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Simulation of dimethyl ether production as LPG Substitute using LNG from Arun Terminal with tri-reforming and direct synthesis method

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ABSTRACT

Increased demand for LNG compels Indonesia to import to meet these needs. Substituting LNG with alternative fuel emerges as a strategy to reduce LPG imports. One such alternative that can be used for LPG substitution is Dimethyl Ether. Dimethyl ether is a colorless compound that possesses a heating value of 30.5 MJ/kg and an energy equivalency with LPG ranging between 1.56 – 1.76. Dimethyl ether can be directly synthesized from synthetic gas produced through natural gas reforming. Production of synthetic gas from natural gas employs the tri-reforming method which integrates steam reforming, dry reforming, and partial oxidation methods in a single reactor offering optimal energy utilization advantages and minimal environmental impact. Dimethyl ether production from synthetic gas uses the direct synthesis method, combining methanol synthesis and dehydration in a single reactor providing high conversion advantages compared to the indirect synthesis method. The simulation was carried out using the process simulator program ASPEN Plus V11. Based on the simulation results, dimethyl ether yield and selectivity is 99.62%. The simulation model resulting from this research can be used for techno-economic analysis as a feasibility study for designing a dimethyl ether plant.

1. Introduction

Liquified Petroleum Gas is a gas fuel commonly consisting of propane or butane or a mixture between those two at room temperature in the gaseous phase, but in high pressure and very low temperature, it will be in the liquid phase. Chemical compounds contained in Liquified Petroleum Gas consist of a mixture of propane, propylene, iso-butane, butylene, and some C_2 and C_5 [1] Liquified Petroleum Gas combustion produces low emissions and greenhouse gases [2].

Liquified Petroleum Gas is commonly used as a fuel in several sectors like household, industry, and transportation [2]. Liquified Petroleum Gas has become a primary need for household gas in Indonesia. Around 82% of households in Indonesia still use Liquified Petroleum Gas as a major household gas [3]. The trend of Indonesia's import and consumption of Liquified Petroleum Gas is showed in Figure 1 [3].

Liquified Petroleum Gas consumption in Indonesia continue to rise until 2022. In 2022, LPG consumption reach 8,2 million metric tons [4]. LPG production in Indonesia cannot meet the consumption needs, which compels Indonesia to import to meet these needs. Over 33% of LPG needs in Indonesia are fulfilled through import activities from another country [5]. One such alternative to reduce import activities is using dimethyl ether as an LPG substitute.

Dimethyl ether is a multi-source fuel, that can synthesized from natural gas, coal, and biomass [6]. Natural gas can be obtained from an LNG terminal. One of the LNG terminals in Indonesia is the Arun Regasification Terminal located in Lhokseumawe, Aceh Province. In the Arun Regasification Terminal, LNG is converted to a gaseous state by heating the liquified gas. Regasified LNG can then be reformed into synthetic gas for dimethyl ether feedstock use.

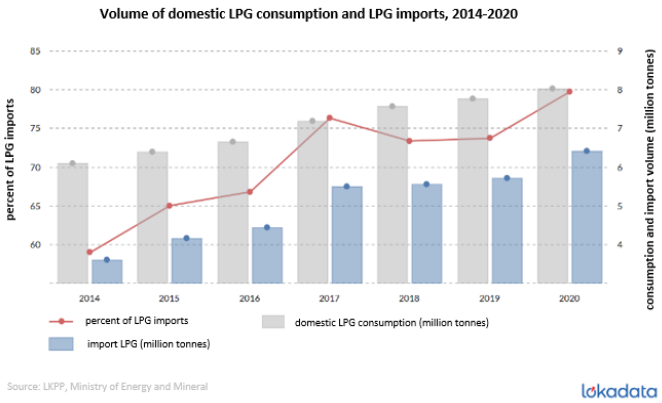

Fig. 1. Indonesia's trend of LPG import and consumption

Dimethyl ether is the simplest ether in a gaseous phase. Dimethyl ether is a colorless gas with an ether smell and is soluble in water or oil. Dimethyl ether is non-toxic and non-carcinogenic. Dimethyl ether has a chemical formula CH_3-O-CH_3 or empirical formula C_2H_6O [7]. The molecular bond of dimethyl ether is shown in Figure 2.

