

Research Article

CO₂ Utilization Process Simulation for Enhancing Production of Dimethyl Ether (DME)

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Increase in the world energy demand also increases the concentration of CO₂ in the atmosphere, which contributes to global warming and ocean acidification. This study proposed the simulation process to utilize CO₂ released from the acid gas removal unit in one of gas processing plants in Indonesia to enhance the production of dimethyl ether (DME) through unreacted gas recycle that can be beneficial in reducing CO₂ emission to the atmosphere. Simulation was developed in Unisim R390.1 using Peng–Robinson–Stryjek–Vera (PRSV) as a fluid package. Simulation was validated by several studies conducted by many researchers and giving satisfactory results especially in terms of productivity, conversion, and selectivity as a function of reactor temperatures in the indirect and the direct DME synthesis processes. Simulation results show that the DME production was enhanced by around 49.6% and 65.1% for indirect and direct processes, respectively, at a recycling rate of 7 MMSCFD. Compressor is required to increase the unreacted gas pressure to the desired pressure in the methanol reactor or dual methanol–DME reactor in both processes. Specific power consumption (SPC) was used as a tested parameter for the effectiveness of recycling unreacted gas. Based on the simulation, the direct DME synthesis process is superior over the indirect process in terms of DME and methanol productions, SPCs, and system energy efficiencies.

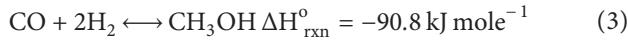
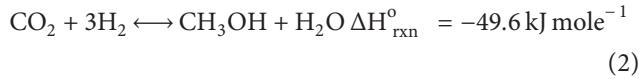
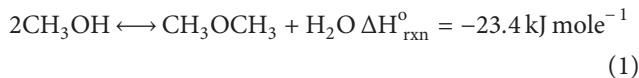
1. Introduction

World population growth and demand for higher living standards require energy resources consumed at a hasty rate. At present, an essential part of the used energy resources, especially for electricity generation and transportation, came from fossil fuels, most of which are consumed by combustion [1, 2]. The increase in the world energy demand also increases the concentration of CO₂ in the atmosphere, which is one of the biggest contributors to global anthropogenic greenhouse gas (GHG) emissions. It is widely known that CO₂ accumulation in the atmosphere contributes to global warming and ocean acidification, which can be a major hazard to the environment and to humanity [3, 4] so that mitigation of CO₂ emissions is very crucial and becomes a common responsibility [5–9]. Technology can effectively reduce CO₂ emissions including Carbon Capture and Storage (CCS) and Carbon dioxide

Capture and Utilization (CCU). However, the main problem that occurs in CCS technology is the limited storage volume, expensive operating costs, and the adverse effects of earthquake incidents [10–13]. Therefore, CCU is more promising to be able to utilize CO₂ as a raw material to react with hydrogen to produce other valuable products such as methanol and dimethyl ether (DME) [6, 14, 15]. However, new problems associated with the CO₂ utilization are with the availability of hydrogen [9], where conventionally hydrogen is also produced from the steam reforming of fossil fuels, which ultimately release CO₂ to the atmosphere [10, 12, 16–19].

DME is a colorless gas at the ambient condition and easily liquefied under low pressure [20]. At present, DME is mainly used as an aerosol propellant or, due to its physical properties close to liquefied petroleum gas (LPG), it can also be used as a LPG substitute for household and industrial purposes [1, 21–23]. Dimethyl ether (DME) is a

potential alternative fuel to diesel used in compression ignition engines [24, 25] due to its higher cetane number (55–60) and lower autoignition temperature compared to those of diesel (235°C) [26, 27]. The DME can be produced through dehydration of methanol over an acidic catalyst, while methanol can be produced by the hydrogenation of CO or CO₂ over a Cu-based catalyst as shown in Reactions (1), (2), and (3) [28–30]. Reaction (4) is a reverse water gas shift reaction [31, 32]. The direct synthesis of DME from CO₂ has an advantage over two-step synthesis by further conversion of the methanol formed in situ to DME, so that over-equilibrium yield can be achieved [33]. In addition, DME production through direct synthesis from syngas using a dual catalyst system permits both methanol synthesis and dehydration in a single process, with no methanol purification [20, 34]:



Several studies have demonstrated that methanol can be synthesized directly from CO₂ captured from many sources such as power and gas processing plants [4]. Problems associated in the direct use of CO₂ on an industrial scale are related to the kinetics of slow CO₂ dehydrogenation and catalyst deactivation [35]. Farsi et al. [36] developed a detail mathematical model for CO₂ conversion to DME based on the coupling methane trireforming. The syngas, which was produced through methane trireforming, was used as a feed to the DME reactor. The simulation results showed that the DME product from the reactor can be increased from 150.9 to 243.5 ton/day through a proper quenching. De Falco et al. [37] built a simulation for DME production through a reactor membrane to convert CO₂ using three types of integrated commercial software. The simulation results succeeded to obtain 60% CO₂ conversion and 60% DME yield by applying a double recycling loop and pure CO₂ external feed. This study aims to examine the direct use of CO₂ for DME production and its thermodynamic constraints through simulations using Unisim R390.1. The simulation targets to produce small-scale DME production by utilizing high CO₂ acid gas released from the acid gas removal unit (AGRU) by optimizing the use of unreacted gases through recycling. Thus green energy sources are expected to be produced, which supports a better environment in the existing oil and gas processing industries. Purification of the DME and methanol products as well as system energy efficiency is also provided in the simulation.

