Carbon dioxide utilization in a gas-to-methanol process combined with CO₂/Steam-mixed reforming: Techno-economic analysis

Chundong Zhang a, Ki-Won Jun a,⇑, Ruxing Gao b, Geunjae Kwak a, Hae-Gu Park a

a C1 Gas Conversion Research Group, Carbon Resources Institute, Korea Research Institute of Chemical Technology (KRICT), Yuseong, Daejeon 34114, Republic of Korea
b Korea Atomic Energy Research Institute, Yuseong, Daejeon 305-353, Republic of Korea
c Quantum Energy Chemical Engineering, School of Engineering, Korea University of Science and Technology (UST), Yuseong, Daejeon 34113, Republic of Korea

Highlights
- Two options of CO₂ utilized gas-to-methanol (CGTM) process are proposed.
- CO₂ is converted via CO₂/Steam-mixed reforming and CO₂ hydrogenation.
- Process simulation and conceptual design are implemented using Aspen Plus.
- Techno-economic analysis is implemented to evaluate the economic feasibility.
- Both options are economically feasible in the plant scale range of 2500–5000 TPD.

Graphical Abstract

Abstract
Conceptual design for two options of carbon-dioxide-utilized gas-to-methanol process (CGTM) was implemented by using process simulation software Aspen Plus. The overall mass and energy stream results as well as the thermal and carbon efficiency were obtained from the developed process models. Before the following economic evaluation and sensitivity analysis, total capital investment (TCI) and total product cost (TPC) of both CGTM options were determined. Then, economic evaluation were conducted to assess the economic profitability of the base cases for both CGTM options, using the economic evaluation indicators such as net present value (NPV), internal rate of return (IRR), and discounted payback period (DPBP). Furthermore, sensitivity analysis as well as break-even analysis were also applied to investigate the economic performance of both CGTM options under different circumstances, by changing parameters such as methanol and NG prices, plant scale, and carbon tax. It was shown that the methanol price, CAPEX, and NG price are the most sensitive factors, and the two CGTM options were economically feasible in the plant scale range of 2500–5000 ton per day, according to the economic evaluation indicators NPV, IRR, and DPBP, and were more economically competitive in the case of higher plant scale and carbon tax.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The increasing atmospheric CO₂ levels and the depleting fossil fuel reserves are regarded as the two major energy-related...
problems facing us in the next 50 years [1]. One strategy to simultaneously address the above two problems is the utilization of CO₂ as a carbon source for the synthesis of liquid fuels and/or petrochemicals [2,3]. In recent years, extensive efforts have been made to develop efficient CO₂ utilization technologies, among which CO₂ reforming and CO₂ hydrogenation have been regarded as more attractive methods for CO₂ conversion [4–6]. It is because of their capability to be applied in the gas-to-liquids (GTL) and gas-to-liquid methanol (GTM) processes on a large scale [7]. For instance, CO₂ reforming can be combined with steam reforming which is widely employed for syngas generation in the current natural gas (NG) industry [8]. In addition, CO₂ hydrogenation can be applied together with CO hydrogenation for the synthesis of various chemicals and/or fuels such as hydrocarbons [9,10], DME [11], and methanol [12].

Methanol is an important primary raw material for the energy and chemical industries, because of its wide applications ranging from energy uses (e.g., as a fuel by itself, or to be blended with gasoline) to chemical uses (e.g., as a solvent, or to be converted to formaldehyde, olefins, acetic acid, esters, etc.) [13,14]. Meanwhile, GTM process has gained extensive attentions since the past decade due to the increasing trend in methanol demand as well as the availability of abundant and cheap NG [15]. Besides, it will attract more attentions in the coming years, owing to the extremely abundant unconventional NG resources such as shale gas and coal-bed methane, which are recently being exploited and utilized [16,17]. Generally, a GTM process consists of three main steps: (1) syngas generation via methane reforming technologies such as auto-thermal reforming (ATR) [18], steam reforming of methane (SRM) [19], partial oxidation of methane (POM) [20], and carbon dioxide reforming of methane (CDM) [21]; (2) syngas conversion through methanol synthesis technology, which produces crude methanol as well as few byproducts (e.g., ethanol and DME) [13,22]; (3) methanol purification via distillation to produce purified methanol with required purity. Among the methane reforming technologies mentioned above, none of them produces syngas with suitable H₂/(2CO + 3CO₂) ratio, as can be directly sent to the following methanol synthesis unit [5]. Hence, the additional syngas ratio conditioning units are necessary. In addition, the ATR and POM technologies need expensive air separation units to generate pure oxygen, which are associated with challenging safety concerns because of the usage of pure oxygen [23]. However, the combination of SRM and CDM, named CO₂/Steam-mixed reforming hereafter, can produce the syngas with flexible H₂/(2CO + 3CO₂) ratios via controlling the two competitive methane reforming reactions SRM and CDM. Thus, no additional syngas ratio conditioning units are necessary in the case of CO₂/Steam-mixed reforming, which could save capital expenditures (CAPEX) and operating expenditures (OPEX) of the GTM process. Meanwhile, CO₂ can be converted in both the reforming and methanol synthesis units to produce final product methanol, which reduces the CO₂ emissions of the GTM process.