Dimethyl ether is an alternative energy used as a transportation fuel, power plant fuel source, chemical (like aerosol and propellant), and precursor for hydrogen production. Dimethyl ether has properties similar to Liquified Petroleum Gas but with good cetane number, low exhaust gas emissions,

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and high energy efficiency, so dimethyl ether can be used as an alternative to substitution for Liquified Petroleum Gas, Liquified Natural Gas, and diesel [8]. Dimethyl ether can be used as a Liquified Petroleum Gas substitute because its properties are similar, so it will not change the specification of a Liquified Petroleum Gas cylinder other than a rubber seal to fit with dimethyl ether. A mixture of 20% dimethyl ether and Liquified Petroleum Gas did not need any change for the cylinder and other equipment [7]. A comparison of dimethyl ether and Liquified Petroleum Gas is shown in Table 1.

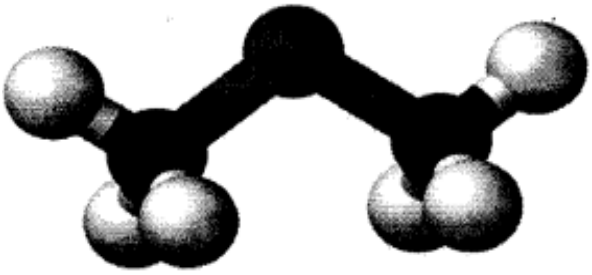

Fig. 2. Molecular bond of dimethyl ether

Table 1. Comparation of DME and LPG

Parameter	DME	LPG	
		Propane	n-Butane
Chemical formula	CH_3OCH_3	C_3H_8	C_4H_{10}
Boiling point (°C)	-25.1	-42	-0.5
Freezing point (°C)	-141.67	-187.61	-138.33
Liquid density (g/cm^3, 20°C)	0.67	0.49	0.57
Specific gravity (vs air)	1.59	1.52	2.00
Heat of evaporation (kcal/kg)	111.7	101.8	92.1
Saturated vapor pressure (atm, 25°C)	6.1	9.3	2.4
Critical temperature (°C)	126.83	126.83	126.83
Critical pressure (bar)	53.7	42.47	37.96
Burning velocity (cm/s)	50	43	41
Ignition energy (MJ)	45	30	76
Flammability limit (%)	3.4 – 17	2.1 – 9.4	2.1 – 9.4
Cetane number	55 – 60	5	10
Net calorific value (kcal/Nm^3)	14200	21800	28300

Dimethyl ether can be synthesized directly from synthetic gas using the direct synthesis method. Direct synthesis combines a methanol synthesis reaction from synthetic gas and methanol dehydration to dimethyl ether. This method is more economical because the reaction is carried out in a single reactor [9]. A reaction occurs in the reactor compromise of four main reactions: (1) Methanol synthesis from CO hydrogenation, (2) CO_2 hydrogenation produces methanol and water, (3) Methanol dehydration produces dimethyl ether and water, (4) Water-gas shift reaction produces CO_2 and H_2 [10].

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (2)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (4)$$

These four reactions are reversible, exothermic, and thermodynamically favorable in low temperature and high pressure. Catalyst used in this method are catalyst with two functions consist of a methanol synthesis catalyst and a solid acid catalyst for methanol dehydration [10].

Synthetic gas used for dimethyl ether synthesis is produce from methane reforming reaction, where methane source is from Liquified Natural Gas. The reforming method that is used is Methane Tri-Reforming. Methane Tri-Reforming is a process to produce synthetic gas that integrates three reactions (5) Methane Steam Reforming, (6) Methane Dry Reforming, and (7) Methane Partial Oxidation [11].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (5)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (6)$$

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \quad (7)$$

These three reactions occur simultaneously in a single catalytic reactor. The advantages of integrating these three reactions are higher economic benefits from steam reforming, higher energy efficiency from partial oxidation, and environmental benefits from dry reforming. A presence of compounds like O_2 and H_2O reduces carbon deposition on a catalyst surface drastically, making the catalyst's lifetime longer. Reactions carried out in a high temperature and atmospheric pressure. Side reactions in Methane Tri-Reforming are (8) Water-Gas Shift, (9) Reverse Water-Gas Shift, and (10) Methane Cracking Reaction [11].

