

A COMPARATIVE STUDY ON SAFETY, EXERGETIC, AND ENVIRONMENTAL ANALYSIS FOR BIOMETHANOL VIA BIOGAS REFORMING

Mattana Santasnachok¹ and Teeranun Nakyai^{2,*}

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Abstract

The energy crisis and global warming caused by fossil fuel combustion have received increasing attention in recent years. Biomethanol is a clean and environmentally friendly energy produced by reforming biogas-derived syngas. To investigate the most suitable and efficient biomethanol production process, this paper compares the biomethanol production via three different biogas reforming processes, namely steam reforming, autothermal reforming, and tri-reforming using Aspen Plus simulator through safety index, energy and exergetic, and environmental analyses. For the process performance, the tri-reforming process achieved the highest energetic and exergetic efficiencies of 63.17% and 41.24%, respectively, due to producing the highest yield of methanol. In the environmental analysis, the steam reforming of the biogas process showed the lowest CO₂ emission intensity of 3.16 ton CO₂/ton methanol. The major source of CO₂ emission is the combustion of biogas. The Dow Fire and Explosion Index was used for the safety aspect. The biomethanol reactor was discovered to be the most hazardous equipment.

Keywords: Biomethanol, biogas reforming, safety indexes, energetic, exergetic, CO₂ emission intensity

Introduction

Over the last few years, the global energy demand has been increasing steadily and is expected to increase by 1.3% each year until 2040 (WEO, 2020). Additionally, the combustion of fossil fuels, i.e., coal, natural gas, and petroleum, generates carbon dioxide, which is a major contributor to global warming (Koo *et al.*, 2012). Therefore, to address the energy crisis and environmental issues, studies

have focused on alternative energies, including wind, solar, hydropower, biomass, and biogas, to substitute conventional fuels as energy sources.

Biogas is an energy source that can be converted into syngas to produce liquid fuels such as ethanol, dimethyl ether, and methanol. Biomethanol is a potential energy source that can be used as an organic solvent, transportation fuel, and

¹ Faculty of Engineering, Burapha University, 169 Longhaad Bangsaen Road, Saensuk, Mueang, ChonBuri 20131, Thailand. E-mail: mattana@eng.buu.ac.th

² Faculty of Public Health, Burapha University, 169 Longhaad Bangsaen Road, Saensuk, Mueang, ChonBuri 20131, Thailand. E-mail: teeranun.na@go.buu.ac.th

* Corresponding author

precursor for chemical production. It can be produced from biogas-derived syngas as a carbon-neutral fuel via steam reforming, dry reforming, autothermal (Minutillo *et al.*, 2020), and tri-reforming processes (Vita *et al.*, 2018). Energy and exergy analysis are powerful tools for indicating the thermal system's efficiency.

Numerous studies conducted energy and exergy analyses to evaluate hydrogen production efficiency. Simpson and Lutz (2007) performed the exergy analysis of hydrogen production via steam methane reforming (SMR). They revealed that the exergy efficiency of the process was approximately 63% and that the reformer had the highest exergy loss. Nakyai and Saebea (2019) also performed the energy and exergy analysis to evaluate the efficiency of syngas production via the tri-reforming process. Minutillo *et al.* (2020) studied hydrogen production plants via biogas steam and autothermal reforming processes using energy and exergy analyses. They discovered that hydrogen separation and compression account for 16%-18% of total exergy losses. As previously stated, most energy and exergy analyses are only applicable to the hydrogen production process; no available studies compared the energy and exergy efficiencies of methanol production of the biogas reforming processes. Although the process performance of systems has been conducted using the energy and exergy method, as mentioned above, environmental friendliness is an important criterion for decision making in manufacturing and process design.

The CO₂ emission intensity was applied to indicate the source of the CO₂ emission in the chemical production process (Milani *et al.*, 2015). Luu *et al.* (2015) studied CO₂ utilization in methanol synthesis with various syngas production technologies. Nakyai *et al.* (2017) conducted the CO₂ emission intensity of the single-step and two-step dimethyl ether production. They reported that

the single-step process has lower CO₂ emission intensity than the two-step process.

Therefore, this study aims to investigate biomethanol production via three different biogas reforming processes: steam reforming, autothermal reforming, and tri-reforming. The influences of parameters (such as reformer temperature and steam) on the H₂/CO molar ratio, operating pressure, and temperature on methanol yield were studied. Furthermore, the energy and exergy approaches were applied to indicate the performance of the biomethanol production process. For the environmental aspect, the CO₂ emission intensity was calculated to determine the source of CO₂ emission. Additionally, the Dow Fire and Explosion Index (F&EI) was applied to assess the hazards of methanol production processes.

