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

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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 C_5–C_{20} 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.

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 (CH_4) to synthetic fuel has attracted much attention because of many advantages of synthetic fuel [2]. In particular, GTL synthetic fuel produced from synthesis gas ($CO+H_2$) 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 (CH_4) 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 stream 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 C_5–C_{20} 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 (CH_4) is converted into synthesis gas ($CO+H_2$) 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.

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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 ($C_{30}H_{62}$) 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 O_2/H_2O 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 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.

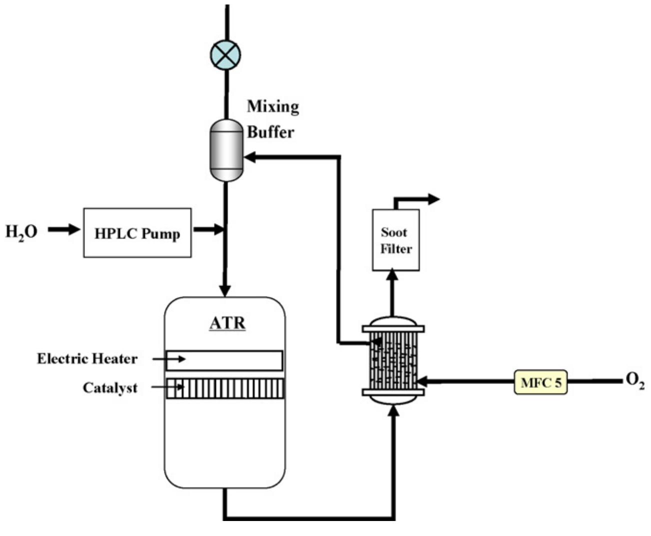

Fig. 1. Scheme for ATR experiment.

Table 1
Several possible reactions taking place in the FT reactor.

Reaction	$\Delta H_{300\,K}$ (kJ/mol)
$CO + 2H_2 \rightarrow -CH_2- + H_2O$	−165.0
$2CO + H_2 \rightarrow -CH_2- + CO_2$	−204.7
$CO + H_2O \rightarrow H_2 + CO_2$	−39.8
$3CO + H_2 \rightarrow -CH_2- + 2CO_2$	−244.5
$CO_2 + 3H_2 \rightarrow -CH_2- + 2H_2O$	−125.2

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].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H_R = 206\,\text{kJ/mol} \tag{1}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2, \quad \Delta H_R = -41.2\,\text{kJ/mol} \tag{2}$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O, \quad \Delta H_R = -519\,\text{kJ/mol} \tag{3}$$

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 ($CO + H_2$) into a mixture of hydrocarbons (synthetic fuel). The FTS reaction can be regarded as hydrogenation of carbon monoxide and is expressed as follows [13].

$$nCO + 2nH_2 \rightarrow -(CH_2)n- + nH_2O, \quad \Delta H_R = -165\,\text{kJ/mol} \tag{4}$$

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 ($CO + H_2$). 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