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (8)$$

$$H_2 + CO_2 \leftrightarrow CO + H_2O \quad (9)$$

$$CH_4 \leftrightarrow 2H_2 + C \quad (10)$$

This research aims to simulate the dimethyl ether production process from liquified natural gas by applying kinetic parameters for designing the process and to obtain methane, CO, H_2 conversion, and dimethyl ether yield and selectivity.

2. Materials and Methods

2.1. Raw material and product

Methane tri-reforming and direct dimethyl ether synthesis are simulated using the process simulator program ASPEN Plus V11. The chemical compound used in this simulation consists of Nitrogen (N_2), Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8), i-Butane (i-C_4H_{10}), n-Butane (n-C_4H_{10}), i-Pentane (i-C_5H_{12}), Carbon Monoxide (CO), Carbon Dioxide (CO_2), Hydrogen (H_2), Water (H_2O), Methanol (CH_3OH), and Dimethyl Ether (C_2H_6O). Liquified Natural Gas from Arun Regasification Terminal is modeled using N_2, CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, and i-C_5H_{12} components. The temperature and pressure of regasified Liquified Natural Gas are set to 65.32°C and 10 bar. Liquified Natural Gas composition from Arun Regasification Terminal is shown in Table 2.

Table 2. Liquified natural gas composition

Component	Mass Fraction (%Mass)
Oxygen	0
Nitrogen	0.22
Carbon Monoxide	0
Carbon Dioxide	0
Methane	96.76
Ethane	2.31
Propane	0.49
i-Buthane	0.09
n-Buthane	0.11
i-Pentane	0.02
n-Pentane	0

Component CO, CO_2, and H_2 are used to model synthetic gas produced from a tri-reforming reactor. Component H_2O, CH_3OH, and C_2H_6O are used to model product formed in a direct dimethyl ether synthesis reactor.

2.2. Fluid package

A fluid package that is used in this simulation is UNIQUAC, based on a simulation developed by Jafari et al [12] for dimethyl ether synthesis from flare gas using Aspen HYSYS V11. UNIQUAC can predict the behavior of LLE and VLE systems.

2.3. Reaction and operating condition

The tri-reforming reaction is modeled using a Gibbs reactor to predict the reaction product using the Gibbs free energy minimization method. The reactor is operated at a temperature of 850°C and pressure of 1 atm. The feed ratio for Methane:Steam:CO_2:O_2 is set to 1:0.282:0.574:0.1 on a molar basis [11].

For the direct dimethyl ether synthesis section, the reaction is modeled using a plug flow reactor with the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model [8]. The reaction rates from Polsen et al [8] are shown below, and kinetics parameters modified from Shim et al [13] and Otalvaro et al [14] are shown in Table 3.

$$r_{CO} = \frac{k_1 f_{CO} f_{H_2}^2 - \frac{k_1}{K_{f1}} f_{CH_3OH}}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^3} \quad (11)$$

$$r_{CO_2} = \frac{k_2 f_{CO_2} f_{H_2}^3 - \frac{k_2}{K_{f2}} f_{CH_3OH} f_{H_2O}}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^4} \quad (12)$$

$$r_{DME} = \frac{k_3 f_{CH_3OH} - \frac{k_3}{K_{f3}} \frac{f_{DME} f_{H_2O}}{f_{CH_3OH}^2}}{(1 + \sqrt{K_{CH_3OH} f_{CH_3OH}})^2} \quad (13)$$

$$r_{WGS} = \frac{k_4 f_{H_2O} - \frac{k_4}{K_{f4}} \frac{f_{CO_2} f_{H_2}}{f_{CO}}}{1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + \sqrt{K_{H_2} f_{H_2}}} \quad (14)$$

Table 3. Kinetics parameters for direct DME synthesis

Parameter	A	B
k_1	8.906528918	-7031.994227
k_2	8.528924114	-8119.91821
k_3	6.967909202	-5228.891027
k_4	2.001155623	-1299.975944
k_1/K_{f1}	32.82479602	-13974.16411
k_2/K_{f2}	32.44719121	-15062.08809
k_3/K_{f3}	9.253636702	-7863.406495
k_4/K_{f4}	6.630415923	-6081.494713
K_{CO}	-12.4501845	6000
K_{CO2}	-13.19600992	6470.411354
K_{H2}	-0.398092354	-778.9271109
K_{CH3OH}	-7.139939575	5799.975944

Operating conditions, reactor dimension, and catalyst properties for direct dimethyl ether synthesis from Polsen et al [8] and Vakili et al [15] are shown in Table 4.

