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MODELLING AND SIMULATION OF FUELS PRODUCTION FROM SYNGAS

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ABSTRACT. Syngas is a very important product, with a variety of uses; it may even become a primary source of fuel, and replace natural gas. This is because, syngas has the building blocks to create all the products and chemicals currently generated in the petrochemical industry. Fuels manufactured from synthesis gas offer special opportunities based both on environmental and energy performance. The aim of the present work is to design and compare different chemical production processes for fuels generation using syngas as raw-material. ChemCAD process simulator software was used as the main tool for process modelling and simulation. The investigation was focused on the conversion of syngas to methanol, dimethyl ether and hydrogen at a large scale. For comparison reasons, the same amount of syngas (e.g. 10000 kmol/h) was used in all three cases under investigation. After comparison, syngas to hydrogen process seems to be the best option from thermal energy point of view and in terms of environmental impact.

Keywords: *syngas, process modelling and simulation, hydrogen, methanol, dimethyl ether (DME)*

INTRODUCTION

Synthetic gas called also syngas is a fundamental chemical intermediate which can be obtained from many sources (e.g. coal, natural gas, biomass, different solid waste, recycled plastics), using different technologies (e.g. gasification, reforming) and can be used in various applications. In its simplest form, syngas is composed of two diatomic molecules, CO and H_2 that provide the building blocks upon which an entire field of fuel science and technology is based. According to PR Newswire global syngas production accumulated to

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116 GWth in 2014 and is projected to reach 213 GWth by 2020 [1]. The important role of syngas in both chemical and petrochemical industries has been widely recognized since it is currently utilized as a main feedstock for producing environment-friendly synthetic fuels and methanol via respective Fischer-Tropsch synthesis [2]. Syngas is a crucial intermediate resource for production of hydrogen and ammonia [3] being also attractive as a fuel for internal combustion engines, gas turbines and high temperature fuel cells, and as a chemical feedstock for the production of methanol, synthetic hydrocarbon fuels [4, 5]. The most important syngas applications are briefly presented in Figure 1.

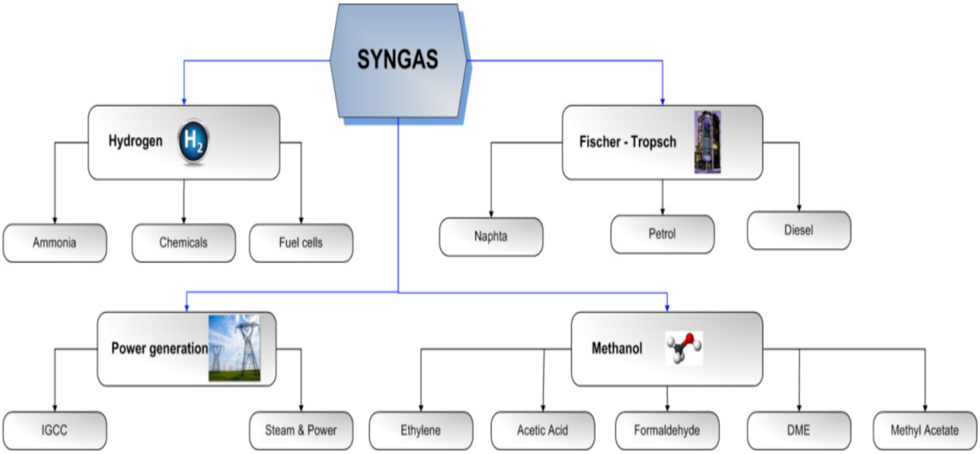

Figure 1. Syngas application in various industrial sectors

The goal of the present work was to investigate and compare the production of different fuels from syngas. The attention was focused on three fuels, more exactly: methanol, dimethyl ether (DME) and hydrogen. A brief overview of the importance, production methods, advantages and disadvantages of the three fuels is presented the next section.

The first fuel investigated was methanol. Methanol is an important chemical intermediate used to produce a number of chemicals, including: formaldehyde, dimethyl ether, methyl tert-butyl ether, acetic acid, olefins and others. Currently, for economic reasons, the majority of methanol is synthesized from syngas that is produced via steam reforming of natural gas. One of the distinct advantages of employing methanol as a sustainable source of fuel is the diverse array of feed stocks from which this simple alcohol can be produced. Besides industrial production from natural gas and coal, methanol can be made from anything that is, or ever was, a plant (e.g. timber waste, landfill gas, trash, pulp mill black liquor, agricultural waste [6]. Fuel methanol has similar properties to gasoline and can be stored and transported in a similar manner.