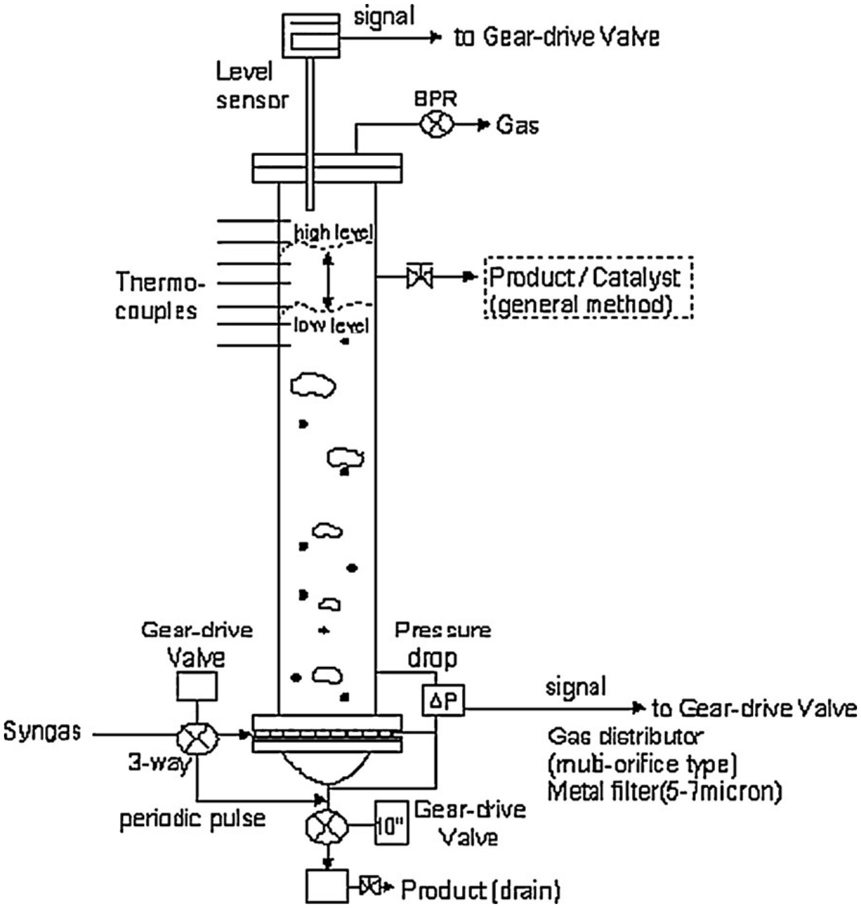

Fig. 2. Scheme for FT synthesis reaction in SBCR (slurry bubble column reactor).

used in most of slurry phase FT reactor models. On the small catalyst particles (less than 50 μm) usually employed in industrial slurry phase reaction systems, intra-particle temperature and concentration gradients are mostly negligible. In this work, therefore, intra-particle mass and heat transfer resistances were neglected. A lot of efforts have been made on FT reaction mechanism and kinetics, which are undoubtedly complex. Several FT kinetic models were studied over Co-based catalysts [18]. The kinetic model was initially coupled through a user-supplied subroutine to the Aspen HYSYS reactor model in order to simulate the slurry phase FT reactor and to validate the model using experimental data [19]. In this work, slurry phase kinetic model was applied to simulate FT reaction, and consequently, to calculate CO conversion. The kinetic model used in this simulation study is express as follows [18].

$$-r_{CO} = \frac{aP_{H_2}P_{CO}}{(1 + bP_{CO})^2} \qquad (5)$$

2.3. Model for FT product distribution

There have been many attempts to model the product distribution of FT process. Hydrocarbon synthesis reaction through FTS can be regarded as a polymerization reaction. Specific selectivity for a particular hydrocarbon and overall product distribution can be described by a chain polymerization kinetics model involving the

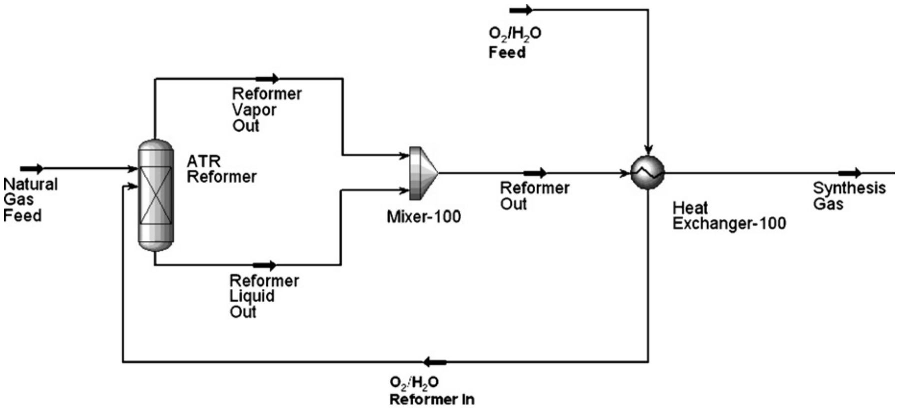

Fig. 3. Simulated PFD (process flow diagram) of ATR for the production of synthesis gas from natural gas (CH_4).

