

# Efficient utilization of carbon dioxide in a gas-to-methanol process composed of CO<sub>2</sub>/steam-mixed reforming and methanol synthesis



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## ABSTRACT

Two process models for a carbon-dioxide-utilized gas-to-methanol (GTM) process (CGTM) that primarily produces methanol were developed using the process simulation software Aspen Plus. Both models comprised a reforming unit, a methanol synthesis unit and a recycling unit, with the feeding point of the fresh feed CO<sub>2</sub> as the principal configurational difference. In the reforming unit, CO<sub>2</sub>/Steam-mixed reforming was performed to generate the targeted syngas in flexible compositions. Meanwhile, CO<sub>2</sub> hydrogenation was conducted over a Cu-based catalysts in the methanol synthesis unit to directly produce the targeted product, methanol. After methanol synthesis, the unreacted syngas was recycled to the methanol synthesis and reforming units to enhance energy efficiency. The simulation results revealed that both CGTM options can favorably improve the energy efficiency and significantly reduce the total CO<sub>2</sub> emissions, compared to a conventional GTM process. The energy efficiency was shown to be highly affected by the recycle ratio and a higher recycle ratio seemed to favorably improve CO<sub>2</sub> conversion, enhance energy efficiency, and reduce CO<sub>2</sub> emissions. However, the split ratio (recycle-to-reforming unit/total recycle) seems to have little effect on the energy efficiency, and the optimum recycle to the reforming unit was determined to be none.

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## 1. Introduction

Gas-to-Methanol (GTM) process based on the methanol synthesis have attracted significant attention over the past decade because of the generally increasing trend in methanol demand and the abundant natural gas supply available at relatively low prices [1]. Methanol is a very important primary raw material for the petrochemical and energy industries because of its wide applications, ranging from chemical uses (e.g., as a solvent or an intermediate for producing olefins, formaldehyde, acetic acid and esters) to energy uses (e.g., as a fuel by itself, blended with gasoline, or for use in direct methanol fuel cells) [2–4]. Methanol will become an even more important commodity in the coming years, thanks largely to the unconventional but extremely abundant natural gas resources, such as shale gas and coal-bed methane which have been recently exploited through the

development of horizontal drilling and hydraulic fracturing technologies [5–8].

Anthropogenic emission of CO<sub>2</sub> is regarded as a major contributing factor in the serious global warming issues [9,10]. To reduce the CO<sub>2</sub> emissions, technologies such as carbon capture and storage (CCS) and carbon capture and utilization (CCU) have been developed and implemented [11–14]. Compared with CCS, CCU seems to be more beneficial because it can not only reduce CO<sub>2</sub> emissions, but also produce valuable fuels and chemicals that will enable the petrochemical industry to recoup the costs of CO<sub>2</sub> capture and conversion [15,16]. Among the CCU strategies, CO<sub>2</sub> hydrogenation and CO<sub>2</sub> reforming have been recently considered as promising methods for CO<sub>2</sub> utilization due to their potential for use in the GTM process on a large scale [8,13,17]. In addition, the GTM technology can also be employed to utilize wasted associated natural gas, another greenhouse gas, that currently goes to waste and is usually flared due to its low economic value, thus generating a large amount of additional CO<sub>2</sub>.

In General, a methanol-synthesis-based GTM process is comprised of three sections. The first section is syngas production, in which the methane reforming reaction occurs via processes such as auto-thermal reforming (ATR), partial oxidation of methane

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## Nomenclature

ASU	Air separation unit
ATR	Auto-thermal reforming
CAPEX	Capital expenditures
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CDR	Carbon dioxide reforming of methane
CFR	Carbon formation reactions
CGTM	Carbon dioxide utilized gas-to-methanol process
$C_{eff}$	Carbon efficiency
DME	Dimethyl ether
F-T	Fischer-Tropsch
GTL	Gas-to-liquids
GTM	Gas-to-methanol
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LHV	Lower heating value
NG	Natural gas
OPEX	Operating expenditures
POM	Partial oxidation of methane
SMR	Steam methane reforming
S/C	Steam-to-carbon
$T_{eff}$	Thermal efficiency
WGS	Water gas shift

(POM), steam methane reforming (SMR), and carbon dioxide reforming of methane (CDR) [18–21]. The second section is methanol synthesis, typically over Cu-based catalysts, which produces crude methanol containing a few byproducts such as dimethyl ether (DME) and ethanol [22,23]. The third section is purification, which separates pure methanol as the final product. Among the aforementioned methane reforming technologies, there are several disadvantages. That is, the obtained  $H_2/(2CO + 3CO_2)$  ratio deviates from 1, which is required for the downstream methanol synthesis. Thus, additional  $H_2/(2CO + 3CO_2)$  ratio adjustment steps are necessary. Moreover, for POM and ATR, an additional expensive air separation unit (ASU) is needed [8]. Therefore, in present study, CO<sub>2</sub>/Steam-mixed reforming was employed for syngas production to generate syngas in flexible

$H_2/(2CO + 3CO_2)$  ratios by adjusting the two competitive methane reforming reactions, SMR and CDR.