The second fuel which arouses our interest is dimethyl ether (DME). This fuel is obtained from methanol, its production process becoming one of the most important issues of the world industry in the recent years. There are different methods of DME production: an indirect synthetic method using the dehydration reaction of methanol, a direct synthetic method from natural gas, gasification of coal, biomass, or electrolysis using solar, wind, hydro or wave energy. DME is more like liquefied petroleum gas (LPG) in its physical properties. But by contrast, it is more suitable for use in a diesel engine due to its high cetanic value. Unlike methanol, it has a sufficient cetanic number without the use of additives or spark assistance. DME has low octane and is not used as a gasoline substitute, in contrast to methanol, which has excellent properties for this use. The calorific value is higher than methanol but lower than conventional fuels. Like methanol, DME can be used directly in gas turbines [7].

The third fuel investigated was hydrogen. Hydrogen can be produced using a number of different processes (e.g. reforming of natural gas, gasification of coal, oil and / or biomass, water electrolysis, fermentation of biomass). Hydrogen, as an important energy carrier in the future has a number of advantages. For example, a large volume of hydrogen can be easily stored in a number of different ways [8]. Hydrogen is also considered as a high efficiency, low polluting fuel that can be used for transportation, heating, and power generation in places where it is difficult to use electricity. The only emissions are water vapour. In some instances, it is cheaper to ship hydrogen by pipeline than sending electricity over long distances by wire [9].

A comparison between the three fuels investigated in the present work, underlining their advantages and disadvantages is presented in Table 1.

Table 1. Advantages and disadvantages of methanol, DME and hydrogen as fuels

Fuel	Facts	Advantages	Disadvantages
CH_3OH	Predominately from syngas made via SMR. Several automakers have developed prototypes using CH_3OH as fuel. Commodity chemical.	Mature technology. Many uses for CH_3OH	Poor solubility in gasoline and phase separation problems. More corrosive than gasoline.
DME	Many potential uses e.g. diesel, cooking fuel, refrigerant, chemical feedstock.	In situ dehydration of CH_3OH to DME increases CH_3OH yields.	DME is very reactive. Sensitive to traces of pollutants.
H_2	Largest use of syngas. Predominately made via steam methane reforming (SMR).	H_2 itself is a clean fuel. Mature technology. High yields.	Delivery price can be significantly higher than plant gate price. Have to compete with mega methanol plants.

RESULTS AND DISCUSSION

The following cases have been investigated in the present work:

Process 1: Methanol from syngas production process;

Process 2: DME from methanol production process;

Process 3: H_2 from syngas production process.

The main streams for *Process 1* are reported in Table 2. Starting from a quantity of 10000 kmol/h (stream 1, Table 2), a quantity of 3331.48 kmol/h of methanol with a purity of 99.9% was obtained, as shown in Table 2 (stream 7).

Table 2. Relevant flows for *Process 1*

Stream Name	**Unit of measure**	**1**	**4**	**5**	**7**	**9**
Temperature	°C	160	221.3	267	38	38
Pressure	bar	29	65	65	105	105
Component flow-rate	kmol/h					
H_2		6667	10255	3591	2.71	3589
CO		3333	5125	1794	1.47	1792
CH_3OH		0	17	3348	3331.48	17
CO_2		0	0	0	0	0
H_2O		0	0	0	0	0
DME		0	0	0	0	0
Total flow	kmol/h	10000	15397	8734	3335.66	5398
Total flow	kg/h	106805	164765	164765	106794	57971

The main streams for *Process 2* are reported in Table 3. In this case the flow-rate of the main product obtained (DME) has a value of 1665.66 kmol/h (see stream 10 from Table 3). The purity of the product obtained is about 99.56%.

The main streams for *Process 3* are reported in Table 4. The quantity of the desired product (H_2) obtained in this case 9670.65 kmol/h (see stream 10, Table 4). The quantity of syngas consumed to produce de desired product is 10000 kmol/h, correspondent to a mass flow-rate of 106805 kg/h (stream 1, Table 4).

Table 3. Relevant flows for *Process 2*

Stream Name	**Unit of measure**	**1**	**5**	**6**	**10**	**23**
Temperature	°C	38	256	364	25	25
Pressure	bar	105	14.7	13.9	11.4	1
Component flow-rate	kmol/h					
H_2		2.71	2.71	0	0	0
CO		1.47	1.47	0.12	0.12	0
CH_3OH		3331.48	4144.03	829.14	7.29	8.77
CO_2		0	0	0	0	0
H_2O		0	16.46	1674.73	0	1658.27
DME		0	18.31	1676.58	1658.26	0
Total flow	kmol/h	3335.66	4182.97	4180.57	1665.66	1667.05
Total flow	kg/h	106794	133987	133979	76631	30155

Table 4. Relevant flows for *Process 3*

Stream Name	**Unit of measure**	**1**	**3**	**7**	**10**	**11**
Temperature	°C	160	325	250	20	20
Pressure	bar	29	16.2	14.7	14.7	14.7
Component flow-rate	kmol/h					
H_2		6667	0	9670.70	9670.65	0
CO		3333	0	329.30	329.29	0
CH_3OH		0	0	0	0	0
CO_2		0	0	3004.03	2984.69	19.33
H_2O		0	3333	328.97	19.57	309.39
DME		0	0	0	0	
Total flow	kmol/h	10000	3333	13333	13004.21	328.78
Total flow	kg/h	106805	60044	166852	160427	6425

The processes presented in the present work use data from literature [11]. All the models have been validated using the initial literature source. After validation, the models have been scaled up to the same syngas flow-rate and composition.

In order to establish which process is the best option from thermal energy point of view, a comparison has been made between the three case studies. Table 5 shows the process values from thermal energy point of view.

Usually, when monitoring the thermal energy, the comparisons and conclusions are made based on the low heating value (LHV). The lower heating value (also known as net calorific value) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which assumes the latent heat of vaporization of water in the reaction products is not recovered [12]. The thermal energy obtained using the flow-rates of fuels derived from process modelling and simulation and from the correspondent LHV values of the fuels considered are reported in Table 5.

Table 5. Thermal comparison for the simulated processes

Processes	**Fuel flow-rate (kmol/h)**	**Fuel flow-rate (kg/h)**	**Fuel LHV (MJ/kg)**	**TE(L) (MW_{th})**
Process 1	3331.48	106607	20.09	594.93
Process 2	1658.26	76280	28.88	611.94
Process 3	9670.65	19341	120.21	645.83

LHV - lower heating value, TE(L) - thermal energy based on the LHV

As shown in Table 5, from thermal energy point of view, *Process 3* is the best option, with a quantity of 645.83 MW_{th} generated compered to *Process 1* and *Process 2* where 594.93 MW_{th} respectively 611.94 MW_{th} are generated. Since for *Process 3*, there is no CO_2 involved in the reaction, in terms of environmental impact, this process is also the best option, compared to *Process 1* and *Process 2* which result in one, respectively two molecules of CO_2 / molecules of fuels emitted by burning CH_3OH and DME.

Further, using the best thermal energy obtained in the three cases back calculations were performed in order to determine the necessary amount of syngas requested to produce the fixed amount of thermal energy (e.g. 645.83 MW_{th}). The results are reported in Table 6.

Table 6. Syngas flow-rate values calculated using low heating thermal energy value

Process	**Syngas (kmol/h)**	**Fuel (kg/h)**	**LHV (MJ/kg)**	**TE(L) (MJ/h)**	**TE (L) (MW_{th})**
Process 1	10855.59	115728.62	20.09	2324988	645.83
Process 2	10553.89	80505.12	28.88	2324988	645.83
Process 3	10000	9670.53	120.21	2324988	645.83

LHV - lower heating value; TE(L) - thermal energy based on the LHV

The syngas flow-rate obtained after using 645.83 MW_{th} of thermal energy increased compared to the initial syngas flow-rates. For *Process 1*, the syngas flow-rates has increased with 8.55% (e.g. from 10000 kmol/h to 10855.59 kmol/h), while for *Process 2* the value increased with 5.54%. For the last process, *Process 3*, syngas flow-rates have the same value as the initial ones, because the highest thermal energy generated, which belongs to this process (syngas to hydrogen) has been used.

