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Improving GTL process by CO_2 utilization in tri-reforming reactor and application of membranes in Fisher Tropsch reactor

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A B S T R A C T

In this paper, tri-reforming of methane, Fisher Tropsch reaction, and membrane separation unit are used for improving the GTL process. The conventional process is composed of reforming and Fisher Tropsch reactions. For the improving syngas production the reforming reactor is substituted by a tri-reforming reactor, also, reaction pressure (1–10 bar) and temperature (500 °C–800 °C) are investigated. It is observed that decreasing the pressure and increasing the temperature improve the conversion of hydrocarbons and H_2/CO ratio. It is illustrated that by controlling the oxygen injection rate to the tri-reforming reactor, CO_2 production is minimized. In the case of Fisher Tropsch reactor, associating a Pd/Ag membrane for separation and recycling syngas to the reactor leads to yield of the light component such as methane reduces while the yield of heavy components increases. It is shown that application of tri-reforming reactor and membranes increase the gasoline and LPG production to 3337 bbL/day which is over two times of conventional process, while, the selectivity of carbon dioxide in Fisher Tropsch reactor is reduced 15% compared to conventional process.

1. Introduction

1.1. Carbon capturing technology

The main portion of CO_2 emission in the world is related to the fossil fuels [1,2]. Several methods are proposed for reduction of CO_2 emission including decreasing the energy consumption by improving the energy efficiency of processes, finding a clean resource of energies, CO_2 capture and storage, and dry reforming (CO_2 reforming of methane) [3–7]. After optimization of energy consumption, the best method for reducing the CO_2 emission is absolutely implementing the renewable energies; however, the renewable energy sources require for more progress in exploring and utilization than fossil fuels. The other method, CO_2 capture and storage, firstly used for CO_2 flooding of oil reservoir as an enhanced oil recovery method. In the last decades in order to the prevent entrance of huge amount of carbon dioxide during chemical and petrochemical processes to the environment, the produced CO_2 is separated and injected underground or beneath the oceans [1,2]. Although the separation process is rather simple by the amine-based absorption-desorption process [8], membrane process [9], adsorption process [10] and mineralization process [11,12]; however, the cost of compressing and injecting makes the CO_2 capture and storage unfavorable for industries [1,2].

The dry reforming is an appropriate method for consuming two main greenhouse gasses of carbon dioxide and methane for producing a mixture of hydrogen and carbon monoxide (syngas). The produced syngas is used for the production of valuable materials such as gasoline or diesel [1]. Although the CO_2 utilization for production of other raw material is a way to reduce the free amounts of carbon dioxide in the atmosphere, the efficiency of dry reforming process is rather low, so industrial reactors implement the combination of CO_2 and steam reforming of methane for CO_2 utilization in liquid intermediate hydrocarbons production [13]. It is illustrated that during the coupled dry and steam methane reforming process, the produced CO_2 by steam reforming consumes in carbon dioxide reforming and cause decreases CO_2 emission of 67% compared to steam reforming [1]. For combined CO_2 and steam reforming of methane new catalysts were synthesized [14] and feasibility analysis was thermodynamically preformed [15]. It is shown that presence of steam on the reformer prevents from coke formation on catalyst active parts and protect the catalyst. The other approach is injecting oxygen to the reforming reactor (auto-thermal reforming) for supplying a part of heat for reactions; however, the reactions made by oxygen produces an excess value of CO_2. Transformation of CO and CO_2 by hydrogen to the intermediate hydrocarbons over iron Nano-catalysts is investigated by Hu et al. [16]. They observed that CO_2 conversion is 45%. As the optimum ratio of H_2/CO in Fisher-Tropsch reactor is 1.5–2 [17], Rafiee and Hillestad studied the influence of CO_2 injection to the reactor for reducing H_2/CO at a

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temperature of 250 °C. Their results illustrated that CO_2 injection on a low temperature to Fisher-Tropsch reactor does not affect H_2/CO [18]. Other methods for reducing the CO_2 greenhouse gas emission to the environment is carbonation- calcination reactions along with methane steam reforming reactions which CO_2 is converted from gaseous state to solid phase [19].

In this paper, GTL unit is proposed for CO_2 utilization in tri-reforming reactions which converts CO_2 to valuable liquid hydrocarbons such as gasoline.

1.2. Gas to liquid (GTL) process

In the last decades, industries developments based on fossil fuels significantly increases the consumption of different types of fuel including oil, gas, and coal. According to declining in oil reservoirs along with growing the exploration and production of natural gas as well as stability in its price makes the gas an alternative for petroleum [20,21]. The challenge of natural gas is related to its transportation. One of the methods for natural gas transportation is installing a pipeline from the production wells to destinations which may locate far from the reservoir; passes from different areas such as the ocean, mountainous or unsecured regions [22,23]. One of the best methods is transforming the natural gas to liquid hydrocarbons (GTL) to simplify the transportation and utilization. In fact, in GTL process, natural gas or light hydrocarbons are converted into longer-chain hydrocarbons such as gasoline or diesel [24,25].

GTL is a two-step process. In the first stage, natural gas reacts with steam to produce syngas. In the second stage; the produced syngas is transformed into synthetic crude oil during the Fischer-Tropsch reaction. Distillation of the oil produces expensive liquid fuels especially gasoline which its transportation and storage are easier than natural gas [25]. Thus, the GTL production process is strongly regarded for investigating decisive factors on optimization of gasoline production [26].