Materials and Methods

The methanol production from three different biogas reforming processes, namely, steam reforming, autothermal reforming, and tri-reforming processes, were studied. The assumptions of the three processes are summarized as follows:

1. Reformer and methanol reactors are operated in isothermal and adiabatic conditions.
2. The processing system is assumed to be in steady-state conditions.
3. Biogas as feedstock instead of methane.
4. The environmental state is at 25°C and 101.325 kPa.

Figure 1 presents the Aspen Plus flowsheet of the biomethanol production via steam reforming, autothermal reforming, and tri-reforming of biogas. In this study, biogas was used as feedstock, and its components, including methane, carbon dioxide, and water, are shown in Table 1.

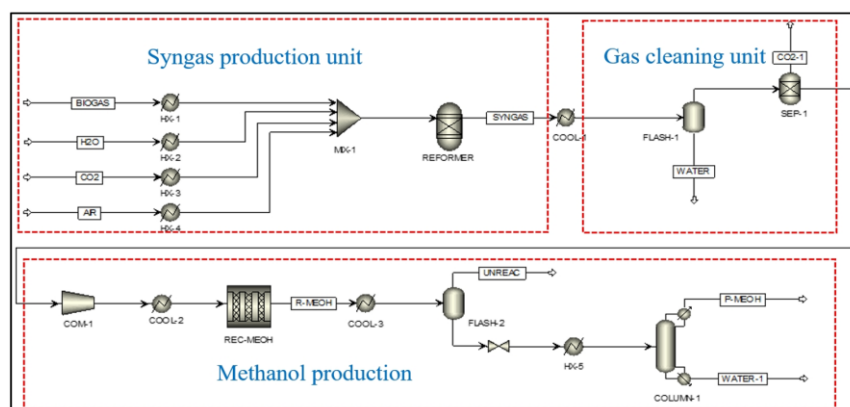


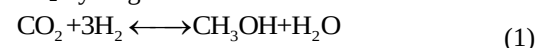
Figure 1. Aspen plus flowsheet for methanol production via reforming of biogas

In the steam reforming of biogas, steam was used as gasifying agent, whereas in the autothermal reforming of biogas, air and water were used as gasifying agents. For the tri-reforming of biogas, air, water, and carbon dioxide were used as gasifying agents. Pure carbon dioxide was obtained from the CO₂ extracted from the exhaust gas after the postcombustion process (Schakel *et al.*, 2018). As depicted in Figure 1, the biogas and gasifying agents were preheated before being fed into the reformer. The reformer was operated in the temperature range of 800°C-1,000°C at atmospheric pressure. The chemical reactions involved in the biogas reforming comprised of SMR, dry reforming of methane (DRM), partial oxidation of methane (POM), reverse CO₂ methanation (RCM), water gas shift (WGS), and complete oxidation of methane (COM), as listed in Table 2. The Peng-Robinson and Soave-Redlich-Kwong fluid packages were selected to simulate syngas and methanol productions, respectively.

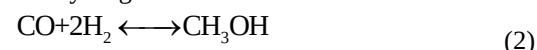
The hot syngas from the reformer was cooled, consequently removing the water. Then, the raw syngas was transferred to a gas cleaning unit to remove the CO₂ content using a membrane before

being fed into the biomethanol reactor. In the biomethanol synthesis unit, the main chemical reactions in the biomethanol reactor were CO₂ hydrogenation, CO hydrogenation, and reverse WGS reactions.

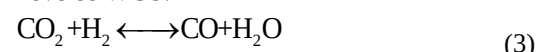
CO₂ hydrogenation:



CO hydrogenation:



Reverse WGS:



The reaction rates of the biomethanol synthesis are given by the literature using Equations (4)-(6) (Graaf *et al.*, 1988).

$$r_{\text{CO}} = \frac{k_1 K_{\text{CO}} (f_{\text{CO}} f_{\text{H}_2}^{3/2} - (f_{\text{CH}_3\text{OH}}/f_{\text{H}_2}^{3/2} K_{\text{P1}}))}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2})(f_{\text{H}_2}^{1/2} + (K_{\text{H}_2}^{-1/2} K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}}))} \quad (4)$$

$$r_{\text{CO}_2} = \frac{k_2 K_{\text{CO}} (f_{\text{CO}_2} f_{\text{H}_2}^{3/2} - (f_{\text{H}_2\text{O}} f_{\text{CH}_3\text{OH}}/f_{\text{H}_2}^{3/2} K_{\text{P2}}))}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2})(f_{\text{H}_2}^{1/2} + (K_{\text{H}_2}^{-1/2} K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}}))} \quad (5)$$

$$r_{\text{WGS}} = \frac{k_3 K_{\text{CO}_2} (f_{\text{CO}_2} f_{\text{H}_2} - (f_{\text{H}_2\text{O}} f_{\text{CO}}/K_{\text{P3}}))}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2})(f_{\text{H}_2}^{1/2} + (K_{\text{H}_2}^{-1/2} K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}}))} \quad (6)$$

where the r is the rate of reaction, f is the fugacity of gases, k is the rate constant of reaction i , K_j is the adsorption equilibrium constant of component j , and K_p is the equilibrium constant of reaction i . The kinetic parameters for methanol synthesis are shown in Table 3 (Graaf *et al.*, 1988).

In this study, the operating temperature and pressure of the methanol reactor were in the ranges of 190°C-260°C and 50-80 bar, respectively. For the methanol distillation column, the total number of stages, crude methanol feed stage, and

Table 1. Components of biogas used in the simulation

Component	Value (mol %)
CH ₄	52.00
CO ₂	42.88
H ₂ O	5.12

Table 2. Chemical reactions involved in the reforming of biogas

Reaction	Equation	ΔH (kJ/mol)
SMR	CH ₄ + H ₂ O $\longleftrightarrow$ CO + 3H ₂	+206
DRM	CH ₄ + CO ₂ $\longleftrightarrow$ 2CO + 2H ₂	+247
POM	CH ₄ + 0.5O ₂ $\longleftrightarrow$ CO + 2H ₂	-36
RCM	CH ₄ + 2H ₂ O $\longleftrightarrow$ CO ₂ + 4H ₂	+165
WGS	CO + H ₂ O $\longleftrightarrow$ CO ₂ + H ₂	-41
COM	CH ₄ + 2O ₂ $\longleftrightarrow$ CO ₂ + 2H ₂ O	-803

Table 3. Kinetic parameter for methanol synthesis

Parameter (unit)	Ai	Bi	Parameter (unit)	Ai	Bi
k_1 (kmol Pa ^{1/2} ·kg ⁻¹ ·s ⁻¹)	4.0638×10 ⁶	-11695	K_{CO_2} (Pa ⁻¹)	1.7214×10 ⁻¹⁰	81,287
k_2 (kmol Pa·kg ⁻¹ ·s ⁻¹)	1.5188×10 ⁻³³	-266010	$K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{1/2}$ (Pa ^{-1/2})	4.3676×10 ⁻¹²	115,080
k_3 (kmol Pa ^{1/2} ·kg ⁻¹ ·s ⁻¹)	9.0421×10 ⁸	-112860	K_{P1} (atm ⁻²)	2.3717×10 ⁻¹³	98,438
K_{CO} (Pa ⁻¹)	8.3965×10 ⁻¹¹	118270	K_{P2} (atm ⁻²)	6.6688×10 ⁻¹¹	54,499
K_{CO_2} (Pa ⁻¹)	1.7214×10 ⁻¹⁰	81287	K_{P3} (-)	2.8118×10 ²	-43,939

reflux ratio were 25, 11, and 1, respectively. The distillation rate and condenser pressure were 20 kg/h and 48 bars, respectively. The types of condenser and reboiler are partial vapor and kettle, respectively. The column's valid phases were vapor-liquid.

Performance Analysis

Safety index

For the safety analysis, the Dow F&EI was used to evaluate relative ratings of the fire and explosion risk involved in the biomethanol process. It is formulated as Equation (7).

$$F\&EI = MF(F_1 \times F_2) \quad (7)$$

where MF is the material factor, F_1 is the general process hazards, which are types of chemical reactions (exothermic or endothermic), material handling and transfer, and drainage and spill control, and F_2 is the special process hazards, such as toxic material, operating area, quantity flammable and unstable material, and leakage. The radius of exposure in meters can be calculated as

$$Raduis_m = 0.256(F\&EI) \quad (8)$$

The degrees of hazard associated with the F&EI value are obtained from the literature.

Energy and Exergy Analyses

Energy efficiency measures were based on the first law of thermodynamics or energy conservation. The total energy (E_{total}) is the sum of physical energy (E^{ph}) and chemical energy (E^{ch}), as calculated using Equation (9) (Nakyai and Saebea, 2019).

$$E_{total} = E^{ph} + E^{ch} \quad (9)$$

The physical and chemical energies can be calculated using Equations (10) and (11).

$$E^{ph} = \sum_{i=1} n_i h_i \quad (10)$$

$$E^{ch} = \sum_i n_i HHV_i \quad (11)$$

where h_i and HHV_i represent the specific enthalpy and higher heating value of component i , respectively. n_i represents the molar yield.

Similar to the energy analysis, the total exergy (Ex_{total}) is the sum of physical exergy (Ex^{ph}) and chemical exergy (Ex^{ch}), as calculated using Equations (12)-(14).

$$Ex_{total} = Ex^{ph} + Ex^{ch} \quad (12)$$

$$Ex^{ph} = \sum_{i=1} n_i ((h-h_0) - T_0(s-s_0)) \quad (13)$$

$$Ex^{ch} = \sum_i n_i (ex_i^{ch} + RT_0 \ln y_i) \quad (14)$$

where h and s represent the specific enthalpy and entropy in the operating condition, h_0 and s_0 represent the specific enthalpy and entropy at the environmental state, T_0 represents the temperature at the environmental state, ex_i^{ch} represents the specific exergy of component i , R represents the universal gas constant, and y_i represents the mole fraction of component i . The energetic (η_E) and exergetic (η_{Ex}) efficiencies are determined using the following expression:

$$\eta_{E,system} = \frac{E_{methanol}}{E_{biogas} + E_{heat} + E_{power}} \times 100 \quad (15)$$

$$\eta_{Ex,system} = \frac{Ex_{methanol}}{Ex_{biogas} + Ex_{heat} + Ex_{power}} \times 100 \quad (16)$$

where E_{heat} and E_{power} are the energy and power supply in the process and Ex_{heat} and Ex_{power} are exergy of heat and power supply in the system.

Environmental Estimation

In the environmental analysis, the CO_2 emission intensity of the methanol production via three different biogas reforming processes was investigated by the following equation (Luu *et al.*, 2015):

$$CO_2 \text{ emission intensity} = \frac{\text{ton } CO_2}{\text{ton methanol}} \quad (17)$$

In Equation (17), the sources of the CO_2 emission consist of CO_2 emission from the biomethanol production process, biogas combustion, thermal duty, and electricity duty. Thus, the total CO_2 emission can be determined by the following equation:

$$\text{ton CO}_2 = \text{CO}_{2,\text{fuel}} + \text{CO}_{2,\text{process}} + \text{CO}_{2,\text{thermal}} + \text{CO}_{2,\text{electricity}} \quad (18)$$

$$\text{CO}_{2,\text{fuel}} = 2.75 \times (\text{CH}_{4,\text{feed}}) \quad (19)$$

$$\text{CO}_{2,\text{thermal, electricity}} = Q_{\text{sup}} \times \text{EF}_{\text{thermal, electricity}} \quad (20)$$

where EF is the CO₂ emission equivalent factor for thermal and electricity duties.

Result and Discussion

Model Validation

To predict the performance of biomethanol production from the biogas reforming process, the Aspen Plus models were validated and verified by the experimental data. For the syngas production unit, the simulation results were compared with the experimental data of Jang *et al.* (2016). Figure 2 displays the comparison of the syngas compositions between simulation and experimental data. As shown in the figure, the results from the Aspen Plus models were closely consistent with the experimental results. For the biomethanol production unit, the simulation results with the plant data of Shiraz Petrochemical Company. The syngas feed components, operating conditions, simulation results, and plant data are shown in Table 4. The results showed that the simulation results are consistent with the plant data, as shown in Table 4.

Syngas and Methanol Production

Influence of steam and Air-to-Biogas ratio on H₂/CO Molar ratio.