CONCLUSIONS

Three processes for fuels production starting from syngas as raw-material have been investigated in the present work. The processes under investigation are: *Process* 1 is the equivalent of syngas conversion to methanol, *Process 2* represents syngas to DME route, and *Process* 3 describes syngas conversion to hydrogen. For all cases under study the same amount of syngas (e.g. 10000 kmol/h) was used. The methanol flow-rate obtained for *Process 1* was 3335.66 kmol/h with a purity of 99.9%, 1665.66 kmol/h DME was obtained in *Process 2*, with a purity of 99.69% respectively 9670.65 kmol/h of hydrogen was obtained in *Process 3*. The three fuels have been also investigated from thermal energy point of view. *Process 3* represents the best option form energy point of view but also from environmental point of view because no CO_2 is released by burning this fuel. The second best option is *Process 1*, followed by *Process 2*.

EXPERIMENTAL SECTION

The three processes have been modelled using ChemCAD process simulator developed by Chemstations [13]. Details about the data used for modelling and simulation are presented in the next section.

The Process flow-diagram for syngas to methanol is presented in Figure 2.

The production capacity of this plant is 2563 tons/day of methanol with a purity of 99.9% at atmospheric pressure. The raw-material syngas is introduced into the process at T = 160°C and p = 29 bar. Syngas enters the heat exchanger E-201 and is cooled to T = 125°C. Further, in order to achieve a pressure p = 45 bar, syngas is compressed in compressor C-201 with an efficiency of 75%. Syngas enters the second compressor C-202, together with the recycled CO and H_2, and it will be compressed to a pressure of 65 bar, with the same efficiency of 75%. The mixture furthermore sent to an equilibrium reactor R-201, where the reaction taking place is:

$$CO + 2H_2 \leftrightarrow CH_3OH$$

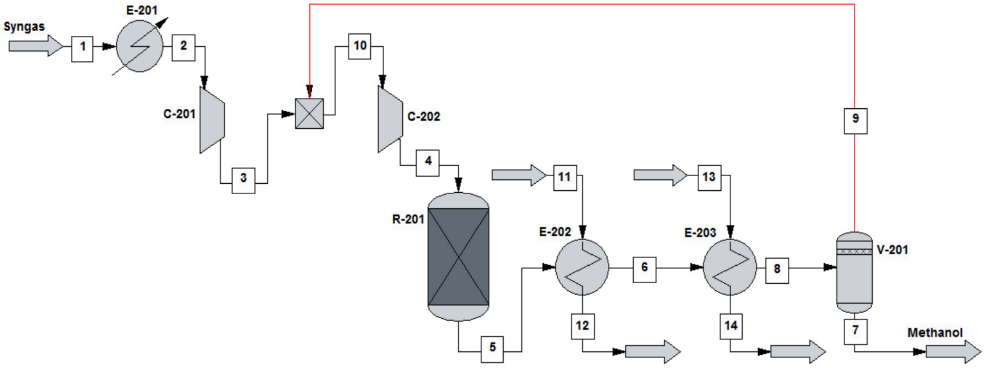

Figure 2. Syngas to methanol process flow diagram (Process 1)

The molar ratio of the reactants is 1:2. The conversion was assumed to be 65% [11]. The mixture exits the reactor at T = 267°C and is further cooled, using a cooling water agent, twice, in heat exchangers E-202 and E-203, until it reaches a temperature of 125°C. Furthermore, methanol is separated from the unreacted syngas through a flash vessel (V-201), and the syngas is recycled to the reactor. The methanol product exits as a liquid at 38°C and 105 bar.

Figure 3 shows the process flow diagram for the DME production using methanol as raw-material.

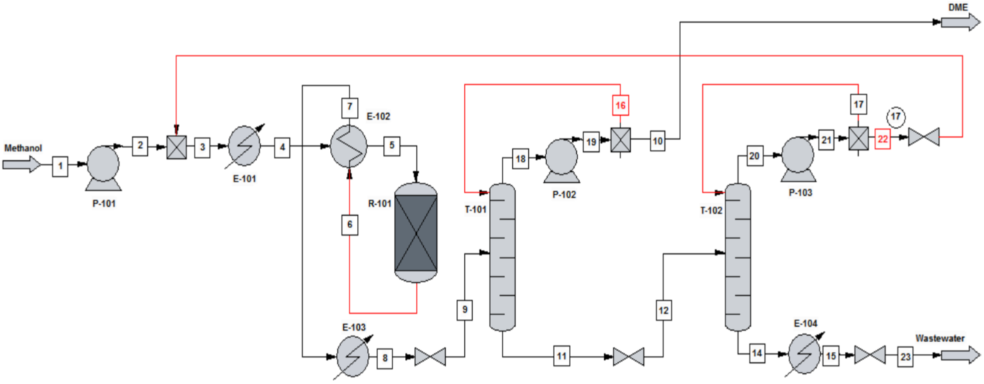

Figure 3. DME production process from methanol (Process 2)

