Methanol production from biogas

Anita Kovac Kralj and Davorin Kralj

Abstract— Methanol is produced from synthesis gas, which is produced from natural gas. Natural gas can be replaced by biogas for the production of synthesis gas. We compare the production of methanol from varieties of raw materials - natural gas and biogas. The basic starting point for comparison is the same mass inlet flow rate of both raw materials under the same operating conditions. Methanol production using natural gas and biogas as the raw material was simulated using an Aspen Plus simulator with real chemical thermodynamic, and 16 146 kg/h crude methanol from natural gas and 14 615 kg/h from biogas could be produced. Methanol production from biogas could also increase by 9.7 % with processed operational and parametric modification using nonlinear programming (NLP). The most important is the conversion of methane in the reformer. Optimal methane conversion could take place by operating with the use of optimal parametric data in a reformer unit (temperature=840 $^{\circ}$C and pressure=8 bar). The optimal production of methanol from biogas was 16 040 kg/h under optimal parameters.

These instructions give you guidelines for preparing papers for conferences or journals. Use this document as a template if you are using Microsoft Word. Otherwise, use this document as an instruction set. The electronic file of your paper will be formatted further at NAUN. Define all symbols used in the abstract. Do not cite references in the abstract. Do not delete the blank line immediately above the abstract; it sets the footnote at the bottom of this column. Page margins are 1,78 cm top and down; 1,65 cm left and right. Each column width is 8,89 cm and the separation between the columns is 0,51 cm.

Keywords—methanol production, biogas, nature gas.

I. INTRODUCTION

Anaerobic digestion is a process in which the biodegradation of organic matter occurs in the absence of dissolved oxygen. It is a well-established and internationally applied technology for stabilizing municipal sewage sludge, treating organic wastes, products and wastewaters from industries, households, and farms [1]. The resulting methane gas is a highly energetic biogas which is used in combined heat and power generators. The development of biogas technology took place at the beginning of the 19th century. However, owing to the energy crises of the 1970s, anaerobic digestion technology underwent significant development [2, 3].

Anaerobic digestion systems for the fermentation of organic matters are widely used with commercial digesters of 70–5000 m^3, small units are used mainly for heating, while large units are used for electricity generation. Much of the technology is based in Europe, with Germany and Denmark

leading the field [4]. According to Nacke and co-authors, by the end of 2005, there were more than 2000 biogas plants in Germany, of different sizes [5].
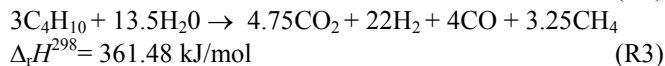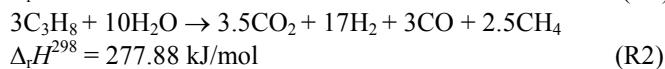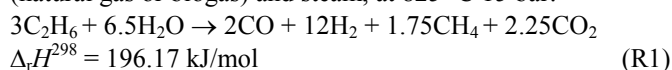
II. METHANOL PRODUCTION

This paper presents the methanol production from biogas. The case study is based on a Lurgi methanol process [7, 9] (Fig. 1). The methanol process is composed of three subsystems:

- production of synthesis gas
- production of crude methanol and
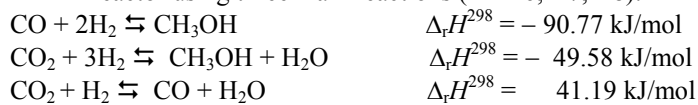- purification of methanol (F301, D301–D304).

We studied the possibility of better conversion regarding synthesis gas in retrofitting the Lurgi process for low-pressure crude methanol production (without purification) from biogas.

