Efficient utilization of carbon dioxide in a gas-to-methanol process composed of CO₂/steam–mixed reforming and methanol synthesis

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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 CO₂ as the principal configurational difference. In the reforming unit, CO₂/Steam–mixed reforming was performed to generate the targeted syngas in flexible compositions. Meanwhile, CO₂ 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 CO₂ 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 CO₂ conversion, enhance energy efficiency, and reduce CO₂ 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 CO₂ is regarded as a major contributing factor in the serious global warming issues [9,10]. To reduce the CO₂ 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 CO₂ emissions, but also produce valuable fuels and chemicals that will enable the petrochemical industry to recoup the costs of CO₂ capture and conversion [15,16]. Among the CCU strategies, CO₂ hydrogenation and CO₂ reforming have been recently considered as promising methods for CO₂ 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 CO₂.

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.

(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 H2/(2CO + 3CO2) ratio deviates from 1, which is required for the downstream methanol synthesis. Thus, additional H2/(2CO + 3CO2) ratio adjustment steps are necessary. Moreover, for POM and ATR, an additional expensive air separation unit (ASU) is needed [8]. Therefore, in present study, CO2/Steam–mixed reforming was employed for syngas production to generate syngas in flexible H2/(2CO + 3CO2) 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 CO2 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 CO2 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 CO2-utilized GTM processes (CGTMs) based on methanol synthesis, which can convert CO2 by both CO2 reforming and CO2 hydrogenation reactions. It was shown that the energy efficiency was increased and the CO2 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 CO2 together with fresh natural gas and steam is first fed to the reforming unit to produce syngas by CO2/Steam–mixed reforming and then to the methanol

![Fig. 1. Schematic process flow diagram of CGTM.](image-url)
synthesis unit to produce the methanol product through CO2 and CO hydrogenation: (2) in option 2, fresh CO2 directly enters into the methanol synthesis unit to produce the targeted methanol through CO2 hydrogenation.

Several basic assumptions together with the criteria used in the established models are described as follows. Methane, ethane, propane, butane, CO2, and N2 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 C2+ 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 C1–C4 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:

- SMR: H2O + CH4 → CO + 3H2, $\Delta H_{298K} = 206 \text{kJ/mol}$ (1)
- CDR: CO2 + CH4 → 2CO + 2H2, $\Delta H_{298K} = 247 \text{kJ/mol}$ (2)
- WGS: CO + H2O → CO2 + H2, $\Delta H_{298K} = -41 \text{kJ/mol}$ (3)
- CFR: CH4 → C + 2H2, $\Delta H_{298K} = 75 \text{kJ/mol}$ (4)
- CFR: 2CO → C + CO2, $\Delta H_{298K} = -172 \text{kJ/mol}$ (5)

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 CO2/Steam–mixed reforming, as mentioned before. In the methanol synthesis reactor, CO2 hydrogenation occurs over a Cu-based catalyst provided suitable hydrogen content (i.e., $H_2/(2CO + 3CO_2) \geq 1$). 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:

- $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \Delta H_{298K} = -49.5 \text{kJ/mol}$ (6)
- $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}, \Delta H_{298K} = -90.5 \text{kJ/mol}$ (7)
- $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}, \Delta H_{298K} = 41.2 \text{kJ/mol}$ (8)

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/m3, 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) is 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 CO2 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 CO2/(CO2 + CO) ratio in the syngas, total CO2 conversion, and energy efficiency. To keep away from severe carbon deposition region, the molar ratio of the fresh feedstock CO2/NG/H2O 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 H2/(2CO + 3CO2) 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 H2/(2CO + 3CO2) ratio in the syngas changes with the recycle ratio, thus in order to maintain the optimum H2/(2CO + 3CO2) ratio in the syngas, the CO2/NG ratio must be adjusted accordingly, as shown in Tables S2–S4.

As shown in Fig. 2, the CO2/(CO2 + CO) ratio in the syngas can be raised via increasing the recycle ratio, because of the much higher conversion of CO than CO2 to methanol in the methanol synthesis unit. Thus, with increasing recycle ratio, increasingly more CO2 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 CO2 accumulation in

![Fig. 2. Influence of the recycle ratio on CO2/(CO2 + CO) ratio in syngas.](image-url)
the syngas, results in a decrease in the total amount of emitted CO$_2$ of the entire process due to the enhanced total CO$_2$ conversion, as shown in Fig. 3. Moreover, for option 2, as the recycle ratio increases to around 0.55, the total CO$_2$ conversion becomes close to zero, however, as the recycle ratio increases to about 0.98, nearly 95% of the fresh CO$_2$ is converted in the two options 1 and 2. This can be ascribed to CO$_2$ hydrogenation as well as CO$_2$ reforming in the methanol synthesis and reforming units, respectively. In the methanol synthesis reactor, a high CO$_2$/H$_2$/(CO$_2$ + CO) ratio combined with an optimum H$_2$/(2CO + 3CO$_2$) ratio improves the conversion of CO$_2$ to methanol via CO$_2$ hydrogenation. Meanwhile, a higher CO$_2$/H$_2$/(CO$_2$ + CO) ratio results in higher per-pass and ultimate CO$_2$ conversions. In addition, the CO$_2$ recycled to the reforming unit is also converted via CO$_2$ reforming. Through the foregoing processes, the recycled CO$_2$ sent to the reforming and methanol synthesis units is converted to either syngas or methanol. Thus, the amount of vented CO$_2$ 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$_2$ 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