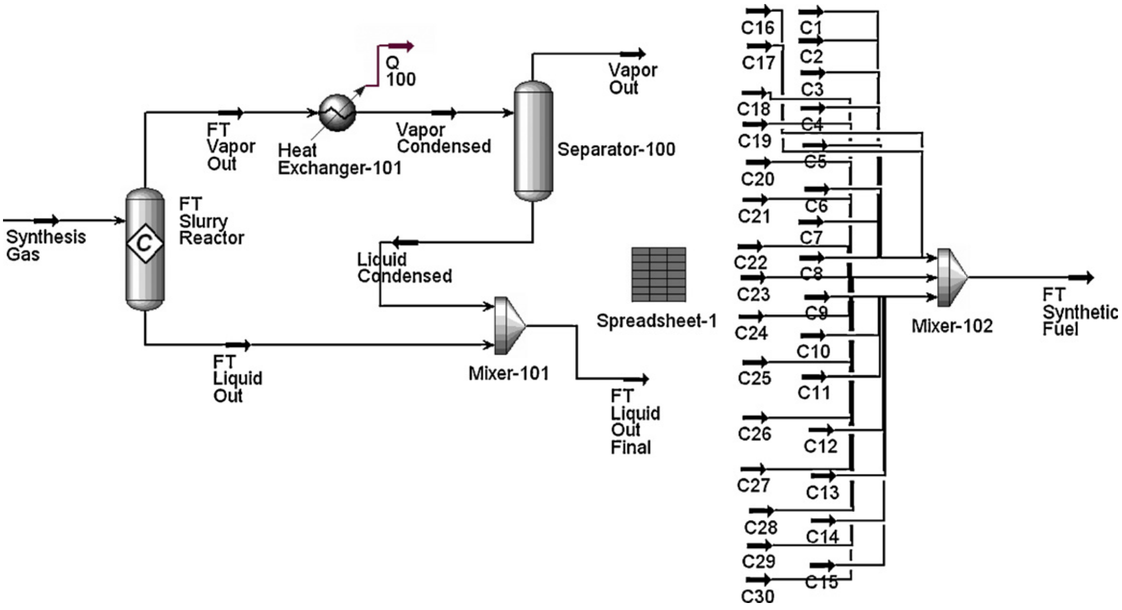

Fig. 4. Simulated PFD (process flow diagram) of FTS for the production of synthetic fuel from synthesis gas (C_1–C_{30}: FTS product stream calculated by kinetics using Aspen HYSYS spreadsheet).

stepwise addition of one carbon to another on the growing chain. In general, product distribution follows some sort of exponential function, with the chain growth probability as an important factor. This model is referred to as Anderson–Schultz–Flory (ASF) model [20], where W_n represents the weight of fraction. Chain growth probability (α) is calculated by the following equation [20].

$$\frac{W_n}{n} = (1-\alpha)^2 \alpha^{(n-1)} \tag{6}$$

2.4. Simulation methodology

It is required to utilize thermodynamic parameters which can be applied to fundamental equation of state for simulating a GTL process by Aspen HYSYS. In the simulation study, accurate model for VLE (vapor–liquid equilibrium) calculation is indispensable. Although many equations of state have been developed, no equation accurately represents all real gases under given conditions. Nonetheless, it is known that RKS (Redlich–Kwong–Soave) equation is useful in calculating VLE thermodynamic properties. Because GTL process is composed of vapor–liquid multicomponents, RKS equation was selected as a governing equation for the determination of thermodynamic parameters in this work. The RKS equation is expressed as follows [21].

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{7}$$

where $a(T) = \{1 + m(1 - T_r^{0.5})\}^2, \quad m = 0.480 + 1.574\omega - 0.17\omega^2$

2.5. Simulation assumptions

Following assumptions were made for modeling of GTL process.

- Process is under steady-state and isothermal conditions.
- Input flow rate of natural gas is constant.
- FTS catalyst is heterogeneous and void fraction between FT catalyst is uniform.
- Catalyst poisoning by H_2S is negligible.

3. Results and discussion

3.1. Comparison of experimental and simulation results for FTS product distribution

Experimental and simulated carbon number distributions of FTS products over Co/Al_2O_3 catalyst are shown in Fig. 5. Upon taking logarithm of Eq. (6), the slope of Eq. (8) becomes $\log\alpha$ (α: chain growth probability) in Fig. 5. Steep slope means that the value of α is small.

$$\log\left(\frac{W_n}{n}\right) = \log\left[\frac{(1-\alpha)^2}{\alpha}\right] + n\log\alpha \tag{8}$$

As shown in Fig. 5, $\log(W_n/n)$ was non-linearly decreased with increasing carbon number in experimental observation. On the other hand, $\log(W_n/n)$ was linearly decreased with increasing carbon number in simulation study. However, the two curves showed the same trend with respect to carbon number. In experiments,

