Modified Two-Step Dimethyl Ether (DME) Synthesis Simulation from Indonesian Brown Coal

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Abstract. A theoretical study was conducted to investigate the performance of dimethyl ether (DME) synthesis from coal. This paper presents a model for two-step DME synthesis from brown coal represented by the following processes: drying, gasification, water-gas reaction, acid gas removal, and DME synthesis reactions. The results of the simulation suggest that a feedstock ratio of coal : oxygen : steam of 1 : 0.13 : 0.821 produces the highest DME concentration. The water-gas reactor simulation at a temperature of 400°C and a pressure of 20 bar gave the ratio of H_2/CO closest to 2, the optimal value for two-step DME synthesis. As for the DME synthesis reactor simulation, high pressure and low temperature promote a high DME concentration. It is predicted that a temperature of 300°C and a pressure of 140 bar are the optimum conditions for the DME synthesis reaction. This study also showed that the DME concentration produced by the two-step route is higher than that produced by one-step DME synthesis, implying that further improvement and research are needed to apply two-step DME synthesis to production of this liquid fuel.

Keywords: *ASPEN HYSYS optimization; ASPEN Plus; feedstock ratio; gasification; Indonesian brown coal; simulation; two-steps Dimethyl Ether (DME) synthesis; water-gas shift reaction.*

1   Introduction

With estimated resources and reserves of 105.2 billion tons and 21.1 billion tons, respectively, Indonesia's coal has a very high potential of meeting domestic energy demand. However, 20.2% belongs to low-rank coal, commonly known as brown coal [1]. Brown coal is usually utilized for mine-mouth power plants to eliminate the need for coal transportation and to avoid pollutant emission [2]. At around 30%, the efficiency of such power plants is fairly low [3] and a higher amount of CO_2 is emitted. Carbon dioxide and other greenhouse gases are a known drawback to the utilization of brown coal [2].

Coal conversion to liquid, known as liquefaction, is expected to solve the problem regarding efficiency. Three routes are commercially available to liquefy coal, namely pyrolysis, direct coal liquefaction (DCL), and indirect coal

liquefaction (ICL). ICL products are flexible, namely methanol (CH_3OH), dimethyl ether (CH_3OCH_3), Fischer-Tropsch (FT) diesel- or gasoline-like fuels, and hydrogen (H_2) [4].

Based on national energy policy as stated in Government Regulation of the Republic of Indonesia No. 79/2014, coal utilization is targeted to reach 30% by 2025. This policy also mandates liquefied coal as a new energy source for the transportation sector.

DME is a potential substitute for diesel fuel, owing to its high cetane number and soot-free combustion. Moreover, at average to high engine load, DME has higher combustion efficiency compared to diesel fuel [5]. Therefore, DME production from coal is expected to overcome some environmental issues caused by coal utilization toward utilization of cleaner coal technology.

DME can be synthesized either by a one-step process or a two-step process. One-step DME has attracted more industrial interest because of its lower thermodynamic limitations as well as higher economic value and theoretical significance [6]. The one-step gas-phase process, however, requires a large exothermic reactor due to the high net heat of the reaction. Hence, a low per-pass conversion is required to maintain the reactor temperature to avoid a short catalyst life due to the large temperature rises associated with these reactions. On the other hand, the currently existing but more traditional two-step process suffers from thermodynamic limitations [7]. To address these limitations, modification of the process is necessary.

A number of patents have shown promising novel approaches to convert syngas to DME, one of which is Haldor Topsoe A/S [8]. This process involves the preheating of syngas to a given temperature and then splitting the inlet stream of methanol, yielding methanol effluent, water and unconverted synthesis gas. The unreacted syngas will then be added to the DME reactor along with the methanol effluent from the synthesis reactor. Obtaining a higher conversion rate is also possible by utilizing three adiabatic reactors with intercoolers in between.

This study was aimed at evaluating modified two-step DME synthesis and to give recommendations for further optimization of the process. A process simulation of DME synthesis can shed light onto the conceptual design of the chemical processes by exploring the conditions to obtain optimum values [9].

2   Methodology

2.1   Process Description

As shown in Figure 1, the following processes represent the DME synthesis model: drying, gasification, water-gas reaction, acid gas removal and DME synthesis reactions. Evaluation was carried out by employing ASPEN PLUS® for processes involving solid state and ASPEN HYSYS® for processes involving gas and liquid state.

Syngas was cooled and expanded for further reaction in a water-gas reactor (WGR) in order to adjust the H_2/CO ratio to the desired value for subsequent downstream processing. For indirect DME production, the optimum H_2/CO ratio in the feed gas to the synthesis reactor is 2 [8,10]. WGR output that contains sulfur has to be cleaned before entering the downstream synthesis step, which requires sulfur content below 1 ppmv to guarantee adequate catalyst life [8]. This sulfur removal was carried out using an absorption column containing Diethanol Amine (DEA) solvent. Rich DEA was regenerated by stripping the solvent from undesirable content and then recycling it in the absorption process.

Compression and heating were carried out subsequently as the sulfur removal step in order to adjust the operating conditions required by the methanol synthesis reaction. Prior to being fed into the DME reactor, stream splitting of the methanol reactor effluent was conducted to control the outlet temperature of the bed, potentially minimizing intercooler load. The methanol produced from the reaction was dewatered by dehydration catalyst, yielding DME as the desired product. The DME was purified further by separation using a flash tank and a distillation column. The purity of the DME obtained at the end of the process was 99.50%-vol [10].

2.2   Simulation Basis

The simulation process assumed a flow rate of 2,000-ton/d air-dried basis of Indonesian brown coal. The characteristics of typical Indonesian brown coal are shown in Table 1. Soave-Redlich-Kwong (SRK) was applied in the simulation for calculating the thermodynamic properties as SRK gives greater accuracy in estimating the physical state than Peng-Robinson (PR) and Redlich-Kwong (RK) [11].

The gasification process was modeled by ASPEN PLUS and consisted of three processes: coal drying, coal decomposition, and char gasification. A gasifier yields the product composition that approaches equilibrium [11]. The gasification design was based on technology of GE/Texaco, a major player in gasifier technology [12,13].
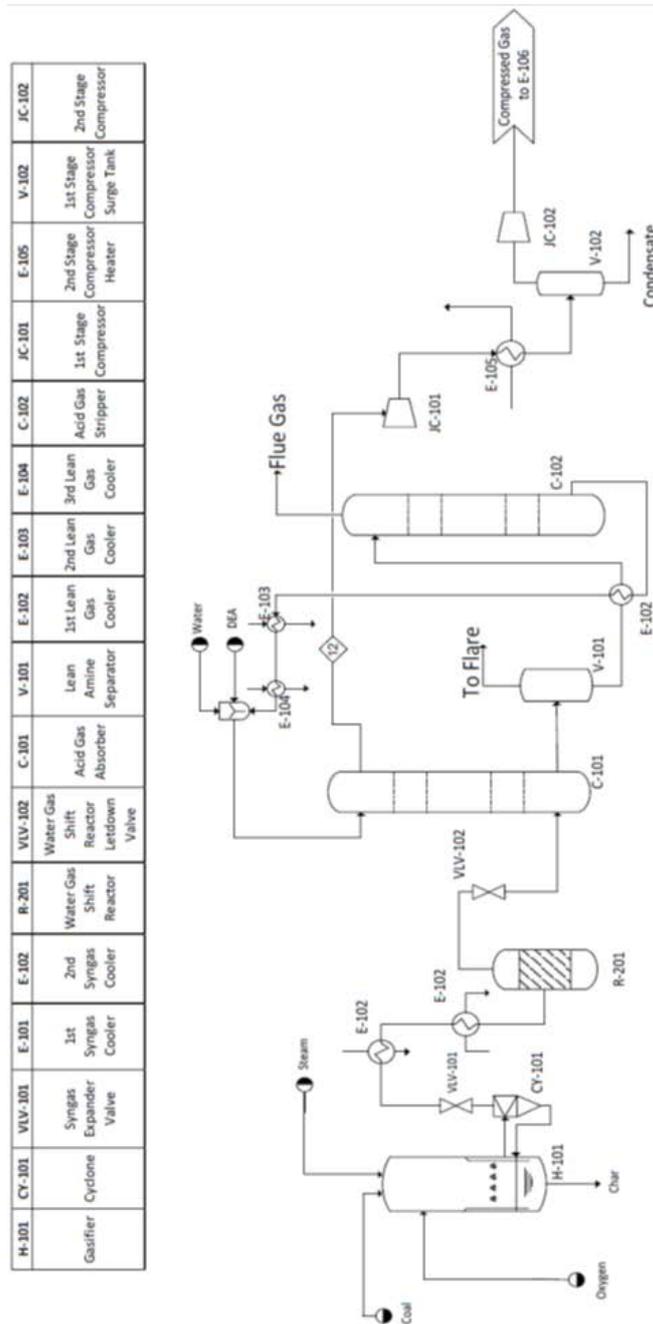
Figure 1 Schematic diagram of DME synthesis model.

E-106	E-107	R-202	E-108	R-103	E-109	V-103	VLV-103	VLV-104	V-104	A-101	C-103
Pre-Mixing Heater	Methanol Synthesis Reactor Pre-heater	Methanol Synthesis Reactor	DME Synthesis Reactor Pre-heater	DME Synthesis Reactor	DME Synthesis Reactor Outlet Heater	Noncondensible Gas Separator	Product Gas Letdown Valve	Noncondensible Gas Letdown Valve	Purge Gas Separator	Purge Wash Tower	Product Recovery Column
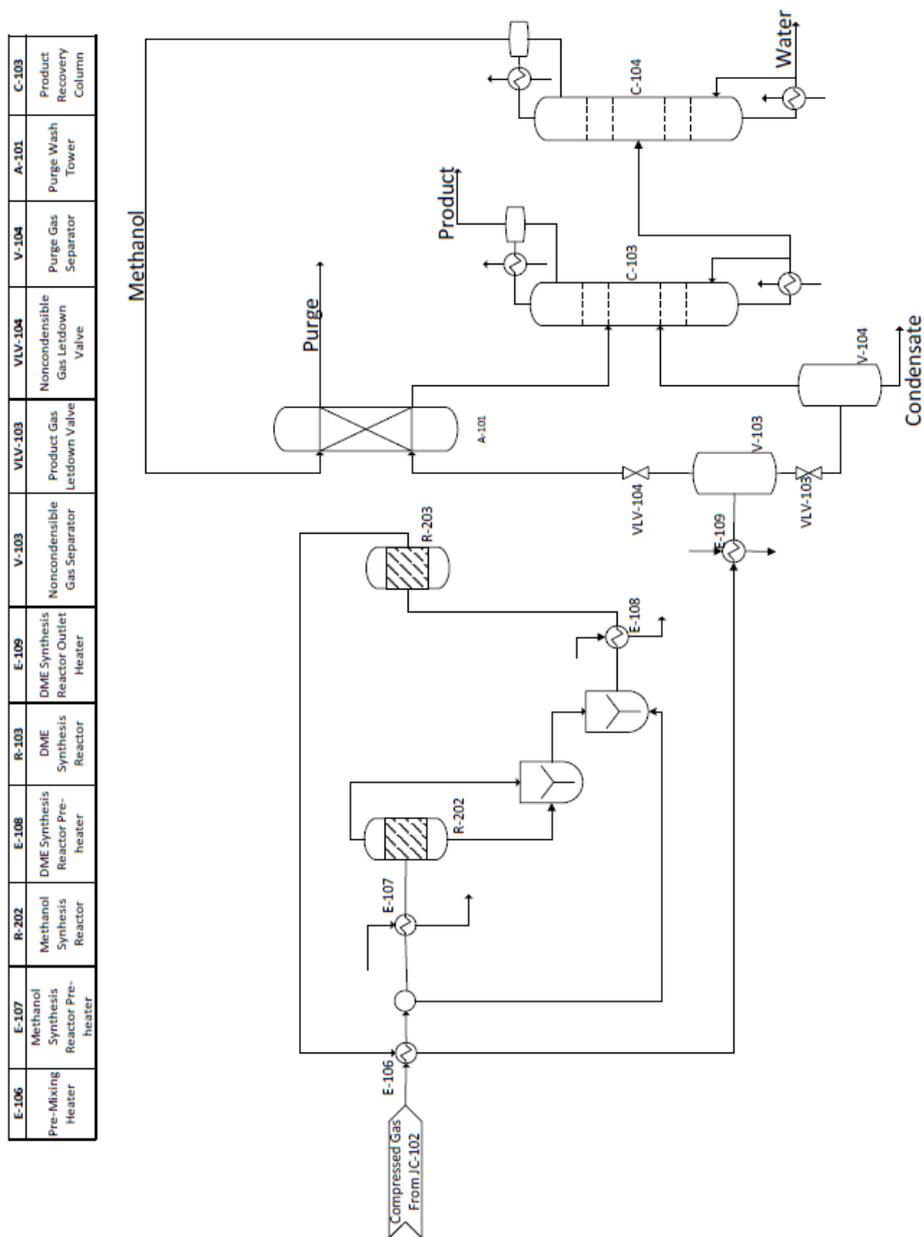
Figure 1 Schematic diagram of DME synthesis model (cont.).