$$T_{\text{eff}} = \frac{\text{LHV of methanol}}{\text{LHV of feed NG}}$$

and

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

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

$$T_{\text{eff}} = \frac{\text{LHV of methanol}}{\text{LHV of feed NG} + \text{heat duty/0.8}}$$

and

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

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

$$= \frac{(\text{heat duty/0.8} - \text{LHV of vent gas}) \times 1.012}{\text{LHV of fuel NG}}$$

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
efficiency values here are mainly due to the improved CO₂ conversion at the high recycle ratio in the methanol synthesis reactor. With the increase in the recycle ratio, more CO₂ is converted to methanol in the methanol synthesis reactor. Thus, the T eff and C eff would increase with increasing recycle ratio. However, in our previous GTL process using a Cu catalyst in the F-T synthesis reactor, CO₂ was generated to a small extent via the WGS reaction. In the current case, with an increasing recycle ratio, more and more CO₂ is generated, which would likely decrease the T eff and C eff.

Fig. 5 depicts the T eff and C eff values for both options at different split ratios. Although T eff and C eff tend to move downward with an increase in the split ratio, however, there is no significant change at different split ratios. T eff and C eff 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 CO₂ 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 eff and C eff 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 CO₂ is reacted to produce CO and H₂, thus decreasing the CO₂/(CO₂ + CO) ratio in the syngas. To keep the H₂/(2CO + 3CO₂) ratio in the optimum range, the fresh feed amount of CO₂ must be adjusted, which can be seen from Tables S5–S7. In addition, as shown in Fig. 6, the vented CO₂ is also reduced as the split ratio increases. However, sending more of the recycle stream to the reforming unit does not benefit the T eff and C eff 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, CO₂ can be converted via the CDR as well as CO₂ hydrogenation in the reformer and the methanol synthesis reactor, respectively. In General, the equilibrium conversion of CO₂ via CDR in the reformer exceeds that via CO₂ 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 CO₂ via CO₂ hydrogenation could be improved by increasing the recycle ratio.

As shown in Fig. 2 and Tables S5–S7, the CO₂/(CO₂ + 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 CO₂ is first converted to CO via the CDR in the reformer, resulting in the decrease of CO₂ content in the generated syngas. However, in option 2, fresh CO₂ is directly fed to the methanol synthesis reactor without CO₂ consumption in the reformer. In addition, option 1 at a steam-to-carbon (S/C) ratio of 1.5 exhibits a lower CO₂/(CO₂ + 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 CO₂ conversion, leading to the lower CO₂/(CO₂ + CO) ratio in the syngas. As shown in Fig. 3, the amount of CO₂ in the vent gas for option 1 is lower than that of option 2. Here, CO₂ consumption via the CDR is found to be much larger than that by CO₂ hydrogenation under the given conditions. Meanwhile, option 1 at a S/C ratio of 1.5 shows the lowest amount of CO₂ in the vent gas, which could be attributed to the improved CO₂ conversion at the lower S/C ratio. However, the difference in the amount of CO₂ in the vent gas between both options 1 and 2 decreases with increasing recycle ratio. This is mainly due to the increased CO₂ conversion in the methanol synthesis reactor of option 2 under
higher CO2/(CO2 + CO) ratios. Moreover, as we can see from Fig. 4, the Teff and Ceff 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 Reff and Ceff 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 CO2 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 Teff and Ceff values of option 2 in the high recycle ratio range 0.8–0.98 is mainly attributed to the higher conversion of CO2 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 CO2 conversion in the methanol synthesis reactor and the reduced consumption of energy in the reforming unit.

In addition, as shown in Fig. 5, the Teff and Ceff 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 CO2 in the methanol synthesis reactor and the lower consumption of energy in the reforming unit for option 2. Meanwhile, the Teff and Ceff 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 Teff and Ceff as well as the CO2 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 CO2 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, Ceff is increased by ca. 5.0–8.3%. Teff 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 CO2, we proposed two CGTM options with the feeding point of the fresh feed CO2 as the principal configurational difference. The effects of the recycle and split ratios on the thermal and carbon efficiencies as well as the total CO2 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 CO2 conversion, enhance the thermal and carbon efficiencies, and reduce CO2 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 CO2 emissions were significantly reduced, because of the efficient utilization of CO2 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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