The production capacity of this plant is 1839 tons/day of DME with a purity of 99.96 % at atmospheric pressure. The raw-material used is composed of fresh methanol and a small amount of water, which enters the process at T = 25°C and p = 1 bar. Further, this mixture is compressed to a pressure of 15.5 bar, in a compressor having an efficiency of 60%. Combined with the recycled reactant, the mixture is preheated by the first heat exchanger E-101 to a temperature of T = 154°C. Then, it is vaporized by the second heat exchanger E-102, prior to being sent to R-101 reactor, having a temperature of T = 364°C and a pressure p = 13.9 bar. The reaction taking place in the reactor is:

$$2CH_3OH \leftrightarrow CH_3\text{–}O\text{–}CH_3 + H_2O$$

Methanol conversion is around 80% [11]. The stream leaving reactor, is then cooled in heat exchanger E-103 (T = 100°C) prior to being sent to the first of the two distillation columns T-101 and T-102. DME product is taken overhead from the first column. Water and methanol enters the second distillation column (T-102) at T = 140°C and p = 7.4 bar, where water from the unused methanol will be separated. The water is sent to wastewater treatment to remove trace amounts of organic compounds while methanol is recycled back to the process.

Figure 4 shows the process flow diagram for the hydrogen production using syngas as raw-material.

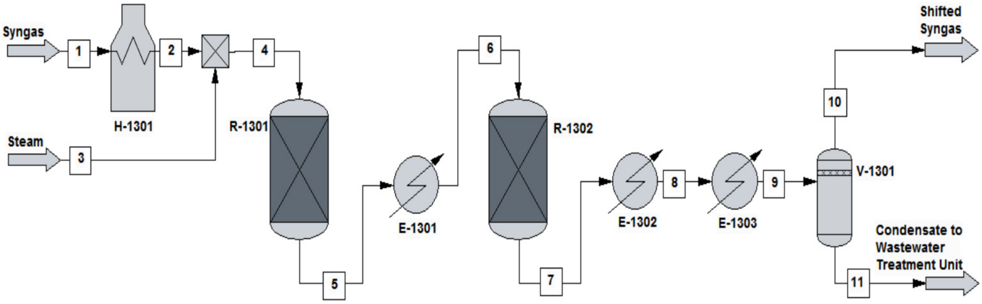

Figure 4. Hydrogen production from syngas (Process 3)

The production capacity of this plant is 464 tons/day of hydrogen with a purity of 98% at atmospheric pressure. The raw-material used is a mixture of carbon monoxide (p = 16.7 bar, T = 115°C) and hydrogen (p = 16.7 bar, T = 115°C) in a molar ratio of 1:1. The mixture is heated up to 320°C using a fired heater. The heated syngas is further mixed with steam (water at T = 325°C and p = 16.2 bar) and enters in the high temperature shift reactor. The reaction taking place in the reactor is:

$$CO + H_2O \rightarrow H_2 + CO_2$$

The conversion considered is 63% [11]. The mixture leaves the reactor R-1301 at T = 425°C and enters a simple heat exchanger E-1301, where is will be cooled to a temperature of T = 250°C. After the temperature is reached, the mixture is transferred to the second stage reactor (R-1302) which operates at T = 250°C and represents the low temperature shift reactor. The reactor effluent is further cooled using cooling water in heat exchangers E-1302 and E-1303, before being sent to the flash separator V-1301. The effluent is first cooled from T = 250°C to 185°C in the first heat exchanger (E-1302), and finally it achieves a temperature of T = 20°C in the second heat exchanger (E-1303). The off-gas resulted in V-1301 flash separator is a mixture of CO, H_2 and CO_2 gases, that is usually sent to a hydrogen-recovery process or to a combustion system, while the bottom product, water, is sent to a wastewater treatment unit. A significant amount of CO_2 is obtained, which is further purified using a CO_2 capture plant. The CO_2 capture rate is about 90%, the CO_2 removal uses an amine-based process. This is a standard industrial process, but not a subject included in the present work. For our process, it is considered that CO_2 was already purified.

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