2. Methods

Unisim Design R390.1 was used to simulate the production of DME through indirect and direct conversion routes using feed gas of hydrogen gas and acid gas which contains high CO₂, a typical gas from AGRU in gas processing plant [30]. In the indirect conversion route, acid gas and hydrogen gas are compressed until the desired pressure in the methanol reactor (PFR-R1_MeOH). CO₂ is then hydrogenated into methanol in the methanol reactor at a given temperature and the product of the reactor is then sent to the separator (V-103). The vapor product of the separator, which is rich in hydrogen and carbon dioxide, will be recycled to the methanol reactor at a certain flow rate. Meanwhile, the bottom product of the separator (V-103) is sent to the methanol purification column (T-100-2-3) to produce methanol with a purity higher than 0.99 in mole fraction basis. The methanol with high purity is sent to the DME conversion packed bed reactor (PFR-R2_DME) to produce DME. The product of the reactor is then cooled, expanded, and separated to produced DME with a purity of 0.99 (mole fraction).

In the direct conversion route, the acid gas and hydrogen gas are compressed until the desired pressured in the dual methanol and DME synthesis reactor (PFR-R1). The mixed gases are sent to a dual-functional reactor (PFR-R1) where both methanol and DME are produced in a single-bed reactor. The product from the reactor is cooled to 30°C and the vapor and liquid formed are separated in the separator (V-106). The vapor product of the separator is dominated by unreacted hydrogen and CO₂ gases as well as DME, while the liquid product is dominated by water and methanol. The vapor product is then sent to the fractionation column (T2_Frac_DME) to produce DME with a purity of around 0.99 (mole fraction), while hydrogen and CO₂-rich gases from the top product of the fractionation column are recycled at a certain flow rate to the dual methanol-DME synthesis reactor. The bottom product of separator (V-106) is sent to the methanol fractionation column (T1_Frac_MeOH) to produce methanol with a purity of around 0.99 (mole fraction).

The production of DME flow diagram through indirect and direct conversion routes is described in Figures 1 and 2, respectively. The acid gas and hydrogen flow rates used in this study are set at 5 MMSCFD and 10 MMSCFD, respectively, while the gas composition and operating condition are presented in Tables 1 and 2, respectively. The composition (Table 1), pressure, temperature, and acid gas flow rate data (Table 2) were based on the acid gas stream from the regeneration unit of the amine compound at the acid gas removal unit (AGRU) in one of the gas processing plants in Indonesia. The challenge of methanol synthesis from CO₂ is the low equilibrium conversion gained in the reactor bed as compared with CO as feed stock. In order to have higher yield of methanol as the reaction is exothermic, the temperature has to be reduced prior to entering the next bed or stage so that the reaction can keep continuing to gain its equilibrium. The more the stages of the packed bed reactor are, the more the H₂ is consumed in the reactor

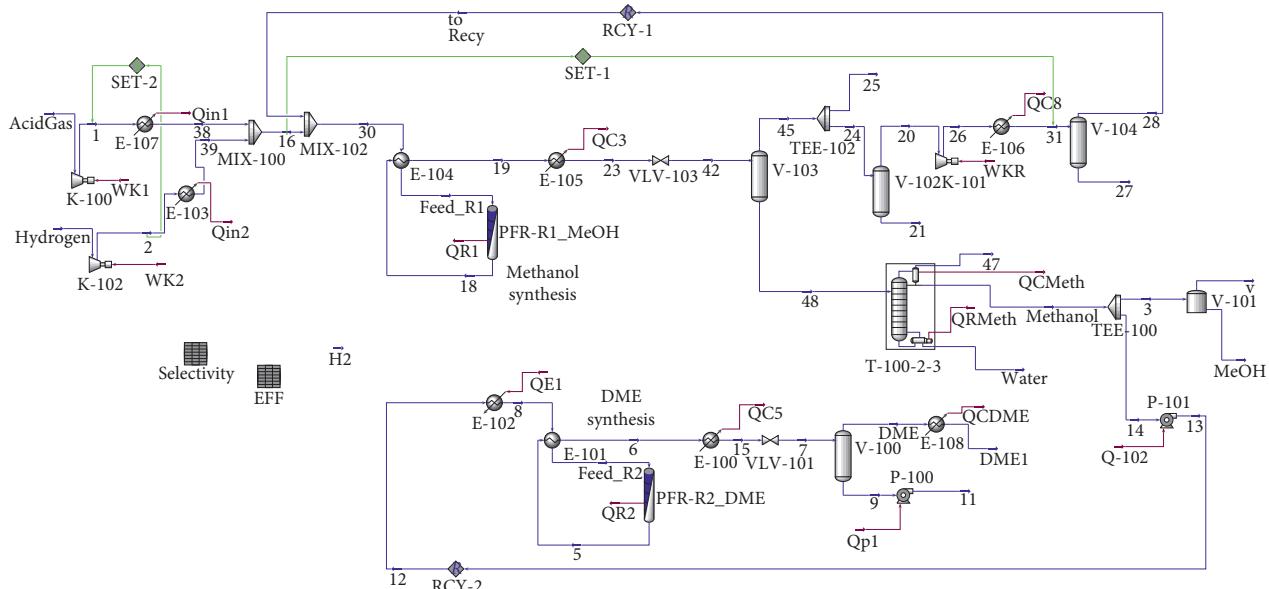


FIGURE 1: Flow diagram of indirect DME synthesis.

