Catalytic methanation of biogas using Ni and Ni-Co based catalysts

Department of Gaseous and Solid Fuels and Air Protection
UCT PRAGUE

Kulas Jan[1,2], Polák Lukáš[1], Tomáš Hlinčík[2]

[1]Department of Hydrogen Technologies and Energy Innovation, UJV Rez, a. s., Husinec-Rez, Czech Republic
[2]Department of Gaseous and Solid Fuels and Air Protection, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic

ABSTRACT

One of the ways to decrease carbon dioxide emissions in natural gas application is to substitute it with biomethane, respectively SNG (Sustainable Natural Gas). In this regard catalytic methanation gains wider acknowledgment due to enabling effective application of surplus energy to produce methane-rich gas. Catalytic methanation is a reaction of carbon dioxide and hydrogen, which produces methane and water. Hydrogen used in this reaction can be produced via electrolysis of water using surplus of renewable electric energy. Flue gases from power plants, biogas, carbon dioxide from industrial processes or air can all be used as sources of carbon dioxide for this reaction. Catalytic methanation of biogas enables simple transformation (upgrading) of biogas into biomethane (resp. SNG) without the need to separate carbon dioxide in advance, which in turn increases efficacy of the whole SNG production process. Another advantage is increased output of SNG due to carbon dioxide located in biogas being transformed into methane. Methane-rich gas produced in this way can be applied to fuel vehicles or injected into nature gas grid to be used for its transportation and storage capacity.

This paper looks into application of catalytic methanation as an alternative method of biogas treatment up to the natural gas level of quality. Four model gases were tested at gauge pressure of 0.55 MPa using Ni and Ni-Co based catalysts. The first model gas served to figure out catalytic activity and selectivity. This gas comprised stoichiometric amounts of hydrogen and carbon dioxide (4:1). The following three model gases had model biogas ratios of CH_4:CO_2 at 20:80, 40:60 and 60:40 respectively and hydrogen in a stoichiometric ratio to carbon dioxide. The results of the experiment show that maximum methane yield was achieved using model gas with CH_4:CO_2 ratio of 60:40 at 340 °C on a Ni based catalyst, where molar fraction of methane in the produced gas reached 98.5 %.

INTRODUCTION

- Biogas is upgraded to biomethane mainly in Germany, Netherland and Switzerland. At the moment in Czech Republic there is one plant, located in Rapotín, that uses CO_2 separation for biomethane production, which in turn is injected into the nature gas grid.
- Biogas that is upgraded and injected in such a way can be distributed to extraction points or used to fuel vehicles or heating gas in natural gas grid.
- Biogas can be upgraded into biomethane via separation of CO_2 or into SNG via direct transformation of CO_2 located in biogas, aka Sabatier reaction:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta_r H = -165\ \mathrm{kj \cdot mol^{-1}}$$

CATALYTIC METHANATION

- Catalytic methanation is most commonly associated with the Power-to-Gas concept, however it can also be applied to biogas upgrading.
- Catalytic methanation yields the so called SNG or Renewable Natural Gas (RNG).
- Hydrogen used in the reaction is produced via electrolysis of water using renewable energy sources.
- Heat produced by a methanation unit, as well as the oxygen, gained from electrolysis can be used in the biogas plant.
- It is important to desulfurized the biogas before it is introduced into the methanation unit, as sulfur compounds act as catalytic poison.

EXPERIMENTAL PART

Tab. 1: Compositions of model gases

Model gas	Composition of inlet gas- mol. fraction [%]			Ratio	Ratio
	Methane	Carbon dioxide	Hydrogen	H_2:CO_2	CH_4:CO_2
1.	0.0	20.0	80.0	4:1	0:100
2.	4.8	19.0	76.2	4:1	20:80
3.	11.8	17.6	70.6	4:1	40:60
4.	23.1	15.4	61.5	4:1	60:40

- Used catalysts – Ni / γ-Al_2O_3 and Ni-Co / γ-Al_2O_3; Synthesized during multiple-impregnation (UCT Prague).
- Composition of catalytic metals:
  - Ni/γ-Al_2O_3 Ni-Co/γ-Al_2O_3
  - Ni - 56 m. % Ni – 33 m. %/Co – 22 m. %
- In order to test catalytic methanation of biogas a pilot unit with a fixed bed was used, which enabled testing various catalysts and ratios of CH_4:CO_2 as well as CO_2:H_2 at maximum temperature of 520 °C and maximum gauge pressure rate of 1.5 MPa.

