Replacing natural gas with biogas in the methanol production

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ABSTRACT

Natural gas may be a replaced by renewable source from a second generation – non-food source for methanol production.

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) with quadratic and linear functions. 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) by using quadratic and linear functions. The optimal production of methanol from biogas was 16 040 kg/h under optimal parameters.

Keywords: methanol production, biogas, natural gas

1 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].

During the time in which the mixture of wastewater stays in the digester, with the microbial population in order, to produce the biogas is called the 'hydraulic retention time' (HRT). This time is very important in the design of biogas digesters [6]. Anaerobic bacteria (the methanogens), are sensitive to those acid concentrations where the optimum pH value is found to be within a range of 6.5–8.5 [4]. In addition, according to Nickolas, the concentration of ammonia increases at the ends of the processes, so the pH level will be between 7.2 and 8.2.

Temperature is an important factor that determines the rate of digestion. Most digesters are operated within the mesophilic range (30–35 °C), but it is possible to operate digesters within the thermophilic range (approximately 55 °C) but with higher operating costs, lower process stability, and more structural requirements [7]. The carbon to nitrogen (C/N) ratio for optimal biogas production should be within the range 25–30. When a batch of waste is received with high C/N ratio, this implies a complex organic matter which is difficult to biodegradable; therefore, some adjustment is required, such as adding a high content of nitrogenous waste. On the other hand, low C/N ratio needs straw or crop residues to be added, so as to adjust the carbon content [8].

According to Koelsch and co-authors, the total solids content range is about 8–13% and 80% of the solids are volatile solids [9]. One-half of the volatile solids (the biodegradable ones) are converted into methane and carbon dioxide. Typical solid separation of the effluent will remove 4% of the solids from the effluent. About one-third of the solids are converted to gas, one-third can be separated out mechanically, and one-third remains in the separated liquid effluent [10].

This paper presents the replacement of raw materials - natural gas with biogas by using quadratic and linear functions.

2 REPLACING NATURAL GAS WITH BIOGAS

2.1 Methanol production from natural gas

Methanol production using natural gas and biogas gas as the raw material was simulated using an Aspen Plus simulator (with real chemical thermodynamic and selected processing units, which are very comparable to existing material and energy flow flows) [11]. The thermodynamic properties of gases can be calculated using different methods and models. These models can estimate fugacity

coefficients, enthalpies, densities, entropies, and free energies. The Grayson-Streed model of corresponding states correlation is used for synthesis gas. Fugacity coefficients, entropies and free energies can be estimated using this model. The Grayson-Streed model is a generalized method for predicting vapour-liquid equilibria in gaseous hydrocarbon and hydrogen mixtures. This method is needed for simulation. The thermodynamic model of component properties is very important for approaching a good simulation. The thermodynamic properties of synthesis gas were estimated by using the Grayson-Streed model with an Aspen Plus simulator, and the results are in relatively good agreement with the experimental data in an existing methanol production plant [12]. Methanol production using natural gas as the raw material was simulated using an Aspen Plus simulator, and 16 146 kg/h crude methanol could be produced. The composition of synthesis gas has a strong effect on the composition of crude methanol mass flow (m_{MeOH} =16 146 kg/h) and the possible production of steam heat flow rate (Q_{steam} =13 309 kW).

2.2 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). The reactions R1-R5 took place in reactor REA-1. 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 quadratic and linear equations, and included in the NLP model. Methanol production from biogas could also increase with processed operational and parametric modification using nonlinear programming (NLP).

2.3 Quadratic mathematical model of methanol production from biogas

Retrofitting of the existing plant is focused on the general mathematical NLP method including many result assumptions by the Aspen Plus simulator.

