In: SHS Web of Conferences. Vol. 83, May 13-14 2020, Bratislava, Slovak Republic (2020).
5. H Kumar, A., Bhaskar, P., Nadeem, S. P., Tyagi, M., Garza-Reyes, J. A.: Sustainability adoption through sustainable human resource management. Int. J. Math. En. Man. Sc *6*, 1014 (2020).
6. Jílková, P.: Sustainable Corporate Strategy: The Role of Human Capital in the Time of COVID-19 Crisis. TEM J. *2*, 699, (2021).
7. G Kramar, R.: Sustainable human resource management: six defining characteristics. Asia Pac. J. Hum. Resour. *60*, 146 (2022).
8. I Vraňaková, N., Gyurák Babeľová, Z., Chlpeková, A.: Sustainable Human Resource Management and Generational Diversity. Sustainability *13*, 8496 (2021).
9. Bednaříková, M., Košťálová, J., Vávra, J., Halamová, D.: Diversity management in the Context of Corporate Social Responsibility. In: 10th International Scientific Conference “Business and Management 2018”, 3–4. 5. 2018, Vilnius, Lithuania, 245, (2018).
10. Kowalski, G., Ślebarska, K.: Remote Working and Work Effectiveness: A Leader Perspective. Int. J. Environ. Res. Public Health *19*, 15326 (2022).
11. Zubr, V., Sokolova, M.: The Level of Job Satisfaction in the Czech Republic. In: 19th International Scientific Conference on Hradec Economic Days, 2-26.3. 2021, Hradec Králové, the Czech Republic, *11*, 957 (2021).
12. García-Carrión, B., Del Barrio-García, S., Muñoz-Leiva, F., Porcu, L.: Effect of social-media message congruence and generational cohort on visual attention and information-processing in culinary tourism: An eye-tracking study. J. Hosp. Tour. Res. *65*, 78 (2023).

WAYS TO IMPROVE THE COLLECTION AND RECYCLING OF SEPARATE WASTE IN THE SELECTED REGION – CASE STUDY

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Abstract

The global shift towards sustainable behaviour is also affecting waste management practices. Recycling is one way to reduce waste. It allows to apply the principles of circular economy by eliminating the single use of different types of materials. The paper deals with waste collection and recycling in a selected region of the Czech Republic and the possibilities of improving these processes. It presents the results of a primary qualitative research conducted in two phases, first in a company engaged in waste collection and sorting, then in a company implementing the recycling process itself. The research involved the collection of primary information through face-to-face interviews according to an interview scenario, which was complemented by observations. The research was aimed at identifying how to implement both the collecting process (in the first phase of the research) and the recycling process (in the second phase of the research), while identifying tools to improve these processes. The revealed tools can be classified into three basic groups, namely tools for the implementation of technical and technological innovations (concentrated mainly on cost savings), improvement of personnel processes (processes related to recruitment and selection of employees, adaptation processes and processes aimed at increasing work-friendliness) and tools enabling the use of optimization methods and models in the management of in-house processes (including the introduction of appropriate information technologies). The research results and their discussion can contribute to improving collecting and recycling not only in the companies where the primary research was conducted, but also in other companies operating in the Czech Republic. They can also be an inspiration for foreign companies, but only after considering the degree of similarity of the conditions under which companies of this type operate.

Introduction

Waste production rates are increasing. It is estimated that 2.24 billion tonnes of solid waste were produced globally in 2020, or approximately 0.79 kg per person per day. At the same time, waste production is expected to increase by 73% from 2020 levels to 3.88 billion tonnes by 2050. Population growth and urbanisation are cited as the main reasons for this increase in waste[1]. It is the difficult-to-accept increase in waste and the concomitant dangers arising from unsustainable waste management, especially in low-income countries, that is leading countries around the world to improve the practices applied in solid waste management[1,2].

Recycling is an important way to stop or even reduce the volume of waste produced. It contributes to the three basic rules of sustainability (reduce, reuse and recycle) and is also key in the transition from a linear to a circular economy[3]. It helps to loop direct flows by contributing to the recovery of virgin resources from used products and their packaging[4]. The ideal outcome of recycling is the gain of material that can be used for the same purpose as the primary resource, e.g., when recycling office paper results in recycled office paper[5]. Recycling has a number of environmental benefits. It prevents waste of potentially useful materials, conserves natural resources (such as wood, water and minerals), reduces the amount of waste taken to landfills and incinerators, reduces energy consumption, reduces and prevents air and water pollution, and helps in job creation[3,6].

The above-mentioned environmental benefits of recycling and its ability to contribute to sustainability have led to a great deal of attention being paid to recycling in recent years. In particular, the focus has been on increasing recycling volumes, on ways to improve recycling processes in relation to different types of materials and on reducing the disadvantages of recycling. These consist mainly in the possible economic inefficiency caused by the high investment costs in building a recycling unit[7], the creation of jobs in an unsuitable working environment, and the difficulty in securing quality of products made from recycled materials[8].

As the issue of obtaining quality of products made from recycled materials is closely linked to the quality of waste sorting, attention is also paid to this process. There are two main ways in which solid waste can be sorted, either at the level of households, which are obliged to sort waste into a certain number of categories, or in specialised sorting facilities. Traditionally, sorting at the household level was considered inconvenient because it takes up space and requires time and effort[9]. However, according to research results[9] there are households that prefer a greater extent of domestic waste sorting, even though third-party sorting allows the same goal to be achieved.

The Czech Republic stands out among the EU countries with one of the most efficient and cheapest sorting systems. 73% of the population actively sorts waste, 77% of packaging is sorted[10,11] and the total annual volume of sorted waste is approximately 755,000 tonnes. In terms of materials, mainly paper, plastics, glass, beverage cartons and metals are sorted[11]. While the figures above are certainly very good, it is nevertheless clear that the sorting system in the Czech Republic leaves much to be desired. The biggest space for improvement is in the sorting of bio-waste, batteries, electrical equipment and metals[12].

This paper focuses on the improvement of waste sorting systems in a selected region of the Czech Republic and the possibilities of improving the preparation of sorted waste for recycling and the recycling process itself in the selected company. It presents the results of a primary qualitative research conducted in two successive phases, first in the company providing the collection of sorted waste from the selected region and then in the company implementing the recycling process itself. The presented research results, their discussion and suggestions for improving the processes implemented in both companies can contribute to the improvement of both waste collecting and recycling processes, especially in the Czech Republic. The recommendations for improvement can be used in other countries as well, certainly after considering the degree of similarity of specific conditions. In effect, the results can therefore be used in improving sustainability.

Simulation and/or experiment

The main objective of the qualitative research was to identify ways to improve the processes implemented in the company providing the collection of sorted waste from the selected region as well as in the company implementing the recycling process itself. The research was carried out as a two-phase research.

The first phase of the research took place in a company that collects waste for recycling, fine-sorts it and prepares it for recycling. The sub-objectives of this phase of the research were to identify:

- the company's customers (municipalities),
- the organisation and implementation of waste collection,
- the method and place of sorting of individual materials,
- buyers of sorted materials,
- problems arising during waste collection and sorting.

The second phase of the research took place in the company implementing the actual recycling processes. The sub-objectives of this research phase were to identify:

- materials entering the recycling process,
- the recycling method and the recycling process,
- the output of the recycling process, its properties and its use,
- the problems of the recycling process.

In both phases of the research, primary data were collected using the in-depth interview method combined with observation. The in-depth interview was conducted according to a pre-prepared scenario. Observations were conducted during field trips in both companies to complement the in-depth interviews. The research took place in the spring months of 2022.

The primary data collection was followed by data processing. The method of data processing was content analysis of both the notes and the voice recording of the in-depth interviews.

Discussion and result analysis

Both phases of the research yielded a number of interesting findings and formed the basis for the formulation of recommendations for improving individual activities related to both the collection of materials for recycling and the recycling process itself.

The company specialised in the collection, fine-sorting and preparation of materials for recycling focuses mainly on plastics, paper, glass, beverage cartons and metals. It collects these materials from approximately 25 municipalities located in the selected region. It serves approximately 25.000 inhabitants. In addition to the collection itself, it provides training, consultancy services and the necessary administration. It is a small enterprise. A description of the activities carried out, the main problems associated with the activities and suggestions for improvement are shown in the following table (Table I.).

Table I.
Description of the individual activities of the collection, fine-sorting and preparation for recycling processes, the problems associated with these activities and suggestions for improvement

Activity	**Description of the activity**	**Problems associated with the activity**	**Suggestions to improve the activity**
Preparing the collection of materials for recycling	Provision of transparent bags for households and individuals doing business in the municipality	-	-
	Collection of sorted materials in transparent bags	Incorrect sorting by some residents	Education
Planning the collection of sorted waste	Manually via "collection cards" (planning respects the requirements of individual municipalities)	Manual planning without the use of software – time loss, elimination of the possibility to optimise transport routes	Introduction of a software tool for: • Collection planning • Waste collection records • Optimization of transport routes • Providing quick information to customers on the volume of sorted materials
Assignment of tasks to collection workers	Collection workers are given collection cards, according to which collection takes place	Shortage of workers, high turnover	Improve staffing activities, in particular: • Recruitment and selection • Training and adaptation Use motivational and incentive tools of human resources management in an extended form
Pick-up of sorted materials.	On the designated day, the transparent bags are placed in front of the houses and collected – the Kerbside collection system is applied	Shortage of workers, high turnover	Improve staffing activities, in particular: • Recruitment and selection • Training and adaptation Use motivational and incentive tools of human resources management in an extended form
Fine-sorting	Manual fine-sorting using a sorting line	Shortage of workers, high turnover	Improve staffing activities, in particular: • Recruitment and selection • Training and adaptation Use motivational and incentive tools of human resources management in an extended form
		The need to sort plastic materials by type of plastic	Shifting, at least partially, the responsibility for more detailed sorting to municipal residents and individuals doing business in the municipality Use of motivational and incentive instruments in relation to the municipal

Activity	Description of the activity	Problems associated with the activity	Suggestions to improve the activity
			population
		High proportion of manual work in a non-ideal working environment	Shifting, at least partially, the responsibility for more detailed sorting to municipal residents and individuals doing business in the municipality
			Use of motivational and incentive instruments in relation to the municipal population
		Staff errors in sorting	Improving the recruitment, selection, training, motivation and stimulation of employees
		Sorting line stops	Increase in the number of sorting lines and cooperation in fault elimination
Preparation of sorted waste for dispatch	Sorted materials are compressed to form transport units.	High proportion of manual work	Cooperation with the customer on transport optimization (application of the P-system for inventory management, connecting collections with other regions)
Transportation of sorted materials to the company carrying out the recycling process.	The activity takes place approximately once a month when the truck is full.	Long storage time for sorted waste	Cooperation with the customer on transport optimization (application of the P-system for inventory management, connecting collections with other regions)
		Variable collection date	Cooperation with the customer on transport optimization (application of the P-system for inventory management, connecting collections with other regions)

The company that carries out the actual recycling processes is engaged in the recycling of plastic waste from municipal sources. It buys input materials from companies engaged in sorting, coming from all over the Czech Republic, but only if specified conditions are met. The output of the recycling process is recycled material, from which it produces its own products. A description of the activities carried out, the main problems associated with the activities and suggestions for improvement are shown in the following table (Table II.).

Table II.
Description of the individual activities of the recycling process, the problems associated with these activities and suggestions for improvement

Activity	Description of the activity	Problems associated with the activity	Suggestions to improve the activity
Planning the recycling process	Planning is based on customer demand. The aim is to produce the required quantity in the shortest possible time	Existing restrictions consisting in the desire: • to minimize stops of production equipment and • to maximise the use of production capacity	Use of mathematical methods and models in planning (e.g. linear programming)

Activity	Description of the activity	Problems associated with the activity	Suggestions to improve the activity
Material input to the recycling process	The input to the recycling process is plastic in two forms, namely as mixed plastic and plastic film	Occurrence of materials degrading the recycled material	Input material control Sanctions against suppliers for repeated detection of mis-sorting
		Increasing amounts of polyethylene terephthalate in inputs to the recycling process	-
		Lack of inputs if the volume of sorted material is reduced	Motivating and stimulating households to sort
Recycling	Mechanical recycling, uninterrupted operation, production to stock	Energy intensity of the process	Use of roofs on the company premises for the location of a photovoltaic power plant. Technological innovation
		High process cost. Rising operating costs. Upward pressure on product prices	Use of roofs on the company premises for the location of a photovoltaic power plant. Technological innovation
		Permanent shortage of staff Low quality of staff	Higher wages Improving the recruitment, selection, training, motivation and stimulation of employees
Creation of products from recycled material (output from the recycling process)	A wide range of products is produced, especially for gardens and industrial applications. Possibility to customize products according to individual customer requirements	Durability of products limits the need to change products, limits the volume of sales in kind and financial units	Marketing communication in relation to potential customers focused on the presentation of product quality
Product assembly and application consulting	The offer includes the possibility of ordering transport and installation	-	-
Consumer complaints	Product quality complaints are handled (caused mainly by improper handling of products by customers, to a lesser extent by imperfections in the recycling process)	The subject of the complaint may be the twisting of the material caused by the poor quality of the input material and/or its storage in a humid environment	Storage of input material under controlled conditions

Conclusion

Recycling and how it can be improved has been a subject of academic interest and corporate practice for many decades. Typically, this interest has focused on discovering ways to improve the technological process itself, i.e., the way the material used is processed. However, improving recycling also has another dimension, namely improving the management of the process. It is then appropriate to consider not only the recycling itself, but also the sorting of the material that will enter the recycling process. The primary research carried out that there is quite significant scope for improving these processes. By deploying methods and tools suitable for managing different business processes, sorting and recycling processes can also be improved. Primarily, these tools can be divided into three basic groups, namely tools applicable in the field of:

- technical and technological innovation (concentrated mainly on cost savings),
- improvement of personnel processes (both recruitment and selection processes and adaptation processes, as well as processes aimed at increasing work-friendliness); and
- the introduction of appropriate information technologies and the use of optimisation methods and models for the management of in-house processes.