Recently, extensive efforts have been made to develop more efficient methanol-synthesis-based GTM processes. Ehlinger et al. investigated the process design, analysis, and integration of the methanol production from shale gas [6]. Bermúdez et al. simulated the production of methanol from coke oven gas by means of CO<sub>2</sub> reforming [24]. Lee et al. modeled three gas-to-liquids (GTL) processes that produced methanol, DME, and F-T diesel, to determine the optimal GTL product selection under uncertain price scenarios [25]. Park et al. carried out a simulation study to find the optimum reaction conditions for the maximum production of methanol [26]. Although a number of process simulations have been implemented to ascertain more efficient methanol-synthesis-based GTM processes, few works to date have addressed the entire GTM process, in which not only energy efficiency but also CO<sub>2</sub> emissions are considered.

Therefore, based on our previous study on F-T synthesis-based GTL process using Fe or Co catalysts [27,28], we now suggest two new CO<sub>2</sub>-utilized GTM processes (CGTMs) based on methanol synthesis, which can convert CO<sub>2</sub> by both CO<sub>2</sub> reforming and CO<sub>2</sub> hydrogenation reactions. It was shown that the energy efficiency was increased and the CO<sub>2</sub> emissions were significantly reduced by recycling a portion of the unreacted syngas to the reforming and methanol synthesis units.

## 2. Material and methods

Generally, a methanol-synthesis-based GTM process comprises a feeding unit, a gas pretreatment unit, a reforming unit, a methanol synthesis unit, and a product separation unit. However, the present study does not include the gas pretreatment and product separation units, since they are well established in current petrochemical industrial practices and their influence on the process performance is relatively small, as also described in our previous work [28,29]. Therefore, we developed two simplified but meaningful CGTM models that mainly consider, as a whole, the feeding, reforming, methanol synthesis and recycling units, together with several separation vessels. As illustrated in Fig. 1, the main difference of the two proposed CGTM options is configurational: (1) in option 1, fresh CO<sub>2</sub> together with fresh natural gas and steam is first fed to the reforming unit to produce syngas by CO<sub>2</sub>/Steam-mixed reforming and then to the methanol

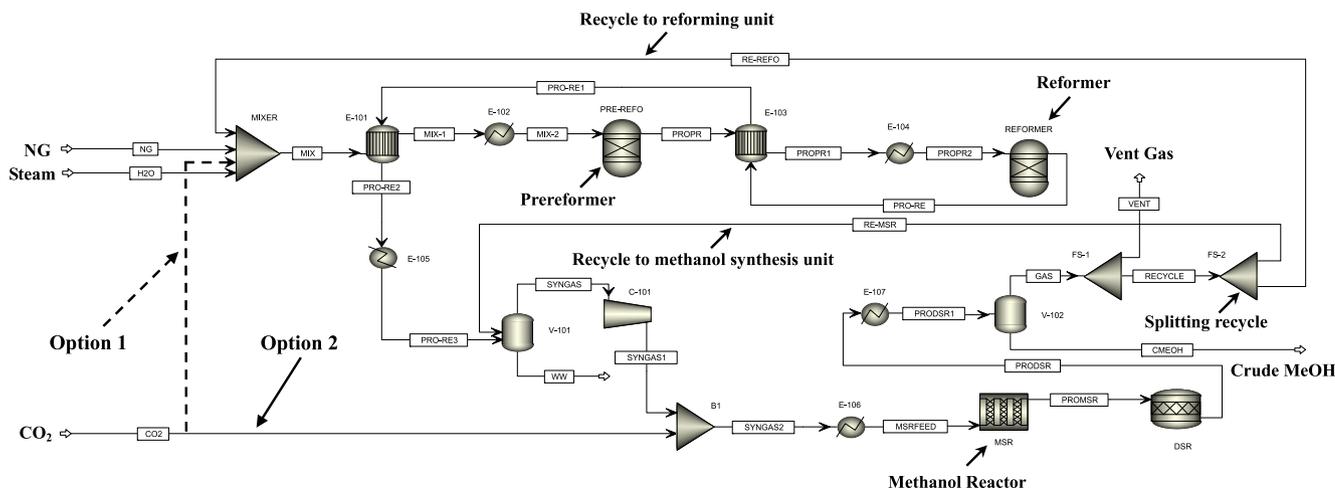
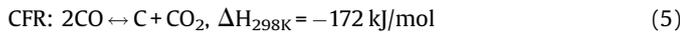
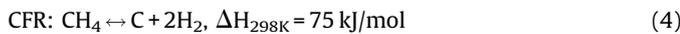
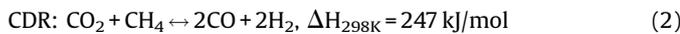
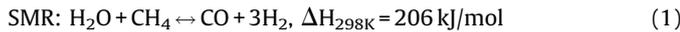