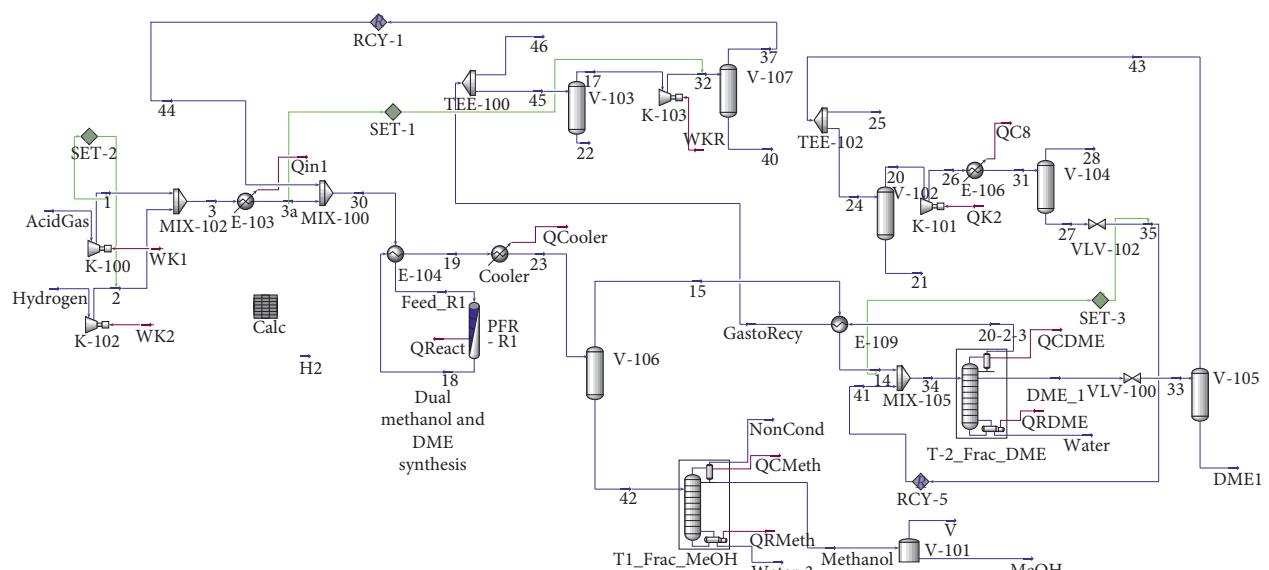


FIGURE 2: Flow diagram of direct DME synthesis.

TABLE 1: Feed gas composition of the acid gas.

Number	Composition	Mole fraction (%)
1	CO ₂	86.5923
2	H ₂ O	11.3495
3	CH ₄	2.0523
4	C ₂ H ₆	0.0057
5	C ₃ H ₈	0.0002

TABLE 2: Feed gas operating condition.

Number	Parameter	Value
1	Pressure (bar)	1.2
2	Temperature (°C)	80.0
3	Flow of acid gas stream (million standard cubic feet per day, MMSCFD)	5.0

[31, 32], thus reducing the remaining H₂ which will be flared/purged at the end of process. Currently, the scope of this study is still utilizing a single-stage packed bed reactor configuration in the process simulation where in future we plan to study the multistage reactor which will further reduce the flared H₂ using a more capital cost investment of multistage packed bed reactor.

The flow of hydrogen-rich gas recycled was varied in both routes to see its effect on the DME production. The pressure in methanol and DME reactors in the basic simulation in the indirect process is set at 40 bar and 19 bar,

respectively. The pressure of DME reactor in the indirect process is set at 19 bar, which is considered as moderate pressure to minimize the investment cost of the reactor and still give high conversion of methanol to DME which is around 0.87.

Meanwhile, the pressure of the dual-functional reactor in the basic simulation in the direct process is set at 40 bar. The kinetic correlation for the methanol and DME syntheses was based on Graaf et al. [38] and Bercic and Levec [39], respectively, as presented in (5)–(8):

$$r'_{\text{CH}_3\text{OH},\text{A}_3} = \frac{k'_{\text{ps},\text{A}_3} K_{\text{CO}} [f_{\text{CO}} f_{\text{H}_2}^{3/2} - (f_{\text{CH}_3\text{OH}})/(f_{\text{H}_2}^{1/2} K_{p_1}^0)]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + ((K_{\text{H}_2\text{O}})/(K_{\text{H}_2}^{1/2})) f_{\text{H}_2\text{O}}]}, \quad (5)$$

$$r'_{\text{H}_2\text{O},\text{B}_2} = \frac{k'_{\text{ps},\text{B}_2} K_{\text{CO}_2} [f_{\text{CO}_2} f_{\text{H}_2} - (f_{\text{H}_2\text{O}} f_{\text{CO}})/(K_{p_2}^0)]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + ((K_{\text{H}_2\text{O}})/(K_{\text{H}_2}^{1/2})) f_{\text{H}_2\text{O}}]}, \quad (6)$$

$$r'_{\text{CH}_3\text{OH},\text{C}_3} = \frac{k'_{\text{ps},\text{C}_3} K_{\text{CO}_2} [f_{\text{CO}_2} f_{\text{H}_2}^{3/2} - (f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}})/(f_{\text{H}_2}^{3/2} K_{p_3}^0)]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + ((K_{\text{H}_2\text{O}})/(K_{\text{H}_2}^{1/2})) f_{\text{H}_2\text{O}}]}, \quad (7)$$

$$-r_{\text{CH}_3\text{OH}} = \frac{k K_{\text{CH}_3\text{OH}}^2 [C_{\text{CH}_3\text{OH}}^2 - (C_{\text{DME}} C_{\text{H}_2\text{O}})/(K)]}{\left(1 + 2(K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}})\right)^{1/2} + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}}, \quad (8)$$

where $k'_{\text{ps},\text{A}_3}$ is the pseudoreaction rate constant for reaction A (mole·s⁻¹·kg⁻¹·Bar⁻¹), $k'_{\text{ps},\text{B}_2}$ is the pseudoreaction rate constant for reaction B (mole·s⁻¹·kg⁻¹·Bar^{-1/2}), $k'_{\text{ps},\text{C}_3}$ is the pseudoreaction rate constant for reaction C (mole·s⁻¹·kg⁻¹·Bar⁻¹), k'' is the pseudo-first-order rate constant based on catalyst volume (s⁻¹), K is the adsorption equilibrium constant (Bar⁻¹), K_{eq} is the pseudo-first-order equilibrium constant, K_p is the chemical equilibrium constant based on partial pressures, and K_C is the chemical equilibrium constant based on concentrations.