Table 4. Simulation parameters for direct dimethyl ether synthesis reactor

Parameter	Value
Temperature	220°C
Pressure	60 bar
Reactor length	14.2 m
Tube diameter	0.046 m
Particle density	1200 kg/m^3
Bed voidage	0.4

2.4. CH_4 conversion

Methane or CH_4 conversion for synthetic gas production can be calculated using equation shown below.

$$X_{CH_4} = \frac{F_{in} y_{CH_4,in} - F_{out} y_{CH_4,out}}{F_{in} y_{CH_4,in}} \quad (15)$$

2.5. CO conversion and dimethyl ether yield

CO and H_2 conversion for dimethyl ether production can be calculated using equations from Moradi et al [9] are shown below.

$$X_{CO} = \frac{F_{in} y_{CO,in} - F_{out} y_{CO,out}}{F_{in} y_{CO,in}} \quad (16)$$

$$X_{H_2} = \frac{F_{in} y_{H_2,in} - F_{out} y_{H_2,out}}{F_{in} y_{H_2,in}} \quad (17)$$

Dimethyl ether yield and selectivity can be also calculated using equations from Moradi et al [9] are shown below.

$$Y_{DME} = \frac{2 F_{out} y_{DME,out}}{F_{in} y_{CO,in}} \quad (18)$$

$$S_{DME} = \frac{2 F_{out} y_{DME,out}}{F_{in} y_{CO,in} - F_{out} y_{CO,out}} \quad (19)$$

3. Results and Discussion

3.1. Methane tri-reforming

Methane Tri-Reforming was chosen to produce synthetic

gas from Liquified Natural Gas using steam, CO_2, and O_2. The reactor operated at a temperature of 850°C and pressure of 1 atm. The ratio of steam, CO_2, and O_2 to methane is 1:0.3:0.3:0.2. A higher ratio of H_2O in the feed stream can increase H_2 yield, so the H_2/CO ratio also increases. A Higher ratio of H_2O can also increase methane conversion. A higher ratio of CO_2/CH_4 can cause a reverse water-gas shift reaction, which makes H_2 consumed and produces more CO, lowering the H_2/CO ratio. Besides that, higher CO_2 content can increase the CO_2/CO ratio, which makes dimethyl ether yield lower. A higher concentration of O_2 can cause methane combustion to H_2O and CO_2, which makes H_2 yield lower [11].

Gibbs reactor is used to model a tri-reforming reactor. Products from the reactor are synthetic gas composed of H_2, CO, CO_2, and H_2O and a trace of methane that are not converted. The mass balance of the tri-reforming reactor is shown in Table 5.

Table 5. Mass balance of tri-reforming reactor

Component	Input		Output	
	Mass flow (kg/hr)	Mole flow (kmol/hr)	Mass flow (kg/hr)	Mole flow (kmol/hr)
N_2	2.2	0.0785	2.2	0.0785
CH_4	1136.29	70.83	168.697	10.5155
C_2H_6	23.11	0.7685	0.01	0
C_3H_8	4.9	0.1111	0	0
i-C_4H_{10}	0.9	0.0189	0	0
n-C_4H_{10}	1.1	0.0155	0	0
i-C_5H_{12}	0.2	0.0028	0	0
H_2O	623.691	34.6201	16.689	0.9264
CO_2	748.54	17.0085	18.933	0.43
O_2	192.997	6.0314	0	0
H_2	0	0	317.014	157.26
CO	0	0	2210.39	78.913

Methane conversion to synthetic gas can be calculated using the equation (15). Based on the calculation results, methane conversion is 94.98%.

The product outlet from the reactor is cooled down to 220°C using a cooler and then compressed to 60 bar using a multistage compressor and intercooler. A cooled and compressed stream is then fed to a direct dimethyl ether synthesis reactor.

3.2. Direct dimethyl ether synthesis

The direct synthesis method was chosen to produce dimethyl ether. The reactor operated at a temperature of 220°C and pressure of 60 bar. A plug flow reactor models a direct dimethyl ether synthesis reactor. The reaction that occurs in the dimethyl ether reactor is exothermic, so it will release the amount of heat that makes the reaction temperature rise. Temperature rise inside the reactor will cause the catalyst to deactivate, so the temperature inside the reactor must be maintained at the same as the inlet temperature. Products resulting from the dimethyl ether reactor are dimethyl ether, methanol, water, and trace amounts of hydrogen and CO_2. The mass balance of the direct dimethyl ether synthesis reactor is shown in Table 6.