The above tools, or the groups of tools specified above, can be used individually to achieve partial (step-by-step) improvements in these processes, or they can be applied on a larger scale, optimally at the same time if the financial and organisational conditions are favourable. In such a case, a step change improvement in both collecting and recycling processes can be expected not only in the companies where the primary research was conducted, but in companies of this focus in general.

References

1. World Bank: Solid Waste Management. Retrieved January 15, 2023, from https://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management
2. Azevedo B.D., Scavarda L.F., Caiado R.G.G., Fuss M.: Waste Manage., *120*, 772 (2021).
3. Niaounakis M.: *Recycling of Flexible Plastic Packaging*. Elsevier, Oxford 2020.
4. Kirchherr, J. Resour. Conserv. Recy. *179(4)*, 106033 (2021).
5. Liu M., Tan S., Zhang M., He G., Chen Z., Fu Z., Luan C.: J. Environ. Manage, *255*, 109859 (2020).
6. Ervasti I., Miranda R., Kauranen I.: Waste Manage., *48*, 64 (2016).
7. Costa C.M., Barbosa J.C., Gonçalves R., H. Castro, H., Del Campo F.J., Lanceros-Méndez S.: Energy Storage Materials, *37*, 433 (2021).
8. Keramitsoglou K.M., Tsagarakis K.P.: Resour. Conserv. Recy, *70*, 55 (2013).
9. Czajkowski M., Kądziela T., Hanley N.: Resource and Energy Economics, *36(1)*, 290, (2014).
10. EKO-KOM: Systém sběru a recyklace obalových odpadů. Retrieved December 20, 2022, from https://www.ekokom.cz/
11. EKO-KOM: Systém EKO-KOM. Retrieved February 20, 2023, from https://www.ekokom.cz/
12. Ministry of the Environment of the Czech Republic: Waste management. Retrieved December 20, 2022, from https://www.mzp.cz/cz/odpadove_hospodarstvi

THE LOGISTICS IN THE CHEMICAL INDUSTRY

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Abstract

For a properly functioning production system of any type, properly functioning logistics is key (it mainly affects the amount of downtime, speed of production, quality of production and, to a large extent, the cost of production and requirements for the amount of capital tied up in inventories). Another important role of logistics is the transformation of the differences between the producer's production and the customer's consumption in place, time and quantity. In addition, logistics in the chemical industry is associated with a number of specifics, such as the transport and storage of flammable and dangerous substances, which require a special regime and safety measures. Or the fact that the heavy chemical industry produces input materials for other manufacturers and therefore it is a business and marketing concept B to B (B2B). Probably the most important input material for the chemical industry is crude oil. It is a key raw material for the functioning of any national economy of an industrially developed state. The problem is that its deposits in the world are very unevenly located, which makes it necessary to transport it in huge volumes over very long distances. The interesting thing is that the solution to this problem on a global scale is not dominated by oil pipelines, but by tankers. In the year 2000, long before the outbreak of the conflict in Ukraine, when a large amount of raw materials were imported to Europe from Russia, pipeline "Družba" transported crude oil and maximum transport capacity was 1.4 million barrels per day. That's a fraction of the 17 million barrels per day that was transported by ocean tankers from the Persian Gulf region to Asia and the US in the same year.

In our paper, we want to analyse some new development trends in logistics with regard to logistics related to the chemical industry, including pointing out the importance of maritime transport in international logistics and global trade. The goal is to describe and demonstrate with specific data how much our civilization is dependent on maritime transport for its existence. And further describe some specifics of logistics in the chemical industry.

Introduction

Any production needs input raw materials that must be brought, stored, transported from the warehouse to the place of production at the moment of their use, during the production process there is manipulation between workplaces and production phases, and when the finished product is created, it is distributed to the customer[8]. All these activities are ensured by logistics[4]. Over the past fifty years, logistics has become a very important field for many reasons. In all developed economies, there has been a qualitative jump in transport, which is able to replace the spatial proximity of individual producers[6]. Today's products are highly sophisticated and consist of a large number of components and in order to create the final product, it is necessary to bring all these components to one place at one time and in the specified quantity[9]. All this must be realized with minimal costs. Logistics routes are often very long and span different countries, as production factories are often decentralized in different parts of the world[6]. It is also a fact that many companies have moved their production to other states where labour costs are lower. This situation was made possible by the development of transport technology, which is capable of large-capacity transport over any distance. And this with relatively low costs, because the transport costs are divided among a large number of transported units precisely because the means of transport have a huge capacity[7]. Another important feature of today's business environment is intense competition. Thanks to the fact that it is possible to transport goods across states with relatively low costs, every manufacturer is confronted with competition from abroad[9]. The customer today has a choice and is well informed. Competition creates pressure on the efficiency of production, and here again logistics inside the production factory is very important, where it is necessary to ensure fast and high-quality production and eliminate excessively high stock levels[8]. With proper organization, it is possible to achieve a reduction in the inventory level, which will not lead to a lack of inventory and stop production[4, 6]. Another very important area of logistics is the distribution of finished products to customers. The customer is demanding and wants to order goods via the Internet and requests their delivery to their home. From what has been described, it follows that logistics is a very important part of business management for any type of production[9]. A number of new industries have emerged within logistics.

The field of logistics is very broad and constantly evolving. In recent years, the issue of environmental protection has been very topical, and logistics is also important here. E.g. in the return flow of waste and especially used packaging and their recycling[10]. At the end of the millennium, half of the world's waste was produced by the USA (5 % of the world's population) and 29 % of this waste was packaging (part of today's logistics are sectors such as: Reverse Logistics, Waste Logistics or Reverse Distribution)[6, 12]. Development and research in the chemical industry can play an important role in the recycling of materials and in the use of new materials that are more easily recycled. Europe produces a large amount of waste, is industrially developed and does not have enough raw materials for its industry, which it has to import. In addition, there is a need to replace the shortage of primary raw materials from Russia. Therefore, today all technologies capable of replacing primary raw materials with alternative materials are very important.

Importance of sea transportation

The development of logistics and international trade is related to the globalization of the world, the volume of world trade has increased sixteen times since the end of the 1970s, and half of world trade takes place over distances of more than 3,000 km, currently there are 50,000 cargo ships of all kinds (including oil tankers and ships transporting liquefied natural gas), maritime transport realizes 90 % of world trade[7].

When it comes to the transportation of goods, they are loaded into sea containers and these are transported using huge cargo ships. The largest ones have a capacity of over 22,000 TUE, where TUE stands for twenty foot equivalent unit, it is the volume of a sea container with standardized dimensions of 20 x 8 x 8.5 feet (approximately 6 x 2.4 x 2.6 meters). This is a huge amount, because one truck can fit either two such 20 feet long containers or one 40 feet long container. The greatest intensity of maritime transport, which carries goods, takes place between the EU states and Southeast Asia, where China dominates. The largest port in Europe is Rotterdam, through which goods with a volume of 14.3 million TUE per year pass, the largest port in the world is Shanghai with 43.5 million TUE per year[7]. Such huge volumes of transport can only be realized with the help of large ships transporting goods in sea containers. Sea containers have standardized dimensions and thanks to this it is possible to load goods into them. Then load the entire container onto a truck or railcar and take it to the port where it is simply loaded onto a ship. When the ship reaches the port, the containers are simply loaded with the goods again onto railway wagons or trucks. This practical system was devised by Malcolm McLean as early as 1956[7]. Since then, the capacities of container seagoing ships have increased until today, when the ship is approximately 480 m long and 60 m wide. Larger ships are not produced, the dimensions have reached their limits because the ship must be able to manoeuvre. This corresponds to the maximum capacity of around 24,000 TUE. Interestingly, the weight of this large ship without cargo is 235,000 tons.

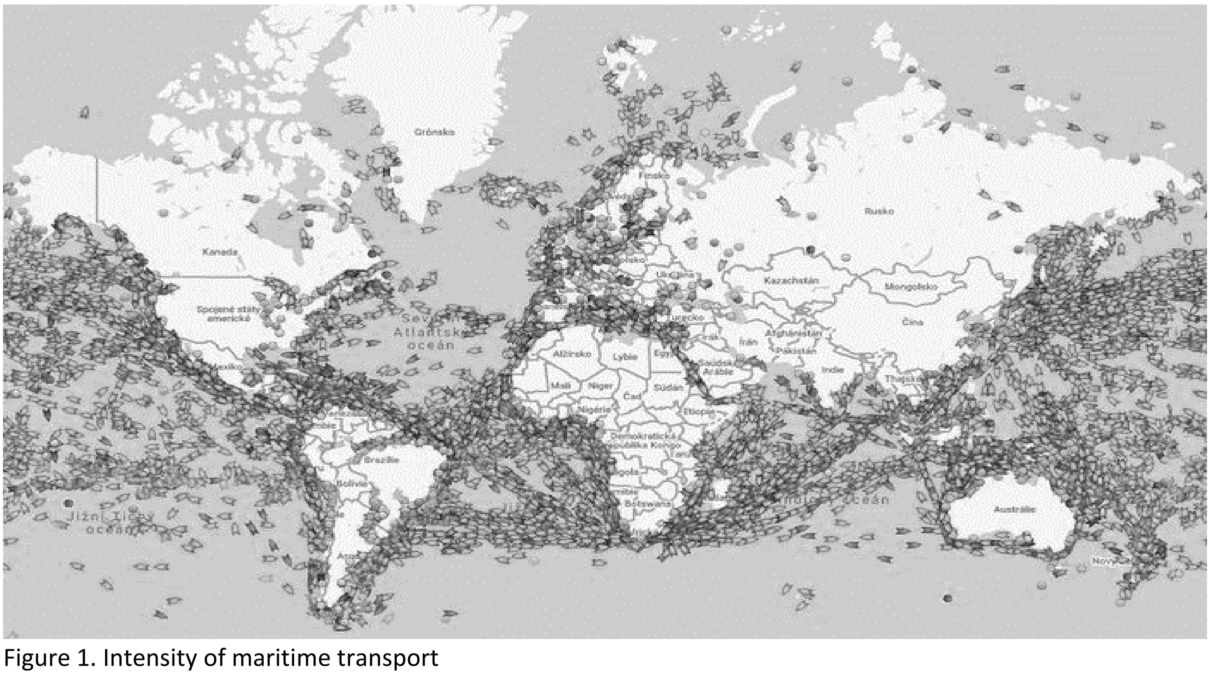

Figure 1. Intensity of maritime transport
Source: https://www.marinetraffic.com/ [11]

The advantage of these large cargo ships is their ability to transport a large volume of goods, on the other hand, the disadvantage is their slow speed, approximately 40 kilometres per hour. Other shipping alternatives are shipping goods from China to the EU by rail. This way is faster. Shipping by cargo ship takes 36 days and shipping by rail takes only 16 days. The problem is that the railway does not have such a large capacity to transport such a large volume of cargo that is transported nowadays. The intensity of current shipping is illustrated in Figure 1, which is a view of a marine radar that shows the current location of all ships on the oceans.

Another problem of land transport is the need to build a modern transport infrastructure in the many countries through which railway tracks run. The problem with such a railway corridor is that when there is a collision e.g. a sandstorm, a fault on the tracks, a fault on the railway machine, the corridor will be blocked. While the breakdown of a cargo ship on the ocean will not affect the transportation of other ships. The exception is the unfortunate event that happened on 23/03/2021, when the cargo ship Ever Given, carrying containers of goods from Asia to Europe, blocked the Suez Canal for nine days.

Another alternative to a sea route between Asia and Europe could be "northern route". The ships would sail north around Russia. The problem with this route is that it is near to the North Pole, which means that there is frost, ice and half a year of darkness.

We can state that the maritime route leading through the Suez Canal (or its alternative with sailing around Africa) cannot be replaced nowadays. The maritime route from the Chinese port of Shanghai to Europe via the Suez Canal currently accounts for 26 % of world trade, in 2019 the Suez Canal transported goods with a total weight of more than one billion tonnes (that was four times more than the Panama Canal)[7].

Crude oil transportation is a special chapter. Crude oil is the basic raw material for the chemical industry and other industries. It is used, for example, in the production of plastics, and nowadays plastics and products from the chemical industry make up around 20 % of the weight of every car produced[3]. It is the main raw material for powering internal combustion engines and because of this it has become a strategically important raw material. Today's globalized world and its economy needs huge volumes of transportation of raw materials, goods, population mobility, air transportation, sea transportation, cargo transportation, etc. It was mentioned above how many goods are transported by sea, and each large cargo ship for the transportation of sea containers consumes every day of sailing at with a full load of 200 to 250 tons of diesel. We have to realize that a ship is only capable of transporting goods by sea, but when it arrives at a port, these large volumes need to be transported further to their destination, and trains and trucks are used, and these trucks need a lot of diesel. It follows that every industrially and economically developed country needs a large amount of diesel for its functioning.

Crude oil deposits are distributed very unevenly in the world. Therefore, it is necessary to transport this important raw material over long distances. Crude oil can be efficiently transported in two ways. Pipeline transport using oil pipelines and shipping by sea using oil tankers. Or a combination of these methods, the oil is transported by tanker to a port, where it is pumped and transported overland by pipeline (e.g. the pipeline from Trieste in Italy). Maritime transport is very important for the transportation of crude oil. Most of the world's crude oil is transported by sea using oil tankers. An example is the situation in 2000, when 1.4 million barrels were transported to Europe from Russia every day, via pipeline system. But at the same time, 17 million barrels were transported by oil tankers from the Persian Gulf region.