The selectivity of DME and methanol products in the direct DME synthesis can be calculated as follows [40, 41]:

$$S_{\text{DME}} = \frac{2n_{\text{DME}}}{n_{\text{CO}} + n_{\text{MeOH}} + 2n_{\text{DME}}}, \quad (9)$$

$$S_{\text{MeOH}} = \frac{n_{\text{MeOH}}}{n_{\text{CO}} + n_{\text{MeOH}} + 2n_{\text{DME}}}, \quad (10)$$

where S_{DME} and S_{MeOH} are DME and methanol selectivity, respectively, while n_{DME} , n_{MeOH} , and n_{CO} are molar flow rates of DME, methanol, and CO in the product stream of the dual methanol-DME reactor, respectively. The CO₂ conversions (X_{CO_2}) for indirect and direct process were calculated based on the methanol and dual methanol-DME reactors, respectively:

$$X_{\text{CO}_2} = 1 - \frac{n_{\text{CO}_2-\text{out}}}{n_{\text{CO}_2-\text{in}}}, \quad (11)$$

where $n_{\text{CO}_2-\text{in}}$ and $n_{\text{CO}_2-\text{out}}$ are molar flow rates of CO₂ entering and leaving the reactors.

3. Results and Discussion

The main difference between direct DME synthesis and indirect DME synthesis is the use of a single-bed reactor for the synthesis of methanol and DME. Another advantage of direct DME production is that 2 products will be yielded, namely, methanol and DME, which have concentrations above 99 mole%. Meanwhile, indirect synthesis only produces DME with concentrations above 99 mole% as the methanol formed is used to synthesize DME in the DME reactor. To determine the feed-flow rate of hydrogen, the first simulation is conducted without recycle for the direct process at the temperature where the DME produced is at its peak. The specific product (SP) was used as parameter to find the feed-flow rate of hydrogen and is defined as

$$\text{SP} = \frac{W_{\text{DME}}}{(\text{H}_2 : \text{CO}_2)(\text{CO}_2-\text{feed})}, \quad (12)$$

where W_{DME} , $\text{H}_2 : \text{CO}_2$, and CO_2-feed are DME produced, feed molar ratio of $\text{H}_2 : \text{CO}_2$, and feed molar flow of CO₂, respectively. Figure 3 shows the effect of $\text{H}_2 : \text{CO}_2$ on the specific product and CO₂ conversion, X_{CO_2} . As shown in Figure 3, the peak of the specific product is at an $\text{H}_2 : \text{CO}_2$ of around 2.3, or based on acid gas feed conditions, the hydrogen feed-flow rate is around 10 MMSCFD. Therefore, the

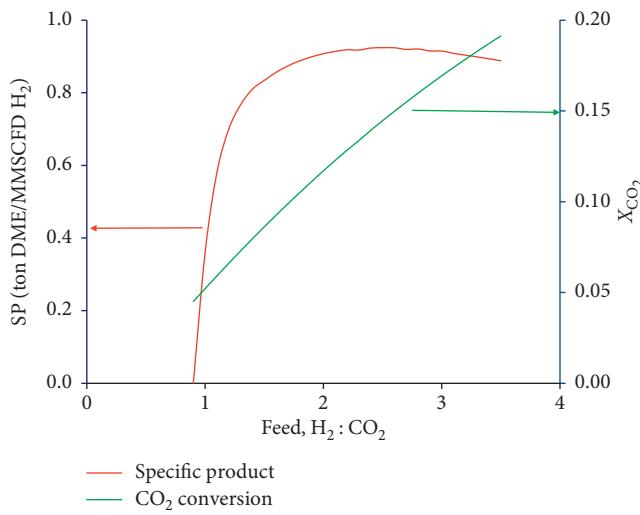


FIGURE 3: The effects of feed molar ratio of $\text{H}_2:\text{CO}_2$ on specific product, SP, and CO_2 conversion, X_{CO_2} .

hydrogen feed-flow rate of 10 MMSCFD will be used as the basis for further simulations.

Figure 4 shows the effect of the unreacted gas recycle rates to the $\text{H}_2:\text{CO}_2$ ratio that enters the reactor and the CO_2 conversion at reactors' pressure of 40 bar. As shown in Figure 4, there is a slight decrease in the ratio of $\text{H}_2:\text{CO}_2$ entering the reactor to the unreacted gas recycle rates for both direct and indirect processes. $\text{H}_2:\text{CO}_2$ ratio that enters the reactor only decreases from around 2.31 to 2.25 and 2.27 or decreases around 2.4% and 1.8% for the direct and indirect process, respectively, when the unreacted gas recycle rates increase up to 7 MMSCFD. Meanwhile, the CO_2 conversion only increases from about 0.136 to 0.141 with an increase of around 3.6% for the direct process, and it is relatively constant for the indirect process, when the unreacted gas recycle rates increase from 1 to 7 MMSCFD. These facts reveal that the unreacted gas recycle rates up to 7 MMSCFD have insignificant effect on the $\text{H}_2:\text{CO}_2$ ratio entering the reactor and CO_2 conversion.

Figure 5 presents the effects of both indirect and direct processes reactor temperatures at a pressure of 40 bar on the methanol production at unreacted gas recycle rates of 1 MMSCFD to 7 MMSCFD. The production of methanol increases with the increase of the unreacted gas recycle rates for both indirect and direct processes. Figure 5 shows that, at temperatures above 204°C, it seems that the methanol production in the indirect process is higher than the direct process. The difference is that in the indirect process only methanol is produced, while in the direct process DME is also produced in addition to methanol.