The retrofitted methanol process by using biogas as raw material can increase synthesis gas conversion and, therefore, the crude methanol conversion. 14 615 kg/h crude methanol production from biogas could be enlarged by using nonlinear programming (NLP). The methanol process parameters are optimized using a nonlinear programming (NLP) model [13]. The parameters in the retrofitted model of methanol production from biogas were simultaneously optimized using the GAMS/MINOS [13]. This NLP can be solved using a large-scale reduced gradient method (e. g. MINOS). The model is non-convex, it does not guarantee a global optimization solution but it quickly gives good results for non-trivial, complex processes. The NLP model contains variables of the process parameters: molar heat capacities, material flow rates, heat flow rates, pressures and temperatures, which are limited by real constraints. The NLP model contains equations which enable methanol and steam production. The most important is the conversion of methane in the reformer. Optimal methane conversion could take place by an operation using the optimal parametric data in a reformer unit. Mathematical problems could include those equations which present synthesis gas composition (equations 1−10), crude methanol production (equations 11−12), and steam production (equations 13−14).

Equation 1 presents the dependence of the composition of methane in the synthesis gas, as a function of pressure in the reformer:

$$m_{CH4,p}^{B} = 1.1454p^2 + 54.2p - 150 \qquad (1)$$

Equation 2 presents the dependence of the composition of carbon dioxide in the synthesis gas, as a function of pressure in the reformer:

$$m_{CO2,p}^{B} = -0.6257p^2 - 5.5214p + 9713.3 \qquad (2)$$

Equation 3 presents the dependence of the composition of water in the synthesis gas, as a function of pressure in the reformer:

$$m_{H2O,p}^{B} = 1.5692p^2 + 62.551p + 21131 \qquad (3)$$

Equation 4 presents the dependence of the composition of carbon monoxide in the synthesis gas, as a function of pressure in the reformer:

$$m_{CO,p}^{B} = -1.6141p^2 - 90.916p + 9403 \qquad (4)$$

Equation 5 presents the dependence of the composition of hydrogen in the synthesis gas, as a function of pressure in the reformer:

$$m_{H2,p}^{B} = -0.47744p^2 - 20.548p + 3576.3 \qquad (5)$$

Equation 6 presents the dependence of the composition of methane in the synthesis gas, as a function of temperature in the reformer:

$$m_{CH4,T}^{B} = 0.0469T^2 - 89.742T + 42990 \qquad (6)$$

Equation 7 presents the dependence of the composition of carbon dioxide in the synthesis gas, as a function of temperature in the reformer:

$$m_{CO2,T}^{B} = -12.61T + 19894 \qquad (7)$$

Equation 8 presents the dependence of the composition of water in the synthesis gas, as a function of temperature in the reformer:

$$m_{H2O,T}^{B} = 0.052T^2 - 94.338T + 64845 \qquad (8)$$

Equation 9 presents the dependence of the composition of carbon monoxide in the synthesis gas, as a function of temperature in the reformer:

$$m_{CO,T}^{B} = -0.08298T^2 + 166.49T - 73188 \qquad (9)$$

Equation 10 presents the dependence of the composition of hydrogen in the synthesis gas, as a function of temperature in the reformer:

$$m_{H2,T}^{B} = -0.01752T^2 + 32.943T - 12084 \qquad (10)$$

Equation 11 presents the dependence of the composition of crude methanol in methanol reactor (REA-2), as a function of pressure:

$$m_{MeOH,p}^{B} = -2.739p^2 - 110.73p - 16890 \qquad (11)$$

Equation 12 presents the dependence of the composition of crude methanol in methanol reactor (REA-2), as a function of temperature:

$$m_{MeOH,T}^{B} = -0.10285T^2 + 197.11T - 77982 \quad (12)$$

Equation 13 presents the dependence of the production of steam flow rate during the methanol process, as a function of pressure:

$$Q_{steam,p}^{B} = -0.13685p^2 - 3.908p + 12735 \qquad (13)$$

Equation 14 presents the dependence of the production of steam flow rate, as a function of temperature:

$$Q_{steam,T}^{B} = 35.882T - 16956 \qquad (14)$$

The objective function (eq. 15) of the NLP model was to maximize the annual profit and included the incomings and depreciation (Table 6). Income include the additional methanol ($m_{MeOH}^{B} - m_{exist}^{B}$) and steam ($Q_{steam}^{B} - Q_{exist}^{B}$) productions depending on the pressure and temperature functions. Temperature and pressure could have an affect on the additional production of methanol and steam, therefore, it could be divided by two as an objective function. The existing methanol mass flow from biogas (m_{exist}^{B}) is 14 615 kg/h under existing unchanged process conditions. The existing steam heat flow from biogas (Q_{exist}^{B}) is 12 646 kW under unchanged existing process conditions. Depreciation is included in the cost of additionally heating the reformer if the temperature is higher than the existing temperature (T_{ex} =825 ^{o}C).

