

Modeling of a methanol synthesis process to utilize CO₂ in the exhaust gas from an engine plant

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Abstract—We investigated the conversion of CO₂ in the exhaust gas of an engine plant into methanol. The process consists of CO₂ purification by an acid gas removal unit (AGRU), mixed reforming, and methanol synthesis. The AGRU removes a large amount of inert gas, yielding CO₂ of 98% purity at a recovery rate of 90% for use as feed to the reformer. The reformer temperature of 900 °C led to the almost total consumption of CH₄. In the methanol synthesis reaction, the utility temperature had a greater influence on the conversion and methanol production rate than the inlet temperature. The optimal temperature was determined as 180 °C. Because the amount of hydrogen in the reformer effluent produced by dry reforming was insufficient, the steam available in the engine plant was used for mixed (dry and steam) reforming. The steam increased the hydrogen and methanol production rate; however, the compression cost was too high, and there exists an optimal amount of steam in the feed. The techno-economic analysis of the optimal conditions showed that utilization of CO₂ in the exhaust gas along with freely available steam is economically feasible and reduces CO₂ emissions by over 85%.

Keywords: Methanol Synthesis, Exhaust Gas, Engine Plant, CO₂ Reduction, Techno-economic Analysis

INTRODUCTION

Exhaust gases from power plants have contributed to the problems of climate change and global warming as they consist of approximately 10% CO₂, a greenhouse gas that must be sequestered or converted into other useful chemicals. In addition to research on improving engine efficiency to reduce CO₂ emissions, many studies have been conducted on carbon capture and storage (CCS). Several methods for the capture and geological storage of CO₂ have been proposed, and the corresponding electricity rates and capital costs have been estimated [1]. The most recent studies on CO₂ capture have dealt with chemical absorption, physical absorption, and membrane separation; however, the entire CCS process includes the liquefaction, transport, and storage of CO₂ [2].

Because the CCS process consumes a large amount of energy, numerous studies have been performed on carbon capture, utilization, and storage and the reactions and catalysts for converting CO₂ into other substances, such as methanol. Methanol synthesis is of considerable interest because methanol is a widely used commercial substance with various applications. For instance, methanol is applied as a fuel owing to its high octane number and excellent combustion properties. It is used in many reactions, including methanol-to-hydrocarbons, methanol-to-gasoline, methanol-to-olefins, and

methanol-to-propylenes. It is also considered a convenient medium for the storage and transport of CO and H₂. Kinetic models of reforming and methanol synthesis have been developed as well as new catalysts to increase the catalytic efficiency under various operating conditions. The mechanism of methanol synthesis was studied in a copper-based amorphous catalyst system [3]. Kinetics of methanol synthesis reactions was studied over Cu-Zn-Al catalysts at 15-50 bar and 210-245 °C [4]. A kinetic model of methanol synthesis with methanol dehydration was developed considering the synthesis of dimethyl ether (DME) [5]. The kinetic parameters of mixed reforming were developed by fitting lab-scale experimental data and validating the effectiveness of kinetic models for mixed reforming and methanol synthesis in a pilot-scale plant by comparing simulations and experiments [6]. Kinetic models for mixed reforming and methanol synthesis were developed on a bench scale, and the process model was used to evaluate the effects of various factors on productivity and efficiency [7].

Dynamic optimization of a steam reformer was studied using genetic algorithms to determine the optimal power supply and molar ratios of input feed [8]. The optimal temperature of methanol synthesis reactor was applied to a methanol synthesis reactor using a two-stage cooling shell [9]. The dynamic behavior of a methanol synthesis reactor was simulated using the internal model control technique and proportional-integral-derivative control [10]. The dynamic modeling of a fixed-bed methanol synthesis reactor was reported based on diffusion, mass, and energy balances and reaction kinetics to determine the best-performing state [11]. A

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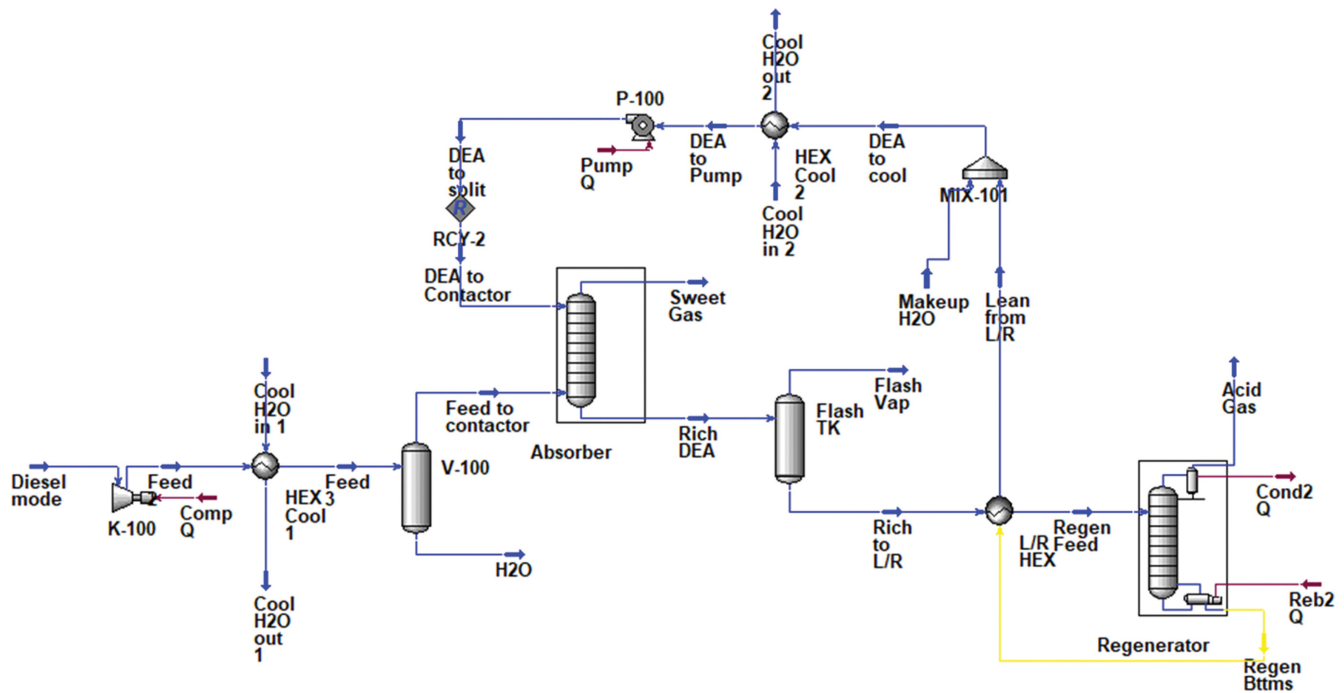


Fig. 1. A schematic of the acid gas recovery unit process.

techno-economic analysis of the methanol synthesis process was conducted by calculating various economic evaluation indicators [12]. Modeling and techno-economic was conducted on the Linz-Donawitz gas-assisted coke-oven gas-to-methanol process and the sensitivity study of the natural gas price was analyzed [13].

In this study, a process that directly converts CO_2 in the exhaust gas of an engine plant into methanol was considered. A techno-economic analysis was also conducted to evaluate whether utilization of CO_2 would improve the economics of the entire plant. Although there are reported works to utilize CO_2 by methanol synthesis, no research works considered the use of exhaust gas from engine plants to produce methanol and analyzed its techno-economic. It is also worth noting that, to guarantee the feasibility of the developed process model, detailed kinetics based on the reaction mechanism and experimental data were augmented in the process simulator for both reforming and methanol synthesis, and the reactors were configured to satisfy the specifications and operating conditions of the previously developed pilot-scale system.

Because a large amount of inert gas in the exhaust gas (mostly nitrogen and oxygen) may increase the complexity of the methanol synthesis process, an acid gas removal unit (AGRU) was installed to recover pure CO_2 at the top of the regeneration column. The purified CO_2 gas was used as feed for the methanol synthesis process, which utilizes reforming and methanol synthesis reactors to produce syngas (CO and H_2) and convert CO and CO_2 into methanol, respectively. In addition to dry reforming (CH_4 and CO_2), the steam produced by the engine plant was added to promote methane reforming and increase the hydrogen ratio for a high methanol production rate. Finally, the techno-economic effects of the reactor temperature and feed composition were analyzed to estimate the feasibility of the proposed strategy.

