



A simulation study on gas-to-liquid (natural gas to Fischer–Tropsch synthetic fuel) process optimization

Yong Heon Kim^{a,b}, Ki-Won Jun^c, Hyunku Joo^d, Chonghun Han^a, In Kyu Song^{a,*}

^a School of Chemical and Biological Engineering, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea

^b Petroleum Technology Institute, Korea National Oil Corporation, Gwangyang-dong, An Yang 431-711, South Korea

^c Korea Research Institute of Chemical Technology, Jang-dong, Yuseong-gu, Daejeon 305-343, South Korea

^d Korea Institute of Energy Research, Jang-dong, Yusong-ku, Daejeon 305-343, South Korea

ARTICLE INFO

Article history:

Received 9 June 2009

Received in revised form 30 July 2009

Accepted 23 August 2009

Keywords:

Natural gas

Synthetic fuel

Fischer–Tropsch synthesis

ABSTRACT

A simulation study on gas-to-liquid (natural gas to Fischer–Tropsch synthetic fuel) process was carried out in order to find optimum reaction conditions for maximum production of synthetic fuel. Optimum operating condition for GTL (gas-to-liquid) process was determined by changing reaction variable such as temperature. During the simulation, overall synthetic process was assumed to proceed under steady-state conditions. It was also assumed that physical properties of reaction medium were governed by RKS (Redlich–Kwong–Soave) equation. ATR (auto-thermal reforming) in synthesis gas production unit and slurry phase reaction over Co-based catalyst in FTS (Fischer–Tropsch synthesis) unit were considered as reaction models for GTL process. The effect of reaction temperature on CO conversion and C₅–C₂₀ hydrocarbon yield in FTS unit was mainly examined. Simulation and experimental results showed that optimum reaction temperature in FTS unit was 255 °C. Simulation results were also compared to experimental results to confirm the reliability of simulation model. Simulation results were reasonably well matched with experimental results.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

GTL (gas-to liquid) process is a promising way to convert gas fuel to synthetic liquid fuel [1]. Recently, conversion of natural gas (CH₄) to synthetic fuel has attracted much attention because of many advantages of synthetic fuel [2]. In particular, GTL synthetic fuel produced from synthesis gas (CO + H₂) through FTS (Fischer–Tropsch synthesis) retains extremely low sulfur and aromatic compounds [3,4]. GTL synthetic fuel also shows low emission of carbon monoxide, nitrogen oxides, hydrocarbons, and other particulates [4]. Thus, GTL synthetic fuel has been considered as a green fuel.

Production of synthetic fuel from natural gas involves two reactions. One is the conversion of natural gas to synthesis gas through reforming reactions. These examples include steam reforming [5], dry reforming [6], partial oxidation [7], and auto-thermal reforming (oxidative steam reforming) [8]. The other is the conversion of synthesis gas to synthetic fuel through FTS. Fe- or Co-based catalysts have been widely employed for FTS [9]. Although Co-based catalysts are relatively expensive, they show high activity in low-temperature FTS and have long life to be able to offer a good balance

between cost and performance. Thus, Co-based catalysts have been widely studied as an efficient FTS catalyst for GTL process [10].

In this work, a simulation study on natural gas (CH₄) conversion to FT (Fischer–Tropsch) synthetic fuel was carried out in order to find optimum reaction conditions for maximum production of synthetic fuel. For this purpose, auto-thermal reforming (a combination of partial oxidation and steam reforming) in synthesis gas production unit and slurry phase reaction over Co-based catalyst in FTS unit were considered as reaction models. Aspen HYSYS software was used for the simulation to see the effect of reaction temperature on CO conversion and C₅–C₂₀ hydrocarbon yield in FTS unit. Simulation results were compared to experimental results to confirm the reliability of simulation model. It is expected that the simulation model developed in this work may serve as a design basis for pilot-scale GTL process.

2. Technical approach and process simulation

A GTL plant examined in this work consists of two main process units; a reforming unit where natural gas (CH₄) is converted into synthesis gas (CO + H₂) and a FTS unit where synthesis gas is converted into synthetic fuel. In this work, ATR (auto-thermal reforming) in synthesis gas production unit and slurry phase reaction over Co-based catalyst in FTS unit were employed as reaction models for simulation of GTL process.

* Corresponding author. Tel.: +82 2 880 9227; fax: +82 2 889 7415.

E-mail address: inksong@snu.ac.kr (I.K. Song).

Nomenclature

ω	acentric factor
W_n	weight of fraction
α	chain growth probability
T_r	reduced temperature
H	enthalpy (kJ/mol)
r	reaction rate (mol/s kg)
P_i	partial pressure of component i (Pa)
a	temperature-dependent constant, the product of surface rate constant and adsorption constant (equation specific)
b	temperature-dependent constant, the product of surface rate constant and adsorption constant (equation specific)

Fig. 1 shows the scheme for ATR experiment. EH (electric heater) was placed in front of the monolith catalyst layer. EH provided the necessary heat to preheat the catalyst layer to the catalytic ignition temperature of the feed mixture for initiation of partial oxidation of methane. Water was fed to the reactor through a HPLC pump (Series II, LabAlliance). Thermocouples were placed inside and outside of the reactor in order to record the temperature profile.

Fig. 2 shows the scheme for FT synthesis reaction in SBCR (slurry bubble column reactor). γ - Al_2O_3 support was obtained by calcining aluminum boehmite (Catapal-B Condea) at 600 °C in an air stream. Co/ γ - Al_2O_3 catalyst was prepared by a conventional wet-impregnation method. The SBCR has 5.08 cm diameter and 2.0 m height with an effective reactor volume of 3.7 L. 1 kg of squalane ($\text{C}_{30}\text{H}_{62}$) was used as a liquid medium. The catalyst/squalane weight ratio was 20/100. The liquid products accumulated in the SBCR were separated by the porous metal plate located underneath the distributor.