Tankers move around the world's oceans in large numbers and each one is capable of carrying around 400,000 tons of crude oil. The US Energy Information Administration (EIA) reports that 60 % of the world's crude oil is transported by sea. The largest crude oil producers in the world are the states in the Persian Gulf region, and from there the crude oil is transported through the strait of Hormuz. 25 % of the world's crude oil production is transported through the strait of Hormuz, and at the same time 30 % of liquefied natural gas (LNG) is transported here[7].

We can say a not very optimistic conclusion that if some unexpected situation were to occur and sea transport routes were blocked for a long time, it would mean the end of our civilization in this form as we know it. At the same time, such a situation is not completely unrealistic, since it would be enough to block one of the strategically important straits or canals.

Specifics of logistics in the chemical industry

The war in Ukraine and the related economic sanctions on Russia represent a new challenge for Europe. There was a logistically complex event where it was necessary to quickly find new suppliers of raw materials such as crude oil, natural gas, coal, fertilizers, etc. and organize their transportation from other places in the world. From September 2022, almost no coal will be imported from Russia to the EU. In 2021, the share of crude oil imported from Russia to Europe was 25 %, a year later it fell to 14 %, the share of natural gas was 30 % and fell to 20 % [1]. For some countries, the dependence was even higher. Coal outages have been replaced by supplies from Colombia, South Africa and Kazakhstan, steel is imported mainly from China, crude oil is imported from a number of countries and there is no single dominant supplier. Natural gas, originally transported by a system of gas pipelines, will now be transported using special cargo ships for liquefied gas from the USA, Great Britain and Algeria[1].

These changes in suppliers caused a price shock especially for energy (sharp growth and partial decline), which had a very negative impact precisely on the chemical industry, which has high energy consumption and, moreover, in combination with requirements to reduce carbon dioxide emissions[3].

In-house logistics in the chemical industry is different from in-house logistics in other industries. A large part of the products and intermediates here are in a gaseous or liquid state. Production processes are connected by pipelines and reservoirs. The dimensioning of these pipelines and reservoirs uses mathematical and simulation models, which are very complex, because parameters change in chemical production, e.g. due to aging of catalysts or clogging of heat exchangers[5]. Knowledge from the field of chemical kinetics is often used, because accurate data on the rate of chemical reactions will enable the correct dimensioning of e.g. the size of chemical devices. Again, sophisticated calculations are used here because the rate of a chemical reaction depends on inputs: concentration of reactants, pressure, temperature, and also on catalysts: radiation, electric field, magnetic field, etc.[2]

Simulation calculations enable cost savings thanks to the optimal setting of pressures, temperatures, device dimensions, accurate information on the amount of input and output substances. They help to create variants with different values of equipment operation costs and equipment acquisition investments. Another question that needs to be solved is how to produce the chemical substance, because there are often more options and to use the production equipment accordingly. It is necessary to assess investment costs, operating costs, prices and availability of the necessary raw materials, e.g. ammonia can be obtained by synthesis of nitrogen and hydrogen, or from ammonium salts (using hydroxides) or by decomposition of an organic substrate with a high nitrogen content[2].

An important area of logistics is transportation and storage. The chemical industry is also specific in that the stored and transported commodities are often dangerous substances. The storage of dangerous substances is associated with higher costs, because the warehouses must have special equipment: Warehouse floors resistant to chemical substances and equipped with drains to sumps, so that in the event of an accident there is no contamination of the environment. Warehouses equipped with thermoregulation capable of maintaining a set temperature range and also with ventilation equipment capable of extracting gases in the event of an accident. There are rules which substances must not be stored together, e.g. acids must not be stored together with hydroxides, flammable substances must not be stored together with oxidants, etc. Stores must be equipped with fire detectors and a fire extinguishing system. Warehouse workers must be trained and have emergency eye flushing and water shower facilities available. Substances must be stored in special containers, shelves and cabinets are equipped with tubs to catch substances in case of leakage. The entire warehouse, its equipment and safety regulations are regularly inspected.

Products and intermediate products of the chemical industry need to be transported and they are mostly dangerous substances. Their transport is again associated with higher costs, as it is necessary to use special equipment such as tank semi-trailers or tank railway wagons. Their transportation is carried out in a mode that must minimize the risks of accidents. The trend is to hire specialized transport companies that have the necessary equipment and certificates[8]. If an accident occurs, there will be great damage, people's lives are at risk, and the environment is damaged. During road and rail transport in the EU, dangerous goods are marked with two orange tables in a black frame. In the upper frame there are numbers that indicate the danger of substances and in the lower frame there are four digits that identify the transported substance (each chemical substance has its own number). E.g. a tanker that carries automobile gasoline has the number 33 in the upper frame and the number 1203 in the lower frame. The number 3 means flammable substance, because there are two numbers 3 means to emphasize the danger. Gasoline has the designation 1203. The designation on the orange frame gives quick information about the substance and the danger. E.g. the number 2 in the upper frame means gas, the number 6 a poisonous substance and the mark "X" before the number means that it is not possible to extinguish with water.

Conclusion

The paper describes the importance of a special area of logistics, namely maritime transport, and its importance for global trade. Without freight shipping, the economy of today's globalized world could not function. From the point of view of the chemical industry, maritime transportation of crude oil and liquefied natural gas is very important. It would be a disaster for crude oil prices on world markets if for any reason there was a halt to shipping in the strait of Hormuz, as tankers carry crude oil from the Persian Gulf through this route. Furthermore, some specifics of logistics in the chemical industry were described. We can say that logistics in the chemical industry has to deal with more complex situations than logistics in other industrial areas and works with a greater number of limiting conditions, including high safety requirements and this is associated with the generation of higher costs.

References

1. Černý P.: *Evropa se zbavuje závislosti na Rusku.* V Statistika a my, vol. 13 (2023) 2.
2. Dufek M., Hoch K.: *Průmyslová chemie*. ČVUT, Praha 1992.
3. Fanta M., Rot A.: *Dopadová studie*. CETA a Svaz chemického průmyslu ČR v Chemagazín. Vol. XXXII (2022) 4.
4. Gros I.: *Logistika.* VŠCHT, Praha 1996.
5. Hovorka F.: *Technologie chemických látek*. VŠCHT, Praha 2005.
6. Pernica P.: *Logistický management*. *Teorie a podniková praxe*. Radix, Praha 1998.
7. Romancov M.: *Námořní slepota*. N Media, Praha 2022.
8. Špaček M., Souček I., Hyršlová J.: *Strategické přístupy v managementu podniků chemického průmyslu*. NAVA, Plzeň 2016.
9. Švecová L., Veber J.: *Produkční a provozní management*. Grada, Praha 2021.
10. Voštová V., Altmann V., Fries J., Jeřábek K.: *Logistika odpadového hospodářství*. ČVUT, Praha 2009.
11. https://www.marinetraffic.com/ [5_6_2023]
12. Zhao CH., Liu W., Wang B.: *Reverse Logistics*. 1st International Conference on information Management, Innovation Management and Industrial Engineering. Taiwan, (2008).

CIRCULAR ECONOMY IN ENTERPRISES OF THE CZECH CHEMICAL INDUSTRY

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Abstract

In recent years, topics of the bio-based/circular economy has been mentioned more and more often among the professional public and in business practice. This concept is rightly in the forefront precisely because it represents one of the possible ways to achieve the goal of a sustainable future. The paper publishes the results of qualitative research on the topic of carried out during 2022 in chosen companies from the chemical industry operating in the Czech Republic, summarizes how this current issue is reflected in attitudes and specific activities related to BBE/circular economy. The results suggest that the primary areas of focus are monitoring the current development of legislation in the Czech Republic and the EU, introducing technologies to reduce the energy intensity of the production process and, last but not least, respecting customer requirements in the field of ISCC.

Introduction

The increasing burden of human activities on the environment, the intensive use of natural resources and the associated gradual depletion of essential raw materials raises questions in virtually all economic sectors about how to cope with this situation in the future. The so-called circular economy, seen as a complex system, appears to be a viable path to sustainability. Although this trend has become increasingly apparent around the world in recent years and its content is intuitively perceived, the true meaning is still the subject of study[1]. A uniform definition of the concept[2] cannot be found, but there is a relatively broad consensus on the concept of the circular economy as a circular economy that, in contrast to the linear economy, seeks to valorise raw materials, materials and already existing products, extend their life span and minimise or eliminate waste.

A comprehensive strategic framework for the circular economy in the Czech Republic is set out in the government document "Circular Czech Republic 2040", according to which the circular economy (circular economy) aims to maintain the value of products, materials and resources for as long as possible in the economic cycle and return them to the production cycle at the end of their lifespans, while minimising waste creation[3]. The expected outcome of the implementation of the principles of the circular economy is significant contributions in the environmental, economic and social fields. The strategic framework focuses on ten priority areas, including products and design, consumption and consumers, waste management, industry, raw materials, construction, energy, bioeconomy and food, circular cities and infrastructure, water, research, development and innovation, education and knowledge and economic instruments.

These areas suggest that the challenges associated with the circular economy are closely related to a wide range of enterprises in the chemical industry. Without transforming the production of basic chemistry, which forms the material and energy basis of our society and economy, it is not possible to achieve the sustainability objective[4]. Industrial symbiosis by producing and useful products in one industry via utilising co- or by-products from another industry has been established within a long time, the innovative concept of circular economy is an opportunity to scale up both biobased economy and green chemistry approaches[5]. By extending the scope of sustainability to the entire life cycle of chemical products, the concept of circular chemistry aims to replace today's linear "produce-sell-consume-dispose" approach with circular processes. By applying this approach in conjunction with the dynamics of technological change, it will ultimately lead to optimisation of resource efficiency across chemical value chains and enable a closed, waste-free chemical industry[6]. Studies suggest that companies in chemical industry can generate circular value in three ways: value addition through cost reduction, revenue migration, and value addition through generation[7].

Currently, the chemical industry in the Czech Republic is facing a fall in revenues caused by the COVID-19 pandemic and taking advantage of opportunities in connection with the implementation of the principles of The European Green Deal and the Chemical Strategy for Sustainability may represent a way to recovery. Priorities of the Czech chemical industry include decarbonisation of energy, decarbonisation of energy-intensive industries and decarbonisation of other consumers, for which it will be necessary to create suitable conditions, which include in particular the availability of electricity, the availability of green electricity and the availability and efficiency of CCSU[8].

The research aim was to contribute to the knowledge of the views of managers of chemical industry enterprises operating in the Czech Republic to the issue of BBE/CE, to analyse whether and how it translates into attitudes and specific activities.

Materials and methods

The qualitative research method, a semi-structured in-depth interview, was used to obtain the data. The research took place during the first half of 2022. A conceptual framework was established and a framework scenario was created on the basis of a literary research. The framework scenario was first verified in a pilot study involving two subjects from the study group. It proved appropriate to add a short structured questionnaire with characteristics of the demographic data of the company to the interview, which the respondents could fill in themselves before the interviewer's own visit. The time needed to fill in the questionnaire was up to 5 minutes. At the same time, the content part of the scenario was modified, the topic of the interview was extended to BBE/CE.

The research sample was selected by a purposeful, selective method. The research involved representatives of companies from different branches of the chemical industry, and respondents across a wide range of management areas were approached to understand the significance and context of BBE/CE for the activity of the chemical companies as a whole. Initially, 45 respondents were approached by email, 18 agreed, most of whom (14) listed a category of 50–249 employees as the size of their company, 3 respondents represented a category of company size up to 49 employees, and 1 respondent represented a company with more than 250 employees. The respondents were subsequently arranged for a visit, for which they were given semi-structured interviews, the duration of the interview being 60–90 minutes. The interviews were conducted on the basis of a framework scenario, which, due to the diversity of the issues examined, was continuously supplemented by the researchers according to the current direction of the interview. The interviews were always conducted in the parent company of the respondent, three interviews were conducted by telephone due to the respondent's time indisposition. The interviews with the respondents were recorded at the moment of implementation with the consent of the respondents, then transcribed and analysed.

Discussion and result analysis

The interview scenario was divided into four thematic units. The first part focused on the perception of the meaning of the terms BBE and CE, not only from the respondent's point of view, but also from the point of view of the whole company. The second part focused on the opportunities in which the respondent encounters the concept of BBE/circular economy in his profession and on the areas covered by the BBE/CE company. The third part is devoted to activities related to BBE/circular economy, knowledge requirements in this particular area and typical tasks of workers (workers). The last part of the interview concerned the projected outlook for the future in the context of the development of the economy, labour markets and technological trends.

Perception of the meaning of BBE/CE concepts

The results of the first part indicate a relatively wide range of perceived meanings of the term circular economy. Most respondents view the circular economy and BBE as two integral parts, often confusing meanings. The characteristics of the terms in their conception can be conceived as an economy built on the targeted recycling of resources and energies, which seeks to reuse with the use of biotechnology natural/basic materials, originally considered as waste.

In only two cases do the respondents strictly separate these terms. They agree on the definition of BBE of a production chain that relies on renewable resources and raw materials (biomaterials) at the input, at the output it produces, in addition to products, waste that is always sought for (bio-based). They see the circular economy as an economy based on the recycling of materials, where inputs can be used from recycled materials or foreign waste, if waste is produced it is sought for further use. This leads to minimisation of consumption and reinforces cooperation between companies throughout the production chain of a particular product. The two areas intersect, merge, but can also exist separately.

