Methanol production from biogas

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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 ^{o}C and pressure=8 bar). The optimal production of methanol from biogas was 16 040 kg/h under optimal parameters.

Keywords**—**methanol production, biogas, nature gas, environmental management, sustainability

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].

2 Environmental Management and Sustainability

The environment management is so the consequence of EU Environmental Policy and Slovene Environmental Policy [11]. Hospital Maribor has engaged actively in environmental protection as a part of sustainability. Environmental management systems guarantee Hospital Maribor environmental protection at all locations. This include putting into practice best environmental practice. One of the most important thing in environmental management is leadership. The whole treat of environment in the administration and leading of professional processes is inevitable condition for the preservation of natural balance in the environment [12]. Leaders establish utility of purpose and direction of the organisation. They should create and maintain the internal environment in which people can become fully involved in achieving the organization's objectives [13]. And environmental objectives are organization's objectives. Specific management representative who, irrespective of other responsibilities, has defined roles, responsibilities and authority for:

- ensuring that environmental management system is established, implemented and maintained,
- reporting to top management on the performance of the environmental management system for review, including recommendations for improvement [14].

Management representative collects data on the environment related aspects of various activities, such as energy consumption. Therefore the greatest opportunities of saving costs should be based on electrical energy management. An energy management plan should include a characterization of the energy type and its applications, characterization of typical consumption, evaluation of facilities and systems, evaluation of supply contract and other possibilities of acquiring energy, identification and evaluation of energy-saving opportunities and, finally, development of an action plan to implement and review the plan. This process should be continuous, being constantly revised in an effort to discover new opportunities [15]. In a typical hospital, water heating, space heating, and lighting account for 61-79 percent of total energy use, depending on climate relative to the number of cooling- and heating-degree days. Energy is a significant factor in the growing percentage of healthcare operating costs, which are increasing at the rate that cannot be offset by increases in reimbursement rates. In order to survive, healthcare facilities must aggressively control costs. Strategies for energy cost controls have led to a trend of dealing with energy supply costs, reliability, and quality as managed risk [16]. Development of Environmental Management System is constantly improving. New environment issues dictate the redefining of The interest of customers, users, developers and others in the environmental aspects and impacts of products is increasing [17]. It is essential for the real effectiveness of environmental management to have appropriate leadership and keep well-regulated interpersonal relations in an enterprise. Congenial and stimulating atmosphere, promoting relaxed free and unimpeded activities, work satisfaction and satisfaction with co-operation with others, are all elements distinguishing excellent performance. When implementing changes, employees should be motivated adequately. There was quite a strong resistance from employees to implementing working groups at the very beginning of this process, which also resulted from the fact that we were unable to present them the sense and benefits of this process, moreover, we were unable to motivate them by the positive aspects of teamwork [18].

3. 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 °C 15 bar (Table 1):

$$3C_2H_6 + 6.5H_2O \rightarrow 2CO + 12H_2 + 1.75CH_4 + 2.25CO_2$$
$$\Delta_r H^{298} = 196.17 \text{ kJ/mol} \qquad \text{(R1)}$$

$$3C_3H_8 + 10H_2O \rightarrow 3.5CO_2 + 17H_2 + 3CO + 2.5CH_4$$
$$\Delta_r H^{298} = 277.88 \text{ kJ/mol} \qquad \text{(R2)}$$

$$3C_4H_{10} + 13.5H_20 \rightarrow 4.75CO_2 + 22H_2 + 4CO + 3.25CH_4$$
$$\Delta_r H^{298} = 361.48 \text{ kJ/mol} \qquad \text{(R3)}$$

$$CH_4 + H_2O \leftrightarrows CO + 3H_2$$
$$\Delta_r H^{298} = 206.08 \text{ kJ/mol} \qquad \text{(R4)}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2$$
$$\Delta_r H^{298} = -41.17 \text{ kJ/mol} \qquad \text{(R5)}$$

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):

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

Component in s.g.	Mass flow /(kg/h)
CH_4	1 737
CO_2	8 915
CO	9 404
H_2	3 648
H_2O	19 821
Others parameters	
m_{MeOH} (kg/h)	16 146
Q_{steam} (kW)	13 309

Table 1: The composition of synthesis gas (s.g.) from natural gas and others parameters at the existing condition T =825 °C and p = 15 bar.

4. 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 (table 2).

Component in s.g.	Mass flow /(kg/h)
CH_4	919
CO_2	9 491
CO	7 678
H_2	(R6) 3 163
H_2O	(R7) (R8) 22 421
Others parameters	
m_{MeOH} (kg/h)	14 615
Q_{steam} (kW)	12 646

Table 2: The composition of synthesis gas (s.g.) from biogas and other parameters at the existing condition T =825 °C and p = 15 bar.

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 (Table 3 and 4). The parameters can be influenced, especially during reactions R4- R5:

$CH_4 + H_2O \leftrightarrows CO + 3H_2$
$\Delta_r H^{298} = 206.08$ kJ/m (R4)

$CO + H_2O \leftrightarrows CO_2 + H_2$
$\Delta_r H^{298} = -41.17$ kJ/mol (R5)

Component in s.g.	Mass flow /(kg/h)
CH_4	315
CO_2	9 630
CO	8 581
H_2	3 383
H_2O	21 726
Others parameters	
m_{MeOH} (kg/h)	15 838
Q_{steam} (kW)	12 696

Table 3: The composition of synthesis gas (s.g.) from biogas and other parameters at T =825 °C and p = 8 bar.

Component in s.g.	Mass flow /(kg/h)
CH_4	531
CO_2	9 055
CO	8 633
H_2	3 289
H_2O	22 163
Others parameters	
m_{MeOH} (kg/h)	15 488
Q_{steam} (kW)	13 905

Table 4: The composition of synthesis gas (s.g.) from biogas and other parameters at T =860 °C and p = 15 bar.

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.

5. 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 [10]. The parameters in the retrofitted model of methanol production from biogas were simultaneously optimized using the GAMS/MINOS [10]. 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:

$$m^{\mathrm{B}}_{\mathrm{CH4,p}} = 1.1454p^2 + 54.2p - 150 \tag{1}$$

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

$$m^{\mathrm{B}}_{\mathrm{CO2,p}} = -0.6257p^2 - 5.5214p + 9713.3 \tag{2}$$

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

$$m^{\mathrm{B}}_{\mathrm{H2O,p}} = 1.5692p^2 + 62.551p + 21131 \quad (3)$$

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

$$m^{\mathrm{B}}_{\mathrm{CO,p}} = -1.6141p^2 - 90.916p + 9403 \quad (4)$$

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

$$m^{\mathrm{B}}_{\mathrm{H2,p}} = -0.47744p^2 - 20.548p + 3576.3 \quad (5)$$

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

$$m^{\mathrm{B}}_{\mathrm{CH4,T}} = 0.0469T^2 - 89.742T + 42990 \quad (6)$$

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

$$m^{\mathrm{B}}_{\mathrm{CO2,T}} = -12.61T + 19894 \quad (7)$$

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

$$m^{\mathrm{B}}_{\mathrm{H2O,T}} = 0.052T^2 - 94.338T + 64845 \quad (8)$$

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

$$m^{\mathrm{B}}_{\mathrm{CO,T}} = -0.08298T^2 + 166.49T - 73188 \quad (9)$$

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

$$m^{\mathrm{B}}_{\mathrm{H2,T}} = -0.01752T^2 + 32.943T - 12084 \quad (10)$$

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

$$m^{\mathrm{B}}_{\mathrm{MeOH,p}} = -2.739p^2 - 110.73p - 16890 \quad (11)$$

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

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

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

$$Q^{\mathrm{B}}_{\mathrm{steam,p}} = -0.13685p^2 - 3.908p + 12735 \quad (13)$$

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

$$Q^{\mathrm{B}}_{\mathrm{steam,T}} = 35.882T - 16956 \quad (14)$$

The objective function (eq. 15) of the NLP model was to maximize the annual profit and included the incomings and depreciation (Table 5). Income include the additional methanol ($m^{\mathrm{B}}_{\mathrm{MeOH}} - m^{\mathrm{B}}_{\mathrm{exist}}$) and steam ($Q^{\mathrm{B}}_{\mathrm{steam}} - Q^{\mathrm{B}}_{\mathrm{exist}}$) 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 ($m^{\mathrm{B}}_{\mathrm{exist}}$) is 14 615 kg/h under existing unchanged process conditions. The existing steam heat flow from biogas ($Q^{\mathrm{B}}_{\mathrm{exist}}$) 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 °C).

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

$$\begin{aligned} V_{\max} &= \frac{(m^{\mathrm{B}}_{\mathrm{MeOH,p}} - m^{\mathrm{B}}_{\mathrm{exist}})}{2} C_{\mathrm{MeOH}} \\ &+ \frac{(m^{\mathrm{B}}_{\mathrm{MeOH,T}} - m^{\mathrm{B}}_{\mathrm{exist}})}{2} C_{\mathrm{MeOH}} \\ &+ \frac{(Q^{\mathrm{B}}_{\mathrm{steam,p}} - Q^{\mathrm{B}}_{\mathrm{exist}})}{2} C_{\mathrm{steam}} \\ &+ \frac{(Q^{\mathrm{B}}_{\mathrm{steam,T}} - Q^{\mathrm{B}}_{\mathrm{exist}})}{2} C_{\mathrm{steam}} \\ &- (T - T_{ex}) C_{heating} \end{aligned} \tag{15}$$

Price of methanol, C_{MeOH}/(EUR/t): 115.0
Price of HPsteam, C_{steam}/(EUR/kWa): 106.0
Cost of additional, C_{heating}/(EUR/K a): 3 000

Table 6: Cost items for the example process.