In the indirect process, at the methanol reactor temperature of 195°C there is relatively no methanol formed. Furthermore, with the increase in the reactor temperature, methanol starts to form at 204°C and continue to increase until it reaches its peak at a temperature of around 213°C due to the enhancement of the reaction rate of methanol formation (see (2)) [42]. Afterward, methanol production decreases with increasing reactor temperature up to 366°C as

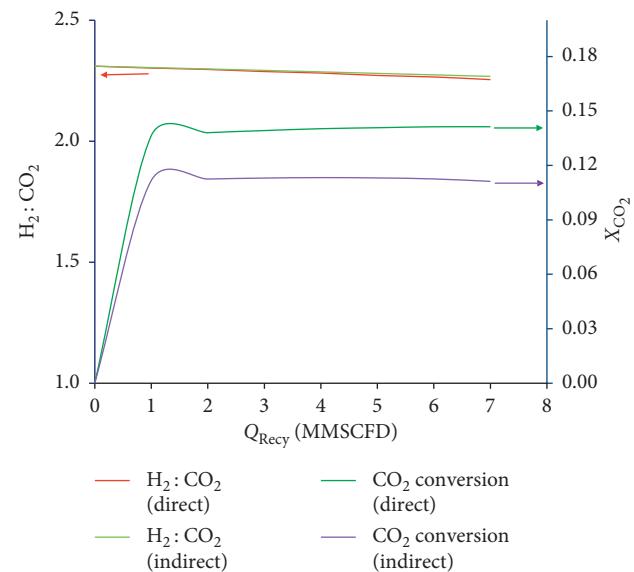


FIGURE 4: Effects of unreacted recycle gas rates, Q_{Recy} , in the indirect and the direct processes on the $\text{H}_2:\text{CO}_2$ ratio and CO_2 conversion, X_{CO_2} .

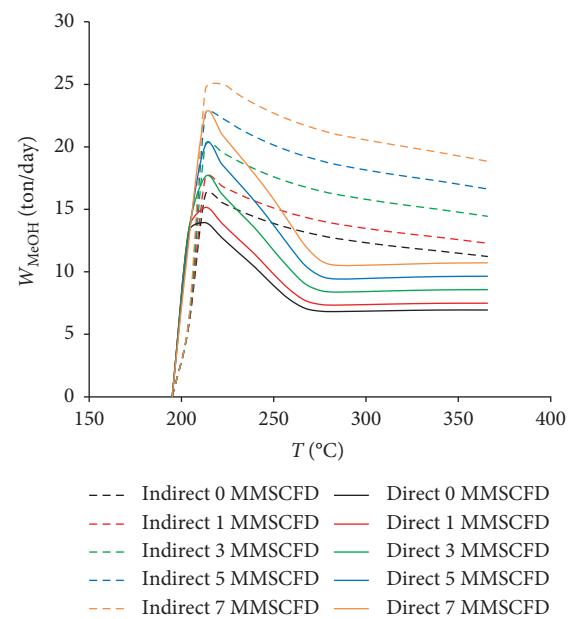


FIGURE 5: Effects of reactor temperature, T , at a pressure of 40 bar in the indirect and the direct processes on the methanol production, W_{MeOH} , at various unreacted gas recycle rates.

the maximum temperature for thermodynamic equilibrium has been achieved [43, 44] and in the temperature range of 213–366°C the reverse water gas shift reaction (see (4)), which is endothermic, could be preferred compared to CO_2 hydrogenation reaction (see (2)) [42]. Thus, the methanol reactor temperature of 213°C in the indirect process is the optimum temperature where there is a balance between kinetic and thermodynamic constraints [45]. The same trend is also reported by Ountaksinkul et al. at reactor pressure of 50 bar, where the methanol production increased in the

range of 200 to 255°C due to enhancement of reaction rate of CO₂ hydrogenation (see (2)) and then decreased with increasing the temperature due to thermodynamic equilibrium of endothermic reaction (see (4)) [42].

There are three curves in the methanol production in the direct process: in the temperature range of 195°C to 204°C, there is an increase in methanol production due to kinetics preference of methanol formation reaction (see (2)); in the temperature range of 204°C to 276°C, there is a decrease in methanol production due to thermodynamic limitation of methanol formation reaction (see (2)) [34, 42] and conversion to DME (see (1)); and in the temperature range of 267°C to 366°C, the methanol production is relatively constant at this temperature region due to the equilibrium between kinetic preference and thermodynamic limitation [30]. At the 40 bar reactor pressure, the maximum methanol production in the indirect and direct process is 16.2 tons/day and 13.9 tons/day, respectively. It seems that the methanol produced in the indirect process is higher than in the direct process. However, the methanol produced in the indirect process will be converted to DME at the DME reactor in the indirect process, while the methanol produced in the direct process is the product that can be yielded in addition to the main products of DME.

The increase in methanol production that can be achieved at peak production for the indirect and direct processes at unreacted gas recycle rates from 0 to 7 MMSCFD is from 16.2 tons/day to 25.0 tons/day and from 6.8 tons/day to 10.5 tons/day, respectively, enhancing methanol productions of 8.8 tons/day and 3.7 tons/day for indirect and direct processes, respectively, or increasing 54.5% and 53.7% in ethanol production for indirect and direct processes, respectively.

Figure 6 presents the effect of reactor temperature in an indirect and direct process at a pressure of 40 bar on DME production at various unreacted gas recycle rates. In the indirect process, the DME is produced at the DME synthesis reactor (see (1)) where the methanol is coming from the methanol synthesis reactor as shown in Figure 4. Therefore, the DME produced follows the profile of methanol formation where DME produced increases from a methanol synthesis reactor temperature of 195°C to 213°C and then decreases to a temperature of 366°C. In general, the process of direct DME synthesis through hydrogenation of CO₂ consists of three reactions: hydrogenation of CO₂ to methanol (see (2)), dehydration of methanol to DME (see (1)), and reversed water/gas shift reaction (see (4)) [46]. DME starts to form at 204°C where the methanol is at the peak of production in the direct process. DME production continues to increase until the DME production equilibrium temperature in the reactor is achieved at around 276°C for dual methanol-DME synthesis reactor pressures of 40 bar due to the balance of both the kinetic and thermodynamic factors. After that, DME production decreases with increasing reactor temperature up to 366°C. DME productions can be estimated thermodynamically [4], since the DME synthesis reaction (see (1)) is reversible and exothermic and the equilibrium conversion is significantly reduced in these ranges of temperatures as shown in Figure 4 [47]. Ereña et al.