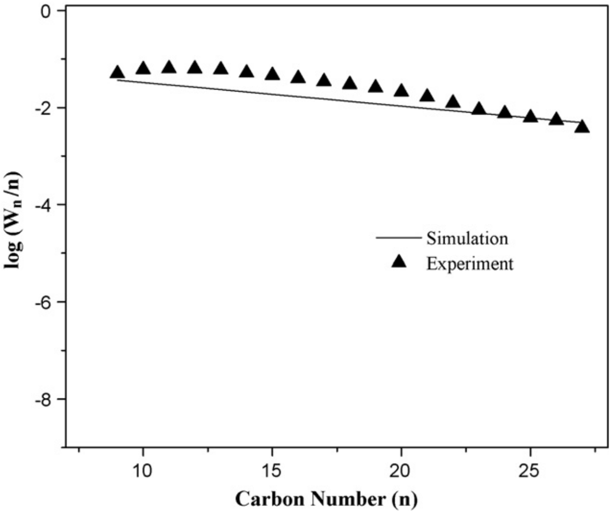

Fig. 5. Experimental and simulated carbon number distributions of FTS products over Co/Al_2O_3 catalyst.

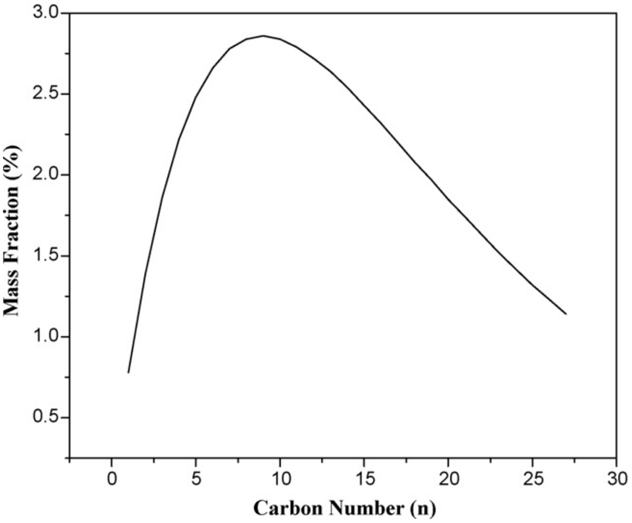

Fig. 6. Mass fraction of FTS products obtained by simulation.

light FT products might be vaporized during the reaction, resulting in non-linear curve. Therefore, it is believed that the slight difference between experimental and simulation results was due to the vaporization of light FT products during the FTS reaction. This can be understood by the fact that the difference between experimental and simulation results became small with increasing carbon number. This result implies that FTS product distribution in heavy carbon number region can be predicted by this simulation model.

Mass fraction of FTS products obtained by simulation is shown in Fig. 6. Mass fraction reached maximum at carbon number around 10. Furthermore, most part of mass fraction was in the range of C_5–C_{20} which serves as useful transportation fuel. In atmospheric condition, hydrocarbons below C_5 are in gas state. The product distribution in such a low carbon number range was not well matched with the ideal distribution due to the occurrence of various secondary reactions. The above results imply that major portion of hydrocarbons was synthetic liquid fuel.

3.2. *Effect of temperature on CO conversion and C_5–C_{20} hydrocarbon yield*

Temperature is one of the major operating variables for CO conversion. CO conversion linearly increases with increasing H_2/CO (feed gas) ratio [22]. However, H_2/CO ratio of 2 is suitable for subsequent FTS process [12].

Fig. 7 shows the effect of temperature on CO conversion in FTS unit. Simulation results showed the same trend as experimental results, with no great difference in CO conversion between two cases. Once again, this result supports that simulation results were reasonably well matched with experimental results. As shown in Fig. 7, both simulation and experimental results revealed that CO conversion reached maximum at around 255 °C. This means that reaction temperature of 255 °C was optimum for FTS reaction. As the FTS reaction is not an equilibrium-limited reaction, there is no limitation on CO conversion theoretically. As reaction temperature goes up, however, bubble formation increases in the slurry phase reactor. This caused the conversion limitation in the FTS slurry phase reaction.

It is known that Aspen HYSYS software has limitation for simulating slurry bed reactor. As shown in Fig. 4, however, simulation for FT slurry bed reaction was conducted using conversion reactor and spreadsheet in order to overcome the limitation of Aspen HYSYS. Conversion in FT slurry bed reactor was linked to spreadsheet. In spreadsheet, the kinetic model for FT slurry bed reactor was used (Eq. (5)). This kinetic model was used for calculating conversion in FT slurry bed reaction. The parameters "*a*" and "*b*" were calculated by FT slurry bed reaction experiments. As the simulation results obtained using spreadsheet conversion link reflected the real situation in a slurry bed reactor, conversion limitation was also observed in simulation results.