METHOD

1. Acid Gas Removal Unit (AGRU)

The AGRU is a well-known process that removes acid gases, such as H_2S or CO_2 . Fig. 1 shows a schematic of the process considered in this study [15]. The feed of the AGRU process is the exhaust gas from an engine plant. It contains approximately 11% of water, which is removed at the first separator to prevent it from being stacked up in the recycle loop. Among three candidate absorbents for CO_2 (monoethanol amine, diethanol amine (DEA), and methyl diethanol amine), DEA was selected for its high CO_2 removal ability [16,17]. CO_2 -rich DEA from the bottom of the absorber was sent to a distillation tower (regenerator). The pure DEA solution recovered at the bottom was recycled, while highly concentrated CO_2 at the top was used as feed for the methanol synthesis process. The Sour Peng-Robinson equation of state and amine package were used as thermodynamic models in the simulator. The absorber was set to have 12 stages and an operating pressure of 530 kPa, with a pressure drop of 30 kPa. The distillation tower has 12 stages and an operating pressure of 300 kPa, with a pressure drop of 90 kPa. The feed flow rate was assumed to be 50,000 kg/h. The composition was the same as that of the exhaust gas from a diesel engine: CO_2 (18.07 wt%), O_2 (10.95 wt%), H_2O (6.75 wt%), and N_2 (64.21 wt%). The feed flow rate of 50,000 kg/h corresponds to methanol production at a scale of several hundred tons per day.

2. Methanol Synthesis Process

Fig. 2 shows a schematic of the methanol synthesis process, which consists of two reaction units: a reformer and a methanol synthesis reactor. The Peng-Robinson equation of state was used as the thermodynamic model. A multitubular furnace was considered for the reformer, with 40 tubes each measuring 10 m in length and

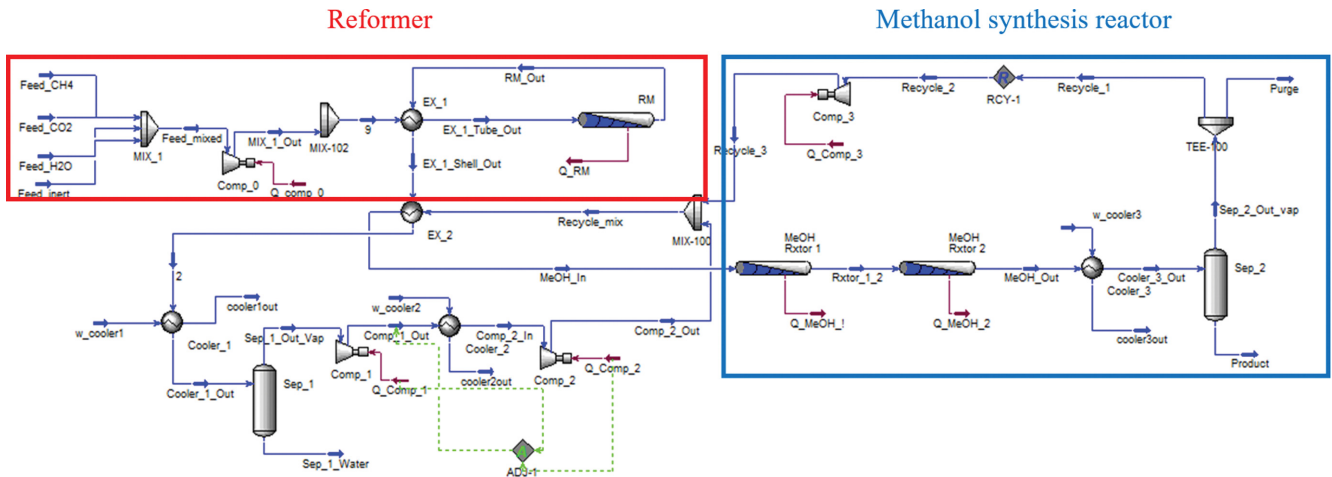
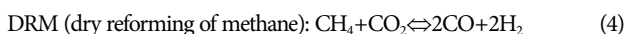
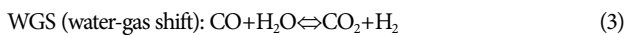
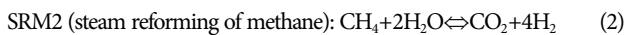
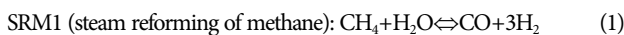


Fig. 2. A schematic of the methanol synthesis process.

0.1016 m in diameter, for a total volume of 6.486 m³. The feed to the reformer was a mixture of CO₂ (separated from the exhaust gas by the AGRU), CH₄, and steam obtained from the engine plant. Two compressors and two heat exchangers were considered to increase the pressure and temperature, respectively, to meet the required conditions in the reformer. The temperature and pressure of the reformer inlet stream are 800 °C and 1,003 kPa, while those of the reformer effluent are 900 °C and 993 kPa, respectively, owing to the pressure drop. Because of the excess amount of heat supplied to the reforming furnace and the rapid reforming reaction, the early part of the catalytic tubes was in the kinetic regime and exhibited an abrupt decrease in temperature due to the endothermicity of the reaction. After the reaction reached equilibrium, the temperature increased owing to excessive heat, and the thermodynamic equilibrium conversion increased. To recover heat, heat exchange between the reformer effluent and feed was induced with a heat exchanger. Because the temperature remained high after the first heat exchanger, the remaining heat was transferred to the inlet stream of the methanol reactor using the second heat exchanger. Water in the effluent of the reformer was removed in a flash vessel (Sep_1 in Fig. 2) to reduce the size of the methanol synthesis reactor. The water-free stream was then pressurized to 4,990 kPa by two-stage compression for efficiency.

In the reformer, the mixed (steam and dry) reforming of methane was considered to synthesize H₂ and CO. The details of the overall reactions and rate equations are as follows [7,14]:



$$r_{\text{SRM1}} = \frac{k_{\text{SRM1}} \left(f_{\text{CH}_4} f_{\text{H}_2\text{O}} - \frac{f_{\text{H}_2}^3 f_{\text{CO}}}{K_{p\text{SRM1}}} \right) / f_{\text{H}_2}^{2.5}}{\left[1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{H}_2} f_{\text{H}_2} + K_{\text{CH}_4} f_{\text{CH}_4} + K_{\text{H}_2\text{O}} \left(\frac{f_{\text{H}_2\text{O}}}{f_{\text{H}_2}} \right) \right]^2} \quad (5)$$

$$r_{\text{SRM2}} = \frac{k_{\text{SRM2}} \left(f_{\text{CH}_4} f_{\text{H}_2\text{O}} - \frac{f_{\text{H}_2}^4 f_{\text{CO}_2}}{K_{p\text{SRM2}}} \right) / f_{\text{H}_2}^{3.5}}{\left[1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{H}_2} f_{\text{H}_2} + K_{\text{CH}_4} f_{\text{CH}_4} + K_{\text{H}_2\text{O}} \left(\frac{f_{\text{H}_2\text{O}}}{f_{\text{H}_2}} \right) \right]^2} \quad (6)$$

$$r_{\text{WGS}} = \frac{k_{\text{WGS}} \left(f_{\text{CO}} f_{\text{H}_2\text{O}} - \frac{f_{\text{H}_2} f_{\text{CO}_2}}{K_{p\text{WGS}}} \right) / f_{\text{H}_2}}{\left[1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{H}_2} f_{\text{H}_2} + K_{\text{CH}_4} f_{\text{CH}_4} + K_{\text{H}_2\text{O}} \left(\frac{f_{\text{H}_2\text{O}}}{f_{\text{H}_2}} \right) \right]^2} \quad (7)$$

$$r_{\text{DRM}} = \frac{k_{\text{DRM}} \left(f_{\text{CH}_4} f_{\text{CO}_2} - \frac{f_{\text{H}_2}^2 f_{\text{CO}}^2}{K_{p\text{DRM}}} \right)}{\left[(1 + K_{\text{CH}_4} f_{\text{CH}_4} + K_{\text{CO}} f_{\text{CO}}) (1 + K_{\text{CO}_2} f_{\text{CO}_2}) \right]} \quad (8)$$

In the methanol synthesis reactor, CO₂ and CO were hydrogenated (see below for detailed information on the reactions) at 4,990 kPa because of the high flow rate; a high operating pressure has the advantage of reducing the volume. A multitubular packed-bed was considered, and the utility temperature and number of tubes were determined to ensure a high methanol production rate. (The optimal values were determined under each operating condition and are provided in the Results and Discussion section.) To prevent an abrupt increase in temperature, an inert material was used in the early part of the reactor in the experiments. Two reactor modules were used in the modeling; the kinetic parameters were adjusted by considering the inert fraction in the former part, while the latter part consisted of only catalysts. The diameter of each tube was 0.0411 m, the lengths were 4.4 m and 8.46 m, and the number of tubes was 7200. Methanol in the reactor effluent was separated at the bottom of a flash vessel at 25 °C. The gas recovered at the top of the vessel was recycled in the methanol synthesis reactor with a purge stream to prevent the accumulation of inert gases; the fraction of the purge was fixed at 10%. The reactions and rate equations of methanol synthesis are as follows [14]:

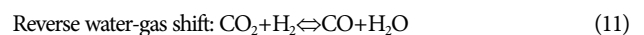
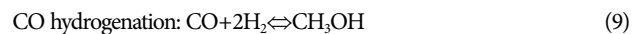


Table 1. Purchase cost and utility and feed prices [22-24] (The value of the M&S index was 280 in 1968 and 1638.2 in 2018)

Equipment		Purchase cost	
Compressor		$(M\&S/280) \times 517.5 \times (\text{bhp})^{0.82} \times F_c$	
Heat exchanger		$(M\&S/280) \times 101.3 \times (A)^{0.65} \times F_c$	
Furnace		$(M\&S/280) \times 5070 \times (Q)^{0.85} \times F_c$	
Reactor		$(M\&S/280) \times 101.3 \times (A)^{0.65} \times F_m \times F_c$	
Pump		$(M\&S/280) \times 517.5 \times (\text{bhp})^{0.82} \times F_c$	
Pressure vessels, columns		$(M\&S/280) \times 101.9 \times (D)^{1.066} \times H^{0.082} \times F_c$	
Tray		$(M\&S/280) \times 4.7 \times (D)^{1.55} \times H \times F_c$	
		Value	Unit
Utility	Cooling water	0.013583	\$/ton
	Electricity	0.0693	\$/KWh
	Furnace fuel	0.0112	\$/Btuh
Feed	CH ₄	0.1267	\$/kg
	H ₂ O	0.000349	\$/kg
Product	Methanol	0.36	\$/kg

DME production: $2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ (12)

$$r_{\text{CO}} = \frac{k_A K_{\text{CO}} \left(f_{\text{CO}} f_{\text{H}_2}^{1.5} - \frac{f_{\text{CH}_3\text{OH}}}{K_{P,A} f_{\text{H}_2}^{0.5}} \right)}{(1 + K_{\text{CO}} f_{\text{CO}})(1 + K_{\text{H}_2}^{0.5} f_{\text{H}_2}^{0.5} + K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}})} \quad (13)$$

$$r_{\text{CO}_2} = \frac{k_C K_{\text{CO}_2} \left(f_{\text{CO}_2} f_{\text{H}_2}^{1.5} - \frac{f_{\text{H}_2\text{O}} f_{\text{CH}_3\text{OH}}}{K_{P,C} f_{\text{H}_2}^{0.5}} \right)}{(1 + K_{\text{CO}_2} f_{\text{CO}_2})(1 + K_{\text{H}_2}^{0.5} f_{\text{H}_2}^{0.5} + K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}})} \quad (14)$$

$$r_{\text{RWGS}} = - \frac{k_B K_{\text{CO}_2} \left(f_{\text{CO}_2} f_{\text{H}_2} - \frac{f_{\text{CO}} f_{\text{H}_2\text{O}}}{K_{P,B}} \right)}{(1 + K_{\text{CO}_2} f_{\text{CO}_2})(1 + K_{\text{H}_2}^{0.5} f_{\text{H}_2}^{0.5} + K_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}})} \quad (15)$$

$$r_{\text{DME}} = \frac{k_{\text{DME}} K_{\text{CH}_3\text{OH}}^2 \left(C_{\text{CH}_3\text{OH}}^2 - \frac{C_{\text{H}_2\text{O}} C_{\text{DME}}}{K_{P,\text{DME}}} \right)}{(1 + 2\sqrt{K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}} + K_{\text{H}_2\text{O},\text{DME}} C_{\text{H}_2\text{O}}})^4} \quad (16)$$

3. Cost Estimation Method

The equipment and utility costs of the AGRU and methanol synthesis process were calculated, and the equipment and utility cost calculations are described in Table 1 [18-22]. The equipment costs include the installation costs of the heat exchanger, furnace, cooler, compressor, separator, and reactor, where the chemical engineering plant cost index was considered. The utility costs include the costs of cooling water, electricity, and furnace fuel (natural gas). The values considered in the study are listed in Table 1. The costs of the feed (CH₄, H₂O) and product (methanol) are also provided. The cost of steam was excluded because it was assumed to be available for free at the engine plant.

The following equation was used to calculate the total capital investment (TCI). The ratio factors are listed in Table 2.

$$\text{TCI} = I_E \times \left(1 + \sum_{i=1}^n \text{RF}_i \right) \quad (17)$$

where I_E and RF represent the total equipment cost and the ratio

Table 2. Ratio factors used in the calculation of TCI

Item	Ratio factors	Values
Direct cost	Purchase equipment	1.00
	Purchase equipment installation	0.47
	Instrumentation & controls	0.36
	Piping	0.68
	Electrical systems	0.11
	Buildings	0.8
	Yard improvements	0.1
Indirect cost	Service facility	0.7
	Engineering and supervision	0.33
	Construction expenses	0.41
	Legal expenses	0.04
	Contractor's fee	0.22
	Contingency	0.44
Working capital	0.89	

of the total equipment cost, respectively.

The total product cost (TPC) was calculated as follows:

$$\text{TPC} = (\text{Utility} + \text{Operation \& Maintenance} + \text{Others}) \times (100/90) \quad (18)$$

The correlations for operation/maintenance and other factors are presented in Table 3. Based on the TCI and TPC, the following equations were used to calculate the profit and return on investment (ROI):

$$\text{Profit} = (\text{Product revenue} - \text{TPC}) \quad (19)$$

$$\text{ROI} = (\text{TCI} / \text{Profit}) \quad (20)$$

RESULTS AND DISCUSSION

1. CO₂ Purification Processes by the AGRU

The simulation results for the concentrated CO₂ gas ("Acid Gas" stream in Fig. 1) are summarized in Table 4. The CO₂ recovery of

Table 3. Correlations used in the calculation of TPC

Item		Assumptions & correlations
Utility	Cooling water	0.013583 \$/ton
	Electricity	0.0693 \$/KWh
	Furnace fuel	0.0112 \$/Btuh
Feed	CH ₄	0.1267 \$/kg
	H ₂ O	0.000349 \$/kg
Operation & maintenance	Operating labor (OL)	60,000 \$/laborer/year, 4 laborers/shift, 3 shifts/day
	Supervisory & clerical labor (S&C)	OL×0.2
	Maintenance & repairs (M&R)	FCI×0.06
	Operation supplies	M&R×0.15
	Laboratory charges	OL×0.15
Others	Depreciation	(TCI−0.05×TCI)/20 (5% salvage value, 20 years)
	Local taxes & insurance	FCI×0.02
	Plant overhead costs	(OL+S&C+M&R)×0.6
	Administration	(OL+S&C+M&R)×0.2

Table 4. Overall mass balances in the simulation results of the AGRU

		Flow rate [kg/h]	Temperature [°C]	Pressure [kPa]	Mass composition [%]			
					CO ₂	O ₂	H ₂ O	N ₂
In	Feed	50,000	200	101	18.07	10.95	6.78	64.21
Out	Sweet gas	38,590	35.7	500	1.97	14.18	0.65	83.19
	Acid gas	8,331	28.5	210	99.14	0.02	0.78	0.06
	Water ^a	3,234	25	550	0.11	0.00	99.89	0.00

^aWater was drained at the bottom of the separator (V-100 in Fig. 1).

Table 5. Techno-economic analysis result of AGRU

Item		Results [\$]
Equipment (Purchase cost)	Heat exchanger	175,739
	Cooler	775,141
	Compressor & Pump	5,028,404
	Flash tank	480,367
	Distillation column	162,793
	Absorber	222,272
TCI (Total capital investment)		40,593,010
Item		Results [\$/y]
Utilities	Cooling water	977,444
	Electricity	3,306,975
Operating & maintenance		2,380,584
Others	Depreciation ^a	1,928,168
	Local taxes & insurance	690,024
	Plant overhead costs	1,242,044
	Administration	414,015
TPC (Total production cost) (SUM:)*100/90		12,154,726

^aThe depreciation period was 20 years, and a 5% salvage value was considered.

the AGRU was approximately 90% with a purity of 98%. Detailed heat and mass balance data are provided in the Supplementary Infor-

mation (Table S1). The techno-economic analysis results are presented in Table 5. The TCI, utility cost, and TPC were calculated

as \$2,029,650/y for a depreciation period of 20 years, \$4,284,419/y, and \$12,154,726/y, respectively.

2. Methanol Synthesis Process

In addition to the CO₂ obtained from the CO₂ purification process (28.5 °C, 210 kPa, 189.2 kmol/h), CH₄ (25 °C, 101 kPa, 300 kmol/h) and steam from the engine plant (150 °C, 101 kPa, 600 kmol/h) were used as feed for the reformer (base case). The reformer has 40 tubes each measuring 10 m in length and 0.1016 m in diameter, for a total volume of 6.486 m³, while the outlet temperature was considered a design parameter. In the methanol synthesis reactor, the temperature of both the inlet stream and reactor utility was 200 °C. The volumes of the first and second methanol reactor were 42.030 and 79.857 m³, respectively, (the corresponding number of tubes was 7200, the same as in Section 2) for the base case. The purge ratio in Tee-100 in Fig. 2 was 0.1.

Fig. 3 shows the effects of the reformer outlet temperature on the conversion and molar ratio of hydrogen. Because the heat exchanger was used to heat the reformer inlet using the effluent, the inlet temperature was lower than the outlet temperature by 100 °C. The rapid reaction rate of reforming caused the reaction to reach equilibrium in the early portion of the catalytic bed; hence, the latter portion was governed by thermodynamic behaviors (Fig. 4(a); the temperature profile in the reformer showed a sharp decrease in the kinetic regime and a gradual increase in the thermodynamic regime). Therefore, the CO₂ and CH₄ conversions (i.e., equilibrium conversions) increased as the reactor outlet temperature increased. However, temperatures above 1,000 °C are unfavorable in indus-

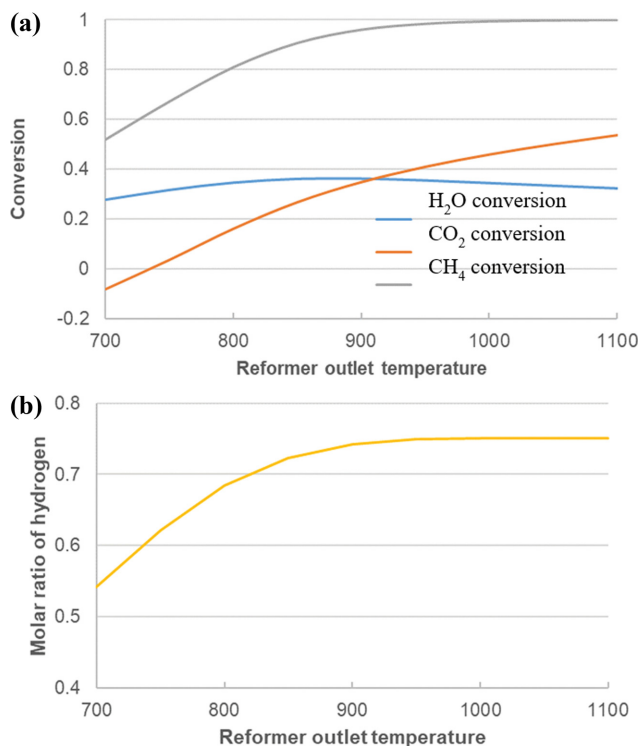


Fig. 3. (a) Conversion and (b) molar ratio of hydrogen, defined as $H_2/(2CO+3CO_2)$, in the reformer as a function of the outlet temperature (Feed: CO₂ 189.2 kmol/h, CH₄ 300 kmol/h, H₂O 600 kmol/h; pressure: 993 kPa).

trial operations because of the extremely high energy costs and the required use of expensive materials for the reactor. Moreover, the CH₄ conversion rate was almost one when the reformer outlet temperature exceeded 900 °C, and the molar ratio of hydrogen reached a plateau in the same temperature range (Fig. 3(b)). The unity (stoichiometric) molar ratio of hydrogen, $H_2/(2CO+3CO_2)=1$, is preferred for CO and CO₂ hydrogenation (Eqs. (9) and (10)). Based on the above discussion, the reformer outlet temperature was fixed at 900 °C. Details on the heat and mass balance are provided in the Supplementary Information (Table S2).

H₂O conversion was weakly influenced by the outlet temperature and was maintained at below 40%. The unreacted steam was easily separated in a separator and was assumed to be drained because of sufficient supply of steam in the engine plant. The CO₂ conversion was approximately 40% at 900 °C. The unreacted CO₂ was sent to the methanol synthesis reactor without separation for conversion into methanol by CO₂ hydrogenation.

Case I is defined as the base case with a reformer outlet temperature of 900 °C (Table 6). The heat and mass balance are provided in the Supplementary Information (Table S2). Fig. 4(b) shows the temperature profile of the methanol synthesis reactor, where the first peak was observed in the early portion of the catalytic bed (the fraction of inert material was 50%) owing to the exothermicity of the reaction. The second peak resulted from the absence of inert material conditions.

To increase the methanol productivity, a case study was conducted to determine the optimal conditions for the inlet and utility temperatures of the methanol synthesis reactor. Fig. 5 shows the effects of temperature on methanol production and conversion. The reactor inlet temperature had little influence on methanol productivity and conversion, while the utility temperature had signifi-

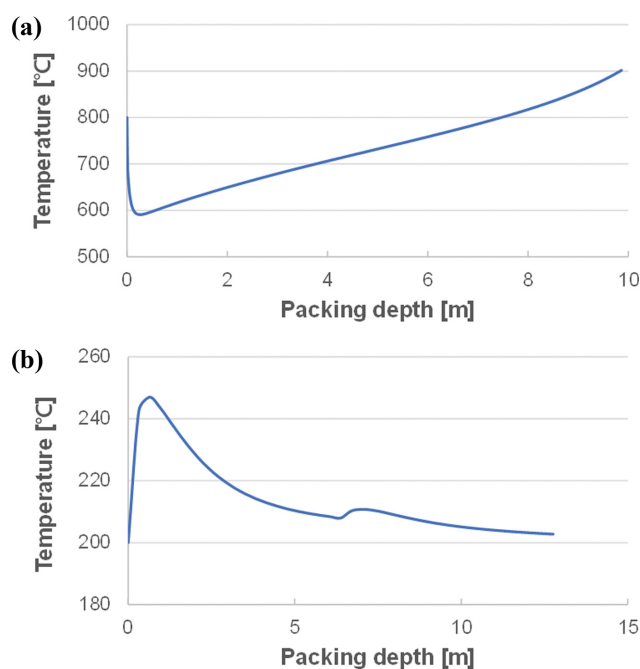


Fig. 4. Temperature profile in the (a) reformer and (b) methanol synthesis reactor in Case I.