Fig. 1. Schematic process flow diagram of CGTM.

synthesis unit to produce the methanol product through CO<sub>2</sub> and CO hydrogenation; (2) in option 2, fresh CO<sub>2</sub> directly enters into the methanol synthesis unit to produce the targeted methanol through CO<sub>2</sub> hydrogenation.

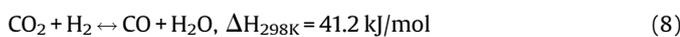
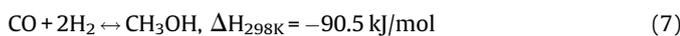
Several basic assumptions together with the criteria used in the established models are described as follows. Methane, ethane, propane, butane, CO<sub>2</sub>, and N<sub>2</sub> were selected as the main components of the fresh feed and fuel natural gas (NG), and the typical composition is shown in supplementary information (SI) Table S1 [28–30]. The thermodynamic method applied in both models was based on the Peng-Robinson equation, which affords accurate results in modeling light gases, hydrocarbons, and alcohols [31,32].

In the reforming unit, a main reformer follows a prereformer, which was operated at 550 °C and 5 bar (gauge). In this circumstance, a Ni catalyst in the reformer converts almost all the C<sub>2+</sub> hydrocarbons in the fresh feed NG and in the recycled gas from the methanol synthesis unit into methane [28,29]. In addition, the RGibbs model based on Gibbs free energy minimization, was selected to simulate the prereformer and chemical equilibria for the C<sub>1</sub>–C<sub>4</sub> hydrocarbons [33–35]. Meanwhile, the RGibbs model was also applied in the reformer and the typical reactions, CDR, SMR, water-gas shift (WGS), and carbon formation reactions (CFR) were considered, as follows:



The reformer was operated at 900 °C and 5 bar (gauge). In this case, because the reaction rates are very fast at elevated temperature, the above reactions (1)–(3) can be assumed to be in chemical equilibrium. Moreover, to better simulate the reformer, the “restricted chemical equilibrium” option was selected in the RGibbs model.

After reforming, the produced syngas is directly sent to the methanol synthesis reactor without using any syngas ratio adjustment units, since the flexible syngas ratios can be obtained via CO<sub>2</sub>/Steam-mixed reforming, as mentioned before. In the methanol synthesis reactor, CO<sub>2</sub> hydrogenation occurs over a Cu-based catalyst provided suitable hydrogen content (i.e., H<sub>2</sub>/(2CO + 3CO<sub>2</sub>) ≥ 1). The methanol synthesis reactor was operated at 250 °C and 80 bar (gauge). The main reactions in the methanol synthesis reactor can be expressed by the following three equations:



The methanol synthesis reactor was simulated with the RPLug reactor model, in which the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model was used to simulate the

above three main methanol synthesis reactions (Eqs. (6)–(8)). The kinetic parameters used in the LHHW model were obtained from our previous experimental results [36]. The packed multi tubular reactor had 11,458 tubes, 12 m in length and 0.03675 m in diameter. The catalyst particle density was 2000 kg/m<sup>3</sup>, and the bed voidage was 0.5.

After methanol synthesis, a gas stream which contains the unreacted syngas, methane and nitrogen is discharged from the reactor top outlet. Meanwhile, a liquid stream which contains the main product (methanol), and the byproducts (water, DME, and ethanol) are discharged from the reactor bottom outlet. A part of the unreacted syngas is recycled to the reforming and methanol synthesis units to enhance the energy efficiency as well as CO<sub>2</sub> conversion. The rest of the unreacted syngas is emitted to suppress the inert gases accumulation, and used as fuel gas to reduce the consumption of fuel NG.