Air and steam as gasifying agents are the key parameters in the biogas reforming process. Therefore, the effect of the air- and steam-to-biogas ratio on the H₂/CO molar ratio was studied in this section, as shown in Figure 3(a)-(b). The reformer temperature and air-to-biogas ratio are kept constant at 900°C and 3, respectively. From Figure 3(a), increasing the steam-to-biogas ratio from 0.5 to 3.0 dramatically increases the H₂/CO molar ratio of steam reforming and autothermal reforming of biogas, whereas the tri-reforming of biogas gradually increases. This can be explained by the fact that the addition of steam favored the SMR and WGS reactions, increasing the hydrogen content. Thus, an increase in the H₂/CO molar ratio was observed. In Figure 3(b), the H₂/CO molar ratio slightly decreased with an increase in the air-

to-biogas ratio. The results reveal that the increase in oxygen provided the occurrence of COM. In the COM reaction, biogas as feedstock reacts with oxygen to produce carbon dioxide and water, decreasing the H₂/CO molar ratio.

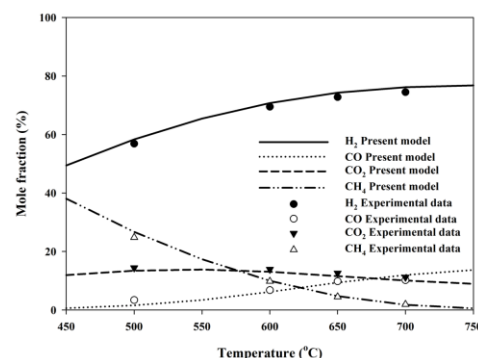


Figure 2. Validation of the tri-reforming of methane as a function of reformer temperature at a (CO₂ + H₂O)/CH₄ ratio of 1.2 and CO₂:H₂O ratio of 1:2.1

Table 4. Operating condition and validation results of the biomethanol synthesis

Component	Reactor inlet ^a (% mol)	Reactor outlet (% mol)	
		Plant data (% mol)	Simulation (% mol)
CO	4.66	1.44	1.26
H ₂	79.55	75.71	76.09
CO ₂	3.45	2.18	2.23
H ₂ O	0.08	1.74	1.71
CH ₃ OH	0.032	5.94	5.61
CH ₄	11.72	12.98	13.13

^a at feed flow rate and temperature of 0.565 mol/s and 503 K, respectively.

Optimum H₂/CO Molar Ratio for Biomethanol Production

The biomethanol process requires an H₂/CO molar ratio of 2. In syngas production, the H₂/CO molar ratio was regulated by diminishing the amount of biogas used as feedstock and gasifying agents. Table 5 shows the proper conditions and syngas yields for all cases.

In Table 5, the tri-reforming of biogas produced the highest syngas yield of 79.95 and 38.89 mol/kg for H₂ and CO, respectively. This is due to the tri-reforming process having the highest conversion of biogas as methane. The syngas yield was 42.08% and 39.76% higher than those of autothermal reforming and steam reforming of biogas, respectively.

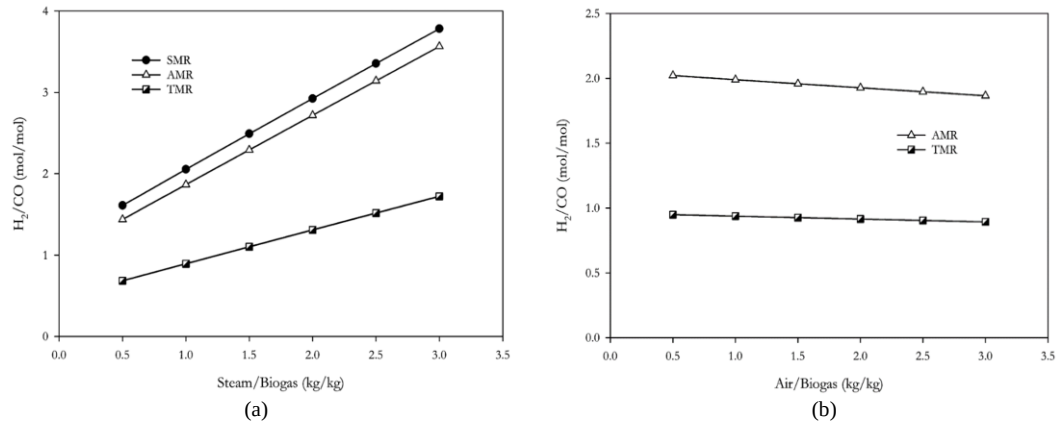


Figure 3. Influence of (a) steam-to-biogas and (b) air-to-biogas ratios on the H_2/CO molar ratio

