CO-PROCESSING OF PYROLYSIS PRODUCTS

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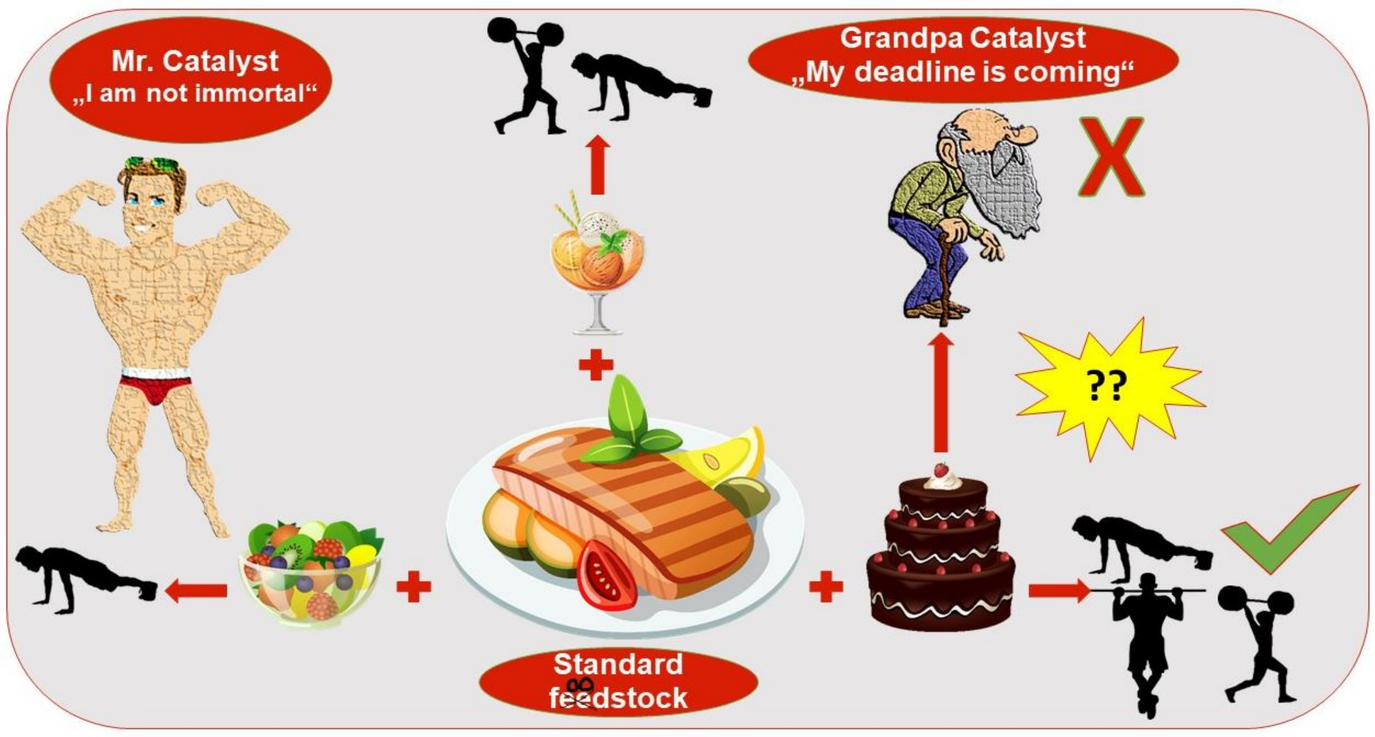
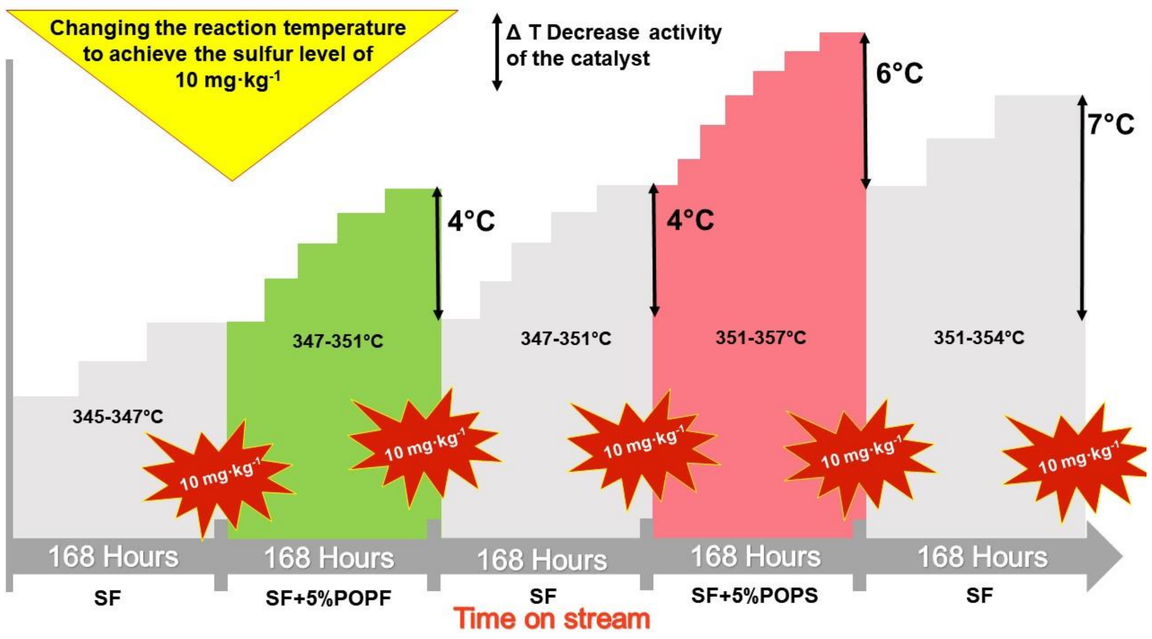
Introduction