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.

6. 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.

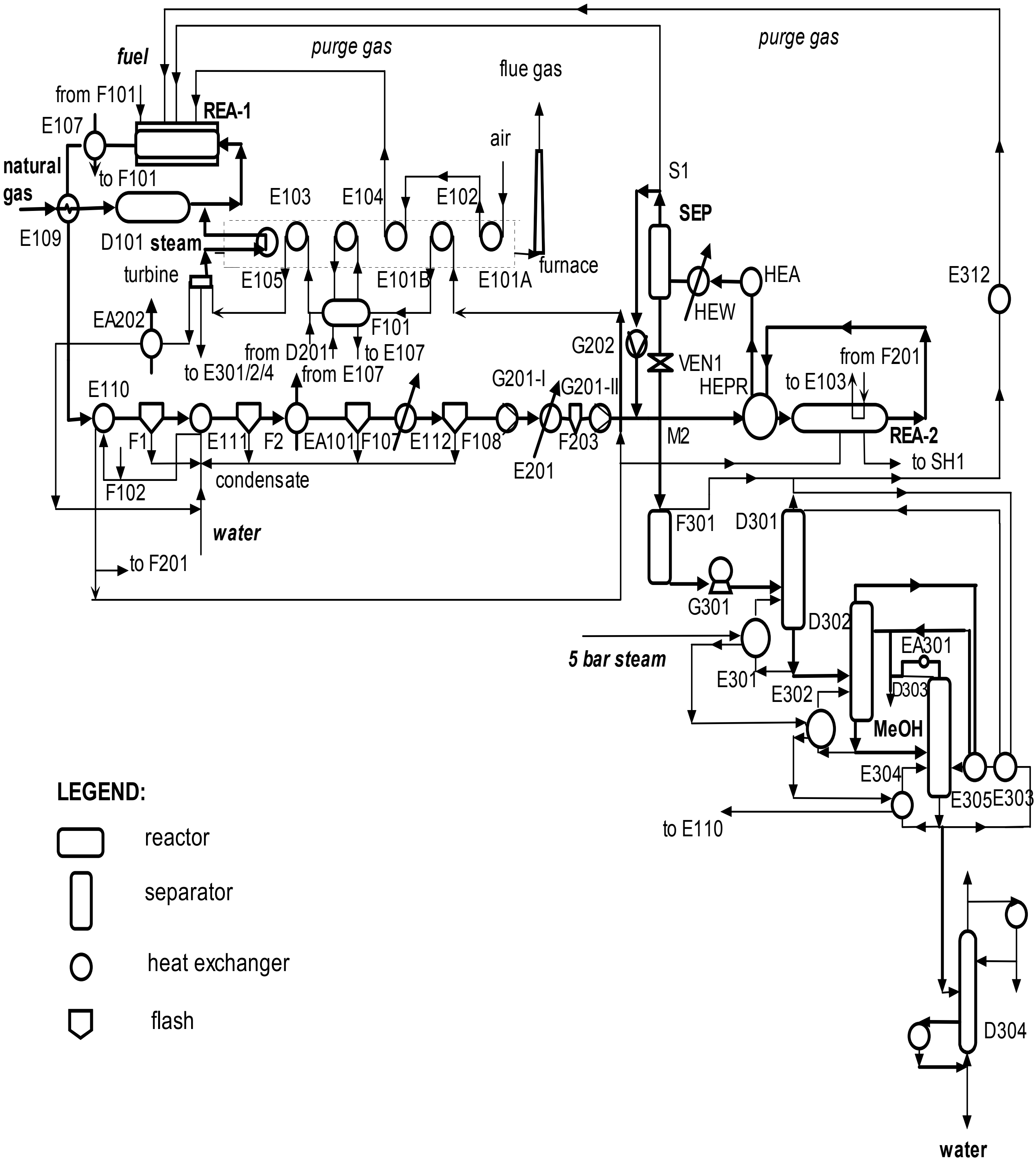

Fig 1: Process flow diagram of a low-pressure Lurgi methanol plant.

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NOMENCLATURES

Abbreviations:

HP	high pressure
NLP	nonlinear programming
n.g.	natural gas
s.g.	synthesis gas

Variables:

m	mass flow, kg/h
p	pressure, bar
T	temperature, K
Q	heat flow rate, W