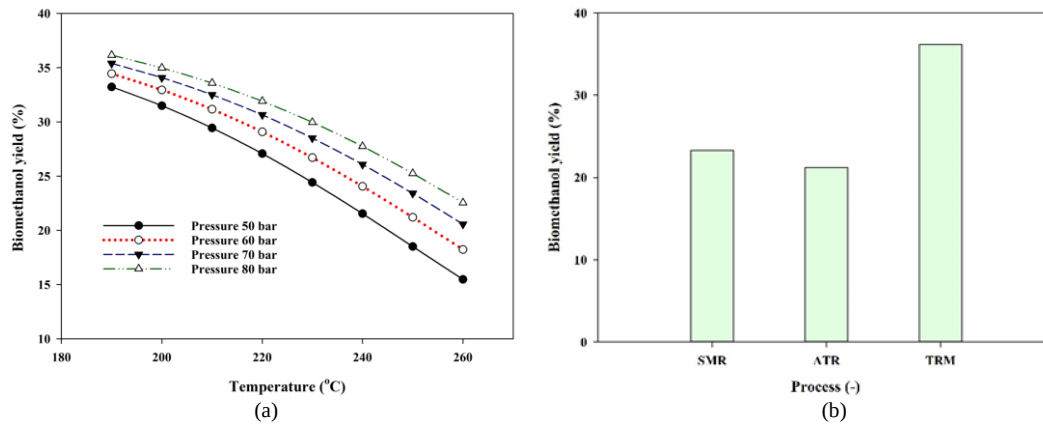


Figure 4. Biomethanol yield (a) Influences of Operational pressure and temperature and (b) process (at 190°C and 80 bars)

Table 5. Operating conditions, syngas compositions, and syngas yield for all cases

Case	S/B (kg/kg)	A/B (kg/kg)	CO_2/B (kg/kg)	H_2/CO (mol/mol)	Syngas composition (kmol/h)			Syngas yield of (mol/kg biogas)	
					H_2	CO	CO_2	H_2	CO
SMR	0.44	-	-	2.0	19.27	9.61	3.70	48.16	24.03
ARM	0.43	0.23	-	2.0	19.27	9.61	4.30	46.30	23.09
TRM	0.83	0.58	0.89	2.0	19.27	9.61	5.31	79.95	39.89

Influences of Operating Pressure and Temperature on Biomethanol Yield.

In the biomethanol synthesis unit, the H_2/CO molar ratio of 2 via reforming of biogas processes was fed into the biomethanol reactor. The influence of operating pressure and temperature on biomethanol yield is depicted in Figure 4(a). The biomethanol synthesis reactor's operation at a higher pressure and lower temperature enhanced the biomethanol yield owing to Le Chatelier's principle and the exothermic nature of methanol synthesis.

As a result, the maximum biomethanol yield was 36.15 mol/kg biogas at a pressure and temperature of 80 bars and 190°C, respectively. Figure 4(b) illustrates the comparison of the biomethanol yield via three different reforming processes of biogas-derived syngas. As shown in the figure, the tri-reforming of biogas achieved the highest biomethanol, followed by steam and autothermal reforming of biogas. This is because the tri-reforming of biogas produced the highest syngas yield (Table 5).

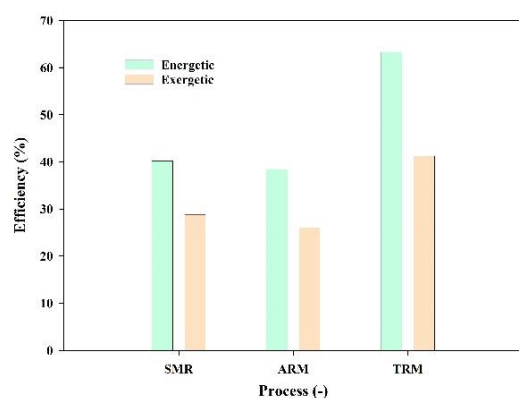


Figure 5. Energetic and exergetic efficiencies of biomethanol for all cases

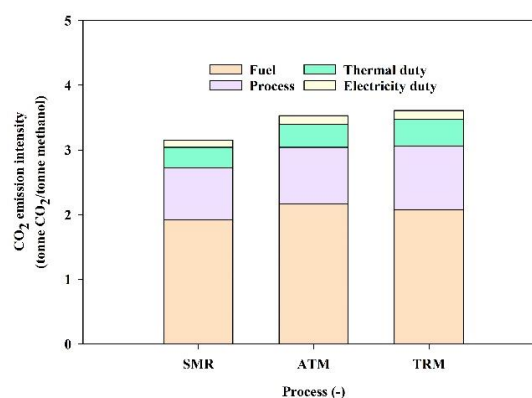


Figure 6. CO₂ emission intensity breakdown for all cases

Table 6. Dow's F&EI results for equipment of bio-methanol production for all cases