The current trend of deeper crude oil processing leads to an increase in the use of secondary products for diesel production. For example higher generation of biofuels or other materials produced from waste by pyrolysis and their processing into products with higher added value. Because of their low quality parameters (the higher amount of heteroatoms and aromatic hydrocarbons) the refinery uses a catalytic hydrogenation process during which the heteroatoms of sulfur and nitrogen are removed from feedstock and quality parameters are improved. The addition of alternative pyrolysis products influences one of the most important properties of a desulfurization catalyst – its activity. Reduced catalyst activity and the presence of pyrolysis products in standard feedstock (SF) affects the quality of products from catalytic hydrogenation. Prior to industrial application, the mentioned aspects are usually tested and verified using experimental pilot units. The aim of work is to evaluate the effect of addition of alternative pyrolysis products on catalyst activity and properties of products from catalytic hydrogenation. The influence of the addition 5% of two alternative pyrolysis products as a component of feedstock was tested. Specifically, it was a product from the steam cracking of petroleum fractions (POPF) and product derived from pyrolysis of sorted waste polystyrene (POPS).

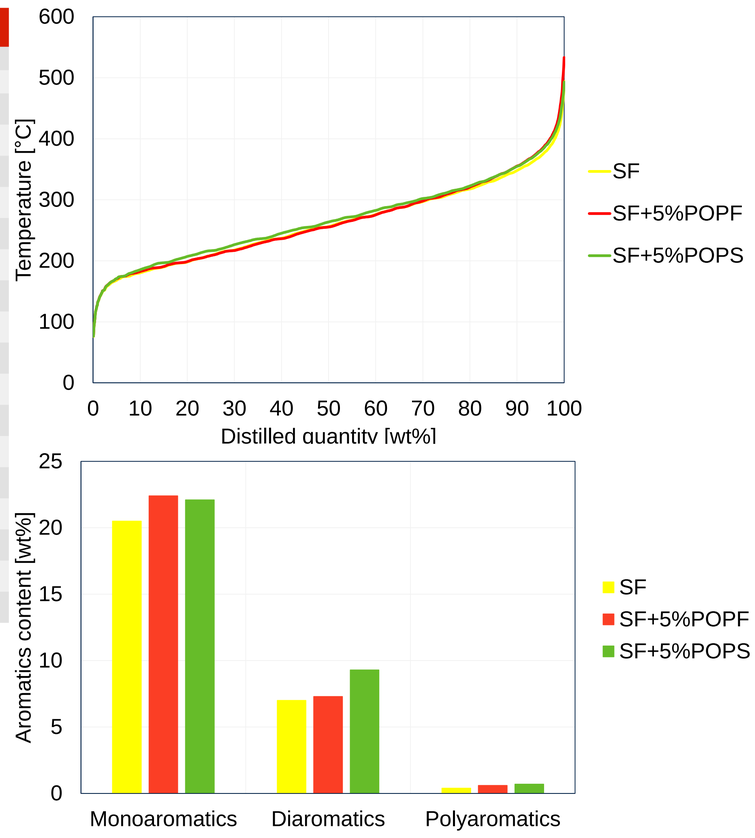
Aim of work



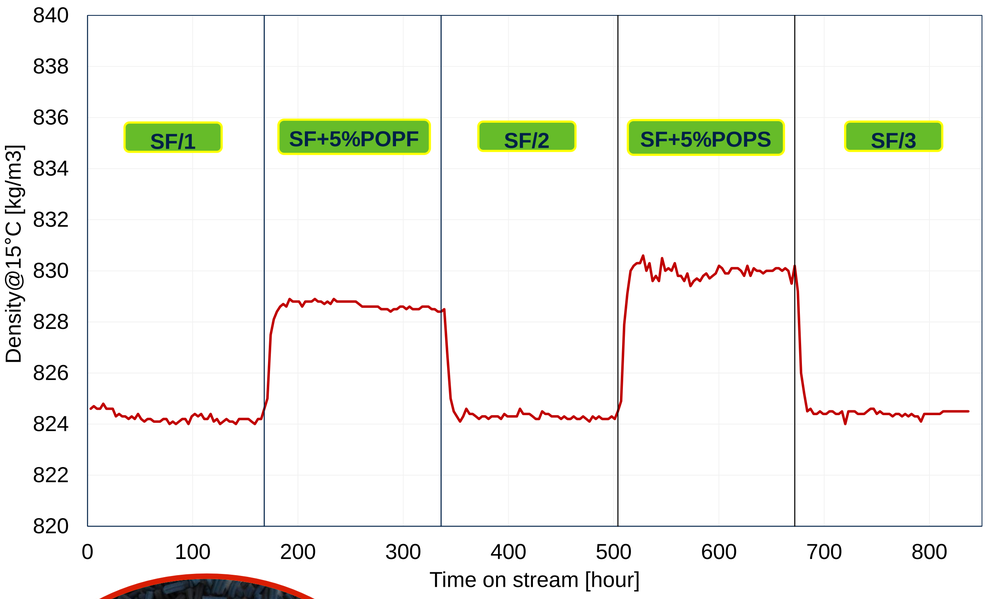
Experimental

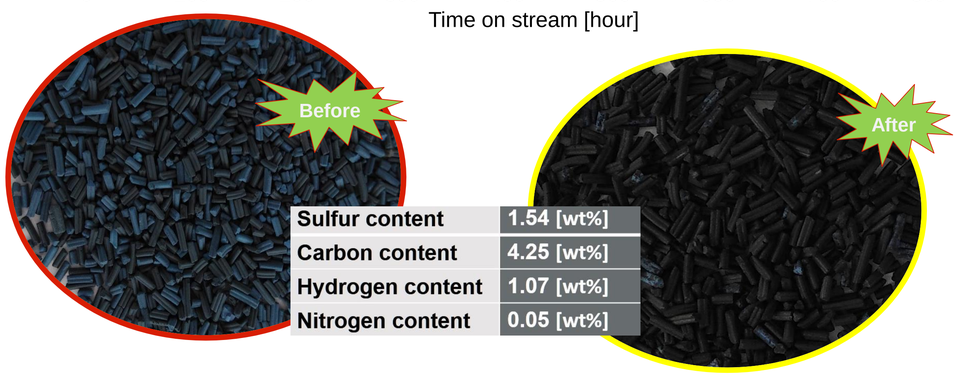


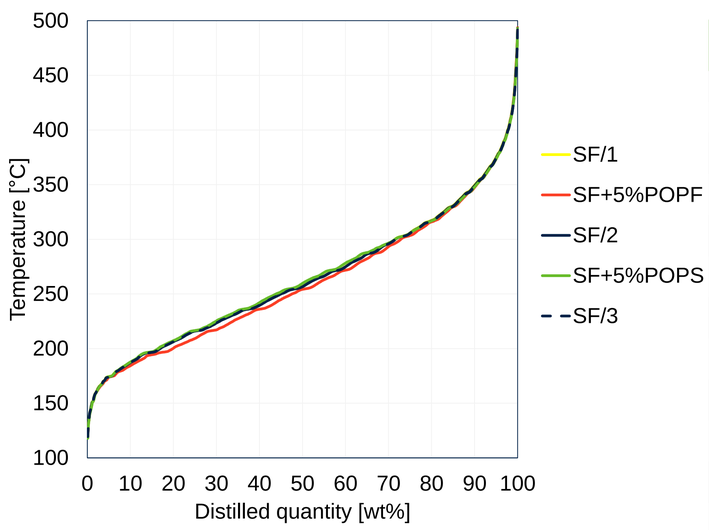
Properties	SF	SF+5%POPF	SF+5%POPS
Density@15°C [kg/m³]	835.8	837.7	838.5
Refractive index 20°C	1.463	1.464	1.466
Colour ASTM D 1500	0.6	0.7	1.2
CP [°C]	-8	-7	-7
PP [°C]	-22	-22	-30
CFPP [°C]	-12	-12	-12
Sulfur content [mg·kg-1]	7444	7081	7116
Nitrogen content [mg·kg-1]	109	106	236
Carbon content [wt%]	86.3	86.1	86.3
Hydrogen content [wt%]	13.6	13.4	13.2
Aniline point [°C]	61	62	62
Monoaromatics [wt%]	20.5	22.4	22.1
Diaromatics [wt%]	7.0	7.3	9.3
Polyaromatics [wt%]	0.4	0.6	0.7
Distillation curve			
IBP [°C]	115.2	115.6	115.3
5 wt% [°C]	168.0	170.6	170.9
95 wt% [°C]	371.3	381.1	379.6
FBP [°C]	442.6	472.1	453.8