Raw material (natural gas or biogas) is first desulphurized (D101) and then heated up in a steam reformer (REA-1), where synthesis gas is produced from raw material (natural gas or biogas) and steam, at 825 $^{\circ}$C 15 bar:

$$3C_2H_6 + 6.5H_2O \rightarrow 2CO + 12H_2 + 1.75CH_4 + 2.25CO_2$$
$$\Delta_r H^{298} = 196.17 \text{ kJ/mol} \tag{R1}$$
$$3C_3H_8 + 10H_2O \rightarrow 3.5CO_2 + 17H_2 + 3CO + 2.5CH_4$$
$$\Delta_r H^{298} = 277.88 \text{ kJ/mol} \tag{R2}$$
$$3C_4H_{10} + 13.5H_2O \rightarrow 4.75CO_2 + 22H_2 + 4CO + 3.25CH_4$$
$$\Delta_r H^{298} = 361.48 \text{ kJ/mol} \tag{R3}$$
$$CH_4 + H_2O \leftrightarrows CO + 3H_2$$
$$\Delta_r H^{298} = 206.08 \text{ kJ/mol} \tag{R4}$$
$$CO + H_2O \leftrightarrows CO_2 + H_2$$
$$\Delta_r H^{298} = -41.17 \text{ kJ/mol} \tag{R5}$$

The hot stream of the synthesis gas is cooled in an E107 boiler, in E109, E110, E111 heat exchangers in an EA101 air cooler, and in an E112 water cooler. The condensate is expanded in flashes: F1, F2, F107, and F108. The synthesis gas is compressed in G201I and G201II two-stage compressors.

In the second subsystem, methanol is produced by the catalytic hydrogenation of carbon monoxide and/or carbon dioxide in a REA-2 reactor using three main reactions (r = R6, R7, R8):

$$CO + 2H_2 \leftrightarrows CH_3OH \qquad \Delta_r H^{298} = -90.77 \text{ kJ/mol}$$
$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \qquad \Delta_r H^{298} = -49.58 \text{ kJ/mol}$$
$$CO_2 + H_2 \leftrightarrows CO + H_2O \qquad \Delta_r H^{298} = 41.19 \text{ kJ/mol}$$

The high-pressure reactor REA-2 is operated within the existing parameters and un-converted gas is recycled. The inlet

stream of the reactor is heated by a process stream (HEPR) or by high-pressure steam (HEST) or a combination of both. The stream leaving the turbine is cooled using air (HEA) and water (HEW) coolers before entering the flash (SEP). The liquid stream of the separation is the product and the recycled gas stream is compressed to 51 bar in a new, two-stage compressor (COMP1, 2) with intermediate water cooling (HEW1). The purge gas is separated from the crude methanol in the flash F301. The purification includes the distillation columns (D301–D304).

III. METHANOL PRODUCTION FROM BIOGAS

Natural gas could be replaced with biogas, which contains 75 % methane (7 895 kg/h), 23% carbon dioxide (2 420 kg/h), and 2 % of hydrogen (210 kg/h), but producing only 14 615 kg/h of crude methanol under existing unchanged process conditions.

Most parameters' effects on material balance were studied, by using an Aspen Plus simulator to determine the material balance of synthesis gas, crude methanol mass flow (m_{MeOH}) and the possible production of steam heat flow rate (Q_{steam}). The most sensitive processing unit for optimizing synthesis gas is a reformer. The reaction of synthesis gas was carried out by using an equilibrium reactor model (RGIBBS; [6]). The reactions R1-R5 took place in reactor REA-1. The conversions of the reactors R1-R3 are 100 %. The outlet stream of reactor REA-1 was observed at different parameters. The parameters can be influenced, especially during reactions R4- R5:

$$CH_4 + H_2O \leftrightarrows CO + 3H_2$$
$$\Delta_r H^{298} = 206.08 \text{ kJ/m} \quad \text{(R4)}$$
$$CO + H_2O \leftrightarrows CO_2 + H_2$$
$$\Delta_r H^{298} = -41.17 \text{ kJ/mol} \quad \text{(R5)}$$

The composition of synthesis gas has a strong effect on the composition of crude methanol mass flow (m_{MeOH}) and the possible production of steam heat flow rate (Q_{steam}). The most important is the conversion of methane in the reformer. Optimal methane conversion could take place by operating with the use of optimal parametric data in a reformer unit. The best methane conversion is under lower pressure and higher temperature.