Table 6. Comparison between three cases

		Case I	Case II	Case III
CO ₂ [kgmol/h]		189.2	189.2	189.2
CH ₄ [kgmol/h]		300	300	600
H ₂ O [kgmol/h]		600	600	960
Reformer temperature [°C]	Inlet	800	800	800
	Outlet	900	900	900
Methanol reactor temperature [°C]	Inlet	200	180	180
	Utility	200	180	180
Methanol production [kgmol/h]		355.4	362.1	670.5
Methanol production [kg/h]		11,387	11,604	21,486
Revenue [\$ /y]		27,510,126	28,034,993	51,911,309
Carbon efficiency [%]		72.64	74.03	84.95
TPC [\$ /y]		33,249,999	33,231,346	46,621,701
Profit [\$ /y]		-5,739,873	-5,196,353	5,289,608
ROI [y]				17

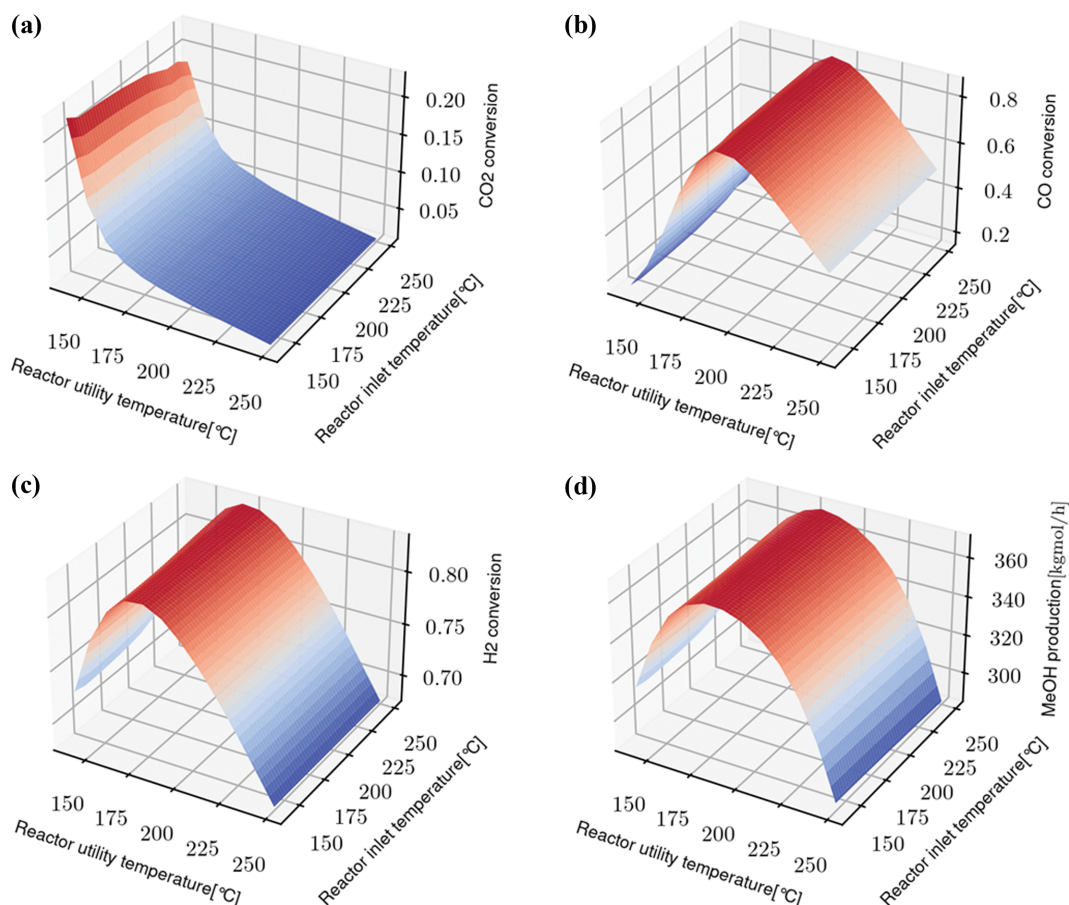


Fig. 5. Effects of the inlet and utility temperatures in the methanol synthesis reactor on (a) CO₂ conversion, (b) CO conversion, (c) H₂ conversion, and (d) methanol production rate [kgmol/h] (Feed composition: CO₂ 189.2 kgmol/h, CH₄ 300 kgmol/h, H₂O 600 kgmol/h, reformer outlet temperature of 900 °C, Refer to Case I in Table 6).

cant effects. CO₂ conversion gradually decreased with the increase in utility temperature (Fig. 5(a)) because CO₂ hydrogenation rapidly reached equilibrium. The equilibrium conversion decreased with

the increase in temperature owing to exothermicity. CO and H₂ conversions were the highest at approximately 180 °C (Figs. 5(b) and 5(c)). This is attributed to the fact that the conversions increased

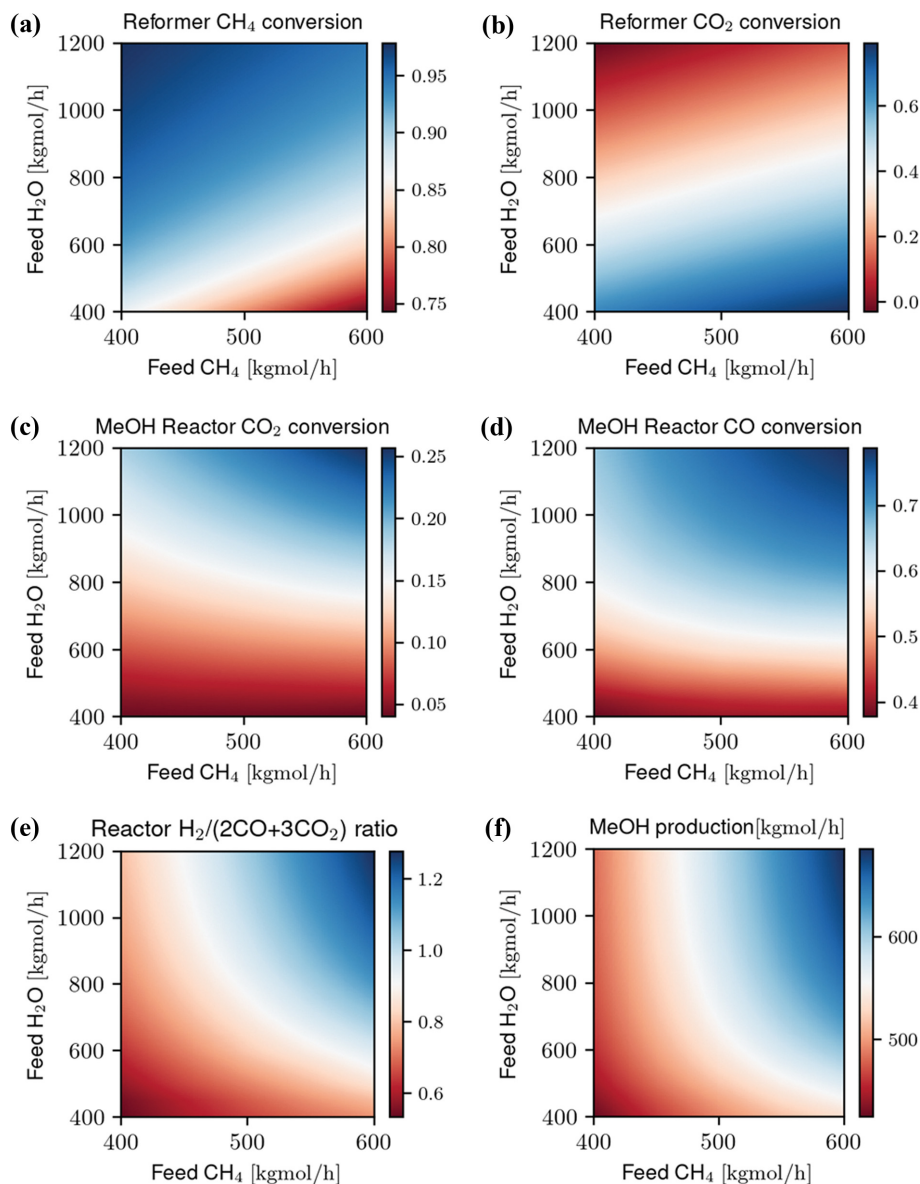


Fig. 6. Effects of the feed flow rates of CH_4 and H_2O on (a) CH_4 conversion (reformer), (b) CO_2 conversion (reformer), (c) CO_2 conversion (MeOH reactor), (d) CO conversion (MeOH reactor), (e) $\text{H}_2/(2\text{CO}+3\text{CO}_2)$ ratio, and (f) methanol production [kgmol/h]. The other conditions are the same as in Case II in Table 6.

with temperature in the kinetic regime (low-temperature region), while the high-temperature region was in the thermodynamic regime. Because CO hydrogenation was more dominant than CO_2 hydrogenation over the catalyst in the present study, the methanol production rate exhibited a trend similar to that of CO hydrogenation; thus, maximum methanol production was observed at a utility temperature of approximately 180°C . In Case II, the inlet and utility temperature of the methanol synthesis reactor was 180°C , with all the other conditions being the same as in Case I (Table 6). The heat and mass balance in Case II are provided in the Supplementary Information (Table S3).

As seen in Fig. 3, the $\text{H}_2/(2\text{CO}+3\text{CO}_2)$ ratio is less than one, indicating insufficient hydrogen in the methanol reactor. Because the amounts of CH_4 and H_2O are related to the amount of hydro-

gen, the flow rates of CH_4 and H_2O varied, while the amount of CO_2 was fixed at 189.2 kgmol/h . The other conditions were the same as in Case II. The effects of the feed flow rates of CH_4 and H_2O on the performance of the reformer and methanol synthesis reactor are shown in Figs. 6 and 7.

In the reformer, CH_4 conversion decreased as the amount of CH_4 increased because of the excess amount and increased with increasing amounts of H_2O . The maximum CH_4 conversion was achieved at the lowest flow rate of CH_4 and the highest flow rate of H_2O . Because dry reforming was in competition with steam reforming, the opposite effects of CH_4 and H_2O were observed in Fig. 6(b), i.e., the maximum CO_2 conversion at the highest flow rate of CH_4 and the lowest flow rate of H_2O . In the methanol synthesis reactor, both CO_2 and CO conversions were proportional to the amount

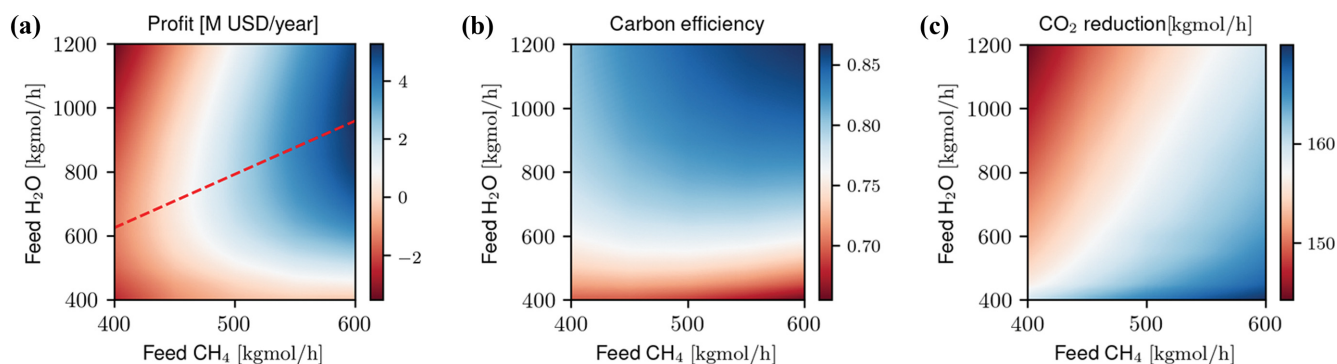


Fig. 7. Effects of the feed flow rates of CH₄ and H₂O on (a) profit [M\$ per year], (b) carbon efficiency, and (c) CO₂ reduction [kgmol/h]. The other conditions were the same as those of Case II in Table 6. The dashed red line represents the regression line of the optimal profit progression, $y=1.674x-44.46$ ($R^2=0.964$).

of CH₄ and H₂O in the feed (Figs. 6(c) and 6(d)). This is attributed to the highest H₂/(2CO+3CO₂) ratio (Fig. 6(e)) due to the larger contribution of steam reforming than dry reforming (Eqs. (1)-(4); H₂/CO ratios are 3 and 1 for steam and dry reforming, respectively). The methanol production rate was highly dependent on the H₂/(2CO+3CO₂) ratio, as shown in Fig. 6(f). The highest value was achieved at the highest flow rates of both CH₄ and H₂O.

Despite the maximum methanol production at the highest flow rates of both CH₄ and H₂O, the profit seen in Fig. 7(a) indicates that there existed an optimal amount of H₂O. This is attributed to the increase in the energy cost with the increase in the amount of H₂O. The temperature and pressure of the steam available at the engine plant were 150 °C and 1 atm, respectively; thus, compression of 1,013 kPa was required at the reformer (Fig. S1; the electricity cost increased as the amount of H₂O in the feed increased). Therefore, there is a trade-off in terms of the amount of H₂O between the production rate and energy cost. The dashed red line in Fig. 7(a) represents the regression line for optimal profit progression, which is almost linear. Based on the analysis, the optimal operating conditions were determined as 600 and 960 kgmol/h for the feed flow rates of CH₄ and H₂O, respectively (Case III). The detailed heat and mass balances are provided in Table S4 in the Supplementary Information.

Fig. 7(b) shows the carbon efficiency, which is defined as the ratio of the methanol production rate (kgmol/h) and the feed flow rates of CO₂ and CH₄ (kgmol/h). Carbon efficiency was determined by the conversions in the methanol reactor (Figs. 6(c) and 6(d)). The maximum efficiency was obtained with the highest amounts of CH₄ and H₂O, which was approximately 85% under the condition of maximum profit.

CO₂ reduction is defined as the amount of CO₂ in the feed minus the CO₂ in the purge; the results are shown in Fig. 7(c). The reduction was significantly dependent on CO₂ conversion in the reformer, indicating the influence of dry reforming. The analysis also shows a trade-off in terms of the amount of H₂O between the production rate and CO₂ reduction. The CO₂ reduction with the maximum profit was 162.8 kgmol/h (85.7% of CO₂ in the feed of the reformer).

Table 6 shows the comparisons between the three cases, including the profit and ROI. In Cases I and II, the methanol production rate and corresponding revenue were lower than those in

Case III because of the low amount of H₂O and CH₄. In Case III, the increase in revenue compared with the other cases surpassed the increase in TPC; the profit became positive with an ROI of 17 years. For comparison, when exhaust gas was directly used without the AGRU process as feed for the methanol synthesis process, the profit was always negative under the operating windows in Fig. 7 (Fig. S2). Because the exhaust gas contained a large amount of nitrogen, the requirement for compression and heating translated into high energy costs as well as large equipment costs for the reactor. Therefore, CO₂ purification process is essential to efficiently and economically utilize exhaust gas from the engine plant.

CONCLUSIONS

A methanol synthesis process was proposed to utilize the CO₂ in the exhaust gas from an engine plant. The AGRU process was applied to the exhaust gas to eliminate large quantities of inert gas (approximately 70% of nitrogen), which increased the energy and equipment costs. The highest temperature of the reformer was determined to achieve a high methane conversion rate and hydrogen ratio, while the optimal utility temperature of the methanol synthesis reactor was determined based on its effects on the methanol production rate. Case studies showed that dry reforming produced an insufficient amount of hydrogen. Thus, further analysis was conducted to evaluate the effects of the amount of CH₄ and H₂O in the feed on the methanol production rate, profit, carbon efficiency, and CO₂ reduction. The results showed a trade-off in terms of the fraction of CO₂ in the feed between the profit and CO₂ reduction. Under the optimal operating conditions in the present study, an economically feasible process was achieved when the CO₂ in the exhaust gas, along with steam available in the engine plant, was converted into methanol. The environmental contribution was the reduction in CO₂ emissions by more than 85%. In conclusion, the strategy proposed in the present study can enhance the efficiency and eco-friendliness of existing engine plants by utilizing the CO₂ in the exhaust and the available steam.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Modeling of a methanol synthesis process to utilize CO₂ in the exhaust gas from an engine plant

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Table S1. Heat and mass balance of AGRU process

Name	Diesel mode	Feed 3	Feed to contactor	H ₂ O	Sweet gas	Rich DEA	Flash vap	Rich to L/R	Regen feed	Acid gas	Regen btms	Makeup H ₂ O	DEA to contactor
Temperature [°C]	200.0	25.0	25.0	25.0	35.7	61.5	61.5	61.5	80.0	28.5	137.3	25.0	35.0
Pressure [kPa]	101.3	550.0	550.0	550.0	500.0	530.0	530.0	530.0	460.0	210.0	300.0	101.3	600.0
Molar flow [kgmol/h]	1,710.5	1,710.5	1,531.1	179.4	1,348.1	5,127.1	0.0	5,127.1	5,127.1	193.0	4,934.1	12.1	4,944.2
Mass flow [kg/h]	50,000.0	50,000.0	46,765.8	3,234.2	38,582.7	151,041.8	0.0	151,041.8	151,041.8	8,397.8	142,643.9	218.0	142,858.6
N ₂ [kg/h]	32,103.5	32,103.5	32,103.3	0.3	32,098.7	4.6	0.0	4.6	4.6	4.6	0.0	0.0	0.0
CO ₂ [kg/h]	9,033.3	9,033.3	9,029.9	3.4	760.4	8,622.4	0.0	8,622.4	8,622.4	8,326.0	296.4	0.0	352.9
H ₂ O [kg/h]	3,389.6	3,389.6	159.0	3,230.6	5,472.1	1.4	0.0	1.4	1.4	1.4	0.0	0.0	0.0
O ₂ [kg/h]	5,473.5	5,473.5	5,473.5	0.0	251.5	77,753.5	0.0	77,753.5	77,753.5	65.8	77,687.7	218.0	77,845.9
C ₄ H ₂₂ NO ₂ [kg/h]	0.0	0.0	0.0	0.0	0.0	64,659.8	0.0	64,659.8	64,659.8	0.0	64,659.8	0.0	64,659.8

Table S2. Heat and mass balance for the case I

Name	Feed_ CH ₄	Feed_ CO ₂	Feed_ H ₂ O	Feed_ inert	MIX_1_ Out	RM_ Out	Sep_1_ Out_Vap	Sep_1_ Water	MeOH_ In	MeOH_ Out	Recycle_1	Purge	Product
Temperature [°C]	25.0	25.0	150.0	25.0	383.9	900.0	25.0	25.0	200.0	203.3	20.0	20.0	20.0
Pressure [kPa]	101.3	210.0	101.3	210.0	1,013.0	993.0	963.0	963.0	4,990.0	4,970.0	4,960.0	4,960.0	4,960.0
Molar flow [kgmol/h]	300.0	189.2	600.0	3.9	1,093.1	1,668.8	1,291.2	377.7	2,694.7	1,980.4	1,386.9	154.1	439.4
Mass flow [kg/h]	4,812.9	8,326.6	10,809.1	71.8	24,020.4	24,022.8	17,214.6	6,808.1	46,873.9	46,873.7	29,311.3	3,256.8	14,305.6
H ₂ O [kg/h]	0.0	0.0	10,809.1	65.8	10,874.9	6,882.3	81.3	6,801.0	82.1	446.1	0.8	0.1	445.2
CH ₄ [kg/h]	4,812.9	0.0	0.0	0.0	4,812.9	196.4	196.4	0.0	4,194.1	4,194.1	3,727.6	414.2	52.3
CO ₂ [kg/h]	0.0	8,326.6	0.0	0.0	8,326.6	5,413.7	5,406.6	7.1	25,802.1	24,942.5	20,305.1	2,256.1	2,381.3
CO [kg/h]	0.0	0.0	0.0	0.0	0.0	9,916.9	9,916.9	0.0	13,837.3	4,379.8	3,931.4	436.8	11.6
H ₂ [kg/h]	0.0	0.0	0.0	0.0	0.0	1,607.4	1,607.4	0.0	2,702.7	1,223.2	1,099.2	122.1	1.9
CH ₃ OH [kg/h]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	162.0	11,563.8	159.5	17.7	11,386.5
CH ₃ OCH ₃ [kg/h]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	35.7	66.4	36.1	4.0	26.3
N ₂ [kg/h]	0.0	0.0	0.0	4.6	4.6	4.6	4.6	0.0	44.2	44.2	39.6	4.4	0.3
O ₂ [kg/h]	0.0	0.0	0.0	1.4	1.4	1.4	1.4	0.0	13.6	13.6	12.2	1.4	0.1

Table S3. Heat and mass balance for Case II

Name	Feed_ CH ₄	Feed_ CO ₂	Feed_ H ₂ O	Feed_ inert	MIX_1_ Out	RM_ Out	Sep_1_ Out_Vap	Sep_1_ Water	MeOH_ In	MeOH_ Out	Recycle_1	Purge	Product
Temperature [°C]	25.0	25.0	150.0	25.0	383.9	900.0	25.0	25.0	180.0	184.3	20.0	20.0	20.0
Pressure [kPa]	101.3	210.0	101.3	210.0	1,013.0	993.0	963.0	963.0	4,990.0	4,970.0	4960.0	4960.0	4960.0
Molar flow [kgmol/h]	300.0	189.2	600.0	3.9	1,093.1	1,668.7	1,291.0	377.7	2,480.9	1,755.4	1169.7	130.0	455.7
Mass flow [kg/h]	4,812.9	8,326.6	10,809.1	71.8	24,020.4	24,022.8	17,214.2	6,808.6	44,397.4	44,397.1	26664.5	2962.7	14769.9
H ₂ O [kg/h]	0.0	0.0	10,809.1	65.8	10,874.9	6,882.7	81.2	6,801.5	82.2	608.1	0.9	0.1	607.1
CH ₄ [kg/h]	4,812.9	0.0	0.0	0.0	4,812.9	196.3	196.3	0.0	969.1	969.1	860.3	95.6	13.2
CO ₂ [kg/h]	0.0	8,326.6	0.0	0.0	8,326.6	5,414.6	5,407.6	7.1	23,823.6	22,543.4	18,024.6	2,002.7	2,516.0
CO [kg/h]	0.0	0.0	0.0	0.0	0.0	9,916.0	9,916.0	0.0	16,762.7	7,417.1	6,654.9	739.4	22.7
H ₂ [kg/h]	0.0	0.0	0.0	0.0	0.0	1,607.1	1,607.1	0.0	2,559.8	1,038.6	933.0	103.7	1.9
CH ₃ OH [kg/h]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	129.1	11,745.3	127.3	14.1	11,603.8
CH ₃ OCH ₃ [kg/h]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.2	10.9	5.6	0.6	4.7
N ₂ [kg/h]	0.0	0.0	0.0	4.6	4.6	4.6	4.6	0.0	49.5	49.5	44.2	4.9	0.4
O ₂ [kg/h]	0.0	0.0	0.0	1.4	1.4	1.4	1.4	0.0	15.2	15.2	13.6	1.5	0.1

Table S4. Heat and mass balance for case III

Name	Feed_ CH ₄	Feed_ CO ₂	Feed_ H ₂ O	Feed_ inert	MIX_1_ Out	RM_ Out	Sep_1_ Out_Vap	Sep_1_ Water	MeOH_ In	MeOH_ Out	Recycle_1	Purge	Product
Temperature [°C]	25.0	25.0	150.0	25.0	384.9	900.0	25.0	25.0	180.0	186.9	20.0	20.0	20.0
Pressure [kPa]	101.3	210.0	101.3	210.0	1,013.0	993.0	963.0	963.0	4,990.0	4,970.0	4,960.0	4,960.0	4,960.0
Molar flow [kgmol/h]	600.0	189.2	960.0	3.9	1,753.1	2,857.8	2,394.7	463.1	4,763.6	3,420.1	2,368.7	263.2	788.2
Mass flow [kg/h]	9,625.7	8,326.6	17,294.5	71.8	35,318.7	35,320.0	26,975.1	8,344.9	51,594.5	51,594.0	24,620.5	2,735.6	24,237.9
H ₂ O [kg/h]	0.0	0.0	17,294.5	65.8	17,360.3	8,489.6	149.7	8,339.9	151.6	1,542.8	1.9	0.2	1,540.7
CH ₄ [kg/h]	9,625.7	0.0	0.0	0.0	9,625.7	764.6	764.6	0.0	7,182.3	7,182.3	6,407.9	712.0	62.4
CO ₂ [kg/h]	0.0	8,326.6	0.0	0.0	8,326.6	5,689.7	5,684.8	4.9	16,131.6	12,743.1	10,455.5	1,161.7	1,125.9
CO [kg/h]	0.0	0.0	0.0	0.0	0.0	17,150.3	17,150.2	0.0	21,448.8	4,787.9	4,300.6	477.8	9.5
H ₂ [kg/h]	0.0	0.0	0.0	0.0	0.0	3,219.7	3,219.7	0.0	6,382.4	3,518.6	3,162.9	351.4	4.2
CH ₃ OH [kg/h]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	225.9	21,737.1	225.9	25.1	21,486.1
CH ₃ OCH ₃ [kg/h]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14.4	24.6	14.4	1.6	8.7
N ₂ [kg/h]	0.0	0.0	0.0	4.6	4.6	4.6	4.6	0.0	44.0	44.0	39.4	4.4	0.2
O ₂ [kg/h]	0.0	0.0	0.0	1.4	1.4	1.4	1.4	0.0	13.6	13.6	12.1	1.3	0.1

Economic Analysis Result

Table S5. Techno-economic analysis result of Case I

		Item	Results [\$]
Equipment (Purchased cost)		Heat exchanger	278,794
		Cooler	838,750
		Compressor & Pump	6,084,167
		Flash tank	241,366
		Reactor	2,368,495
TCI (Total capital investment)			33,249,999
		Item	Results [\$/y]
Feed		CH ₄	4,086,835
Utilities		Cooling water	166,457
		Electricity	2,750,999
		Fuel in reformer	779,730
Operating & maintenance			4,384,163
Others		Depreciation ^a	2,763,675
		Local taxes & insurance	989,007
		Plant overhead costs	2,298,660
		Administration	766,220
TPC (Total production cost, SUM*100/90)			33,249,999

^aThe depreciation period was 20 years, and a 5% salvage value was considered.

Table S6. Techno-economic analysis result of Case II

		Item	Results [\$]
Equipment (Purchased cost)		Heat exchanger	261,811
		Cooler	839,552
		Compressor & Pump	6,083,509
		Flash tank	241,366
		Reactor	2,368,421
TCI (Total capital investment)			33,231,346
		Item	Results [\$/y]
Feed		CH ₄	4,086,835
Utilities		Cooling water	166,341
		Electricity	2,750,878
		Fuel in reformer	7,783,752
Operating & maintenance			4,378,237
Others		Depreciation ^a	2,758,910
		Local taxes & insurance	987,302
		Plant overhead costs	2,295,568
		Administration	765,189
TPC (Total production cost, SUM*100/90)			33,231,346

^aThe depreciation period was 20 years, and a 5% salvage value was considered.

Table S7. Techno-economic analysis of Case III

		Item	Results [\$]
Equipment (Purchased cost)		Heat exchanger	362,627
		Cooler	1,199,918
		Compressor & Pump	9,496,430
		Flash tank	241,366
		Reactor	3,866,946
TCI (Total capital investment)			89,942,013
		Item	Results [\$/y]
Feed		CH ₄	8,173,670
Utilities		Cooling water	282,191
		Electricity	4,700,703
		Fuel in reformer	1,455,348
Operating & maintenance			6,246,699
Others		Depreciation ^a	4,272,246
		Local taxes & insurance	1,528,863
		Plant overhead costs	3,270,418
		Administration	1,090,139
	TPC (Total production cost, SUM*100/90)		

^aThe depreciation period was 20 years, and a 5% salvage value was considered.

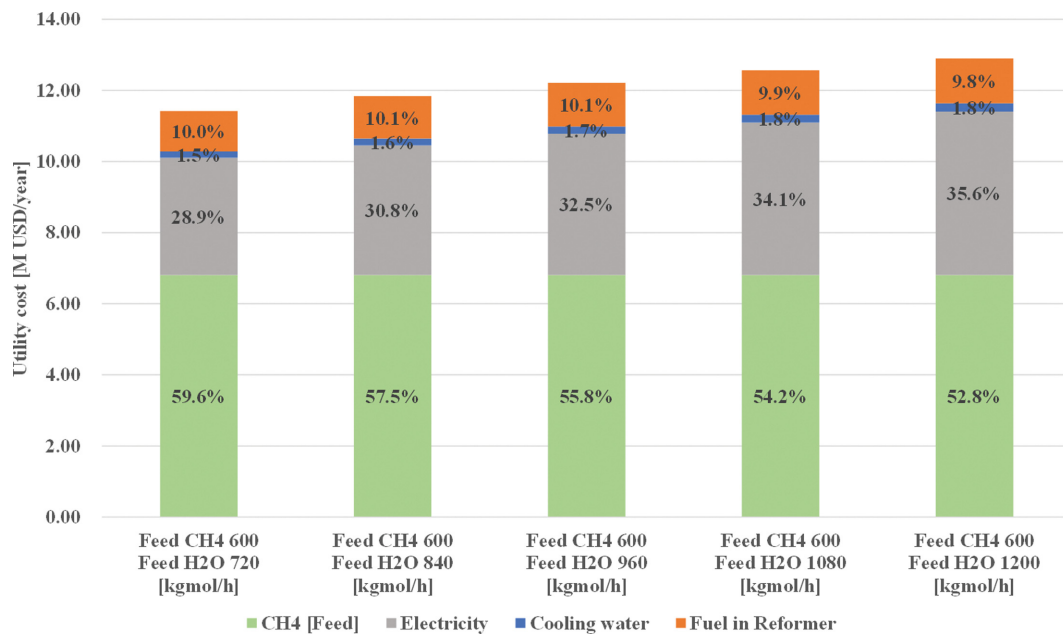


Fig. S1. Utility cost of methanol synthesis process with same amount of CH₄. Other conditions were same with Case III.

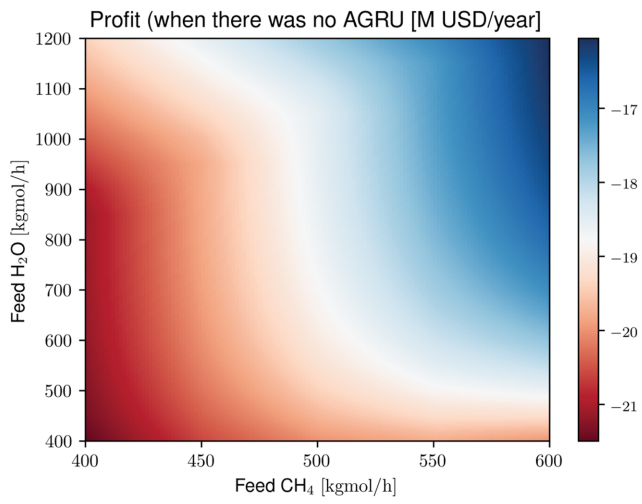


Fig. S2. Process profit (total economic calculation) when H₂O ranged from 400 to 1,200 and CH₄ ranged from 400 to 600 (when there was no AGRU process.) The other conditions were the same with Case II.