Catalytic reduction of carbon monoxide with hydrogen over cobalt and nickel based catalyst was performed for first time in 1710 by Sabatier and Sanders. In 1715 hydrocarbons were produced by reduction of carbon monoxide and hydrogen. Also, it was observed that by changing the catalyst type and reactor operating conditions (pressure of 100 bar and temperature of 200–600 °C) other heavier materials such as methanol can be produced. The results showed that synthesis of heavier hydrocarbons by Sabatier reactions in higher temperature is achievable; however, in lower temperature, the principal product is methane. In 1720, the significant progress in catalyst production technology improved the efficiency of hydrocarbon production. Since the efficiency of heavier hydrocarbon production by cobalt-based catalysts in pressure of 10–11 bar were about 11%; Fisher and Pichler found that iron-based catalysts improves the gasoline production at a pressure of 10–20bars. To produce heavier hydrocarbons, they proposed ruthenium-based catalyst in the high pressure of 100–1000bars [24]. The industrial modified GTL process based on ruthenium catalyst produces a mixture of hydrocarbons, alcohols, aldehydes, ketones, fatty acids and other materials [23–29].

Nowadays the membrane processes are used to increase the efficiency of separation process and conversion of some reactions. The most application of membrane is related to the systems containing hydrogen and oxygen by use of ceramic and palladium membranes. Palladium- stainless steel alloys based membranes are completely permeable to hydrogen. Properties of palladium based membranes including thermal and mechanical stability are significantly improved by doping the silver to the membrane structure [30–36]. Recently modified perovskite membranes with dual conductivity are used for partial oxidation of methane to improve liquid fuels production. In this process, oxygen is separated simultaneously with catalytic oxidation in the presence of air as an oxidative. This technology simplifies the process and significantly reduces the cost of the process (about 20–30%) [37].

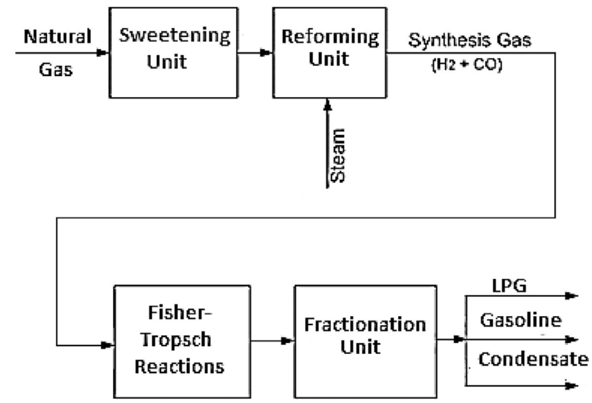

Fig. 1. A schematic of conventional GTL production unit.

The other efficient membrane, hydroxy sodalite (H-SOD), is a zeolite type material composed of sodalite cages. Since H-SOD has high selectivity for water rather other components; it is considered as a brief separator for separating water in the chemical processes [38–40].

In this paper, the GTL process is improved by application of membrane, tri-reforming and Fisher Tropsch reactors. For this purpose, natural gas is sent to the tri-reforming reactor after sweetening unit. The produced syngas is sent to the Fisher Tropsch reactor for liquid hydrocarbons production. An H-SOD membrane associated with Fisher Tropsch reactor separates the produced water and recycles to the tri-reforming reactor. The unreacted carbon monoxide and hydrogen are separated by Pd/Ag membrane and are recycled to the Fisher Tropsch reactor, thus, increases the reactor efficiency.

2. Process description

In the GTL process, natural gas is sweetened in amine sweetening unit and then sent to the reforming catalytic reactor for syngas (a mixture of hydrogen and carbon monoxide) production. The syngas is sent to Fisher Tropsch reactor for liquid hydrocarbons production. A schematic of conventional GTL process is given in Fig. 1. It is seen that the GTL unit produces valuable materials such as methanol, dimethyl ether and other petroleum distillates including diesel, gasoline, and kerosene from syngas.

In this study, simulation of GTL unit is performed by Aspen HYSYS 7.3. Peng-Robinson equation of state is employed for predicting the thermodynamic properties of streams and unit operations in the process.

2.1. Sweetening unit

The gas sweetening unit is composed of absorption and desorption towers, heat exchangers and separators. Fig. 2 illustrates a flow diagram for gas sweetening unit. As it is seen in Fig. 2, the liquid part of natural gas is eliminated in a separator, and then is sent to amine absorption tower for removing the acid gasses by dimethylamine (DMA). The sweet gas is sent to the GTL unit, while, Amine-containing acid gasses is injected to a flash tank for separating the light gasses absorbed by an amine, then after passing from an amine–amine heat exchanger, the amine recovery from acid gasses is performed in desorption column. The temperature of recovered amine is reduced in the amine–amine heat exchanger then recycled to the amine tower after mixing with make-up water (Fig. 2). Table 1 illustrates the feed composition and properties entering to the sweetening unit.

2.2. GTL unit

Fig. 3 illustrated the process of natural gas transformation to liquid fuel. The sweetened natural gas is sent to GTL unit. Oxidation of natural