This design uses partial oxidation of the coal in oxygen generated in an air separation unit to provide the required heat to drive the gasification reactions. The flow-rate ratio between coal, oxygen and steam was fixed at 1 : 0.866 :

0.241 [12]. The oxygen temperature was 230.79°C, while the steam temperature was 236.59°C [14].

Table 1   Indonesian brown coal analysis.

Proximate Analysis (% *air dried basis*)		Ultimate Analysis (% *air dried basis*)		Sulfur Analysis (% *air dried basis*)	
Moisture	6.8	Ash	3.6	Pyritic	0.41
Fixed Carbon	48.1	Carbon	69.4	Sulfate	0.25
Volatile Matter	41.3	Hydrogen	5.09	Organic	0.25
Ash	3.8	Nitrogen	1.55		
		Sulfur	0.91		
		Oxygen	19.45*		
		Chlorine			

* Calculated

Water-gas reaction, methanol synthesis and DME synthesis were modeled by an equilibrium reactor on ASPEN HYSYS. The downstream process design was based on the technology of Haldor Topsoe A/S, a leading commercial developer of fixed-bed DME synthesis reactor designs [15,16].

Gasification was simulated at 47 bar and 1371°C, WGR at 20 bar and 400°C, methanol synthesis reactor at 104.9 bar and 274°C, and DME synthesis reactor at 104.9 bar and 280°C. The operating conditions for the main process are shown in Table 2.

Table 2   Simulation basis of coal gasification and DME.

Process	Used model	Pressure (bar)	Temperature (°C)	Reaction
Gasification	*Yield reactor, Gibbs Reactor*	47	1371	
Water-gas Reaction	*Equilibrium Reactor*	20	400	$CO + H_2O \leftrightarrow CO_2 + H_2$
Methanol synthesis	*Equilibrium Reactor*	104.9	274	$CO + 2H_2 \leftrightarrow CH_3OH$
DME synthesis	*Equilibrium Reactor*	104.9	280	$CO + 2H_2 \leftrightarrow CH_3OH$ $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$

2.3   Simulation Validation

This section summarizes the results of the modeling approach and validation effort in two main sections: gasification and synthesis. Prior to the simulation, a validation of the DME synthesis model was carried out by comparing model prediction and experimental results from the literature. The experimental results were obtained from Haldor Topsoe A/S process data and thus the coal characteristics used by Haldor Topsoe A/S were assigned to the model first.

Then, the experimental and the modeling results were compared. If these only show a slight difference, the model can be considered valid.

First, validation of the gasification process was conducted. A comparison between gasification product composition and simulation of GE/Texaco gasifier result is shown in Table 3. The composition and its experimental output product composition were obtained from the works of Larson & Tingjin [10].

Table 3 Coal characteristics and comparison of gasification product composition.

Coal ultimate analysis (Haldor Topsoe A/S)	Composition (%)	Component	Product composition, experiment (%)	Product composition, simulation (%)
Ash	9.9	CO	41.67	41.75
Carbon	69.58	H_2	27.95	28.33
Hydrogen	5.31	CO_2	8.77	8.56
Nitrogen	1.26	H_2O	18.69	18.44
Chlorine	0.09	H_2S	0.99	1.00
Sulfur	3.87	N_2	1.84	0.69
Oxygen	9.99	COS	0.07	0.07
Moisture	12.03	CH_4	0.01	0.01

Table 3 shows that the chemical equilibrium-based simulation that was conducted can accurately predict product gas composition. The experimental data were based on GE/Texaco gasification technology; however, other gasifier designs and arbitrary coal types can also be used in this modeling approach. The differences between the composition obtained from the experiment and the simulation were relatively small, as shown in Table 3. For example, the predicted hydrogen and CO compositions from the experiments were 27.95% and 41.67 % respectively, while the simulation predicted hydrogen and CO compositions of 28.33 % and 41.75%, respectively.

For the two-step DME synthesis process, the model was also based on Haldor Topsoe A/S. In many respects, a DME/methanol raw product mixture rich in DME is sufficient and thus preferred to a pure DME product if obtained at a lower cost than by methanol dehydration [14]. Table 4 shows the results of the DME synthesis reactor output predicted from simulation in comparison to the experimental results. Again, the difference between the experimental and the simulation results was reasonably small. For instance, the predicted methanol and DME compositions from the experiments were 29.6% and 24.38% respectively, while the simulation predicted hydrogen and CO compositions of 26.36% and 24.39%, respectively. A comparison between the composition output of the DME synthesis reactor at the output of the knockout tank (V-103)

from the experimental results obtained by Haugaard & Voss [15] and that from the model is shown in Table 4. Based on the validation result, the simulation model can be used to accurately predict the output of the modified two-step DME synthesis process.