Results







Average samples	SF/1	SF+5%POPF	SF/2	SF+5%POPS	SF/3
Density@15°C [kg/m³]	824.2	828.6	824.3	829.6	824.5
Refractive index 20°C	1.457	1.459	1.457	1.461	1.457
CP [°C]	-8	-7	-9	-8	-6
PP [°C]	-22	-22	-22	-30	-23
CFPP [°C]	-11	-12	-11	-12	-11
Sulfur content [mg·kg-1]	9.5	10.0	10.2	10.3	10.1
Nitrogen content [mg·kg-1]	7.07	8.38	9.48	15.2	10.9
Monoaromatics [wt%]	23.2	24.0	23.8	25.2	22.7
Diaromatics [wt%]	2.0	2.0	2.2	4.4	2.2
Polyaromatics [wt%]	0.2	0.2	0.1	0.2	0.1
Distillation curve					
IBP [°C]	140.3	137.9	139.7	137.8	139.9
5 wt% [°C]	174.4	173.8	174.1	174.3	174.0
95 wt% [°C]	375.1	373.4	374.4	373.4	374.0
FBP [°C]	451.0	450.3	447.7	446.8	445.4

Conclusion

- During the test temperature inside the catalytic bed was changed to achieve the sulfur level of 10 mg·kg^{-1}.
- Temperature after first 168 hours of standard feedstock feeding had to be increased by 2°C to achieve the sulfur level of 10 mg·kg^{-1} at 347 °C. During the next phase, when the standard feedstock (SF) with addition of 5% pyrolysis oil from steam cracking (POPF) was fed, temperature had to be increased by 4°C to 351°C. Although, the amount of sulfur in the SF+5%POPF is lower than in the SF, but the sulfur is sterically hindered. That is why the desulfurization was more difficult. In the case of long-term feeding of the feedstock, the temperature difference could be even higher. During the third phase, the standard feedstock was feeding again. In the beginning the temperature was decreased to the temperature at which the desired sulfur level was achieved in the first phase. We found that to achieve the sulfur level of 10 mg·kg^{-1} it is necessary to increase the temperature by 4°C to 351°C. This indicates that the presence of pyrolysis oil POPF affected the activity of the catalyst. In the fourth phase the feedstock was changed to standard feedstock with addition of 5% of pyrolysis oil from polystyrene (POPS). Temperature had to be increased by 6°C to 357°C. In this case, the drop in catalyst activity could be caused by less degradable species of sulfur, aromatics and increased amount of nitrogen in the SF+5%POPS. In the last phase the standard feedstock was fed again. The presence of pyrolysis oil from polystyrene affected the activity of the catalyst and therefore the temperature had to be increased by 3°C to 354°C. The temperature required to achieve 10 mg·kg^{-1} sulfur content was 3°C lower than in the fourth phase of testing. Because of the change of feedstock, which had, among other differencies, lower amount of nitrogen and different species of sulfur and aromatics. At the end of the testing, the temperature required to achieve the sulfur level of 10 mg·kg^{-1} had to be increased by 7°C.
- The products density increased and decreased during the test depending on the used feedstock. The highest density had products from processing of SF+5%POPS.
- The parameters of products were affected by feedstocks properties. Increased amount of nitrogen in SF+5%POPS also occurs in the average sample from this condition. Increasing amount of nitrogen can be observed during the test in average samples incurred from the processing of standard feedstock. Using the catalytic hydrogenation process the amount of aromatic hydrocarbons has been reduced, especially content of polyaromatic compounds.

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