### 3. Results and discussion

#### 3.1. Influence of recycle ratio on the performance of the present CGTM

We implemented a series of case studies under the operating conditions, as shown in Tables S2–S4 (see SI). During the case studies, for each CGTM option, seven different recycle ratios were evaluated to investigate their effects on the CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio in the syngas, total CO<sub>2</sub> conversion, and energy efficiency. To keep away from severe carbon deposition region, the molar ratio of the fresh feedstock CO<sub>2</sub>/NG/H<sub>2</sub>O was fixed within the range of (0.3–0.5): 1: (1.5–2.5). Furthermore, the operating conditions were properly chosen to avoid carbon formation [37,38]. In the reforming unit, the syngas is generated in flexible compositions, and the optimum H<sub>2</sub>/(2CO + 3CO<sub>2</sub>) ratio in the syngas for methanol synthesis using Cu catalyst is in the range of 0.99–1.1 (see Tables S2–S4), which can be achieved by changing the molar ratio of the fresh feedstocks in the aforementioned reasonable range. The H<sub>2</sub>/(2CO + 3CO<sub>2</sub>) ratio in the syngas changes with the recycle ratio, thus in order to maintain the optimum H<sub>2</sub>/(2CO + 3CO<sub>2</sub>) ratio in the syngas, the CO<sub>2</sub>/NG ratio must be adjusted accordingly, as shown in Tables S2–S4.

As shown in Fig. 2, the CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio in the syngas can be raised via increasing the recycle ratio, because of the much higher conversion of CO than CO<sub>2</sub> to methanol in the methanol synthesis unit. Thus, with increasing recycle ratio, increasingly more CO<sub>2</sub> accumulates in the syngas stream which is fed to the following methanol synthesis reactor inlet. However, it is noteworthy that the increase in the recycle ratio, despite the CO<sub>2</sub> accumulation in

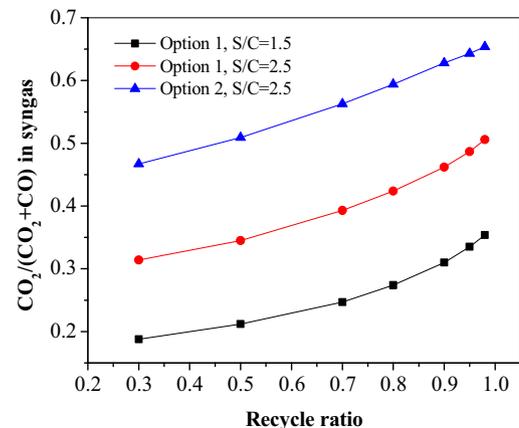


Fig. 2. Influence of the recycle ratio on CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio in syngas.

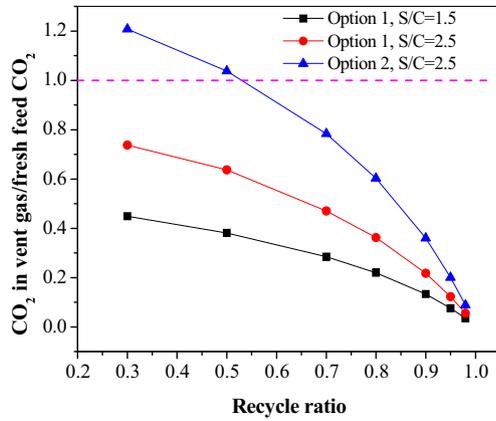


Fig. 3. Influence of the recycle ratio on total CO<sub>2</sub> conversion.

the syngas, results in a decrease in the total amount of emitted CO<sub>2</sub> of the entire process due to the enhanced total CO<sub>2</sub> conversion, as shown in Fig. 3. Moreover, for option 2, as the recycle ratio increases to around 0.55, the total CO<sub>2</sub> conversion becomes close to zero, however, as the recycle ratio increases to about 0.98, nearly 95% of the fresh CO<sub>2</sub> is converted in the two options 1 and 2. This can be ascribed to CO<sub>2</sub> hydrogenation as well as CO<sub>2</sub> reforming in the methanol synthesis and reforming units, respectively. In the methanol synthesis reactor, a high CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio combined with an optimum H<sub>2</sub>/(2CO + 3CO<sub>2</sub>) ratio improves the conversion of CO<sub>2</sub> to methanol via CO<sub>2</sub> hydrogenation. Meanwhile, a higher CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio results in higher per-pass and ultimate CO<sub>2</sub> conversions. In addition, the CO<sub>2</sub> recycled to the reforming unit is also converted via CO<sub>2</sub> reforming. Through the foregoing processes, the recycled CO<sub>2</sub> sent to the reforming and methanol synthesis units is converted to either syngas or methanol. Thus, the amount of vented CO<sub>2</sub> can be significantly reduced by recycling.