The pressure and temperature effects on synthesis gas conversions were determined by using an Aspen Plus simulator and were modelled using equations, and included in the NLP model. Methanol production from biogas could also increase with processed operational and parametric modification using nonlinear programming (NLP; [8]).

The primary objective of retrofit is to change the raw material with a minimum of additional cost and maximize the production of methanol and steam. The optimal production of methanol was 16 040 kg/h at optimal parameters (temperature=840 °C and pressure=8 bar) in the reformer. Optimal steam production was 13 230 kW. Additional cost only included the additional heating of the reformer with 0.045 MEUR/a. The total annual income was 1.36 MEUR/a. Methanol production from biogas could be increased by 9.7 % with processed operational and parametric modification using nonlinear programming (NLP). The profit was 1.315 MEUR/a depending on optimized conditions. The total methanol mass flow from biogas under optimal conditions was identical to that of the total methanol mass from natural gas.

IV. CONCLUSIONS

Natural gas may be replaced by renewable sources of second generation - nonfood sources. Natural gas can be replaced by biogas for the production of synthesis gas. Methanol is produced from synthesis gas, which is produced from raw material - natural gas or biogas. A comparison of methanol production from two varieties of raw materials – were made – natural gas and biogas. The basic starting point for comparison is the same mass inlet flow rates for both raw materials under the same operating conditions. Methanol production using natural gas and biogas as the raw materials was simulated using an Aspen Plus simulator with real chemical thermodynamic, and 16 146 kg/h crude methanol from natural gas and 14 615 kg/h from biogas could be produced. Methanol production from biogas could also increase by 9.7 % with processed operational and parametric modification using nonlinear programming (NLP). The NLP model contains equations which enable methanol and steam production, and parametric optimization. The most important is the conversion of methane in the reformer. Optimal methane conversion could take place by operating by the use of optimal parametric data in a reformer unit. Mathematical problems could include equations which present synthesis gas composition, crude methanol, and steam productions. The primary objective of retrofit is to change the raw material with a minimum of additional cost and maximize the production of methanol and steam. The optimal production of methanol was 16 040 kg/h under optimal parameters (temperature=840 °C and pressure=8 bar) in the reformer. Optimal steam production was 13 230 kW. The total methanol mass flow from biogas under optimal conditions was identical with the total methanol mass from natural gas.
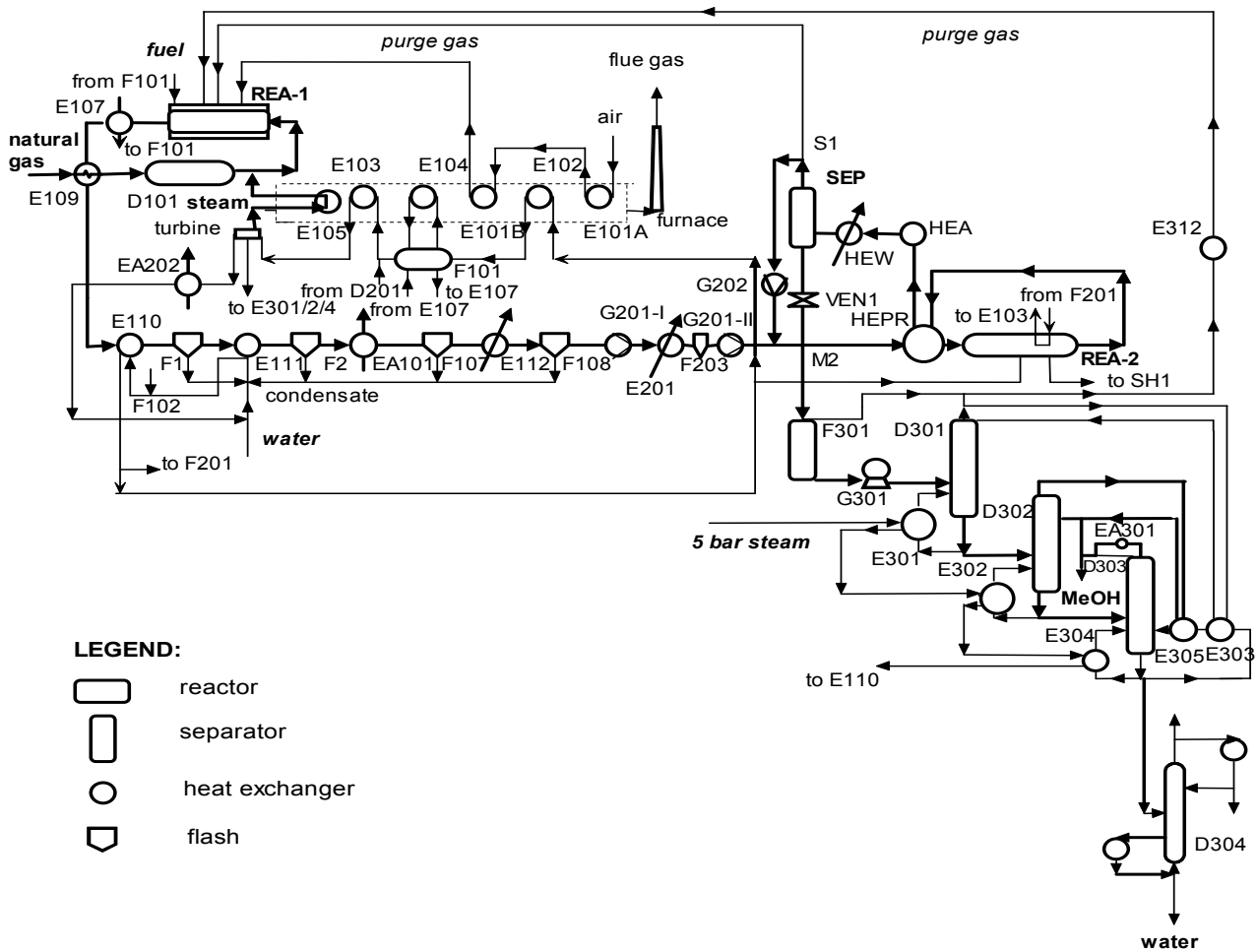
Fig 1: Process flow diagram of a low-pressure Lurgi methanol plant.