Table 4 Syngas characteristics and comparison of DME synthesis reactor output composition.

Component	Synthesis gas (%)	Output composition, experiment (%)	Output composition, simulation (%)
H_2	66.24	0.55	0.82
CO	24.65	0.15	0.43
CO_2	5.15	2.2	1.06
N_2	3.77	0.74	0.03
Methanol		29.6	26.36
DME		24.38	24.39
H_2O	0.18	42.38	46.91

It must be noted that as elicited from the works of Haugaard & Voss [15], an approximately equivalent mole fraction of DME and methanol, as shown in Table 4, will be obtained from the methanol reactor effluent, which undergoes 15% splitting for temperature control purposes.

3   Results and Discussion

3.1   Coal Gasification

Oxygen and steam are gasifying media required to drive the gasification reaction. Oxygen is often used as it produces syngas of higher quality [17]. However, steam can be introduced to limit the excess temperature occurring in the gasifier [6]. Steam is also an important factor that determines the DME concentration and governs the gas composition exiting the gasifier. Figure 2 illustrates the effects of both ratios of steam-to-coal and oxygen-to-coal to DME concentration. The stoichiometric oxygen ratio is defined as the amount of oxygen for complete combustion. It was shown that the DME concentration is affected by the steam-to-coal ratio and the H_2/CO ratio of the product exiting the gasifier. The simulation predicted that a high DME concentration is obtained at a steam-to-coal ratio of approximately 0.130 to 1, while the oxygen ratio per stoichiometric oxygen is at 0.442 to 1.

The carbon monoxide composition was predicted to decrease with the increase of steam-flow rate parallel to the increase of the carbon dioxide composition, which was similar to that in a previous work [18]. With the same steam-to-oxygen ratio, an increase in steam-flow rate results in an increase of H_2 leaving

the gasifier, which leads to a higher H_2/CO ratio. It must be noted that an exorbitant steam-flow rate reduces the DME concentration (Figure 2). It is recommended to maintain the steam-to-coal ratio higher than 0.5.
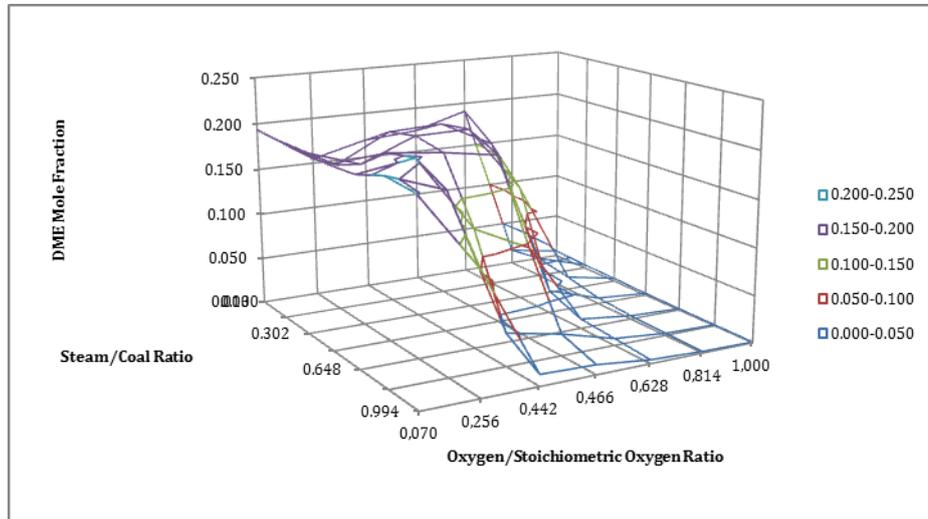
Figure 2 Effect of steam and oxygen on two-step DME synthesis concentration.

Oxygen can be set at low or high flow rates, but it is recommended to determine the optimum coal-to-oxygen ratio as it ensures the optimum H_2/CO ratio. A high oxygen concentration turns the gasification reaction into a combustion reaction, characterized by the absence of carbon monoxide. In this simulation, complete combustion occurred at an oxygen flow rate of 172,800 kg/h.