As illustrated in Fig. S1 (see SI), the methanol productivity increases with increasing recycle ratio. It is obvious that more methanol could be generated by recycling unreacted syngas due to the improved total conversion of the fresh feedstocks. The volume flow rates at the reformer outlet and the methanol synthesis reactor inlet also increase with an increasing recycle ratio, as shown in Figs. S2–S3 (see SI), because of the increased amount of recycled syngas. If the recycle ratio increases, from a technical point of view, the methanol productivity could be improved, higher energy efficiency as well as lower amount of vented CO<sub>2</sub> could be realized. However, from an economic point of view, to meet the increased volume flow rates, the size of the two reactors must be increased since the space velocity is assumed to be the same for all cases. This might greatly increase both the capital expenditures (CAPEX) and operating expenditures (OPEX) of the reactors. Taking both technical and economic aspects into consideration, an optimum value of recycle ratio should be determined under defined conditions, to maximize the economic benefit.

### 3.2. Thermal and carbon efficiencies

Before going further, two important energy efficiencies, thermal efficiency ( $T_{\text{eff}}$ ), and carbon efficiency ( $C_{\text{eff}}$ ) must be considered in detail. In a burner-type reformer, NG is typically used as a fuel gas, but to improve the energy efficiency, the vent gas could also be used to power the burner to reduce the consumption of fuel NG. Thus,  $T_{\text{eff}}$  and  $C_{\text{eff}}$  can be further improved. For some cases in the present study (generally, when the recycle ratios were less than 0.7 for option 2 and 0.5 for option 1), the heat energy required by the reformer could be fully compensated by the vent

gas. However, in other cases, the heat energy derived from the vent gas was deficient for the reformer, particularly when the recycle ratio was increased to or exceeded 0.7 for option 1 and 0.8 for option 2. In other words, at a high recycle ratio, additional fuel NG was generally necessary. Therefore,  $T_{\text{eff}}$  and  $C_{\text{eff}}$  should be calculated in two different ways under the aforementioned different conditions, as also described in our previous work [28]. The specific methods for the calculation of  $T_{\text{eff}}$  and  $C_{\text{eff}}$  are described in detail as follows:

If the lower heating value (LHV) of the vent gas exceeds the value of heat duty/0.8, then

$$T_{\text{eff}} = \frac{\text{LHV of methanol}}{\text{LHV of feed NG}} \quad (7)$$

and

$$C_{\text{eff}} = \frac{\text{total moles of C atoms in methanol}}{\text{total moles of C atoms in feed NG}} \quad (8)$$

Conversely, if the LHV of the vent gas is less than the value of heat duty/0.8, then

$$T_{\text{eff}} = \frac{\text{LHV of methanol}}{\text{LHV of feed NG} + \text{heat duty}/0.8 - \text{LHV of vent gas}} \quad (9)$$

and

$$C_{\text{eff}} = \frac{\text{total moles of C atoms in methanol}}{\text{total moles of C atoms in feed NG} + \text{total moles of C atoms in fuel NG}} \quad (10)$$

where the total moles of carbon atoms in the fresh feed NG is given by

$$\begin{aligned} & \text{total moles of C atoms in fuel NG} \\ &= \frac{(\text{heat duty}/0.8 - \text{LHV of vent gas}) \times 1.012}{\text{LHV of fuel NG}} \end{aligned} \quad (11)$$

In Eqs. (9) and (11), the number 0.8 is the estimated overall heat transfer efficiency of the reforming unit [34], and “heat duty” stands for the total heat duty of the main endothermic units such as the reformer and pre-heater in the reforming unit, as shown in Fig. 1. The number 1.012 in Eq. (11) refers to the moles of carbon atoms per mole of the fuel NG used in present study.

Fig. 4 shows the  $T_{\text{eff}}$  and  $C_{\text{eff}}$  for both options at different recycle ratios. Both values monotonously increase with increasing recycle ratio, even in the high recycle ratio region (e.g., recycle ratio = 0.8–0.98), which is similar to that observed in our previous GTL process that used an Fe catalyst in the F–T synthesis unit [28]. But, it is different from our previous GTL process which employed a Co catalyst in the F–T synthesis unit at a high recycle ratio, where the energy efficiency was slightly decreased [27,39]. The improved

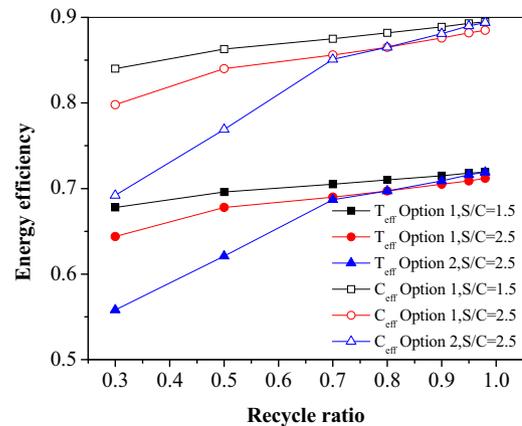


Fig. 4. Influence of the recycle ratio on energy efficiency.

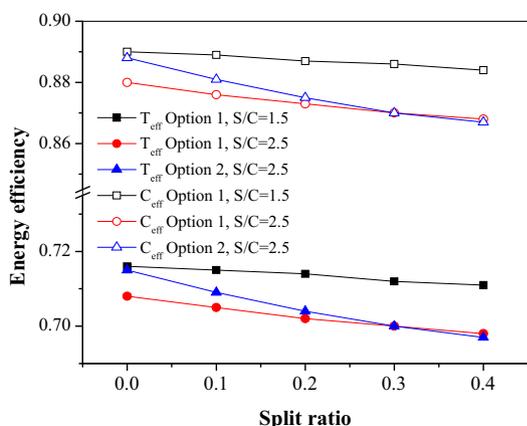


Fig. 5. Influence of the split ratio on energy efficiency (recycle ratio=0.9).

efficiency values here are mainly due to the improved CO<sub>2</sub> conversion at the high recycle ratio in the methanol synthesis reactor. With the increase in the recycle ratio, more CO<sub>2</sub> is converted to methanol in the methanol synthesis reactor. Thus, the T<sub>eff</sub> and C<sub>eff</sub> would increase with increasing recycle ratio. However, in our previous GTL process using a Co catalyst in the F-T synthesis reactor, CO<sub>2</sub> was generated to a small extent via the WGS reaction. In the current case, with an increasing recycle ratio, more and more CO<sub>2</sub> is generated, which would likely decrease the T<sub>eff</sub> and C<sub>eff</sub>.

Fig. 5 depicts the T<sub>eff</sub> and C<sub>eff</sub> values for both options at different split ratios. Although T<sub>eff</sub> and C<sub>eff</sub> tend to move downward with an increase in the split ratio, however, there is no significant change at different split ratios. T<sub>eff</sub> and C<sub>eff</sub> reach their highest values when the split ratio decreases to zero. This is due to the fact that the CDR is a highly endothermic reaction, and sending more CO<sub>2</sub> to the reformer requires more energy, even though, additional syngas is concurrently generated with the increasing split ratio. It seems that the contribution of heat duty to the T<sub>eff</sub> and C<sub>eff</sub> values is dominant as the split ratio increases. Thus, based on this observation, a low split ratio seems to benefit the energy efficiency of the present CGTM options.

### 3.3. Influence of split ratio on the performance of the present CGTM

We also conducted a series of case studies with five different split ratios for each option to determine the influence of the split ratio on the performance of the present CGTM. The specified conditions as well as some simulation results are shown in Tables S5–S7 (see SI). With an increasing split ratio, a larger amount of unreacted syngas is recycled to the reforming unit and due to the CDR reaction, more CO<sub>2</sub> is reacted to produce CO and H<sub>2</sub>, thus decreasing the CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio in the syngas. To keep the H<sub>2</sub>/(2CO + 3CO<sub>2</sub>) ratio in the optimum range, the fresh feed amount of CO<sub>2</sub> must be adjusted, which can be seen from Tables S5–S7. In addition, as shown in Fig. 6, the vented CO<sub>2</sub> is also reduced as the split ratio increases. However, sending more of the recycle stream to the reforming unit does not benefit the T<sub>eff</sub> and C<sub>eff</sub> because of the highly endothermic nature of CDR, as mentioned before. Meanwhile, as shown in Tables S5–S7 (see SI), the flow rate of the reformer increases whereas that of the methanol synthesis reactor decreases with increasing split ratio, since the quantity of recycle to the reformer is increased.

### 3.4. Performance comparison of both CGTM options and conventional GTM process

As mentioned earlier, CO<sub>2</sub> can be converted via the CDR as well as CO<sub>2</sub> hydrogenation in the reformer and the methanol synthesis

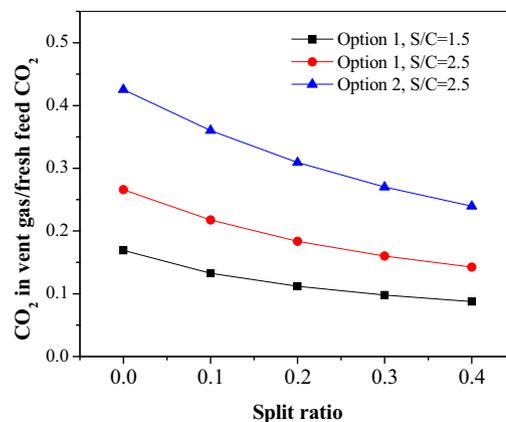


Fig. 6. Influence of the split ratio on overall CO<sub>2</sub> conversion.

