

# 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 <sub>eff</sub>	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 <sub>eff</sub>	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

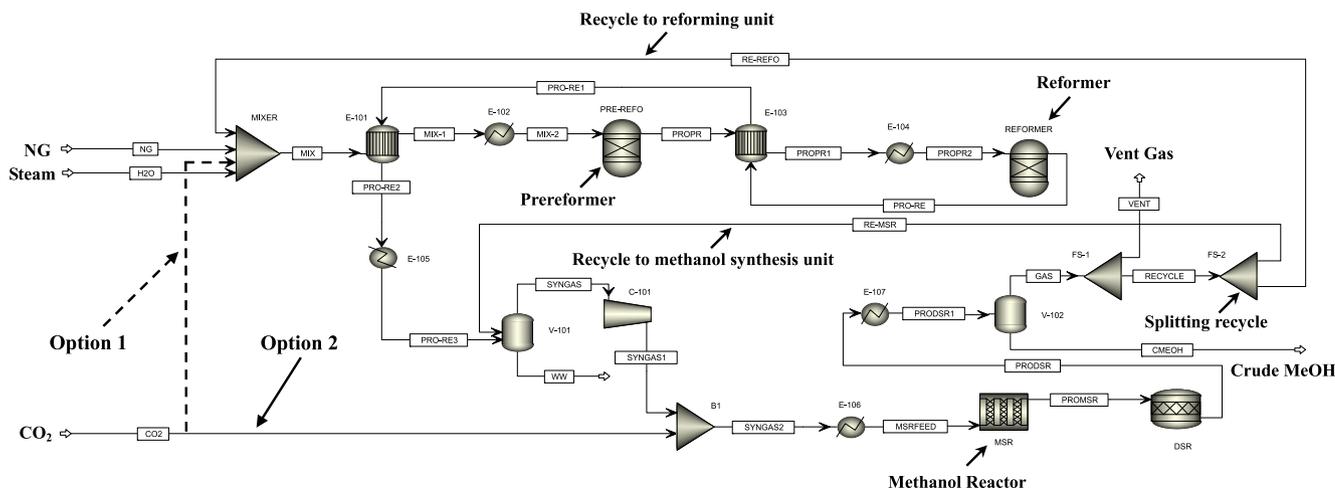


Fig. 1. Schematic process flow diagram of CGTM.

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