Table 6. Mass balance of direct dimethyl ether synthesis reactor

Component	Input		Output	
	Mass flow (kg/hr)	Mole flow (kmole/hr)	Mass flow (kg/hr)	Mole flow (kmole/hr)
CO	2210.39	78.913	0	0
CO_2	18.933	0.43	27.691	0.629
H_2	317.014	157.26	0.0592	0.0294
H_2O	16.689	0.926	721.24	40.035
CH_3OH	0	0	3.192	0.0996
C_2H_6O	0	0	1810.85	39.307

Synthetic gas conversion to dimethyl ether is calculated using CO and H_2 components. Based on the calculation results, CO conversion is 100%, and H_2 conversion is 99.98%. Dimethyl ether yield and selectivity is calculated using DME and CO components. Based on the calculations results, dimethyl ether yield and selectivity is 99.62%. According to Polsen et al [8], when the pressure reaction is increased to 60 bar, the dimethyl ether mole fraction is also increased. An increase in dimethyl ether mole fraction means more dimethyl ether is produced from the reaction. The increase in pressure also makes the dimethyl ether concentration in the outlet stream higher [17].

The product outlet from the reactor is depressurized to 6 bar and cooled down to 134.345°C. Off gas from the product stream is then separated in pressure swing adsorption.

3.3. Dimethyl ether separation and purification

A pressure swing adsorption is used to separate small amounts of off gas that are composed of CO_2 and H_2. Off Gas comes out from the top outlet, and the product stream contains dimethyl ether, water, and a small amount of methanol coming out from the bottom outlet of pressure swing adsorption.

Dimethyl ether, water, and methanol from the bottom outlet of the pressure swing adsorption are then fed to the distillation column to purify the dimethyl ether. The distillation column is used to separate dimethyl ether as a top product and water as a bottom product. The amount of dimethyl ether

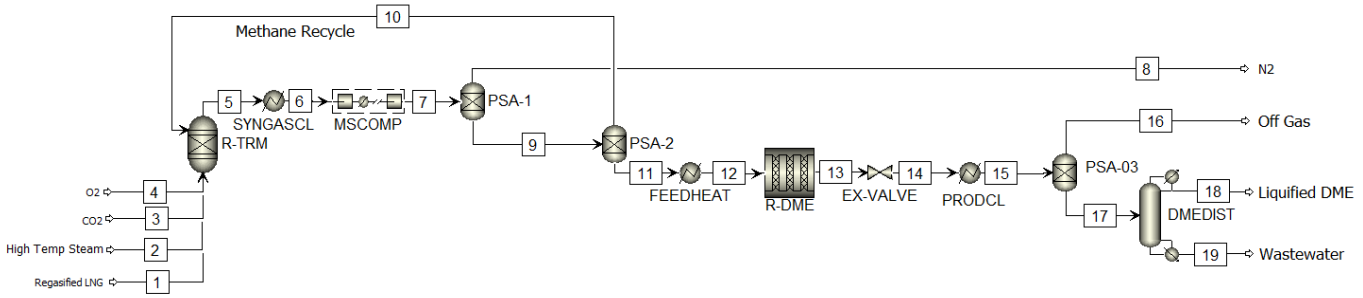

Fig. 3. Process simulation flowsheet for dimethyl ether synthesis from natural gas reforming

gained from the distillation column is near 99% [18]. Dimethyl ether from the top product of the distillation column is sent to a storage tank. Water and methanol from the bottom product of the distillation column are then sent to wastewater treatment.

A complete process flowsheet for simulation of dimethyl ether synthesis from Liquified Natural Gas is shown in Figure 3.

4. Conclusion

The direct dimethyl ether synthesis simulation from synthetic gas using kinetic parameters using Langmuir-Hinshelwood Hougen-Watson (LHHW) was studied using Aspen Plus V11. Dimethyl ether can be directly synthesized from synthetic gas, produced from natural gas tri-reforming using the direct synthesis method. The tri-reforming method can produce a higher H_2/CO mole ratio, and direct synthesis methods can produce more dimethyl ether with a shorter process. The simulation model resulting from this research can be used for techno-economic analysis as a feasibility study for designing a dimethyl ether plant.

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