Maximal additional annual profit (V_{max}) for retrofit:

$$\begin{aligned}
V_{max} &= \frac{(m_{MeOH,p}^{B} - m_{exist}^{B})}{2} C_{MeOH} \\
&+ \frac{(m_{MeOH,T}^{B} - m_{exist}^{B})}{2} C_{MeOH} \\
&+ \frac{(Q_{steam,p}^{B} - Q_{exist}^{B})}{2} C_{steam} \qquad (15) \\
&+ \frac{(Q_{steam,T}^{B} - Q_{exist}^{B})}{2} C_{steam} \\
&- (T - T_{ex}) C_{heating}
\end{aligned}$$

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 ^{o}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.

2.4 Linear mathematical model of methanol production from biogas

Instead of a quadratic model was optimized in the linear model (Fig. 1 and Fig. 2). The problem is simplified, but the results are the same as in the quadratic model.
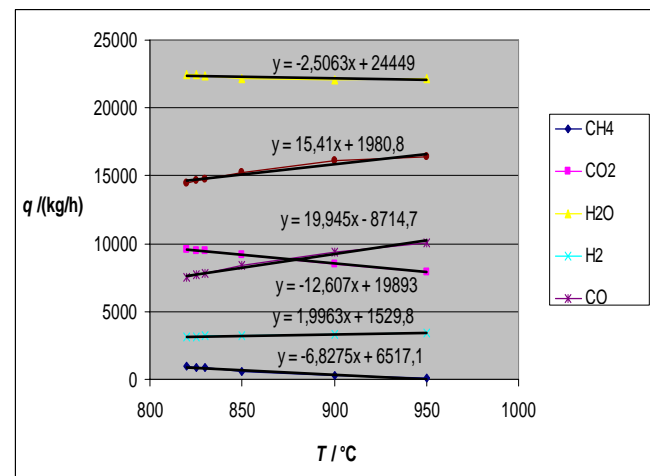

Figure 1: Temperature as a linear function of different component's mass flow.
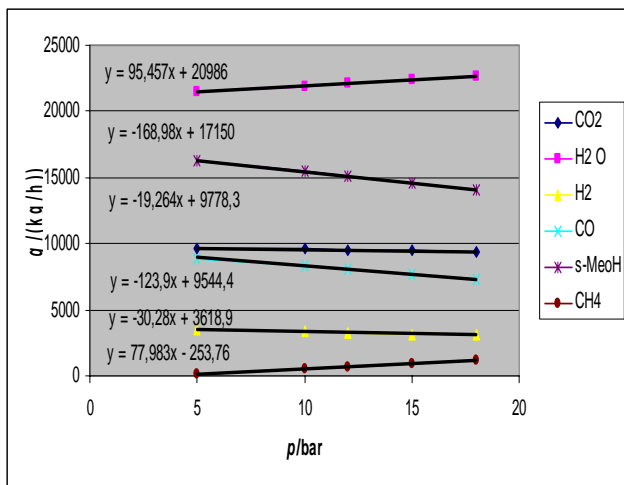
$y = 95{,}457x + 20986$

$y = -168{,}98x + 17150$

$y = -19{,}264x + 9778{,}3$

$y = -123{,}9x + 9544{,}4$

$y = -30{,}28x + 3618{,}9$

$y = 77{,}983x - 253{,}76$

Figure 2: Pressure as a linear function of different component's mass flow.

3 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) with quadratic and linear functions. 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 $^{\circ}$C and pressure=8 bar) in the reformer by using quadratic and linear functions. 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.

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