reactor, respectively. In General, the equilibrium conversion of CO<sub>2</sub> via CDR in the reformer exceeds that via CO<sub>2</sub> hydrogenation in the methanol synthesis reactor over a Cu catalyst, particularly under the low recycle ratio used in present study. However, the CDR is a highly endothermic reaction. Furthermore, it should also be noted that the conversion of CO<sub>2</sub> via CO<sub>2</sub> hydrogenation could be improved by increasing the recycle ratio.

As shown in Fig. 2 and Tables S5–S7, the CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio of option 1 is always lower than that of option 2 under the same conditions, which is due to the different process configurations. In option 1, fresh CO<sub>2</sub> is first converted to CO via the CDR in the reformer, resulting in the decrease of CO<sub>2</sub> content in the generated syngas. However, in option 2, fresh CO<sub>2</sub> is directly fed to the methanol synthesis reactor without CO<sub>2</sub> consumption in the reformer. In addition, option 1 at a steam-to-carbon (S/C) ratio of 1.5 exhibits a lower CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio, compared with option 1 at a S/C ratio of 2.5, because of the competition between the CDR and SMR reactions in the reformer, that is, the lower S/C ratio could improve the CO<sub>2</sub> conversion, leading to the lower CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratio in the syngas. As shown in Fig. 3, the amount of CO<sub>2</sub> in the vent gas for option 1 is lower than that of option 2. Here, CO<sub>2</sub> consumption via the CDR is found to be much larger than that by CO<sub>2</sub> hydrogenation under the given conditions. Meanwhile, option 1 at a S/C ratio of 1.5 shows the lowest amount of CO<sub>2</sub> in the vent gas, which could be attributed to the improved CO<sub>2</sub> conversion at the lower S/C ratio. However, the difference in the amount of CO<sub>2</sub> in the vent gas between both options 1 and 2 decreases with increasing recycle ratio. This is mainly due to the increased CO<sub>2</sub> conversion in the methanol synthesis reactor of option 2 under

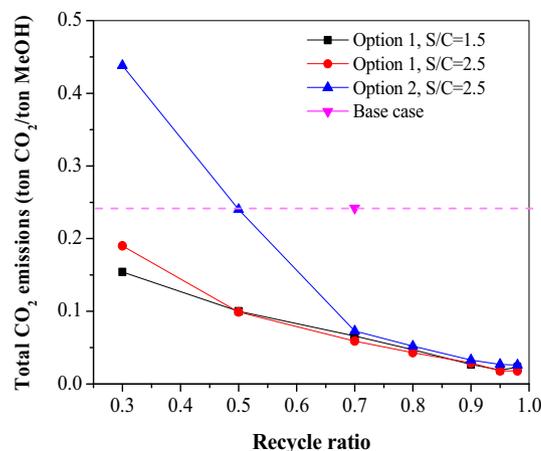


Fig. 7. Influence of the recycle ratio on total CO<sub>2</sub> emission.

**Table 1**  
Performance comparison of both CGTM options with conventional GTM process.<sup>a</sup>

Op.	S/C ratio	R <sup>1</sup>	S <sup>2</sup>	R1 <sup>b</sup>	R2 <sup>c</sup>	CO <sub>2</sub> (kmol/h)	H <sub>2</sub> O (kmol/h)	NG (kmol/h)	MeOH (kmol/h)	T eff.	C eff.	Reformer (kmol/h)	MSR (kmol/h)
1	1.5	0.95	0.1	0.335	1.005	43.0	159	100	124.53	0.718	0.893	374.06	875.73
1	2.5	0.95	0.1	0.487	1.009	45.0	253	100	123.64	0.709	0.882	493.36	1035.9
2	2.5	0.95	0.1	0.643	1.014	42.5	253	100	120.55	0.716	0.890	469.59	1275.2
1	1.5	0.7	0.1	0.247	1.008	37.0	159	100	103.98	0.705	0.875	350.16	625.68
1	2.5	0.7	0.1	0.393	0.997	40.0	253	100	100.04	0.690	0.856	464.81	705.85
2	2.5	0.7	0.1	0.563	1.011	38.0	253	100	90.28	0.687	0.851	436.63	816.28
Base case	2.5	0.7	0.1	0.323	2.099	0	253	100	83.54	0.662	0.820	436.59	779.21

<sup>a</sup> Note: (1) R = recycle/(recycle + vent); (2) S = recycle-to-reformer/recycle (see Fig. 1).