Equipment	SMR		ARM		TRM	
	FE&I	Radius(m)	FE&I	Radius(m)	FE&I	Radius(m)
HX-1	98.40	25.19	98.40	25.19	98.40	25.19
HX-2	4.80	1.23	4.80	1.23	4.80	1.23
HX-3	0.00	0.00	0.00	0.00	1.92	0.49
HX-4	0.00	0.00	1.92	0.49	1.92	0.49
Reformer	97.20	24.88	101.09	25.88	101.52	25.99
cool-1	117.10	29.98	117.10	29.98	117.10	29.98
Flash-1	77.49	19.84	77.49	19.84	77.49	19.84
Sep-01	77.49	19.84	77.49	19.84	77.49	19.84
Com-1	77.49	19.84	77.49	19.84	77.49	19.84
Cool-2	77.49	19.84	77.49	19.84	77.49	19.84
Reac-MeOH	118.80	30.41	120.38	30.82	119.86	30.68
Cool-3	65.60	16.79	65.60	16.79	65.60	16.79
Flash-2	65.60	16.79	65.60	16.79	65.60	16.79
Hx-5	65.60	16.79	65.60	16.79	65.60	16.79
Column-1	95.78	24.52	95.78	24.52	95.78	24.52

Energy and Exergy Analyses

Figure 5 shows the energetic and exergetic efficiencies of syngas and biomethanol production processes for steam reforming, autothermal reforming, and tri-reforming of biogas processes. As shown, the ranges of the energetic and exergetic efficiencies are 40.18-63.17 and 28.79%-41.24%, respectively. The tri-reforming of biogas consumes the highest energy because of the preheating of the gasifying agents. The energy consumption is 1.86 and 1.92 higher than those of autothermal reforming and steam reforming of biogas processes. In Figure 5, the simulation results showed that the tri-reforming of biogas has the highest energetic and exergetic efficiencies of 63.17% and 41.24%, respectively, although it consumes the highest energy. This is because the tri-reforming of biogas has the highest yield of the methanol, thereby increasing the chemical exergy and efficiency of the system.

Environmental Assessment

The total CO₂ emission intensities of the three different processes associated with fuel, process, and thermal and electrical duties are illustrated in Figure 6. As shown in this figure, the tri-reforming and steam reforming of biogas processes have the highest and lowest total CO₂ emission intensity, accounting for 3.60 and 3.16 tons of CO₂ per 1 ton of methanol, respectively. Therefore, when considering the CO₂ emission breakdown of the three processes, the major source of CO₂ emission intensity is the carbon dioxide emission from the combustion of biogas, followed by carbon dioxide from the biomethanol production process and electricity and thermal duties.

Safety Assessment

In this section, the F&EI was used to evaluate the safety of biomethanol production. The F&EI indexes were investigated based on material factors,

general hazards, and special hazards. Table 6 reports the safety indexes and radius of exposure of equipment for biomethanol production for all cases. As listed in this table, the F&EI value and radius of exposure are in the ranges of 4.80-120.38 and 1.23-30.82 m. The biomethanol reactor was identified as the most hazardous equipment for all cases (classified as intermediate level). The difference in the FE&I value of the biomethanol reactor and reformer in three different biogas reforming processes is due to the exothermic and endothermic reactions.

Conclusions

In this study, biomethanol production via three different reforming processes of biogas-derived syngas was studied through energetic and exergetic, environmental, and safety analyses. The results revealed that the tri-reforming of methane yields the highest energetic and exergetic efficiencies of 63.17% and 41.24%, respectively. For the environmental aspect, the steam reforming of biogas had the lowest CO₂ emission intensity (3.16 ton CO₂/ton methanol). In the safety analysis, the biomethanol reactor was the most hazardous equipment, classified as intermediate in terms of potential hazards. From all results, the tri-reforming of biogas showed a suitable process for biomethanol production. However, CO₂ emissions should be considered. In the future, the authors look forward to comparing the three different reforming processes of biogas in terms of economics and investigating the best process for biomethanol production.

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