Figure 2 suggests that oxygen and steam as gasification media and coal as feedstock interact with each other and result in a varying DME concentration. It is concluded that the optimum ratio of coal : oxygen : stoichiometric oxygen is 1 : 0.07 : 0.821, or expressed in coal : oxygen : steam, the optimum ratio is 1 : 0.13 : 0.821, noted by the color of the purple region, with DME mol fraction at 0.15 to 0.2.

Another factor that affects the DME concentration is the H_2/CO ratio, which is a function of pressure and temperature in the gasifier. The pressure in the gasifier was varied from 1 to 100 bar. It is shown in Figure 3 that a lower pressure favors a higher H_2/CO ratio. Therefore, it is implied that gasification can be carried out at a low pressure in order to achieve a higher H_2/CO ratio from the gasifier.
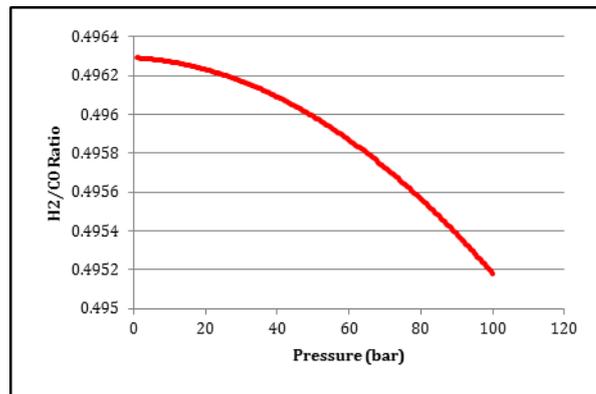
Figure 3 Effect of gasifier pressure on H_2/CO ratio.
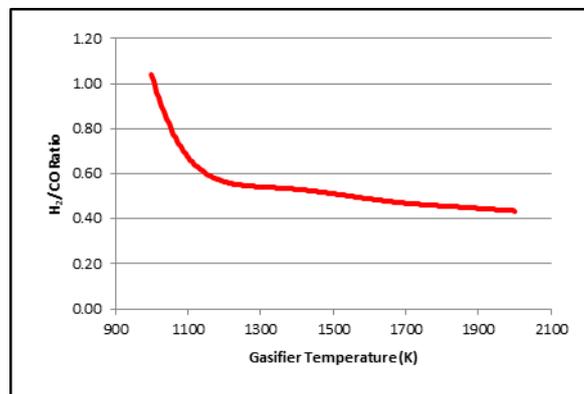
Figure 4 Effect of gasifier temperature on H_2/CO ratio.

Figure 4 shows the effect of the gasification temperature at a fixed pressure of 1 atm. The simulation predicts that an increase in temperature significantly reduces the H_2/CO ratio. To obtain the ideal H_2/CO ratio for DME synthesis, which is valuated at 1, gasification should be carried out at a temperature of approximately 950°C. Achieving the ideal H_2/CO ratio means no additional cost for capital investment in a WGR. Operating conditions must also be optimized as a different pressure and temperature implies different behavior of respective poisonous components, namely NH_3, HCN, HCl, COS, H_2S [2]. Operating at 950°C keeps the concentrations of poisonous species such as COS and HCN low, as well as resulting in the optimum H_2/CO ratio.

Operating as low as 950°C can also benefit energy utilization as less heating utilities are needed. The majority of the operating gasifiers in coupled one-step DME synthesis operate in excess of 1000°C [10]. Therefore, this study suggests

that the temperature and pressure are recommended to be lowered to 950°C to obtain minimum toxic gas production and the optimum H_2/CO ratio.

3.2   Water Gas Shift Reaction

The H_2/CO ratio is an important factor in controlling the DME concentration. A WGR is required to adjust the H_2/CO ratio. The adjustment of the H_2/CO ratio is sought to approach 2, as this is the optimum ratio between H_2 and CO in the feed gas for methanol synthesis. It is desired to obtain a reasonable amount of methanol to promote a higher DME concentration. The ratio must be kept at the closest value possible to the optimum ratio because of the possible interference of CO conversion. This interference causes the CO not to react, resulting in unreacted H_2 and reducing the extent of its conversion [19].
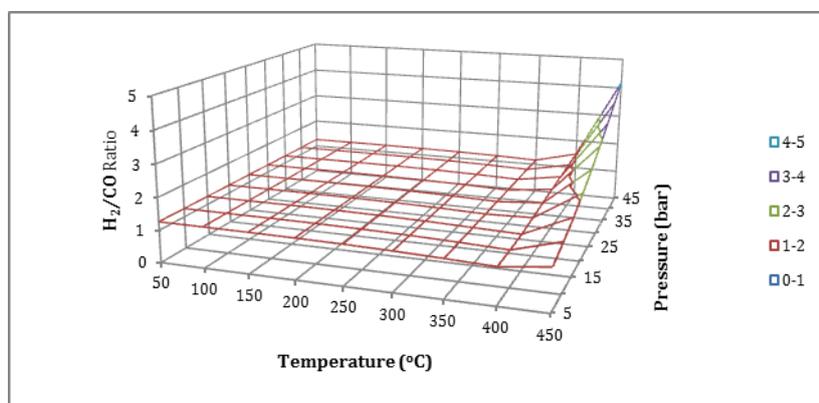
Figure 5   Effect of temperature and pressure of WGR on H_2/CO ratio.