REFERENCES

[1] DeBaere L. (2000). State-of-the- art of anaerobic digestion of solid waste in Europe, Water Science and Technology 41, 283–290.

[2] Alvarez J.M. (2003). Biomethanization of the organic fraction of municipal solid wastes (1st ed.), IWA Publishing.

[3] Strik D., Domnanovich A., Zani L., Braun R. and Holubar P. (2005). Prediction of trace compounds in biogas from anaerobic digestion using the MATLAB Neural Network Toolbox 20, Environmental Modeling & Software, 803–810.

[4] Nickolas J., Themelis S. and Verma S. (2004). Anaerobic digestion of organic waste in MSW, Waste Management World, January–February, 41–47.

[5] Nacke T., Brückner K., Göller A., Kaufhold S., Nakos X. and Noack S. (2005). New type of dry substances content meter using microwaves for application in biogas plants, Anal Bioanal Chem 383, 752–757.

[6] Aspen Technology (2002). ASPEN PLUS User Manual Release 11.1, Aspen Technology Inc., Cambridge, MA 02139, USA.

[7] Kovač Kralj A., Glavič P. and Kravanja Z. (2000). Retrofit of complex and energy intensive processes II: stepwise simultaneous superstructural approach, Comput. chem. Engng 24/1, 125–138.

[8] Brooke A., Kendrick D. and Meeraus A. (1992). GAMS: A User's Guide, Palo Alto, Scientific Press.

[9] McKetta J. J., W. A. Cunningham (1985). Encyclopedia of chemical processing and design. Vol. 29, Marcel Dekker, New York, 418–474.