<sup>b</sup> R1 = CO<sub>2</sub>/(CO<sub>2</sub> + CO).

<sup>c</sup> R2 = H<sub>2</sub>/(2CO + 3CO<sub>2</sub>), here, R1 and R2 refer to syngas compositions at the inlet of the methanol synthesis unit.

higher CO<sub>2</sub>/(CO<sub>2</sub> + CO) ratios. Moreover, as we can see from Fig. 4, the T<sub>eff</sub> and C<sub>eff</sub> for option 1 were calculated to be higher than those of option 2 (S/C = 2.5), when the recycle ratio locates in the range of 0.3–0.8. However, the opposite results were found when the recycle ratio locates in the range of 0.8–0.98. The higher T<sub>eff</sub> and C<sub>eff</sub> values of option 1 (S/C = 2.5) in the low recycle ratio range of 0.3–0.8 is mainly due to the higher conversion of CO<sub>2</sub> in the reformer via the CDR reaction and the sufficient heat recovered from the vent gas which can fully satisfy the energy required by the reforming unit. In contrast, the higher T<sub>eff</sub> and C<sub>eff</sub> values of option 2 in the high recycle ratio range of 0.8–0.98 is mainly attributed to the higher conversion of CO<sub>2</sub> in the methanol synthesis reactor and the lower consumption of energy in the reforming unit when additional fuel NG is required. Moreover, the option 1 (S/C = 1.5) shows the highest energy efficiency, which is mainly due to the low S/C ratio. However, at a high recycle ratio (R ≥ 0.9), option 2 (S/C = 2.5) can be comparable with option 1 (S/C = 1.5), which is due to the improved CO<sub>2</sub> conversion in the methanol synthesis reactor and the reduced consumption of energy in the reforming unit.

In addition, as shown in Fig. 5, the T<sub>eff</sub> and C<sub>eff</sub> of option 1 (S/C = 2.5) were calculated to be slightly lower than those of option 2 at low split ratios, which can be also interpreted by the higher conversion of CO<sub>2</sub> in the methanol synthesis reactor and the lower consumption of energy in the reforming unit for option 2. Meanwhile, the T<sub>eff</sub> and C<sub>eff</sub> values of option 2 are slightly lower than those of option 1 (S/C = 1.5) at different split ratios, mainly due to the low S/C ratio. Considering both the T<sub>eff</sub> and C<sub>eff</sub> as well as the CO<sub>2</sub> emissions for options 1 and 2 at the S/C ratio of 2.5, option 2 seems to have more advantages for CGTM, particularly at a high recycle ratio (e.g., R = 0.8–0.98).

As illustrated in Fig. 7, the total CO<sub>2</sub> emissions of the present CGTM options are much lower than that of the base case of a conventional GTM process, at the same recycle and split ratios. Moreover, Table 1 presents the results of performance comparison between the two CGTM options studied here and a conventional GTM process. For the current CGTM options at recycle ratios of 0.7 and 0.95, C<sub>eff</sub> is increased by ca. 5.0–8.3%, T<sub>eff</sub> is increased by ca. 4.8–7.9% and methanol production is increased by ca. 17.4–47.1%, compared with the base case of the conventional GTM process.

#### 4. Conclusion

For efficient utilization of CO<sub>2</sub>, we proposed two CGTM options with the feeding point of the fresh feed CO<sub>2</sub> as the principal configurational difference. The effects of the recycle and split ratios on the thermal and carbon efficiencies as well as the total CO<sub>2</sub> conversion of the two proposed CGTM options were investigated in detail. Besides, the performance comparison of both CGTM options and the conventional GTM process was also implemented. As we can see from the simulation results, the thermal and carbon

efficiencies were sensitive to the recycle ratio and a higher recycle ratio seemed to favorably improve CO<sub>2</sub> conversion, enhance the thermal and carbon efficiencies, and reduce CO<sub>2</sub> emissions. However, the split ratio seems to have little effect on the thermal and carbon efficiencies, and the optimum recycle to the reforming unit was determined to be none. Furthermore, compared with a conventional GTM process, the thermal and carbon efficiencies of both CGTM options were shown to be successfully improved and the total CO<sub>2</sub> emissions were significantly reduced, because of the efficient utilization of CO<sub>2</sub> in the reforming and methanol synthesis units of both proposed CGTM options.

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#### Appendix A. Supplementary data

Additional contents as noted in the text can be found via the Internet at <http://www.sciencedirect.com>.

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