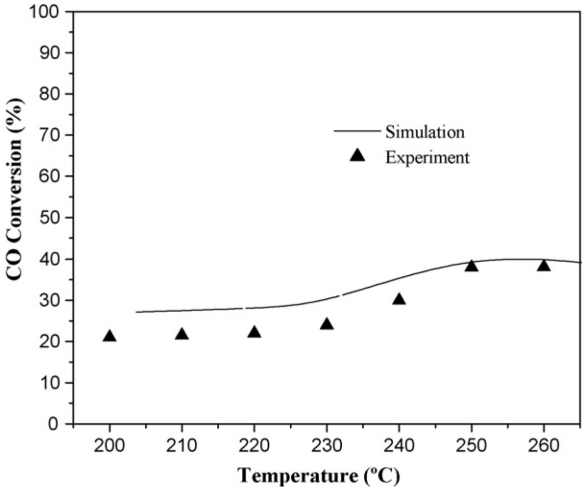

Fig. 7. Effect of temperature on CO conversion in FTS unit.

C_5–C_{20} hydrocarbon selectivity was calculated according to Eq. (9). In simulation, C_5–C_{20} hydrocarbon selectivity was determined by kinetic parameter which was a function of temperature.

$$C_5\text{–}C_{20}\ \text{hydrocarbon selectivity} = \frac{\text{weight of } C_5\text{–}C_{20} \text{ hydrocarbon produced}}{\text{weight of total hydrocarbon produced}} \quad (9)$$

To find an optimum reaction temperature, CO conversion to C_5–C_{20} hydrocarbons was examined by simulation. Fig. 8 shows the effect of temperature on CO conversion to C_5–C_{20} hydrocarbons in FTS unit. CO conversion to C_5–C_{20} hydrocarbons means the yield for C_5–C_{20} hydrocarbons. CO conversion to C_5–C_{20} hydrocarbons was calculated according to the equation 10. As shown in Fig. 8, CO conversion to C_5–C_{20} hydrocarbons showed a volcano-shaped curve with respect to reaction temperature. Maximum CO conversion to C_5–C_{20} hydrocarbons was observed at 255 °C, in good

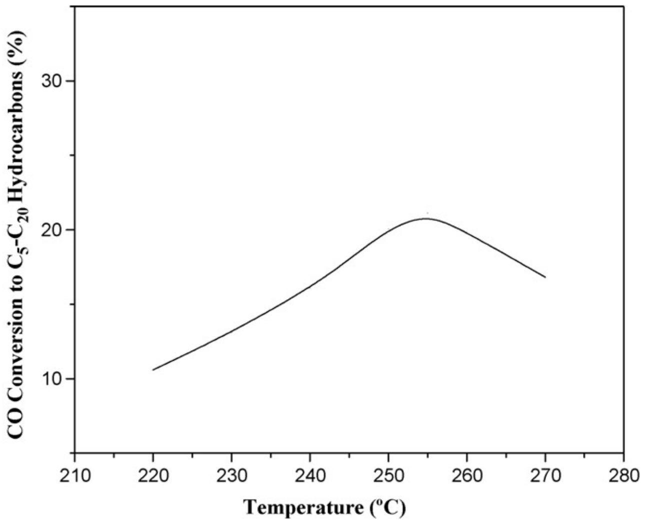

Fig. 8. Effect of temperature on CO conversion to C_5–C_{20} hydrocarbons in FTS unit.

agreement with the result shown in Fig. 7. Thus, optimum reaction temperature in FTS unit was found to be 255 °C.

$$\begin{aligned}&\text{CO conversion to } C_5\text{–}C_{20} \text{ hydrocarbon}\\&\quad = (\text{overall CO conversion} - \text{CO conversion to } CO_2)\\&\quad \times (C_5\text{–}C_{20} \text{ hydrocarbon selectivity})\end{aligned} \tag{10}$$

4. Conclusions

A simulation study on natural gas conversion to FT synthetic fuel was carried out in order to find optimum reaction conditions for maximum production of synthetic fuel. ATR 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 simulation. Optimum reaction conditions for FTS unit were determined by changing reaction variable such as temperature. Optimum reaction temperature in FTS unit was found to be 255 °C. Simulation results were reasonably well matched with experimental results. Thus, simulation model for slurry phase FTS reaction could be utilized to predict FTS performance under different reaction conditions.

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