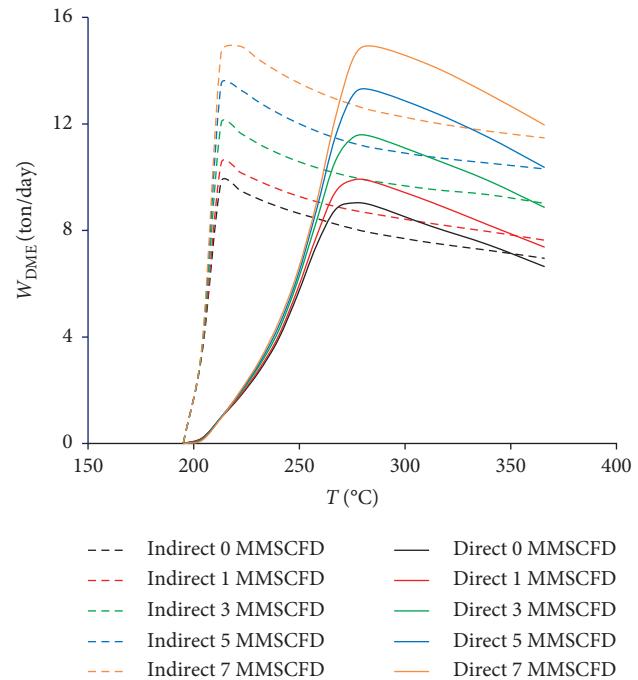


FIGURE 6: Effects of reactor temperature, T , at a pressure of 40 bar in the indirect and the direct processes on the DME production, W_{DME} , at various unreacted gas recycle rates.

[29] found that the yield of DME was at the peak condition at reaction temperature and pressure of 275°C and 40 bar, respectively, which is closed to the simulation result for direct DME synthesis at 40 bar in this study. The DME production in the direct process is higher than the indirect process at temperatures higher than 276°C. The increase of DME production at the peak condition is as a result of the presence of 7 MMSCFD gas recycled for indirect and direct processes from 9.8 to 14.7 tons/day and 9.0 to 14.9 tons/day, respectively. This means that there is an increase in DME production of 49.6% and 65.1% for the indirect and direct processes, respectively.

Figure 7 shows the effect of temperature of the methanol synthesis and the dual methanol-DME synthesis reactors on CO₂ conversion at reactor pressures of 40 bar at various unreacted gas recycle rates. The conversion of CO₂ in the methanol synthesis reactor involves the reaction of methanol formation (see (2)) and the reverse water/gas shift reaction (see (4)) [31, 32]. As with methanol production in the indirect process, CO₂ conversion increases from 195°C to 213°C due to the increased reaction rate [48], reaching a maximum value of 0.11 at a temperature of 213°C. Afterward, the CO₂ conversion decreases up to 366°C due to thermodynamic equilibrium limitation at higher temperatures [43, 44]. Meanwhile, CO₂ conversion in the direct process increases from temperatures of 195°C, reaching a maximum value of 0.13. The increase is due to the kinetic preference of methanol formation (see (2)) and DME formation (see (1)) by consuming methanol formed. Afterward, the conversion is slightly decreased until 366°C where in this range of temperatures the methanol production is slightly increased, while the DME production is slightly decreased.

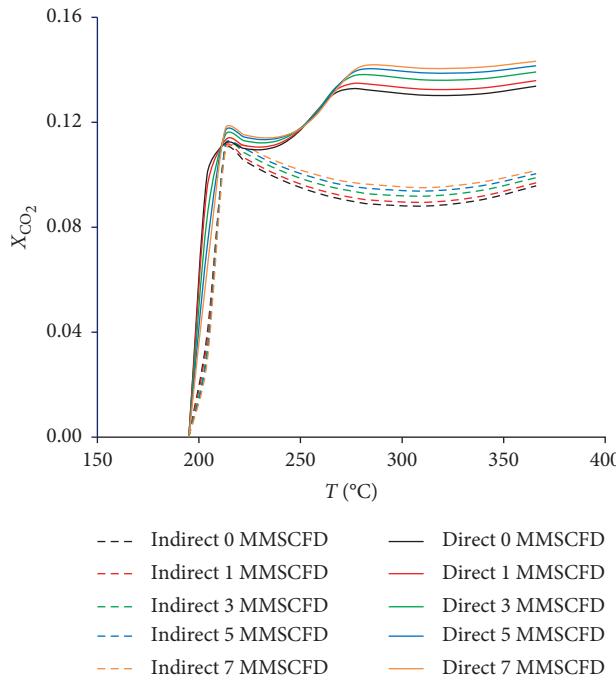


FIGURE 7: Effects of reactor temperature, T , at a pressure of 40 bar in the indirect and the direct processes on the CO_2 conversion, X_{CO_2} , at various unreacted gas recycle rates.

The same phenomena are also reported by Ren et al. [40], when using Cu-ZnO catalyst for methanol and DME synthesis through CO_2 hydrogenation. Ren et al. informed that the CO_2 conversion first increased with the reaction temperature and then decreased. Ren et al. found that the highest conversions were obtained at temperature of 240°C and 260°C, when the reaction pressures were at 21 bar, 28 bar, 35 bar, and 42 bar, respectively, while the highest CO_2 conversions based on the simulation results in this study were at reaction temperatures and pressure of 267°C at 40 bar.

The increase of CO_2 conversion is as a result of unreacted gas recycle rates of 7 MMSCFD from 0.1096 to 0.1111 and from 0.1328 to 0.1419 for indirect and direct processes, respectively. It means that there are 1.3% and 6.8% increase in conversion for indirect and direct processes, respectively. Based on the productions of DME and methanol and conversions that can be achieved from the simulation results, the direct process is more advantageous for producing DME in utilizing CO_2 emissions from AGRU in the oil and gas industries.