Therefore, based on the above considerations and our previous technical study on the CO₂ utilized GTM process (CGTM) [24], in the present work, we mainly focused on the techno-economic analysis for the two proposed CGTM options. During the economic analysis, several economic evaluation indicators such as net present value (NPV), internal rate of return (IRR), and discounted payback period (DPBP) were determined for the base cases of both proposed CGTM options. Besides, the effects of several factors, such as methanol price, plant scale, NG price, and carbon tax were further investigated in detail. It was shown that the two CGTM options were economically feasible in the plant scale range of 2500–5000 ton per day (TPD), according to the evaluation indicators NPV, IRR, and DPBP, and were more economically competitive in the case of higher plant scale and carbon tax.

2. Material and methods

2.1. Process modeling

Generally, a GTM process is usually comprised of several units: units for feeding, gas pretreatment, reforming, methanol synthesis, and methanol purification. However, in this work, the gas pretreatment and methanol purification units were not investigated in detail since they are already well established in the current NG industry and their effects on the performance of the whole CGTM process is relatively small, as also described in our previous study [3,7,23,24]. Therefore, two simplified but meaningful CGTM options were instead proposed, mainly focusing on the feeding, reforming, methanol synthesis and recycling units combined with several separation units, as illustrated in Fig. 1 [24]. Here, the main difference between the two CGTM options is the feeding method of the fresh feed CO₂. More specifically, in option 1, fresh CO₂ was fed to the reforming unit to produce syngas via CO₂/Steam-mixed reforming first, and then to the methanol synthesis unit to produce methanol via hydrogenation of CO₂ and CO. While, in option 2, fresh CO₂ was fed to the methanol synthesis unit directly to produce methanol without entering into the reforming unit.

The criteria as well as some important assumptions applied in the process models are outlined as follows: methane, ethane, propane, butane, CO₂, and nitrogen were selected as the main components in the fresh and fuel NG, and its typical composition is shown in Table S1 of the Supplementary Information (SI). In both established process models, Peng-Robinson equation of state was selected as the thermodynamic calculation method, which guarantees accurate calculation results in modeling light gases, alcohols, and hydrocarbons [7,25]. Before conducting the detailed process modeling, we carefully compared the simulation results of the main units such as the reformer (e.g., CH₄ conversion, CO₂ conversion, and H₂/(2CO + 3CO₂) ratio in the generated syngas), and the methanol synthesis reactor (e.g., CO conversion, CO₂ conversion, and methanol yield) with our experimental results to ensure the accuracy of the proposed models. Besides, the other details about the process modeling can be found in our previous study [24].

The reforming unit in both proposed options is composed of two parts, namely, a prereformer and a reformer. The prereformer is applied to convert all the C₂– hydrocarbons contained in the fresh feed NG into methane over a Ni catalyst, under reaction temperature 550 °C and pressure 5 bar (gauge). Meanwhile, the equilibrium type reactor model RGibbs is used to simulate the prereformer, according to the Gibbs free energy minimization [7,8]. In addition, the RGibbs equilibrium reactor model is also applied to simulate the reformer, and three typical reactions for SRM, CDM, and water-gas shift (WGS) are shown as follows:

$$\text{SRM: } \text{H}_2\text{O} + \text{CH}_4 \leftrightarrow \text{CO} + 3\text{H}_2, \quad \Delta H_{298 K} = 206 \text{ kJ/mol}$$

(1)

$$\text{CDM: } \text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CO} + 2\text{H}_2, \quad \Delta H_{298 K} = 247 \text{ kJ/mol}$$

(2)

$$\text{WGS: } \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2, \quad \Delta H_{298 K} = -41 \text{ kJ/mol}$$

(3)

The reformer is operated under reaction temperature 900 °C and pressure 5 bar (gauge). Under this condition, the three reactions mentioned above can be assumed to reach chemical equilibrium, given that the reaction rates are very fast at such an elevated temperature. Meanwhile, “restricted chemical equilibrium” option is selected to better simulate the reformer.

After reforming, the generated syngas directly enters into the methanol synthesis unit without using any syngas ratio conditioning unit, since the flexible syngas ratios can be achieved by adjusting the two competitive methane reforming reactions SRM and CDM, as mentioned above. In the methanol synthesis reactor, hydrogenation of CO₂ and CO occurs over a Cu-based catalyst
دریافت فوری
متن کامل مقاله

امکان دانلود نسخه تمام متن مقالات انگلیسی
امکان دانلود نسخه ترجمه شده مقالات
پذیرش سفارش ترجمه تخصصی
امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
امکان دانلود رایگان ۲ صفحه اول هر مقاله
امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
دانلود فوری مقاله پس از پرداخت آنلاین
پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات