



Efficient utilization of carbon dioxide in gas-to-liquids process: Process simulation and techno-economic analysis



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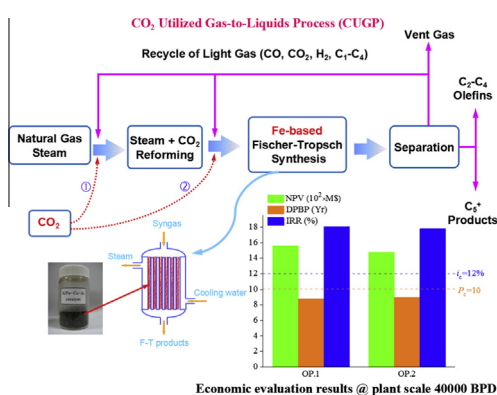
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HIGHLIGHTS

- Two options of CO₂ utilized gas-to-liquids process using Fe-based F–T catalyst were proposed.
- CO₂ was utilized via CO₂/Steam mixed reforming and RWGS reaction.
- Process simulation as well as conceptual design were implemented using Aspen Plus.
- Techno-economic analysis was conducted to evaluate the economic feasibility.
- Both options are economically feasible at the plant scale of 40,000 BPD, and are more competitive in case of high carbon tax.

GRAPHICAL ABSTRACT



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ABSTRACT

Conceptual design of two options of carbon dioxide utilized gas-to-liquids process (CUGP), which mainly produces light olefins and Fischer–Tropsch (F–T) synthetic oils, has been implemented with the aid of Aspen Plus software. The mass and energy stream results as well as the process efficiencies and CO₂ emissions of the proposed options were obtained from the developed models. The capital investment and the product cost estimations were conducted before the following economic analysis. Several indicators such as net present value (NPV), discounted payback period (DPBP) and internal rate of return (IRR) were calculated to evaluate the profitability of the two proposed options. In the economic analysis, sensitivity analysis as well as break-even analysis was carried out. In addition, effects of several sensitive factors such as the prices of synthetic oil, olefin and natural gas, capital investment, carbon tax and plant scale on the IRR of each option were analyzed in detail. It was found that the CUGP, regardless of option, was economically feasible at the plant scale of 40,000 BPD and was more competitive compared with conventional GTL processes, in case of high carbon tax.

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1. Introduction

The increasing CO₂ in the atmosphere is regarded as the main reason for the serious global warming issues [1]. Proposals such as CO₂ capture and storage (CCS) and CO₂ utilization have been implemented to reduce CO₂ emission. Compared with CCS, CO₂

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utilization seems to be more attractive because it can not only reduce CO₂ emission, but also produce valuable chemicals and fuels [2]. Among the CO₂ utilization strategies, CO₂ reforming and CO₂ hydrogenation have received much attention because of their potential to be used for CO₂ utilization in large scale [3]. CO₂ reforming could be used together with the steam reforming which is widely applied for syngas production in the current natural gas (NG) industry [4]. Meanwhile, CO₂ hydrogenation could be combined with CO hydrogenation to produce liquid fuels, such as methanol, dimethyl ether (DME) and hydrocarbons [5–8].

Interests in the Gas-to-Liquids (GTL), as well as Coal-to-Liquids (CTL) and Biomass-to-Liquids (BTL) processes have been increasing in the past decade due to its potential to produce ultra-clean fuels and valuable petrochemicals [9–12]. Generally, there are three main steps in the GTL process: syngas generation through methane reforming, syngas conversion via F–T synthesis and product upgrading by catalytic hydrocracking [13]. F–T synthesis is the key step in the GTL process, because its conversion and selectivity have vital effects on the energy efficiency of the GTL process [14]. Typically, Co-based catalyst is used in the GTL process due to its high activity and selectivity to long chain hydrocarbons [15]. Meanwhile, extensive efforts have been made to develop GTL process with Ni-based CO₂/steam-mixed reforming for syngas generation and Co-based F–T synthesis for syngas conversion [4,16,17]. However, Co-based catalyst is not active for reverse water gas shift (RWGS) reaction, therefore, it has low ability to convert the unconverted CO₂ from the reforming unit. Thus, the unconverted CO₂ should be separated and recycled to the reforming unit or re-emitted to the air. However, if the Fe-based catalyst with high CO₂ containing syngas is used in the F–T synthesis, then the thermal and carbon efficiencies could be further improved because of the enhanced CO₂ conversion with the aid of the RWGS reaction [18]. Based on this consideration, we proposed two new CO₂ utilized GTL processes (CUGP) using Fe-based catalyst, converting not only CO but also CO₂ to hydrocarbons in the F–T synthesis unit via RWGS and general F–T reactions. With recycling the unconverted syngas to the reforming and the F–T synthesis units, successfully improved process efficiencies and significantly reduced CO₂ emissions were realized [19].

Therefore, on the basis of our previous technical study [19], in this work, we have mainly analyzed the two proposed CO₂ utilized GTL processes from the techno-economic point of view. The two processes were analyzed in terms of net present value (NPV), discounted payback period (DPBP) and internal rate of return (IRR). Effects of several factors, such as prices of natural gas, synthetic oil and olefins, capital investment, carbon tax and plant scale were investigated for the economic analysis. It was found that the two environmentally friendly processes were economically feasible at the plant scale of 40,000 BPD, according to the indicators NPV, DPBP and IRR, and more competitive than conventional GTL in case of high carbon tax.

2. Material and methods

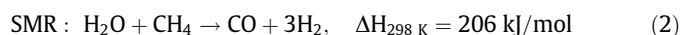
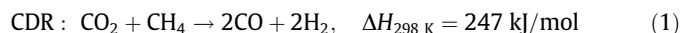
2.1. Process modeling

A GTL process is usually comprised of several units, such as feeding unit, gas cleaning unit, reforming unit, F–T synthesis unit, product upgrading unit and product separation unit. However, the gas cleaning, product upgrading and separation units were not investigated in detail in this work, since they are well established in current petrochemical industry and their influence on the process performance is relatively small, as shown in our previous work [4,19]. Therefore, we established two simplified but meaningful process models mainly dealing with the feeding, reforming,

F–T synthesis and recycling units combined with several separation sections as a whole, which are shown in Fig. 1. As illustrated in Fig. 1, the main difference between the two proposed models is as follows: (1) In model 1, fresh CO₂ combined with fresh feed NG and steam is fed to the reforming unit to produce syngas by CO₂/steam-mixed reforming first and then to the F–T synthesis unit to produce targeted hydrocarbons through RWGS and general F–T synthesis; (2) In model 2, fresh feed CO₂ directly enters into the F–T synthesis unit to produce targeted hydrocarbons through RWGS and general F–T synthesis without entering into the reforming unit.

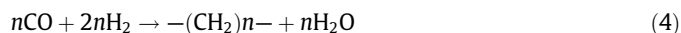
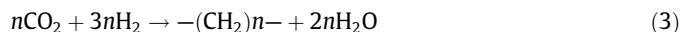
The important assumptions as well as the criteria used in the process models are outlined as follows. Methane, ethane, propane, butane, CO₂ and N₂ were selected as the main components contained in the fresh feed NG, and the typical composition is shown in Table S0 of Supplementary information (SI). The thermodynamic method used in this model is Peng–Robinson equation. In addition, the other details for the process model development can be found in our previous work [19].

The reforming unit in both models includes two parts, one is pre-reformer and the other is reformer. The pre-reformer is operated under $T = 550\text{ }^{\circ}\text{C}$ and $P = 5\text{ bar}$ (gauge). In this case, the pre-reformer using a Ni-based catalyst can convert almost all the C₂₊ hydrocarbons contained in the fresh feed natural gas and in the recycled light gas from the F–T unit into methane. The RGibbs model using chemical equilibrium for C₁–C₄ hydrocarbons is applied to simulate the pre-reforming process according to Gibbs free energy minimization. Furthermore, the RGibbs equilibrium model is also used in the reformer and two typical reactions for CO₂ reforming (CDR) and steam reforming (SMR) are considered as follows:



The reformer is operated under $T = 850\text{ }^{\circ}\text{C}$ and $P = 5\text{ bar}$ (gauge). In this case, the CDR as well as SMR could be assumed to be in chemical equilibrium, since the reaction rates are very fast at elevated temperature. Moreover, “Restricted chemical equilibrium” option was selected in the RGibbs model in order to simulate the reforming process well.

After reforming, the syngas directly enters into the F–T synthesis unit without using any CO₂ removal unit, since CO₂ is also one kind of reactant in the F–T synthesis unit using an Fe-based catalyst on condition that the syngas has high CO₂/(CO + CO₂) ratio (typically higher than 0.5) and sufficient hydrogen content (i.e., $\text{H}_2/(2\text{CO} + 3\text{CO}_2) \geq 1$) [7,19]. The F–T synthesis reactor are operated at $T = 300\text{ }^{\circ}\text{C}$ and $P = 10\text{ bar}$ (gauge). The main overall reactions for high CO₂ containing syngas on an Fe-based catalyst can be regarded as hydrogenation of CO₂ and CO, which are expressed as follows:



Meanwhile, several typical chain growth and RWGS reactions are considered based on the conversion of syngas and selectivity of targeted hydrocarbons obtained from our experimental results [7]. The representative reactions for producing paraffins and olefins are listed in Table S1 (see SI). In addition, the by-product oxygenates were not considered in present work on the basis of our previous experimental study since the selectivity toward oxygenates is typically as low as 1% [7]. Thus, it could be neglected without causing any significant effects on modeling the whole process. The F–T synthesis unit was modeled by RStoic reactor in which fractional conversion was designated. Besides, the

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