The water-gas reaction is an equilibrium and exothermic reaction and occurs in the gas phase causing H_2/CO ratio changes as the pressure varies. The effects of temperature and pressure in the WGR towards the H_2/CO ratio are shown in Figure 5. An increase in temperature ranging between 50°C and 350°C does not cause a significant effect on the H_2/CO ratio, while an increase in temperature ranging between 350°C and 450°C significantly increases the H_2/CO ratio. Based on Figure 5, an H_2/CO ratio closest to 2 can be obtained at a temperature of 400°C and a pressure of 20 bar.

3.3   DME Synthesis

Among the factors that affect the DME concentration in the output of the reactor are the operating conditions of the DME synthesis reactor, because the DME synthesis reaction is an equilibrium and endothermic reaction. The reaction takes place in the gas phase and therefore temperature and pressure

have a significant effect on theDME concentration. Figure 6 shows the effect of temperature and pressure in the DME synthesis reactor on the output of the DME concentration.
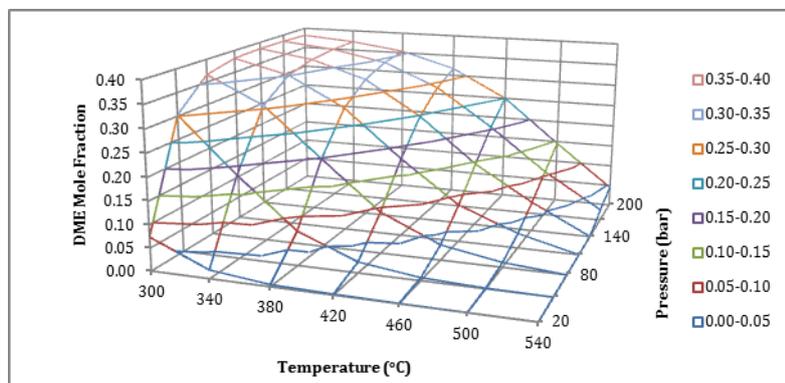
Figure 6 Effect of temperature and pressure of DME synthesis reactor on two-step DME synthesis concentration.

The increase in pressure in conjunction with the decrease in temperature raises the DME concentration. It was found in the simulation that a temperature of 300°C and a pressure of 140 bar are the optimum conditions for the DME synthesis reaction, up to 0.39 mole fraction. Higher temperatures promote faster kinetics, but with compensation of the catalyst's activity.

The model's prediction suggests that at a given temperature and pressure, the DME concentration produced by two-step DME synthesis is higher than that produced by one-step DME synthesis. For example, at 300°C and 100 bar, the DME mole fraction for two-step DME synthesis predicted by the simulation was 0.39, while for a typical produced DME concentration from one-step DME synthesis it is 0.21 [6]. The operating conditions of the DME reactor are similar to those of one-step DME, and could even be lowered, so the process will not suffer from low cold-gas efficiency. Further evaporation is also unnecessary as the given reactor conditions will result in the methanol reaction occurring mainly in the gas phase, further benefitting cold-gas efficiency. Separation will also require less energy, as the effluent is readily available in the gas phase [7].

4   Conclusions

It can be concluded from this modeling study that the ratio of coal : oxygen : steam is an important factor affecting DME synthesis. The simulation suggests that the optimum ratio of coal : oxygen : steam ratio is 1 : 0.13 : 0.821. Lowering temperature and pressure may benefit the process considering the

kinetics of the gasification process. Controlling the water-gas reaction is also important for DME synthesis as it can be used to adjust the H_2/CO ratio. An H_2/CO ratio of 2 is the ideal ratio for DME synthesis. It can be obtained at a temperature of $400^{\circ C}$ and a pressure of 20 bar. The DME synthesis reaction is remarkably influenced by the operating conditions of the reaction. High pressures and low temperatures may result in a higher DME concentration, e.g. at a temperature of 300°C and a pressure of 140 bar.

References

[1] Soelistijo, U.W., Wibowo, A.P. & Abdullah, M., *The Potential Share of Coal Liquefaction in The Indonesian Economy in 2025*, Earth Science, **2**(6), pp. 149-157, 2013.

[2] Bhattacharya, S., Kabir, K.B. & Hein K., *Dimethyl Ether Synthesis from Victorian Brown Coal Through Gasification – Current Status, and Research and Development Needs*, Progress in Energy and Combustion Science, **39**, pp. 577-605, 2013.

[3] Hashimoto, T., Sakamoto, K., Yamaguchi, Y., Oura, K., Arima, K. & Suzuki, T. *Overview of Integrated Coal Gasification Combined-cycle Technology Using Low-rank Coal*, Mitsubishi Heavy Industries Technical Review, **48**(3), 2011.

[4] Kabir, K.B., Hein, K. & Bhattacharya, S., *Process Modelling of Dimethyl Ether Production from Victorian Brown Coal – Integrating Coal Drying, Gasification and Synthesis Processes*, Computers and Chemical Engineering, **48**, pp. 96-104, 2013.

[5] Khunaphan, S., Hartley, U.W. & Theinnoi, K., *Characterization and Potential of Dimethyl Ether (DME) as Dual Fuel Combustion in a Compression Ignition Engine*, International Journal of Engineering Science and Innovative Technology (IJESIT) **2**(3) pp. 79-85, 2013.

[6] Chen, H.S., Fan, C.W. & Yu, C.S., *Analysis, Synthesis, and Design of a One-Step Dimethyl Ether Production Via a Thermodynamic Approach,* Applied Energy, **101**, 449-456, 2012.

[7] Ohno, Y., Yagi, H., Inoue, N., Okuyama, K. & Aoki, S., *Slurry Phase DME Direct Synthesis Technology-100 tons/day Demonstration Plant Operation and Scale up Study*, A.B. Editor et.al (ed(s)), Elsevier B. V/ Ltd., pp. 1-12, 2005.

[8] Voss, B., Joensen, F. & Hansen, J.B., *Preparation of Fuel Grade dimethyl ether*, US Patent, 5908963, 1999.

[9] Babu, B.V., *Process Plant Simulation*, New Delhi: Oxford University Press, 2004.

[10] Larson, E.D. & Tingjin, R., *Synthetic Fuel Production by Indirect Coal Liquefaction*, Energy for Sustainable Development, **VII**(4), pp. 79-102, 2003.

[11]   Bell, D.A., Towler, B.F. & Fan, M., *Coal Gasification and Its Application,* University of Oxford, United Kingdom, 2011.

[12]   National Energy Technology Laboratory, *Gasification 2010 Worldwide Database*, US Department of Energy, 2010.

[13]   Govind, R. & Shan, J., *Modeling and Simulation of an Entrained Flow Coal Gasifier*, American Institute of Chemical Engineers, **30**(1), pp. 79-92, 1984.

[14]   Hoffman, Z., *Simulation and Economic Evaluation of Coal Gasification with Sets Reforming Process for Power Production*, Lousiana State University, United States of America, 2005.

[15]   Haugaard, J. & Voss, B., *Process for the Synthesis of a Methanol/Dimethyl Ether Mixture from Synthesis Gas*, US 6,191,175 B1. United States Patent, 2001.

[16]   Wen, C.Y. & Chaung, T.Z., *Entrainment Coal Gasification Modeling*, Industrial & Engineering Chemistry Process Design and Development, **18**(4), pp. 684-695, 1979.

[17]   Speight, J.G., *The Chemistry and Technology of Coal, 3rd edition*, Taylor & Francis LLC, Florida, pp. 610, 2013.

[18]   Nikoo, M.B. & Mahinpey, N., *Simulation of Biomass Gasification in Fluidized Bed Using ASPEN PLUS*. Biomass and Bioenergy, **32**(12), pp. 1245-1254, 2008.

[19]   Shim, H.M., Lee, S.J., Yoo, Y.D., Yun, Y.S. & Kim, H.T. *Simulation of DME Synthesis from Coal Syngas by Kinetics Model*, Korean Journal of Chemical Engineering, **26**(3), pp. 641-648, 2009.