Opportunities and areas of occurrence of the BBE/CE concept in the company

The results of the second part point to a number of opportunities where respondents in their profession encounter the concept of a BBE/circular economy (from this part, for interviews, the two terms are seen as two possible definitions of the same, no distinction is made). Among the most frequently mentioned opportunities are company innovation projects aimed at reducing the volume of waste and its further use, minimising, sorting and recovery of municipal waste, collection of biowaste, minimisation of waste water. Also the use of waste from animal production and/or from processing of agricultural raw materials for the production of electricity or liquid motor fuels. Furthermore, companies focus on continuous improvement of production leading to a reduction in the consumption of raw materials, materials and energy and look for possibilities of further valorisation of complementary and by-products. At the same time, companies strive for the use of renewable energy sources such as wind, sun, biomass. There is a visible effort to look for possibilities of application of biotechnology, research and production of bioplastics, etc. Last but not least, there is a need to perceive opportunities in the strategic orientation of the company itself, management and implementation of legislative regulations.

From the point of view of determining the most mentioned area, which is dealt with in the investigated companies BBE/CE, none can be stated unambiguously. Research shows that activities usually overlap across the whole company, different departments, different levels of management. They start at the level of strategic management of the enterprise, they continue through the area of legislation and economic management, where through analyses of the market, demand and production possibilities they try to identify the potential for new projects. Implementation of theoretical principles into the specific conditions and specifics of the enterprise takes place in conjunction with R&D, the extensive BBE/CE gender is usually also carried by the production section, which leads to revision and continuous improvement of production. It is also impossible to ignore the control of the production process, its management, regulation, teams often solve partial tasks, such as increasing the production of valuable substances, their isolation and purification. The topic also appears in the optimization of logistic processes. The segment of renewable energy declares an eminent interest in the possibilities of circular economy and the use of waste for energy production.

Activities, tasks and required knowledge related to BBE/CE

The summary of the results of the third part is first devoted to activities related to the BBE/CE and associated knowledge requirements in this particular area, then to typical tasks of employees (workers). The most frequently mentioned activities include monitoring of the sustainability and efficiency of the production process, consumption of raw materials and energy. The carbon footprint, calculation of emissions of the production process, energy intensity are monitored. Furthermore, the current development of legislation in the Czech Republic and the EU and the requirements of customers in the area of ISCC are monitored. Projects are introduced for technical support of production, technologies to reduce the energy intensity of the production process with the aim, for example, to reduce water consumption, increase production and replace used non-renewable resources with renewable ones. Cooperation with project promoters, administration and coordination of projects, selection of applied research projects for a specific user, market research, where to direct applied research are required.

Typical tasks of workers in the technical area include compliance with technological procedures, control of the production process, minimization of waste, control of energy leaks and responsibility for energy consumption according to ever-tightening standards, ensuring trouble-free operation of the production equipment, responsibility for max. yield of the main product, minimization of losses. In the administrative area, emphasis is placed on cooperation and technical support of all new projects, control and calculation of GHC emissions (LCA within activities in the production of biodiesel), implementation of sustainability certificates (ISCC), evaluation of benefits from new activities and new projects from both economic and environmental point of view.

Required knowledge and skills are most often related to detailed orientation in legislation, especially in the field of environmental protection, the ability to respond to changing demands of customers and global trends and generally flexibility in case of an acute demand for change was accentuated. An overview of modern trends in applied technologies, a cross-cutting knowledge of technologies and material flows are considered important, knowledge of production processes, bottlenecks are beneficial.

Vision of future development

The final part was devoted to expert prediction of future developments in three key areas – the economic environment, the labour market and technological trends in the chemical industry sector. Some aspects of the development proved to be relevant for respondents in all three areas of interest, for better understanding of respondents' opinions and views they were left there during the evaluation. In summary, the trends are generally perceived rather positively, and revolutionary changes are expected.

As the main trends in the economy, respondents mentioned the context of The European Green Deal, especially the pressure on applied technologies and on expertise, which entails higher demands on all employees across the company. The share of renewable resources for production of products and energy will grow, energy dependence on fossil fuels will continuously decrease. Efforts will continue to permanently reduce the energy intensity of existing production processes, the development of new and more environmentally friendly technologies. Efforts to minimise waste while maximising its further use will continue to be at the centre of attention. Interest in monitoring CO2 emissions will also grow in sectors other than traditional ones (such as biofuels). The advent of artificial intelligence and more complex digitisation is seen as a significant trend, which in the end will lead, for example, to the elimination of paper form of documentation between companies. Lack of supply of new investments, lack of design and engineering capacities, lack of supply of suppliers of investment units are seen as a persistent problem in the future. Furthermore, there is a persistent problem with supply of capacities in ICT at their increasing importance. Concerns also exist in the area of EU legislation, which practically changes conditions in a shorter cycle than the real time of implementation and return on industrial investments. Related to this is the problem of the real possibility of calculating the return on investments in many sectors, as e.g., the calculation of the return using energy price outlooks or emission allowances or generally environmental requirements is not realistically possible and can be replaced only by an objective increase in the level of project risk, which in turn leads to results, when most projects look like irretrievable.

Respondents approached the estimate of expected changes in the labour market and in working conditions with a generally considered approach, assessing them in a broader context. The main current trend with an overlap in the future they consider the lack of labour and the related need for their above-standard stabilisation through the creation of specific stabilising conditions, then the completely inappropriate structure of new graduates, meaning the lack of technically oriented university and secondary education people. On the part of employees will continue to decrease the willingness to work in the exchange regime, will decrease the willingness to work in technical fields, will be more missing professions promising for the chemical industry, will continue to lack personalities for ICT thanks to high demand. At the same time, pressures on increasing the supply of provided benefits, specific working conditions such as “home office”, part-time jobs, working outside the normal working rhythm, concurrent work engagements, etc. will grow. The introduction of automation and the introduction of new technologies will require higher expertise after the operator, from employers will increase pressure on employees. Greater autonomy and above all responsibility, flexibility and the ability to adapt and learn will be required. Responsibility for education and education of employees with good professional knowledge will pass into the competence of the companies themselves. Modernization of processes will bring improvement of working conditions, will reduce risks for workers, which will be reflected in an excellent OSH. Manual work will be replaced by automata, which will bring about a change in the structure of the labour market.

Views on the development of technological trends vary according to the orientation of the chemical company. However, respondents generally agree that the importance of information technology will continue to grow, but this will also be linked to a potential increase in security risks. Workers will need continuous education and training in the field of technological and environmental security. A higher degree of automation and use of more complex control systems is expected, expansion of 3D printing possibilities, massive take-up of electromobility, 5G technology. Technological development will go towards more efficient use of local energy sources and products, i.e. reducing dependence on central sources.

Conclusion

The theme of bio-based economy/circular economy resonates more and more strongly in the social space, its importance gradually penetrates into the wider structures of society. Although the chemical industry is perceived by the general public as a subject at least debatable from the point of view of the principles of BBE/CE, it cannot be expected in any case to obtain a kind of “exception”, thanks to which it will not have to react to this issue. The aim of the submitted research was to analyse, from the point of view of managers, whether and how the current issue of BBE/CE is reflected in the attitudes and specific activities of companies of the chemical industry operating in the Czech Republic.

Due to the uneven representation of companies of different sizes in the survey, it is not possible to draw conclusions regarding differences in attitudes and activities, the results can only be summarised. The results of the survey among representatives of chemical companies at various levels of management showed that this is a topical and bearish topic, which is actively engaged in companies, focusing on the implementation of related activities and taking steps to expand them further. They realize that BBE/CE is one of the possible ways to achieve the goal of a sustainable future in terms of perceptions of the meaning of these two terms, they mostly view them as two integral parts, often mixing the meanings. The opportunities with which the concept is most associated include waste management, reduction of consumption of raw materials and reduction of energy intensity, or inclusion of a greater share of renewable sources. Typical tasks of employees in the technical area include mainly implementation of new technological procedures and compliance with existing ones, in the administrative area is highlighted evaluation of benefits from new activities and new projects from economic and environmental point of view, cooperation and implementation of sustainability certificates (ISCC). The required missing knowledge and skills most often relate to knowledge of valid legislation of the Czech Republic and the EU in the field of environmental protection.

The circular economy is economically demanding in terms of investment and operation, an important prerequisite for successful implementation is the creation of sufficient own resources. The EU intends to use the crisis for ecological restoration after the end of the COVID-19 pandemic, it offers large investment funds for investments in the environment, and it would be a shame not to use them in the chemical sector as well.

The research results indicate that the concept is not considered a threat to the functioning and future development of the company, managers view it more as a challenge, thanks to which it will eventually be possible to optimize business processes, make the use of material and energy resources more efficient and minimize the impacts of the company's activities on the environment.

References

1. Cattelan Nobre G., Tavares E.: J. Clean. Prod., *314*, 127973 (2021).
2. Velenturf A. P. M., Purnell P.: Sustain. Prod. Consum., *27*, 1437 (2021).
3. Ministerstvo životního prostředí: Cirkulární Česko 2040 (2023).
4. AnastaDs P. T., Zimmerman J. B.: Curr. Opin. Green Sustain. Chem., *13*, 150 (2018).
5. Kaur G., Uisan K., Ong K. L., Lin C. S. K.: Curr. Opin. Green Sustain. Chem., *9*, 30 (2018).
6. Keijer T., Bakker V., Slootweg J.: Nat. Chem., *11*, 190 (2019).
7. Lacy P., Long J., Spindler W.: *The Circular Economy Handbook*. Palgrave Macmillan, London 2020.
8. Souček I.: ICCT 2023, in press.

ONLINE REPUTATION MANAGEMENT IN COMPANIES OPERATING IN THE CHEMICAL INDUSTRY IN THE CZECH REPUBLIC

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Abstract

This paper analyses the importance and use of selected Online Reputation Management tools in companies operating in the chemical industry which are members of the Association of Chemical Industry of the Czech Republic. The results of primary research mapping the use of selected forms of online communication between companies and stakeholders and identifying the intensity of use of various proactive and reactive Reputation Management techniques in the online environment are presented here. In conclusion, on the basis of the research performed, recommendations are proposed for chemical companies outlining guidance on how to effectively promote a positive online reputation through paid and owned content, while at the same time monitoring and responding to received (shared) online content in such a way that the desired corporate image is highlighted while at the same time minimising the impact of any negative online publicity on the company's reputation.

Introduction

Online Reputation Management (ORM) actively shapes and controls the information which appears about a person or organisation on the Internet. It includes monitoring of online mentions, addressing feedback, both positive and negative, and actively promoting positive information about the company. Effective ORM requires companies to comprehensively monitor the online environment and proactively disseminate information through the appropriate online communication channels. It seems that many industrial companies still consider websites to be the most important online communication tool, this certainly being one of the basic online communication platforms. Recently, it has however become apparent that use of social media is also increasing among industrial companies. This trend mirrors the situation found among ordinary users, with more and more people joining social networks and for some, these even becoming their primary medium of communication. It is clear that the field of online communication is an extremely dynamic and rapidly changing environment which deserves deeper analysis, especially in light of the fact that industrial companies traditionally focused on B2B markets have traditionally lagged somewhat behind B2C-oriented businesses in online communication. The current situation of this modern issue is also revealed by the research presented here.

Theoretical background

Creating a positive corporate reputation is a frequently discussed issue in the markets of today. This relates to the issue of its effective management, which in its very essence comes up against a lack of clarity of its definition. As Khan and Digout[1] note, an inconsistent definition of corporate reputation makes it very difficult to measure and establish. Despite the vagueness of the definition, most researchers seem to agree that a company's reputation results from the collective perceptions or evaluations of stakeholders[2]. On the basis of this finding, Olmedo-Cifuentes and Martínez-León[3] proposed that corporate reputation be defined as follows: Reputation is "the estimate of the overall perception different stakeholders have about a company, evaluated through a set of dimensions and attributes that create value that are linked to the organisation and distinguish it from the rest". This definition underlines the importance of reputation for companies, which consists in generating an inimitable competitive advantage which gives the company a unique distinctness on the market. This is confirmed by Harrison[4], who claims on the basis of research that a positive reputation is proven to give a company a sustainable competitive advantage, bring new market opportunities, strengthen its market position and increase the value of the brand as a whole.

In view of the obvious crucial importance of a positive reputation for the competitiveness of companies in the markets of today, it is necessary to establish a permanent process in these companies for establishing, managing and monitoring it. As a consequence of this requirement, a separate field has been created, so-called Reputation Management (RM), which represents long-term strategy for measuring, controlling and managing a company's reputation as an asset[5]. RM was developed on the basis of Fombrun's theory by Doorley and Garcia[6] and in their understanding, it can be considered to be a comprehensive framework for management of corporate reputation. At present, in relation to the development of digitalisation of most activities, a logical adaptation of Reputation Management to the online environment is also occurring and we are seeing the emergence of so-called Online Reputation Management (ORM). Online Reputation Management (ORM) includes a set of techniques which help to monitor and improve the public image of an entity (companies, products and institutions) on the Internet. The aim is to minimise the negative impact of information about the entity while at the same time maximising positive content in such a way as to make it as trustworthy as possible for stakeholders[7].

It is clear from the definitions of Online Reputation Management that it can generally be understood to be the controlled monitoring and influencing of a company's online reputation and that it can most commonly be implemented via websites, blogs[8] and social network[9].

Websites are one of the cheapest and most effective means of promoting a company, and are therefore one of the most important tools for establishing a reputation in the online environment. Websites constitute a fundamental part of a company's business card and are often a key channel for customers and other stakeholders in terms of communication and orientation[8].

Blogs are web-based journals where companies publish educational and other interesting texts to attract stakeholders and make themselves more visible in the online environment. Companies also use blogs to present the latest company news, new products or information from the given sector. The articles usually deal with highly searched topics and help companies to promote awareness of themselves and support their reputation and to ensure their name is ranked at the top of the search results[10].

Social networks are now becoming one of the most important places to publish your own online content and therefore also a key tool for ORM. The most important benefit of the world of social media for Corporate Reputation Management is its interactivity, a factor which allows companies to respond immediately and actively promote positive user perceptions of the company. At the same time, it forces companies to constantly monitor user communications with each other[11] in such a way as to utilise positive mentions and eliminate negative mentions. In the Czech Republic, but also globally, the most widely used social media currently include Facebook, YouTube, Instagram, Twitter, LinkedIn and TikTok[12].

In the world of the Internet, information can be created and disseminated through all the channels described above, but also using other online platforms. In order to manage a company's online reputation, it is necessary to monitor and effectively manage all types of information, be this data outside the company's direct control, i.e. data from external sources, which can subsequently be used and shared, or information fully under the control of the company, i.e. data created or paid for by the company. The tools which ORM uses for these purposes can be divided into proactive and reactive tools according to the way in which they affect the company's reputation.

Proactive Online Reputation Management tools allow a company to actively participate in the creation of its own online reputation. This category includes:

- *creation of in-house content in the online environment* – this activity is one of the most important ORM tools as it is the best and most controllable way for a company to reach its customers, help or advise stakeholders and show its uniqueness[13]. Messages created in-house by a company usually come in two basic forms – text and audiovisual. The most common text publications created by the company for online communication include press releases and articles for online media, which can also include interviews[14]. The basic audiovisual forms of online communications published by companies include podcasts and videos[8]. The company can also actively create an interactive environment for dissemination of its own content by organising online events in the form of online seminars and workshops.
- *sharing of desirable content in the online environment* – shared and acquired content represents online information about a company or its products which does not require the company to pay for it or write it itself. The category of shared content includes online reviews, sharing of information about a business on social media or resharing content and brand mentions, both in text and audiovisual form (for example, a video). This also includes external articles, press releases and various forums[15]. It is important for a company not only to disseminate positive information of its own accord, but also to encourage its dissemination among other users. The aim is to create so-called electronic word-of-mouth (eWoM)[16].
- *search engine optimisation (SEO)* - SEO represents the process of influencing top search engine positions by optimising website promotion, content and other forms of media in such a way as to increase a company's online visibility[17]. The key to successful SEO is using a combination of on-page (internal) and off-page (external) activities. On-page activities are measures which are implemented directly in the content of the website. This, for example, concerns optimisation of content, keywords, headings, meta description, alternative text, domains or the URL, etc. Off-page SEO concerns external

factors which are separate from the website but which lead back to the company's website, such as backlinks from social networks, forums, blogs or third-party websites[18].

Reactive ORM tools respond to the already published mentions of the company. These tools are designed to help the company monitor its online reputation, deal with content relating to the company but published by other users, and to present itself in the best possible light. Reactive ORM tools include:

- *monitoring of content relating to the company in the online environment* – Within the framework of ORM, it is necessary to monitor all social media, websites, blogs and forums which are available online. Monitoring mentions of the company is crucial for the business because this is also essential for other ORM tools, both for the ability to share desirable content online and also for management of reviews or crisis ORM[19].
- *management of online reviews* – online reviews are a key element of ORM as they are the most widely used and most accessible electronic source for communicating experience online. They provide information about products and services and often serve as recommendations. They also represent a source of free feedback for the company[20].
- *Crisis Online Reputation Management (Crisis ORM)* – Crisis ORM helps organisations to deal with sudden and negative events presented or taking place in the online environment. This concerns Online Reputation Management during a crisis and also efforts to prevent crisis situations[21].

Simulation and experiments

On the basis of a literature search which we performed, primary quantitative research was prepared and conducted with the aim of determining the degree of use of Reputation Management tools recommended in the literature in the online environment by companies operating in the chemical industry in the Czech Republic. The survey method used was an electronic online survey conducted using a questionnaire created in the Lime Survey system. The questionnaire was sent to all of the companies associated in the Association of Chemical Industry of the Czech Republic which are engaged in production or distribution of chemical products. This method of selecting respondents was chosen because the Association of Chemical Industry of the Czech Republic is the largest association of chemical companies in the Czech Republic and it can be assumed that all of the major companies involved in chemical production and distribution will be included. 82 companies were asked to fill in the electronic questionnaire by email on the basis of the database which was compiled. The email was targeted at corporate online communications and PR managers, with the request asking them to complete the questionnaire being repeated once, these two requests being sent 14 days apart. In the end, a total of 31 fully completed questionnaires were received, this constituting a return rate of 37.8%. The data were statistically processed and analysed using descriptive statistical methods. IBM SPSS Statistics software was used for statistical processing.

Discussion and result analysis

In order to better specify the research sample, survey respondents were asked to state the basic characteristics of their companies. Data was ascertained about the size of the respective company from the point of view of the number of employees, the target markets of the company, the focus of the company and the type of company (i.e. whether this concerns a national or international company). The structure of respondents is characterised in Table I below.

Table I
Structure of respondents by company size and target markets.

Company size	Relative frequency	Target markets	Relative frequency
Small (less than 100 employees)	22.5%	B2B	52%
Medium (100 to 500 employees)	42%	B2C	6%
Large (more than 500 employees)	35.5%	B2B and B2C	42%

It is evident from Table I that predominantly medium and large companies oriented towards serving B2B markets participated in the survey. 77% were manufacturing companies (23% were non-manufacturing companies) and 61% were companies with an international orientation (39% were national companies).

One of the sub-objectives of the research was to find out how companies use online communication channels and the extent in which the managers who were contacted believe that these means of communication are important for the company in establishing its positive reputation in the online environment. Websites, company blogs, Facebook, Instagram, Twitter, LinkedIn, YouTube and TikTok were analysed. A four-point scale was used to evaluate importance: very important – quite important – not very important – not important at all. The existence of differences in the perceived importance of the individual online communication channels which were compared was tested using the Friedman test. Its significance was less than 0.05, indicating that the respondents do not consider the online communication channels included in our research to be of equal importance. The results of the ascertained importance of individual online communication channels in establishing a positive reputation of the companies under investigation are shown in Table II.

Table II
Importance of individual online communication channels in creating a positive corporate reputation.

Online communication channel	**Relative frequency in %**				Median	Average
	Very important	Quite important	Not very important	Not important at all		
Website	**81**	13	6	0	4	3.70
LinkedIn	**48**	32	13	7	3	3.15
Facebook	26	**35**	23	16	3	2.70
YouTube	13	26	42	19	2	2.26
Instagram	10	23	35	32	2	2.07
Twitter	6	19	36	39	2	1.93
Company blogs	13	10	29	48	2	1.78
TikTok	0	0	26	74	1	1.26

(Scale used: 4 – very important, 3 – quite important, 2 – not very important, 1 – not important at all)

It is evident from Table II that the most important online communication channel for chemical companies in their online presence is the website. Nearly half (48%) of the companies also consider LinkedIn to be very important, and more than a quarter (26%) also consider Facebook to be very important. All three online communication channels mentioned above are very or quite important for more than half of the analysed chemical companies in disseminating information to create a positive online reputation. Other online communication channels included in our research are considered by the majority of respondents to be quite important or not important at all.

Another aim of the research was to map the means used by companies to actively establish their positive reputation on the Internet. The results of the survey are summarised in Table III.

Table III
Level of use of selected proactive ORM tools for establishing the reputation of the companies included in our research on the Internet.

Tools	**Companies which use the given tool**	
	Absolute frequency	**Relative frequency in %**
Press releases	25	81
Articles for online media	22	71
Resharing content and brand mentions	17	55
Paid promotion	17	55
SEO	15	48
Paid channels	12	39
Online events	10	32
Podcasts, sharing videos	8	26
Promotion by influencers	3	10

It is evident from Table III that from among the tools for establishing a positive online reputation included in our research, companies make the most use of press releases and articles for online media. More than half of the companies also focus on resharing of content or brand mentions and paid promotion. The least popular means of promoting a positive online reputation among the analysed companies are podcasts and sharing videos as well as promotion by influencers.

Apart from actively disseminating and sharing appropriate information about the company online and using SEO, companies must also closely monitor what is happening in the online environment and respond appropriately to information, discussions, reviews and reactions, etc. disseminated by other Internet users which could affect the online reputation of the company. It is important to focus in particular on detecting and removing information which is misleading, false or otherwise damaging to the company. A chapter in its own right is constituted by management of online communication in the event of a corporate crisis. A further aim of the research was therefore to find out which tools from the field of reactive ORM are used by the companies under investigation. The use of reactive Online Reputation Management tools is shown in Table IV.

Table IV
Degree of use of selected reactive ORM tools for establishing the reputation of the companies included in our research on the Internet.

Tools	**Companies which use the given tool**	
	Absolute frequency	**Relative frequency in %**
Monitoring mentions of the company in the online environment	22	71
Adequate response to critical mentions of the company	15	48
Analysis of reviews	10	32
Applying the principles of online crisis communication	10	32
Active participation in online discussions	7	23

Table IV shows that one of the most used reactive ORM tools among the companies included in our research is monitoring of mentions of the company. Almost half of the companies also try to respond adequately to critical mentions of the company. The other reactive ORM tools which were investigated tend to be used somewhat marginally by the companies included in our research.

Conclusions and recommendations

On the basis of the results of the research, recommendations were proposed to make online communication by the chemical companies included in our research more effective in future.

The research found that for most of the companies which we analysed, Facebook is the most important social media for establishing their reputation. This is however a mistake from the point of view of the latest research, as the evolution of social media users is moving in a somewhat different direction. Based on the long-term development of the popularity of individual social networks, it can be recommended that chemical companies start **using Instagram more**, a channel which still tends to be seen as not very important from the point of view of the companies under investigation. Instagram in particular seems to have great potential for the future, as its number of users continues to grow, especially among the younger generations. In this context, it is also necessary to advise the companies under investigation to closely monitor trends in changes relating to user interest in various online media. Developments in this area are extremely dynamic and businesses which fail to respect societal trends can quickly fall behind in their efforts to manage their online reputation.

The research shows that just under half of the chemical companies which took part in the research use SEO as a proactive tool to manage their reputation in the online environment. This can be assessed as insufficient. Consistent **implementation of SEO** will be crucial in the future as stakeholders increasingly use various internet search engines to get answers to their questions, within the framework of which effective SEO is a primary source of commercial success. Other proactive ORM tools which are currently rather neglected by the companies included in our research but promise significant potential in the future include **podcasts, online events, the use of paid promotion and establishment of collaboration with influencers**.

An alarming finding from the research was that only 32% of the companies included in our research use analysis of reviews (see table IV). This is completely inadequate from the point of view of optimal Online Reputation Management. Reviews tend to be the primary source of information for the vast majority of online shoppers today. For this reason, effective **handling of review management** is crucial to the success of a company and establishment of a positive online reputation for it. A company should learn not only how to use positive reviews to its advantage, but also how to respond to customer reviews correctly and how to deal with negative reviews[20]. On the Internet, it is in particular speed and interactivity which are crucial factors, enabling companies to communicate with stakeholders individually. This is why companies should also focus more on **active participation in online discussions**, where the company can directly answer questions, resolve any potential problems and effectively develop its relationships with stakeholders in order to preserve and develop its reputation[22].

The main limitation of our research is the relatively small research sample which did not allow for more in-depth analysis of the results. Increasing the number of companies under investigation and also specifying information of interest to different groups of stakeholders in the online environment would be useful suggestions for further follow-up research.

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References

1. Khan S., Digout J.: Corp. Reputation Rev., *21*, 22 (2018).
2. Ajayi O.A., Mmutle T., Chaka M.: Corp. Reputation Rev., *25,* 287 (2022).
3. Olmedo-Cifuentes I., Martínez-León I.M.: Rev. Eur. de Direccio´n y Economı´a de la Empresa, *20*, 77 (2011).
4. Harrison K.: Cutting edge PR. 2020 [cited 2023 Feb. 20]; Available from: https://cuttingedgepr.com/articles/good-corporate-reputation-is-vital-especially-during-covid-19-times/
5. Doorley J., Garcia H.F.: *Reputation Management.* Routledge, New York 2015.
6. Doorley J., Garcia H.F.: *Reputation Management.* Routledge, New York 2020.
7. Rodriguez-Vidal J., Carrillo-de-Albornoz J., Gonzalo J., Plaza L.: J. Assoc. Inform. Sci. and Technol. *72*, (2021).
8. Janouch V.: *Internetový marketing*. Computer Press, Brno 2020.
9. Šenkapoun, P. *Webcopywriting pro samouky*. Zoner Press, Brno 2015.
10. Raposo A.E., Mainardes E.W., Bastos da Cruz P.: Int. Rev. Retail, Distrib. Consum. Res., *32*, 266 (2022).
11. Becker K., Lee J.W.: J. Asian Financ., Econ. Bus., *6*, 231 (2019).
12. Žáková D.: Beneficio Blog. 2023 [cited 2023 March 2]; Available from: https://beneficio.cz/clanky/co-rezonovalo-na-socialnich-sitich-v-roce-2022
13. Procházka D., Řezníček J.: *Obsahový marketing*. Computer Press, Brno 2014.
14. Bednář V.: *Internetová publicistika.* Grada Publishing, Praha 2011.
15. Kroon A.C., Van der Meer T.G.: Commun. Res., *48*, 51 (2021).
16. Doi N., Hayakawa H.: Int. J. Econ. Bus., *27*, 303 (2020).
17. Mladenović D., Rajapakse A., Kožuljević N., Shukla Z.: Online Inform. Rev*., ahead-of-print* (2022).
18. Lopezosa C., Codina L., Díaz-Noci J., Ontalba, J.A.: Comunicar, *28*, 65 (2020).
19. Dogra V., Verma S., Kavita, Chatterjee P., Shafi J., Choi J., Ijaz M.F.: Comput. Intel.Neurosc., *1883698* (2022).
20. Mun H., Lee C.H., Jung H., Yasin, C.: Inform. Technol. Manag., *24*, 55 (2023).
21. Kitchin P.J., Paramio-Salcines J.L., Walters, G.: Sport Manag. Rev., *23*, 66 (2020).
22. Amichai-Hamburger Y., Gazit T., Bar-Ilan J., Perez O., Aharony N., Bronstein J., Dyne, T.S.: Comp. Hum. Behav., *55*, 268 (2016).