The effects of dual DME-methanol reactor temperatures and unreacted gas recycle rates on the DME and methanol selectivity in the direct DME synthesis are shown in Figures 8 and 9. The DME selectivity increases with reaction temperatures, reaching the maximum of 59.3% at reactions temperature of 267°C. The simulation result at reaction pressure of 40 bar was closed to that by Ereña et al., which obtained about 60% DME selectivity, when the reactions temperatures and pressures were at 275°C and 40 bar, respectively, feed gas flow rate of 1 mmole/min (molar ratio of $\text{H}_2 : \text{CO}_2$ at 5 : 1), and 1 g catalyst loading (mass ratio of CZA

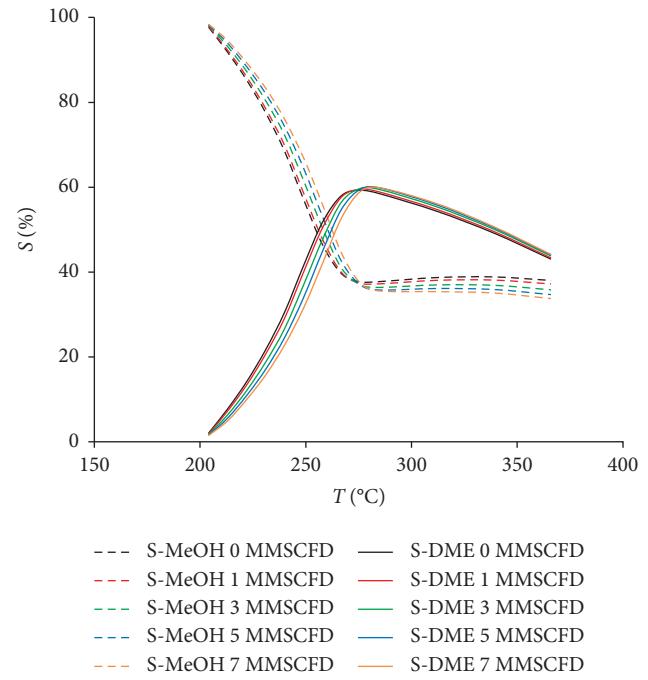


FIGURE 8: DME and methanol selectivity, S , as a function of the temperature of dual DME-methanol reactor at various unreacted gas recycle rates.

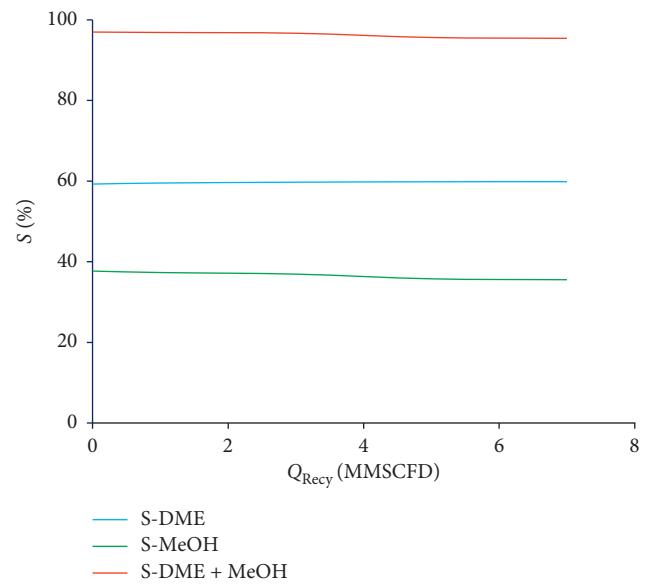


FIGURE 9: Selectivity of DME and methanol production, S , as a function of the unreacted gas recycle rates, Q_{Recy} .

to NaHZSM-5 at 4 : 1) [29]. Ren et al. also reported that the DME selectivity increased initially with an increase in the reaction temperature from 220 to 240°C (the highest DME selectivity ranging from 65.2% to 74.3%) and then decreased, when the temperature increased further and the reaction pressures were less than 35 bar. Meanwhile, at a reaction pressure of 42 bar, the highest DME yield was obtained at 260°C [40]. Sánchez-Contador et al. also reported the similar

trend to this study for DME selectivity in the reaction temperature range of 250–325°C, where the DME selectivity increased with increasing reaction temperature up to 300°C and then decreased, when the temperature further increased to 325°C [47].

The peak of methanol selectivity is at 204°C, while the peak of DME selectivity is at 276°C. Figure 8 shows that the DME selectivity slightly increases and methanol selectivity slightly decreases with increasing the flow rates of recycling unreacted gas. The DME selectivity increases from 59.3% to 59.9%, while methanol selectivity decreases from 37.7% to 35.6%, when the unreacted gas recycle rates increase from 0 to 7 MMSCFD, respectively. Overall, the total selectivity of DME and methanol slightly decreases from 97.0% to 95.4%, when the unreacted gas recycle rates increase from 0 to 7 MMSCFD as shown in Figure 9, respectively. It reveals that the unreacted gas recycle rates only slightly affect the selectivity of DME and methanol in the dual methanol-DME synthesis reactor.

Figure 10 presents the DME productions and increments in both indirect and direct process and the methanol production in the direct process as a function of the unreacted gas recycle rates at the peak DME productions. The production of DME in the indirect process is higher than the direct process until the flow rates of recycled hydrogen of 6 MMSCFD. However, the direct process also produces a significant amount of methanol as shown in Figure 10. Meanwhile, the increase in the DME production for the direct process is higher than the indirect process as presented in Figure 10.

In general, unreacted recycling can enhance DME production and CO₂ conversion in both indirect and direct processes. However, a compressor is needed to recycle hydrogen-rich gas from the previous processes. Therefore, the compressor power is also an important parameter in determining energy consumption in the process of making DME with recycling. The energy consumption for DME production can be expressed as a specific power consumption, which is defined as the power needed by the compressor for recycling gas to produce 1 ton of DME per hour. Therefore, the specific power consumption, η , can be expressed as

$$\eta = \frac{\text{compressor power}}{\text{DME produced}/h}, \quad (13)$$

The analysis of the energy system involves system energy requirements and the system energy output. The system energy requirements include the energy of the compressor, heater, and cooler as well as the energy needed in the condenser and reboiler in the DME and methanol purification columns. Meanwhile, the system energy output includes energy extracted in the form of DME and methanol and unrecycled hydrogen energy by assuming that it can be utilized as fuel by 60% [35].

Figure 11 shows the effect of unreacted gas recycle rates on specific power consumption (SPC) and system energy efficiency at peak condition for indirect and direct processes. The compressor power increased linearly to the increase of the gas recycled flow rates, while the DME production rate also increased but with a gradient lower than the compressor power and led to the increase in the specific

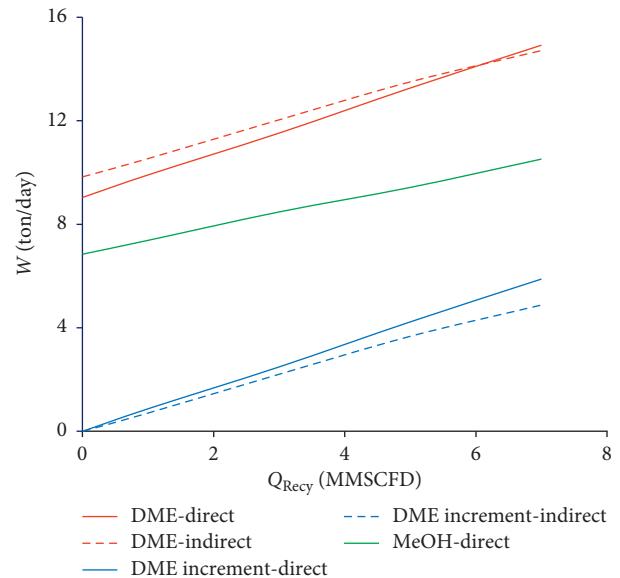


FIGURE 10: DME and methanol production, W , as a function of the unreacted gas recycle rates, Q_{Recy} .

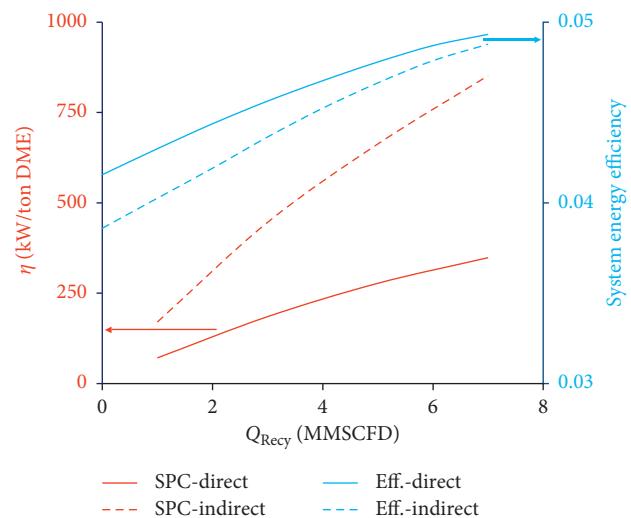


FIGURE 11: Effects of unreacted gas recycle rates on specific power consumption (SPC) and system energy efficiency at peak DME condition for indirect and direct processes.

power consumption as presented in Figure 11. Figure 11 also shows that the specific power consumption for the indirect process is higher than the direct process due to the lower suction pressure of recycling gas in the indirect process. Similar phenomena also occur with efficiency where the direct process has higher efficiency compared to the indirect process as presented in Figure 11, indicating that direct process is superior to indirect process, when there is a recycling of unreacted gas from the processes.

4. Conclusion

This study has been conducted to simulate DME production through direct and indirect processes. In the indirect

process, there are two synthesis reactors, namely, methanol and DME synthesis reactors, whereas the direct process of methanol and DME formation occurs in one reactor known as the dual methanol-DME synthesis reactor. The results of the process simulation have been validated with several research results [29, 30, 34, 40, 42–47, 49] and provide satisfactory results, especially in terms of the productions, conversions, and selectivity of DME and methanol for both processes. Simulation results showed that the DME production can be enhanced by recycling unreacted hydrogen and CO₂ gases. The DME production in indirect and direct processes can be increased by around 49.6% and 65.1%, respectively, at a recycling rate of 7 MMSCFD. However, for this purpose, a compressor is needed to increase the unreacted gas pressure to the desired pressure in the methanol reactor or dual methanol-DME reactor in the indirect process and direct processes. Therefore, compressor work is an important parameter to see the effectiveness of recycling unreacted gas expressed as specific power consumption. The simulation results show that, based on DME and methanol productions, SPCs, and system energy efficiencies, the direct DME synthesis process is superior over the indirect synthesis process.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Table 1: simulation results of DME synthesis through indirect process at methanol reactor pressure of 40 bar and recycled gas flow rate of 1 MMSCFD. Table 2: simulation results of DME synthesis through indirect process at methanol reactor pressure of 40 bar and recycled gas flow rate of 3 MMSCFD. Table 3: simulation results of DME synthesis through indirect process at methanol reactor pressure of 40 bar and recycled gas flow rate of 5 MMSCFD. Table 4: simulation results of DME synthesis through indirect process at methanol reactor pressure of 40 bar and recycled gas flow rate of 7 MMSCFD. Table 5: simulation results of DME synthesis through direct process at dual DME-methanol reactor pressure of 40 bar and recycled gas flow rate of 1 MMSCFD. Table 6: simulation results of DME synthesis through direct process at dual DME-methanol reactor pressure of 40 bar and recycled gas flow rate of 3 MMSCFD. Table 7: simulation results of DME synthesis through direct process at dual DME-methanol reactor

pressure of 40 bar and recycled gas flow rate of 5 MMSCFD. Table 8: simulation results of DME synthesis through direct process at dual DME-methanol reactor pressure of 40 bar and recycled gas flow rate of 7 MMSCFD. (*Supplementary Materials*)

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