Fig. 3 shows the simulated PFD (process flow diagram) of ATR for the production of synthesis gas from natural gas (CH_4). Main feed stream is methane. Methane fed into the ATR reformer together with oxygen and steam is converted into synthesis gas. Heat from the ATR reformer is recovered by Heat exchanger-100 to raise temperature of $\text{O}_2/\text{H}_2\text{O}$ feed stream.

Fig. 4 shows the simulated PFD (process flow diagram) of FTS for the production of synthetic fuel from synthesis gas. Synthesis gas with H_2/CO ratio of 2 is fed to the FT slurry phase reactor. Slurry

Table 1

Several possible reactions taking place in the FT reactor.

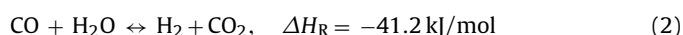
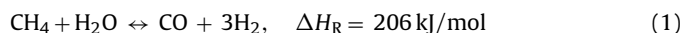
Reaction	$\Delta H_{300\text{K}}$ (kJ/mol)
$\text{CO} + 2\text{H}_2 \rightarrow -\text{CH}_2- + \text{H}_2\text{O}$	-165.0
$2\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + \text{CO}_2$	-204.7
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$	-39.8
$3\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + 2\text{CO}_2$	-244.5
$\text{CO}_2 + 3\text{H}_2 \rightarrow -\text{CH}_2- + 2\text{H}_2\text{O}$	-125.2

phase reactor is known to be efficient for removing heat of reaction in the FTS. Vapor of the reactor is condensed by Separator-100 and final FT synthetic fuel is produced. In FTS process simulation, it was very difficult to simulate entire FT products by kinetics. Therefore, CO conversion was calculated in the FT slurry phase reactor of Fig. 4 using spreadsheet of Aspen HYSYS. Final FT product was distributed to streams from C_1 to C_{30} by spreadsheet, and then mixed to FT synthetic fuel stream.

2.1. Reaction mechanism for GTL process

2.1.1. ATR process

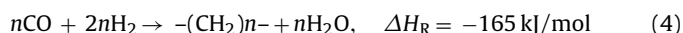
ATR consists of steam methane reforming, water gas shift reaction, and partial oxidation. The overall reactions taking place in the ATR reactor can be expressed as follows [11].



ATR technology is the most heat effective technology for natural gas conversion into synthesis gas. ATR process produces synthesis gas with H_2/CO ratio of 2, which is suitable for subsequent FTS process [12].

2.1.2. FTS process

FTS is a catalytic process that converts synthesis gas ($\text{CO} + \text{H}_2$) into a mixture of hydrocarbons (synthetic fuel). The FTS reaction can be regarded as hydrogenation of carbon monoxide and is expressed as follows [13].



There are also other reactions taking place in the FT reactor, but the detailed behavior of the reactions is not well known. Several possible reactions are listed in Table 1. Because these reactions are highly exothermic, sufficient cooling of the reactor is very important to secure stable reaction conditions [14]. The total heat of reaction corresponds to 25% of the heat of combustion of synthesis gas [14], leading to a limitation on the maximum efficiency of FT process.

Co-based catalysts at low-temperature Fischer–Tropsch (LTFT) synthesis have advantages of high activity and long life [15]. Moreover, Co-based catalysts have been successfully applied to the industrial processes due to their high FT activity and their low oxygenate selectivity, which makes them suitable for the conversion of H_2 -rich synthesis gas (obtained by reforming of natural gas) to synthetic fuel. In this work, therefore, Co-based catalyst was chosen as an efficient model LTFT catalyst for a slurry phase reactor.

2.2. Reaction kinetics for GTL process

Aspen HYSYS was used for simulation. In ATR process, natural gas (CH_4) is converted into synthesis gas ($\text{CO} + \text{H}_2$). In FTS process, it is known that first-order FT kinetics is a good approximation when hydrogen conversion is below 60% [16]. Except for a few more detailed approaches [17], however, linear kinetics has been

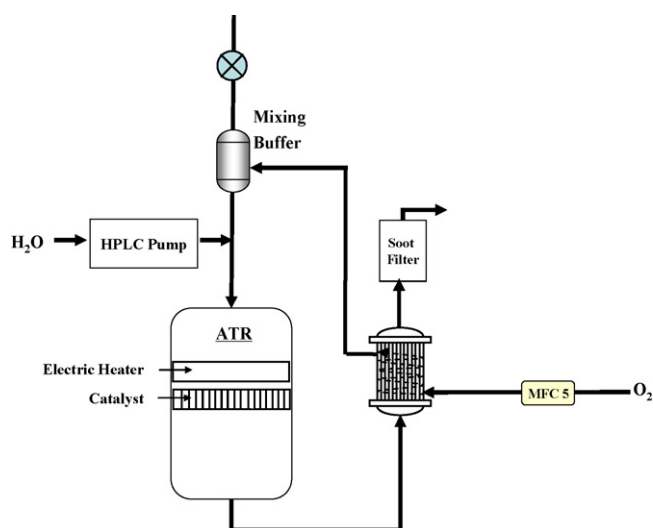


Fig. 1. Scheme for ATR experiment.

Download English Version:

<https://daneshyari.com/en/article/153354>

Download Persian Version:

<https://daneshyari.com/article/153354>

[Daneshyari.com](https://daneshyari.com)