INDICATORS OF SUSTAINABLE PRODUCTION IN CHEMICAL ENTERPRISES

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Abstract

The growing pressure of the public on the sustainable behavior of companies is causing changes in the product portfolio as well as changes in production processes in all industries. The ongoing digitization of business processes facilitates production, helps monitor production processes, and ensures high quality and competitiveness. Chemical production companies are also adapting to the transformation of the industry and, even concerning the rising prices of resources, they are trying to produce sustainably. The sustainability of production and products needs to be monitored through appropriate indicators. Their use and utilization were mapped by qualitative research in a selected chemical company. The dimensions of sustainability were identified according to the triple-bottom-line concept and the key indicators of production sustainability evaluation were verified in them.

Introduction

In connection with legislative and social pressure in the field of sustainable development, manufacturing companies are increasingly faced with the necessity of implementing sustainable production procedures. As a result of globalization and technological progress, the size of the consumer and industrial markets is growing, but for industrial sectors, this fact also means a sharp increase in competition[1]. Companies are thus forced, both legislatively and for economic and social reasons, to adapt their production to current trends – especially in sustainability. To differentiate their product from the competition and meet all legislative requirements, manufacturers are switching to more sustainable production processes that allow them to increase the added value of products and services, which makes them more attractive to customers, but at the same time, they can reduce the consumption of resources entering the production process (materials, water, energy, etc.)[2]. This approach positively affects the economic efficiency of the company, social satisfaction, and environmental responsibility of the company[3].

The idea of sustainable production first appeared in the literature at the end of the 20th century, the term sustainable production and consumption was officially introduced at the 1992 environmental conference in Rio de Janeiro[4]. The document that resulted from this conference became Agenda 21, which, in connection with sustainable production, states that the main global cause of continued environmental degradation is unsustainable patterns of production and consumption, especially in industrialized countries[5]. For that reason, two main areas have been identified in this document, firstly: focusing on unsustainable patterns of production and consumption; and second, the development of national policies and strategies to support changes in unsustainable consumption patterns.

Sustainable production can currently be understood as the creation of goods and services using processes and systems that do not pollute the environment, save energy and other environmental resources, are economically viable, and at the same time safe for workers and consumers[6]. According to the current trend towards an economically, environmentally, and socially sustainable industry, most industrial enterprises have the ambition to save resources (material, energy, time, labor), become carbon neutral in processes and supply networks, and at the same time produce new, carbon neutral and circular products that are necessary to mitigate climate change[7]. The requirements of systematic optimization at all levels from production to value networks in the process of industrial transformation and autonomous production are mentioned by Uygun and Ilie[8]. Characteristic modern approaches, methods, and tools to achieve autonomous sustainable production currently include e.g., circular economy, cleaner production, pollution prevention, best available techniques (BAT), process optimization, recycling, reuse, repair, higher use of renewable resources, integrated supply chain, life cycle assessment, environmental accounting, promoting social responsibility and more[9]. There is general agreement that the concept of sustainable production must be anchored in three dimensions of sustainability: economic development, environmental protection, and social development[10].

The economic sustainability of production is conditioned by added value creation based on cost and revenue components[11], which also include the costs of implementing environmentally and socially friendly technologies, but also possible revenues from the successful implementation of these innovations[12]. The fundamental condition for the creation of added value is represented by innovations that constantly improve economic, energy, but also environmental performance in various areas of production and ensure the acquisition of a competitive advantage on the market[13].

The environmental dimension of sustainable production is defined according to the long-term environmental problems of humanity: Global warming and climate change; Stratospheric ozone depletion; Human health, Human toxicity, Ecotoxicity, Acidification, Eutrophication, Formation of photo oxidants, Depletion of raw materials, and Use of landscape[14].

The social dimension of sustainable production is usually based on the identification and definition of relevant social aspects that concern individual stakeholders[15].

Indicators of sustainable production

Evaluation of the economic performance of the company (or production) is one of the priorities and traditional requirements of investors and company owners. In the development of sustainable production systems, the ability to assess the creation of added value is a crucial step[16]. In addition to the evaluation of the creation of added value, methods of financial analysis, and market performance of the company (market share, sales volume, etc.) are also applied, as well as methods including non-financial aspects of evaluation, such as the Balanced Scorecard (BSC) or Economic Added Value (EVA). Economic evaluation methods also include metrics such as Customer Lifetime Value and Customer Potential Value.

The assessment of environmental performance is usually based on legislative norms and standards governing obligations that the company should respect and consider when identifying environmental aspects. The most common include air emissions; leakage of substances into the water; leakage of substances into the soil; use of raw materials and natural resources; energy use; energy release (e.g., heat, radiation, vibration/noise, light); generation of waste and/or by-products; use of space, etc.[17]. Based on the defined environmental aspects, a set of indicators are subsequently defined, with the help of which it is possible to evaluate the level of sustainable production.

The manufacturing industry must ensure a balance not only between economic and environmental, but also social aspects to maintain the existence of the market, however, social aspects are often difficult to quantify[11]. In today's perception, the traditional concept of social aspects connected with safety for workers and consumers extends to some other stakeholders (Local communities, other supply chain actors, Children, and Society). For the formulation of indicators for social aspects shared with these stakeholders, it is appropriate to use the Social Life Cycle Assessment (S-LCA) methodology, however, compared to the economic and environmental dimensions, it is more difficult to find objective quantitative indicators[18].

The evaluation of economic sustainability is objectively essential for the survival of the company, however, for effective decision-making, the performance of the economic, environmental, and social dimensions must be assessed in a balanced and mutual way. One of the pilot attempts to evaluate sustainable production was presented by Veleva and Ellenbecker[19] already in 2001 with a set of 21 indicators based on the then view on the sustainability of production using the Lowell Center Indicator Framework model, a three-dimensional evaluation model was proposed in 2003 by Krajnc[20], which, however, was not balanced – he proposed ten indicators for the social dimension, compared to 16 economic and 63 environmental ones. In 2005, Hauschild, Jeswiet, and Alting mentioned the need to consider the product in its entire life cycle in sustainable production models[21]. The necessity of implementing environmental management systems and evaluating environmental aspects during production is mentioned by Hillary[22]. Paju connected the traditional Value Stream Mapping (VMS) method with the Life Cycle Assessment (LCA) method and formulated the Sustainable Manufacturing Mapping method[23]. The importance of the environmental dimension and environmentally conceived product in the entire value network is demonstrated by Giri and Bardhan[24], to which Lee adds that green solutions even smaller producers are leaning towards gaining a competitive advantage in global markets[25]. Faulkner and Badurdeen proposed a methodology that extends the usual Value Stream Mapping technique for lean manufacturing with added metrics to measure the sustainability of environmental and social impacts, known as Sus-VSM[26]. A model connecting the requirements of lean production with the Cleaner Production environmental approach was proposed by Ramos[27]. The concept was further extended by Jamil et al. (2020, p. 342) when they defined a summary of indicators that can be used to evaluate the performance of manufacturing companies in all three pillars of sustainability.

Mengistu and Panizzolo identified a total of 1013 indicators across different scientific and business publications for the three basic dimensions of production sustainability assessment, which they say implies a lack of consensus for their application to measure industrial sustainability[28]. There is still a need to establish a concise set of basic indicators that will be universal, uniform, or can be specified according to the needs of a given type of industry.

Research methodology

Academic research and studies from the relevant fields of research, sustainable production and consumption, lean management, and environmental and social assessment are used to address the validity of theoretical assumptions regarding the formulation and implementation of sustainable production indicators in business practice.

A form of qualitative research with representatives of a large chemical production company was chosen for the research itself. The intention was to address representatives of a multinational corporation with demonstrable experience with environmental, social, and sustainability assessment. The pre-selection was made based on press releases and awards received in the field of sustainability approach, on the assumption that a large multinational company has sufficient resources for sustainability assessment, development, implementation, and maintenance of indicators.

Based on a theoretical basis qualitative research was carried out as structured one-to-one interviews with three managers of a chemical company producing basic construction materials. Respondents represented individual dimensions of corporate sustainability – Business Excellence Manager, Environmental Manager, and HR manager. The research was carried out in the period January 2023 – April 2023. Information obtained was processed using content analysis. The first set of questions investigated the company's general approach to sustainability and its impact on competitiveness. The second set of questions investigated the assessment of economic sustainability. The third set of questions was focused on the evaluation of environmental sustainability, and finally, the fourth set of questions investigated the evaluation of the social sustainability of production, or products.

Research findings

The first set of questions first confirmed that the issue of sustainable development is one of the main priorities for the company. The strategic decision-making of the company is mainly driven by global trends, which are very closely connected with sustainability – currently, it is mainly the issue of climate change, lack of natural resources, or digitization and lifestyle. The entire corporation, therefore, focuses on the continuous improvement of its industrial processes to optimize its performance while protecting the environment and participating in general social development. This interest is thus fundamentally reflected in the company's behavior concerning any decisions in the field of development, supplier selection, product design proposals, production process planning, and the implementation of new technologies. Therefore, all these areas always include the criterion of sustainability as an essential element in decision-making, i.e., the requirement that any implemented change must support the achievement of set corporate goals in the field of sustainability.

The basic goal in the area of economic sustainability of production (second set of questions) is the efficient allocation of funds for the company and its owners, while the company's approach is primarily focused on the implementation of an investment policy that takes advantage of growth opportunities in key markets. The basic indicators by which the company evaluates the economic side of the sustainability of the production process and the success of the stated priority goal are the indicators related to the measurement of market performance. For this purpose, the company most often uses traditional financial indicators, which are then also part of the company's financial statements. These are mainly the volume of sales of individual products, cost of production, variances analysis, operating margin, profitability, productivity, Overall Equipment Efficiency (OEE) measurement, market share, Return on Investment (ROI), return on shares, increase in sales, and others.

In the area of the environmental impact of the production process, the company focuses its attention both on the inputs coming into production and on the output flows and emissions. In this context, a significant challenge for the company is the systematic support of circularity, the deviation from linear patterns of the production cycle, and the effort to accelerate the transition to a circular economy. With specific indicators, it monitors water consumption, which is further divided into potable, underground, and recirculated water. Energy consumption is monitored – electricity, compressed air, gas, and steam. In the area of material consumption, the ratio of recycled inputs at the expense of primary raw materials is monitored. For all the mentioned groups of inputs, the company also evaluates the production of related outputs, whether wanted or unwanted. It regularly and systematically evaluates the amount of product on the amount of supplied inputs, the sale of forced by-products of production, or the proportion of waste intended for recycling and the proportion of waste returned to production. In the case of emissions, the company pays particular attention to the creation of CO2 emissions, and special indicators are assessed as preventive measures in connection with environmental protection.

The evaluation of corporate production in the field of social sustainability is based on the identification of the requirements and needs of individual groups of stakeholders, which are divided into six groups in total: "Employees", "Market", "Civil society", "Local community", "Regulatory authorities", and "Investors". The social area of the sustainability of the production process in the company is focused most intensively on employees (Employees) and customers (Markets), for whom it conducts regular targeted surveys, which aim to systematically reassess and verify the fulfillment of the set quantitative goals associated with social policy. For the other categories, it formulates a general and qualitative assessment based on the general principles of corporate culture – respect for others, safety and health protection, respect for rights and freedoms, integrity, loyalty, and solidarity.

Table I. shows an overview of sustainable production indicators for each dimension.

Table I.

Overview of sustainable production indicators

Economic indicators	Environmental indicators	Social indicators
Sales	Material consumption	Health and safety risks
Cost of production	Energy consumption	Injuries and accidents
Variances	Water Consumption	Remuneration and benefits
Operating margin, Value Added	Environmental risks	Noise emissions
OEE	Product output	Diversity
Productivity	Waste	Human Rights and Freedoms
Profitability, (ROI)	Emissions, CO_2	Employees’ loyalty
Market share	LCA	Customers’ satisfaction
Return on shares	Biodiversity	Philanthropy and solidarity

While the company uses objective quantitative indicators for the economic and environmental dimensions, in the social dimension it much more often uses the methods of qualitative indicators, often benchmarking or descriptive evaluations.

Discussion and result analysis

In terms of the level of sustainability assessment of the production process, the company covers almost all relevant aspects of sustainable production. Despite this fact, due to the growing global interest in this issue, areas were identified where the strategy of measuring the sustainability of production could be expanded.

Based on the interviews conducted and the analysis of the corporate report on sustainability, it can be stated that a lot of attention is paid to the transition to energy sources that aim to fulfill the corporate goals in the area of carbon neutrality, specifically electricity. For this reason, the company has very well mapped any emissions coming from production, even from its parts. However, increased attention should be focused on the specific origin of the consumed electricity and monitoring of energy ratios from individual sources (e.g., nuclear, thermal, wind energy, etc.). At the same time, this would enable the company to do a deeper analysis of indirect CO2 emissions, i.e., emissions that do not occur in the company, but because of its activities.

On the side of unwanted production outputs, the company primarily focuses on the carbon footprint, thereby evaluating its level of contribution to global warming. In the area of emissions, however, due to the nature of the production process, which largely produces thermal energy, it would be appropriate to focus attention also on the release of thermal emissions, for example, the temperature of the water leaving the environment. However, also in the case of other energy emissions, it would be appropriate to monitor other quantitative indicators – e.g., light, noise, or odor emissions or specific business metrics for evaluating the impact of production on the natural ecosystem and efficiency in the use of the landscape area. The company does not use the evaluation of emissions with an impact on e.g., acidification, eutrophication, tropospheric ozone, and other forms of environmental aspects.

In the social dimension, the vast majority of methods used are generally qualitative, based on interviews, feedback, consultations, and benchmarking, often of an informal nature, but the formalization and quantification of the information obtained and the promotion of more objective evaluation indicators, for example, the satisfaction index, could be beneficial for the company. the number of complaints/lawsuits, etc. This would lead to overall support for the evaluation of the social area of sustainable production across industrial enterprises, and the comparison with competing enterprises would thus become significantly more efficient in this area. In the social areas: Human rights and freedoms, Employees' loyalty, Customers' satisfaction, Philanthropy and solidarity, quantitative indicators are not used, and the evaluation is only qualitative and descriptive.

Conclusion

Industrial enterprises are currently motivated to implement sustainable production mainly by strict legislation in resource consumption and waste production and emissions, but also by social pressure to develop sustainable products and sustainable production processes. Effective management of sustainable production cannot be achieved without control in the form of measuring factors that affect the sustainable side of production. Setting indicators of sustainable production for a fair evaluation of whether the production or the product itself is viable in the long term, environmentally friendly, and socially responsible is essential for the future positive perception of the company.

During the qualitative research, it was found that the level of evaluation of the sustainability of the production process in the selected company is very high. The company takes a responsible approach to measuring economic sustainability, using for this purpose both conservative assessment methods that only monitor the financial perspective of production efficiency and methods that also include non-financial elements - benchmarking and economic added value. The company constantly strives to reduce the consumption of resources, both by preventing waste, and by using recycled material and incorporating solutions that support circularity into the product design. Increased emphasis is placed on the issue of controlling the reduction of CO_2 emissions, in all areas related to the production process. In the social area of sustainability of the production process, the company constantly adapts its efforts to current social trends and changing lifestyles, community standards, and civil society.

In conclusion, it can be stated that the research confirmed a proactive approach in the evaluation of the economic and environmental dimensions of sustainable production, as well as partial shortcomings in the form of a low representation of some quantitative indicators, which would increase the effectiveness of the evaluation process, especially in the social dimension. However, the company achieved a very advanced form of assessment in the assessment of the sustainability of production and the product itself, which proves that it is aware of the importance of individual sustainability domains for the future competitiveness of its products on the market.

Acknowledgement

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References

1. Becerra M., Markarian G., Santalo .: Strateg. Manag. J., *41 (11),* 2126 (2020).
2. Grubic T., Varga L., Hu Y., Tewari A.: J. Clean. Prod., *247,* 119091 (2020).
3. Aleksić M., Bjekić R., Rodić M.: J. Eng. Manag. Compet., *10 (2)*, 81 (2020).
4. Moldan B., Dahl L. A.: *Challenges to Sustainability Indicators*, ISLAND PRESS, Washington, D.C. 2007.
5. UNCED: U.S. Department of State dispatch, *3*, 28 (1992).
6. Miehe R., Waltersmann L., Sauer A., Bauernhansl T.: J. Adv. Manuf. Process., 3 (2), n/a (2021).
7. Salminen K., Viljakainen A., Virkkunen R., Helaakoski H., Kokkonen A., Vita J., Alahuhta P.: *Towards Sustainable Manufacturing: How is autonomy paving the way towards a sustainable industry?* Espoo, VTT group, Finland 2022.
8. Uygun Y., Ilie M.: *Digitalisierung im Einkauf – Autonomous Manufacturing-related Procurement in the Era of Industry 4.0,* Springer Fachmedien Wiesbaden, Wiesbaden. 2018.
9. Glavič P.: Sustainability, 13 (16), 1 (2021).
10. Gbededo A. M., Liyanage K., Garza-Reyes J. A.: J. Clean. Prod., *184,* 1002, (2018).
11. Jacoby A., Braet J.: *ISPIM Conference*, Barcelona, 16, 2012.
12. Chong Y. T., Teo M. K., Tang C. L.: Renewable Sustainable Energy Rev., *56*, 797, (2016).
13. Kumar M., Mani M.: Front. Sustain., *3*, n/a, (2022).
14. Kočí V.: *Posuzování životního cyklu Life Cycle Assessment – LCA,* Vodní zdroje Ekomonitor, Chrudim, 2009.
15. Luthin A, Traverso M., Crawford R. H.: J. Clean. Prod., *386,* 135725, (2023).
16. Jamil N., Gholami H., Saman M. Z. M., Streeimikiene D., Sharif S., Zakuan N.: Renewable Sustainable Energy Rev., *33 (1)*, 331, (2020).
17. Komoto, H., Furukawa Y.: Procedia CIRP, *107,* 1011, (2022).

18. Vávra J., Munzarová S., Bednaříková M.: *Social Life Cycle Assessment – Assessment of Social Impacts of Chemical and Food Products,* Springer Publishing, Singapore, 2015.
19. Veleva V., Hart M., Greiner T., Crumbley C.: J. Clean. Prod., *9*, 519, (2001).
20. Krajnc D., Glavic P.: Clean Technol Environ Policy, *5*, 279, (2003).
21. Hauschild M., Jeswiet J. Alting L.: CIRP annals, 54, 1. (2005).
22. Hillary R.: J. Clean. Prod., *12*, 561, (2004).
23. Paju M., Heilala J., Hentula M., Heikkila A., Johansson R., Leong S., Lyons K.: *2010 Winter Simulation Conference,* IEEE, 3411, 2010.
24. Giri B. C., BardhanS.: Int. J. Syst. Sci.: Oper. Logist., *4,* 76, (2013).
25. Lee H., Park S., Jeong H.: J. Mech. Sci. Technol., *27*, 219, (2013).
26. Faulkner W., Badurdeen F.: J. Clean. Prod., *85*, 8, (2014).
27. Ramos A. R., Ferreira J. C. E., Kumar V., Garza-Reyes J. A., Cherrafi A.: J. Clean. Prod., *177*, 218, (2018).
28. Mengistu A. T., Panizzolo R.: *International Conference on Industrial Engineering and Operations Management,* IEOM Society International, Rome, 65, 2021.

IMPLEMENTATION OF ENERGY SAVING PROJECTS IN CHANGING ENVIRONMENT

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Abstract

Energy saving efforts lead to increased demand for materials used in projects. Technical solutions require the use of thermal insulations in all sectors of the economy but the demand is particularly high in the construction industry. The demand depends on the decision of the owners about the implementation of the project. The paper uses decision-making based on project evaluation where standard economic criteria are used with considering goals for energy consumption decreasing during certain time interval. The solution, described in the paper, is based on the development of the model describing the dynamic behavior of the system. Exogenous variables are changes of the subsidy used for the support of the project and changes of energy prices and investment costs. The investigated field is the refurbishment of the existing building stock which will influence the demand for thermal insulation and main output parameter is the refurbishment rate during the observed time interval.

Introduction

The European Commission's 2030 targets for energy savings, emissions reductions and renewable resources share increasing have raised discussions on how to meet them. The most ambitious target is a reduction in energy consumption by 32.5%. Consumption is to be reduced by this amount compared to the 2007 forecast for 2030. For us, this means a reduction of 8% compared to current consumption.

After five years of growth, domestic consumption of EPS (Expanded polystyrene) last year decreased by 6.2 % compared to 2021. 53000 tons were consumed in the Czech Republic, it is 9,000 tons less than the previous year. In 2020 this figure was 60200 tons. In Europe, 2.2 million tons of EPS were consumed in 2022. 85% of this amount is used in the construction industry. For the consumption of ESP, the amount of energy saving projects is the key issue. Due to energy savings targets, an increase in demand can be expected in the future. EPS is the most used material for building shell insulation (the share is 60%).

For the prediction of the future changes in the EPS demand it is necessary to understand the present situation of the building stock in the Czech Republic. In 82% of buildings the energy consumption was decreased (valid for 2017)[1]. However, a detailed analysis of the technical solutions reveals that in a significant number of buildings only windows were replaced in the envelope and therefore there is still room for further reduction in consumption[2]. In most cases, more advanced and expensive technical arrangements will be required. The standard solution is to decrease the energy demand by adding external thermal insulation.

Typical problem for manufactures and distributors of the thermal insulation materials is the prediction of the future demand. The solution requires system approach considering the changes in exogenous parameters. The wider environment with different stakeholder objectives is described in Figure 1.

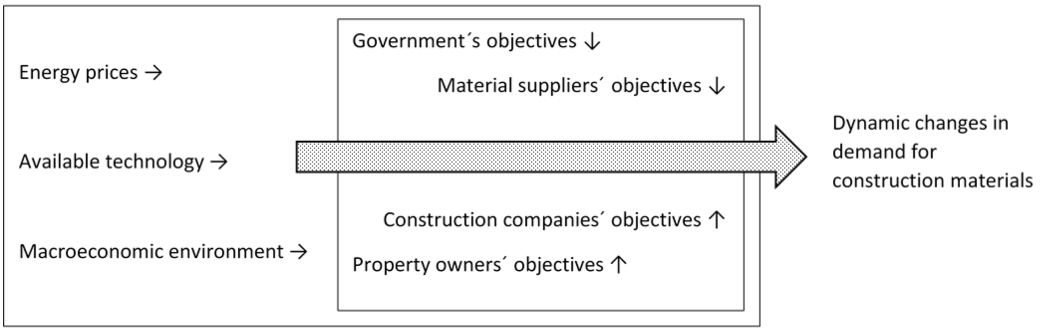

Figure 1. Description of the environment with elements influencing the demand for thermal insulation materials.

The general objective of the paper is to understand the dynamics of the market and to predict the construction materials market behavior. Specific objective is to develop the dynamic model for the calculation of the amount of renovation works and consequently the demand for the thermal insulation material.

Method

The key feature of the investigated system is the existence of time-dependent parameters. It means that it is necessary to consider the system as dynamic system. It is typical behavior for energy prices, construction works prices, interest rates influencing the availability of the loans. Another very important input is the subsidy for supporting energy saving projects. This parameter is very important for decision making concerning launching projects. The used method is the observation of changes in the system during past subsidy programs which include finding opinions of material inputs produces and distributors. Consequently, the hypothesis that it is possible to describe the dynamic behavior by system dynamics model has been set. Next step is to perform experiments by means of this model.

System dynamics is the main tool for calculation of changes in the investigated system[1]. The dynamic model uses stock and flow elements which calculates internal parameters in the system[2]. In our problem situation, the stock element is the stock of buildings with certain parameters. The convertor parameters provide auxiliary calculations and decisions[3]. The model is an interpretation of the structure and all parameters calculations are based on the system of equations. In our case, the main output parameter is the refurbish rate which will describe the changes in the building stocks in the Czech Republic. According this value it is possible to find the demand for thermal insulation materials. The solution of the problem is not one set of output parameters calculated by the designed model but the model should be considered as the tool for finding these parameter values by persons responsible for decision making in the all distribution chain elements.

Model

The model structure is depicted in Figure 2. The main stocks are: *Existing building stock* – five stocks of existing buildings divided according to the construction period, Refurbished stock 1 – refurbished existing and new standard buildings and *Refurbished stock 2* – refurbished buildings in the next step according to increased requirements. Another stocks included in the model are *New buildings standard* and *New buildings low en* – low energy and passive buildings built from 2011 year. The main flows are flows which include *refurbish rate 1* and *refurbish rate 2*. The valves of these flows are controlled through investors' decisions about project implementation. Decision about implementation is based on the ratio between energy cost savings and investment costs which calculates the efficiency of the investment. In this case the investment is the energy saving project. All calculations are related to floor area of the buildings (in the family houses and the apartment buildings). It is evident that the financial output depends on the price of the energy (higher price means higher output).

The significant outputs are the amount of the floor area in the refurbished buildings but also the refurbish rate (floor area in m^2 per time unit) which will be used for the assessment of the required construction materials in every time period.

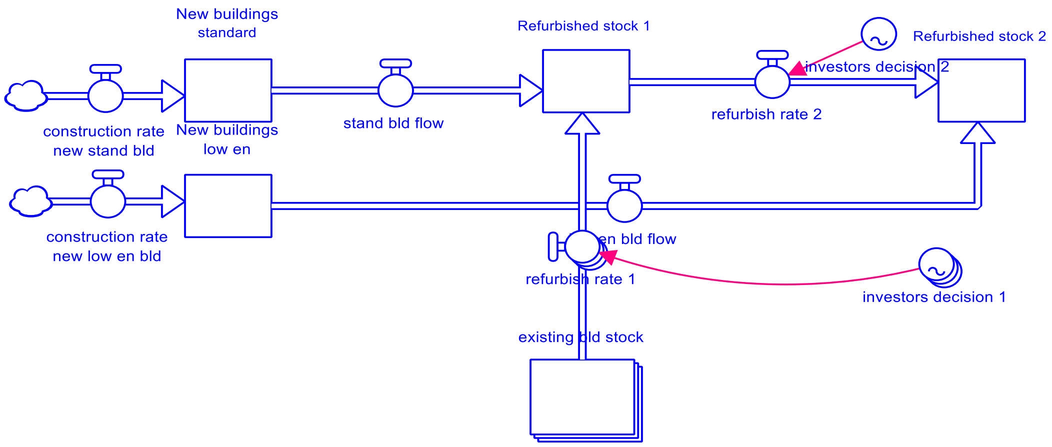

Figure 2. Structure of the model – the essential building stocks.