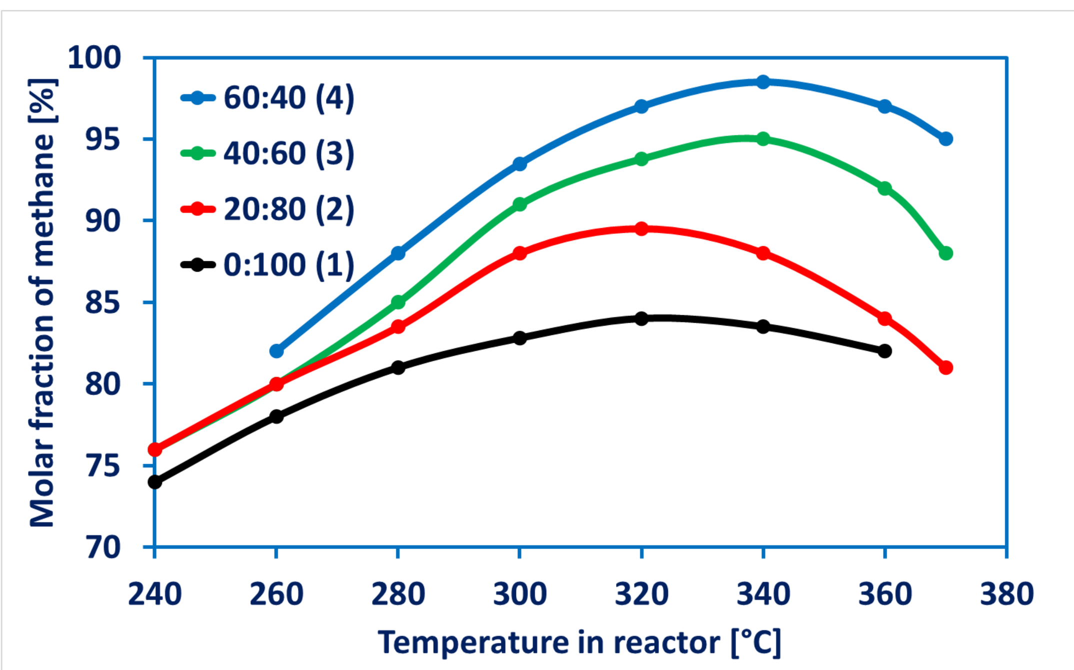

Fig. 1: Dependance of molar fraction of methane on temperature at gauge pressure 0.55 MPa on a Ni based catalyst.

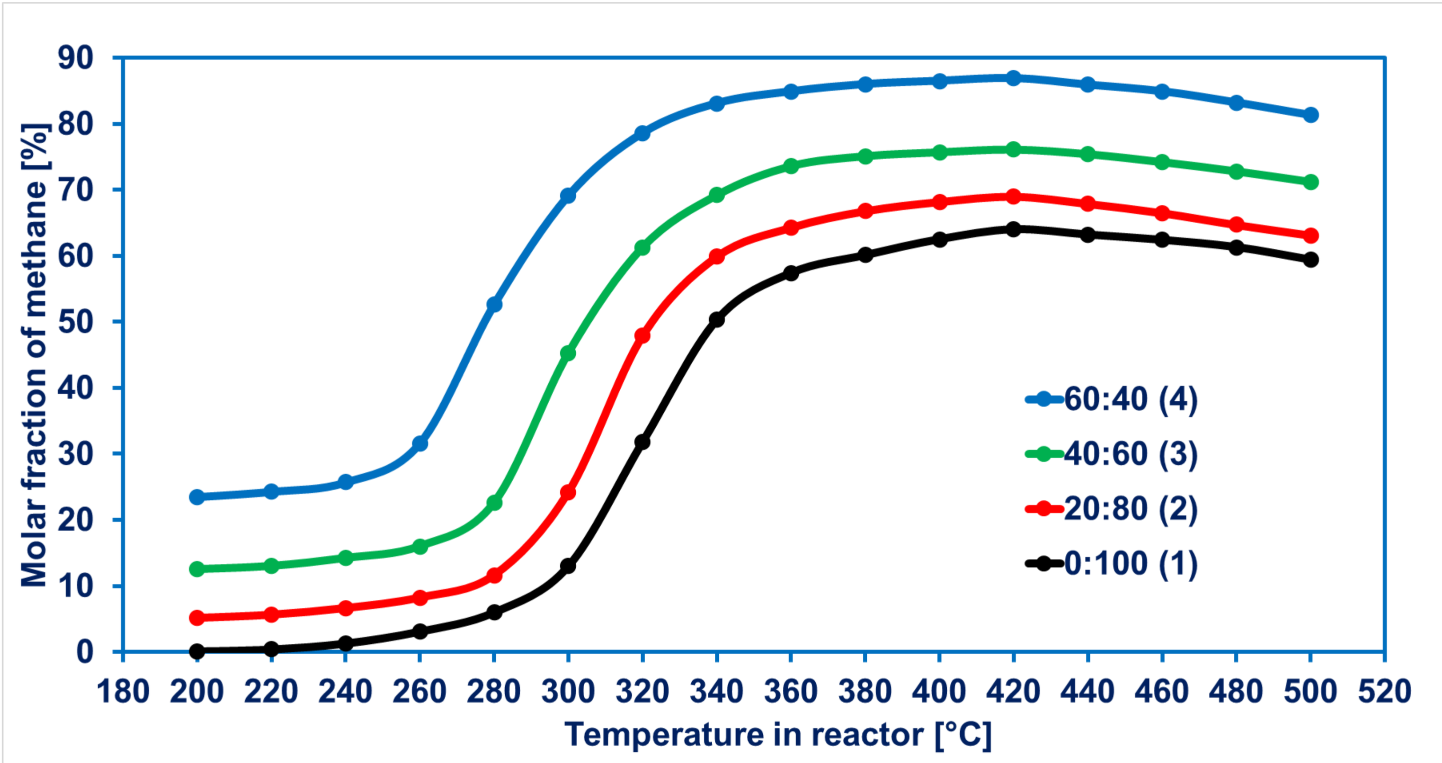

Fig. 2: Dependance of molar fraction of methane on temperature at gauge pressure 0.55 MPa on a Ni-Co based catalyst.

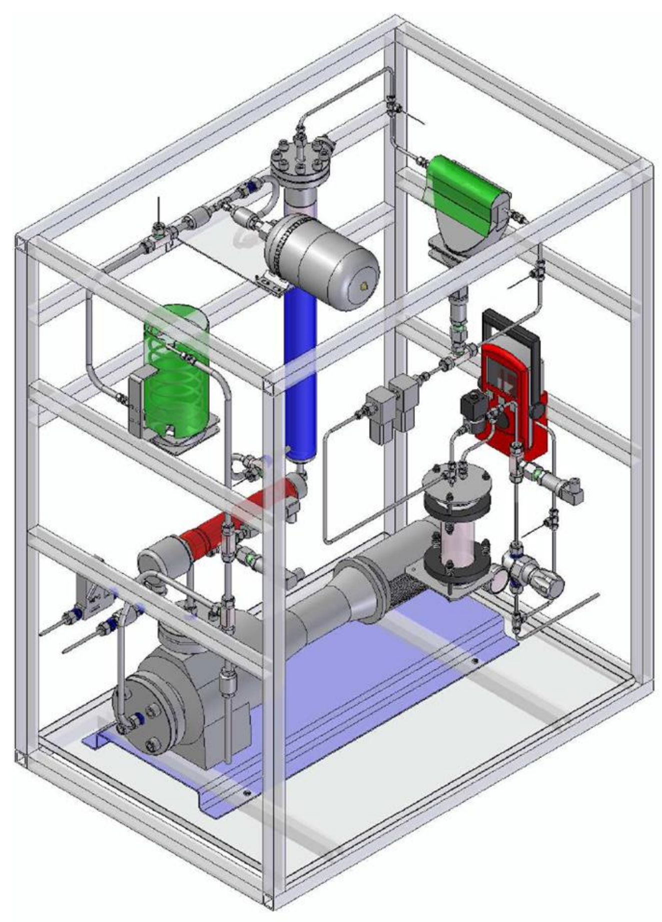

Fig. 3: Pilot unit scheme.

CONCLUSION

- Catalytic methanation enables effective transformation of biogas into SNG with molar fraction of methane reaching up to 98.5 % at 340 °C using a Ni based catalyst, while Ni-Co based catalysts achieved methane purity of 86.9 % at 420 °C. In both cases the desired gauge pressure was 0.55 MPa.
- Ni based catalyst is preferable due to it being cheaper, having higher methane-oriented selectivity, but is more vulnerable to catalytic poisoning by sulfur opposed to Ni-Co based catalysts.
- Application of SNG allows for storing considerable amounts of surplus electric energy in the existing nature gas grids.
- Upgrading biogas to SNG is one the ways of transitioning from fossil fuel sources to renewable energy sources.
- In Czech Republic SNG could cover up to 10 % of annual consumption of natural gas.

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