Another big issue connected with this problem situation is project financing. The model allows to finance the projects only by owners´ financial resources or with the help of the external resources. In this case by means of subsides. The support can be changed from 0 to 100 %. Initial amount of the parameter *Financial resources* (it means external resources) depend on the government objectives and strategy in the field of energy savings or carbon dioxide reduction. The financial resources are spent according the refurbishment rates and the amount of the support. Consumed resources are in the stock *Financial resources spent*. The subsystem *Financing* is presented in Figure 3.

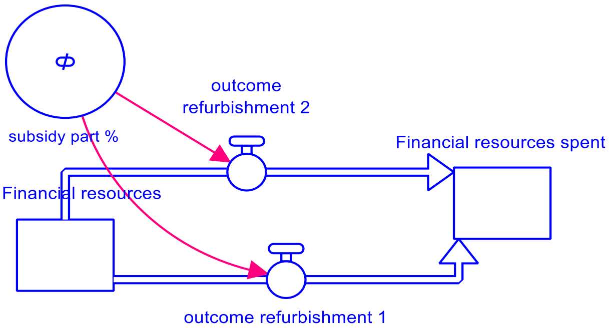

Figure 3. Structure of the model – financing.

Investigated cases and results from simulation

The simulation was performed for the time period 10 years. The aim was to find out amount of refurbished floor area (stock) but for the purpose of finding the demand for materials the refurbish rate (flow) was assessed. The first set of simulations was done to find how certain parameters are sensitive. Under investigation the changes of energy prices, construction work prices and subsidy level were considered. The most important parameter was subsidy level. Therefore, further investigation was focused on this parameter. It is necessary to mention that rational decision making is considered. The ratio between financial incomes and outcomes (with the influence of subsidy) is calculated. Theoretically, another influence is the existence of the subsidy itself. Potential investors consider the advantage of saving the investment costs. Strictly rational decision-making is characteristic only for companies.

The price of energy is 3 CZK·kWh^{-1}. Description of investigated cases:

Case 1: Implementation takes place without financial support from external sources

Case 2: The financial resources for the support of projects are 50 billion CZK and the subsidy is considered to be 20% of the investment costs

Case 3: Financial resources for the support of projects are 50 billion CZK and the subsidy is 40%

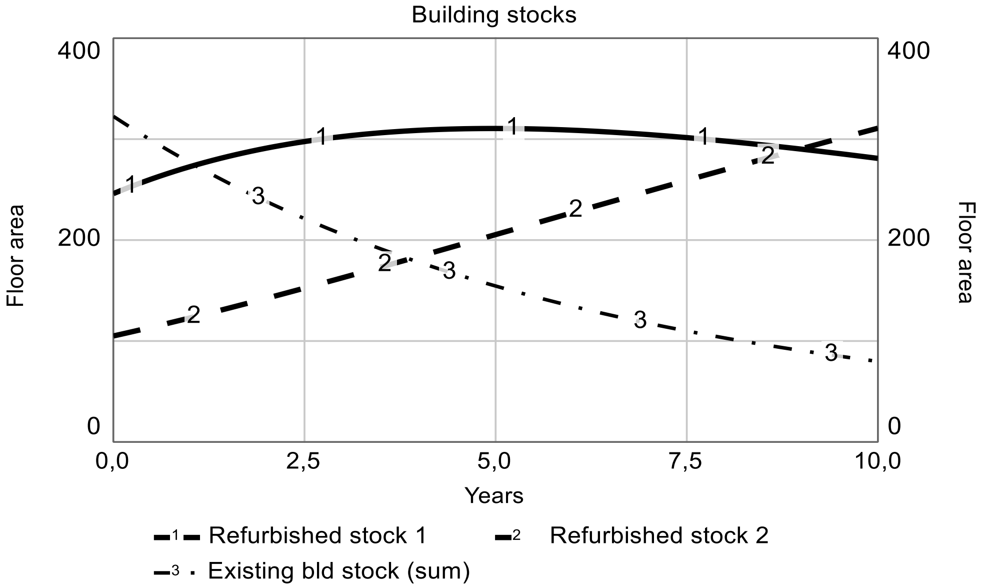

Figure 4. Building stocks for the case 1 expressed as floor area changes during time considered, [10^6 m^2].

The results from simulation are depicted in Figure 4-7. Figure 4 presents the changes in building stocks for the case 1. Next figures demonstrate the changes in the refurbish rates and the financial flows for all cases. These results are more important for the purpose of further use.

Existing building stock parameter dropped from 323.10^6 m^2 to 80.10^6 m^2 for the case 1. For the case 3 this parameter is 74.10^6 m^2. *Refurbished stock 2* parameter was increased from 311.10^6 m^2 to 319.10^6 m^2. In figures where refurbish rates are presented it is possible to observe the step change in this parameter evoked by the consumption of financial resources.

These results are the basis for the prediction of the demand for thermal insulation material with considering that 85% of the EPS production is used in the construction industry. The EPS thermal insulation will cover 60 % of the demand.

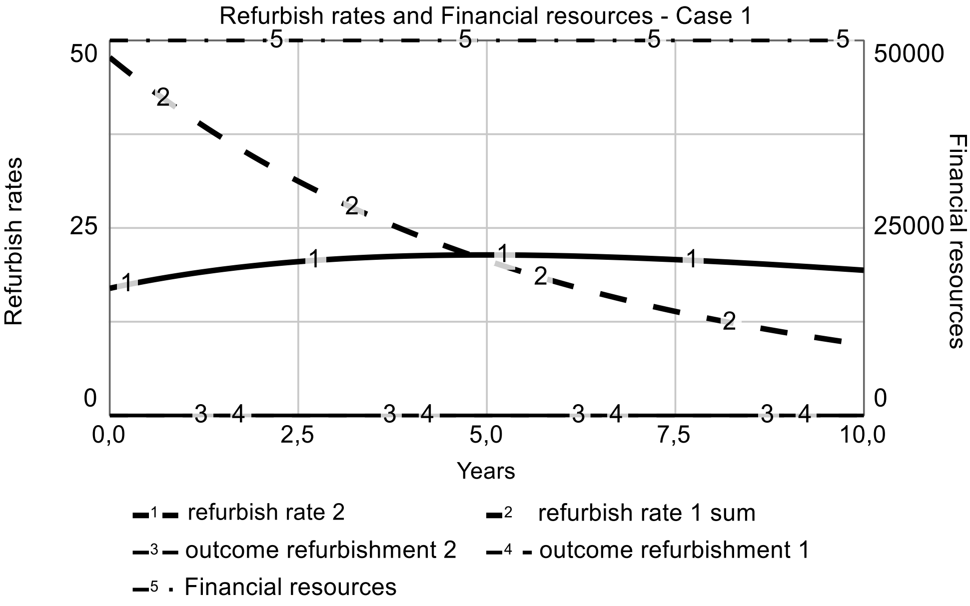

Figure 5. Refurbish rates [10^6 $m^2 \cdot year^{-1}$] and changes of financial flows [10^6 CZK] (right axis) for the case 1.

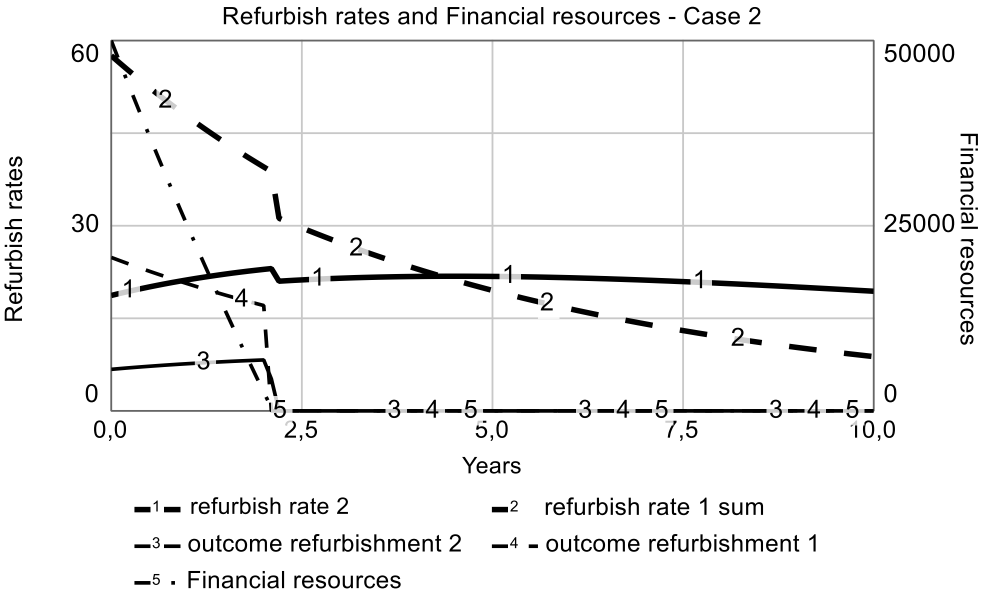

Figure 6. Refurbish rates [10^6 $m^2 \cdot year^{-1}$] and changes of financial flows [10^6 CZK] (right axis) for the case 2.

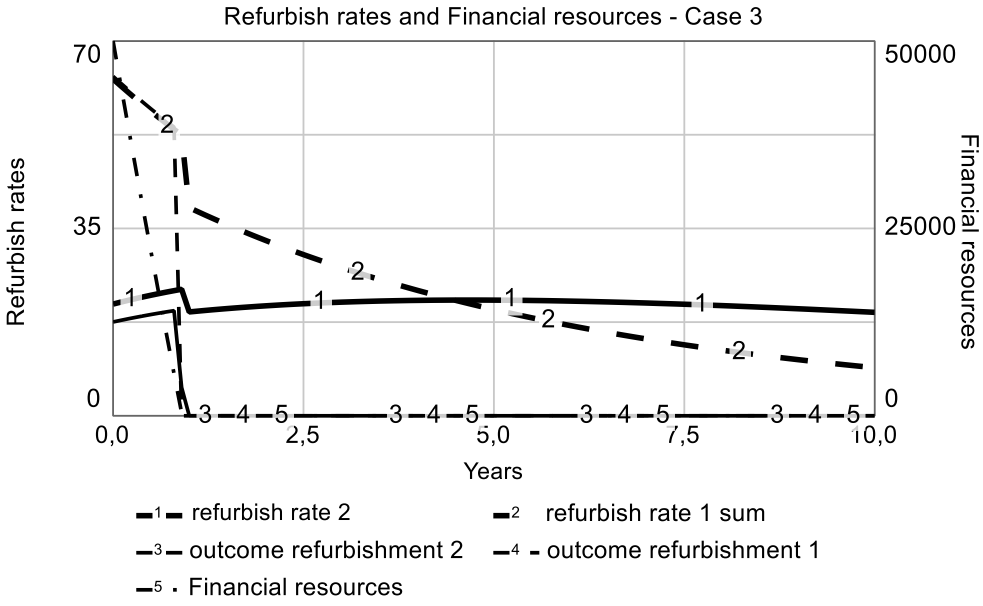

Figure 7. Refurbish rates [10^6 $m^2 \cdot year^{-1}$] and changes of financial flows [10^6 CZK] (right axis) for the case 3.

From results it is possible to see that *refurbish rate 1* parameter decreased during the period of simulation. It is understandable because the stock of not refurbished buildings will be lower. On the contrary, *refurbish rate 2* parameter (ageing of new standard buildings and another improvement of parameters after the first step of existing buildings refurbishment) is stable.

Conclusions and discussion

The system dynamics model for describing changes in investigated system has been developed. The results from simulation makes possible to find main driving forces of changes in the demand for thermal insulation materials with the focus on the EPS. In the Czech Republic there are the subsidy programs which evoke the main changes in the parameters values. Step change in financing energy saving programs is the typical feature. The economic systems have difficulty in dealing with these rapid changes. EPS manufacturers and distributors should respond to the changes described. However, rapid response in production capacity is difficult because the rate of change is significant. As it was mentioned above, the main output is the system dynamics model and calculated refurbished rates which describe year changes of the reconstruction works. The resultant values of the stocks are the important parameters for finding the strategy of the energy consumption decreasing but not for the described problem.

The economic dimension of sustainability focuses on running cost and life cycle costs. Now new issue must be addressed and this is the stable rate of financing. This is new aim of sustainability. The model considered the amount of the financial resources for the subsidies 50 billion CZK but to refurbish the all stock of existing buildings will require more financial resources. The decreasing in the refurbish rates which will occur when the funds are consumed is 23 % and 25 % for the parameters Refurbish rate 2 and Refurbish rate 1.

A fundamental modelling problem in these complex systems is data availability. Although there are many studies that have mapped the building stock, one has to accept that accurate data for the parameters you need to calculate the results are difficult to find or are available with a delay. Very often they exist in different breakdowns or from different years and need to be recalculated and adjusted.

The very important problem is how to introduce owner decision-making if to start the project. Normally only of few owners deals with this issue and it is assumed that if the state has financial resources for the subsidies, owners will refurbish the buildings. However, the question of the return on investment is nowadays, at least simplistically, addressed by everyone who is thinking about reducing energy consumption. There may be more than one reason for the improvement of thermal properties of buildings, but the basic reason is to assess the payback based on the future revenues.

References

1. Holub P., Antonín J. Building Renovation Strategy, Aliance Šance pro budovy, 4-8, 2014.
2. Antonín J. The Survey of the Building Stock and Possibilities of Energy Savings, Aliance Šance pro budovy, 11-30, 2013.
3. Sterman J.D.: *Business Dynamics – System Thinking and Modeling for a Complex World*. McGraw-Hill, Boston 2000.
4. Pidd M.: *Tools for Thinking – Modelling in Management Science*. Wiley, Chichester 2000.
5. Morecroft J.: *Strategic Modelling and Business Dynamics – A Feedback Systems Approach*. Wiley, Chichester 2008.