

GTL Process optimization Simulation Study

[Yong Heon Kim](#)^{1,2}, [Heoung Yeoun Lee](#)¹, [Ki-Won Jun](#)³, [Hyunku Joo](#)⁴, [Chonghun Han](#)¹ and [In Kyu Song](#)¹, (1)School of Chemical and Biological Engineering, Seoul National University, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul, 151-744, South Korea, (2)Petroleum Technology Institute, Korea National Oil Corporation, 1588-14 Gwanyang Dong, An Yang, 431-711, South Korea, (3)Alternative Chemicals/Fuel Research Center, Korea Research Institute of Chemical Technology, 100 Jang-dong, Yuseong-gu, Daejeon, 305-343, South Korea, (4)Air Pollution Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yusong-ku, Daejeon, 305-343, South Korea,

* Corresponding author

Email address : inksong@snu.ac.kr

Tel : + 82-2-880-9227

ABSTRACT

GTL(Gas to Liquids), especially natural gas to FT(Fisher-Tropsch) synthetic fuel, process optimization study was performed in order to find optimum parameters for optimum production. The minimum required energy and optimum operating conditions of GTL process are determined through the changes of system variables, such as temperature, H₂/CO ratio, etc. During the simulation, the overall synthetic processes are assumed to proceed with steady-state reaction of GTL, and catalyst and the physical properties of reacting medium are governed by Redlich-Kwong-Soave (RKS) equation. The reaction model of GTL process are assumed to be composed of ATR syngas(synthesis gas) reforming unit and FTS(Fisher-Tropsch Synthesis) reactor unit.

The simulation procedures are carried out to determine optimum condition of GTL process while varying syngas composition and operating temperature of the reactor. According to simulation results, optimum operating parameters of GTL process are temperature of 255°C and H₂/CO ratio of 2. The simulation results will be compared to the actual experimental data from the lab-scale GTL process which is composed of ATR(Auto Thermal Reforming) reaction and FT slurry phase reaction.

Key Words: GTL, Synthetic Fuel, Synthesis gas, FTS, ATR, Simulation

1. Introduction

There is increasing need about energy conversion process as high oil price lasts. GTL process is one of the most promising way to convert other energy than oil to synthetic fuel. The interest in GTL processes as a way of utilizing associated and remote natural gas is growing. Furthermore, natural gas is a relatively evenly distributed resource. Proven world natural gas reserves, which currently exceed 5,000 trillion cubic feet (TCF), have been growing at a faster rate than proven oil reserves. These gas reserves currently represent over 83% of the energy equivalence of proven oil reserves, of which about 75% is considered to be the less desirable heavy crude. However, for using natural gas pipelines must be constructed and LNG infrastructure which has

manufacturing, shipping, receiving and transporting is indispensable. Therefore, there are many the stranded gas resources not for development by economic reason. About 3,000 TCF of such gas reserves is considered to be stranded; i.e., accessible by drilling but located too far from potential markets for economical transportation to those markets.

GTL process is to convert natural gas to environmental friendly naphtha, kerosene and light oils. GTL synthetic fuel has been suggested recently as a clean alternative fuel. GTL synthetic fuel is a well-known alternative fuel for diesel, gasoline engines due to its good properties, such as environmental advantage. The GTL diesel fuel has near zero sulfur content and aromatic components and a very high cetane number. Thus, this technology contributes to environment and diversification of oil oriented energy usage.

GTL technology generally entails the chemical conversion of natural gas into readily transportable liquids such as methanol or conventional petroleum refinery type distillate fuels. More recently the term GTL has also been more loosely applied to physical conversion processes such as that for liquefied natural gas (LNG) as well as for chemical conversion processes that produce products which may not be in a liquid state under ambient conditions, such as dimethylether (DME). In this paper, we focus on GTL process optimization based on the production of diesel fuel via syngas production, which is consisting primarily of a mixture of CO + H₂, and FTS.

FTS generally involves the synthesis of hydrocarbons and oxygenates from syngas. The types of hydrocarbons produced can include olefins such as ethylene and propylene, and an extremely wide range of saturated hydrocarbons ranging from methane and ethane to long straight chain paraffinic waxes. The oxygenated materials that are produced consist primarily of alcohols such as methanol and ketones such as acetone. When configured to maximize the production of paraffinic hydrocarbons, the resulting intermediate product mix is often described as synthetic crude oil(syncrude). Such syncrudes can be readily refined into desirable distillate fuel fractions such as kerosene, naphtha, and heating oil using conventional petroleum refining techniques. The kerosene can be further refined or blended into high quality diesel or jet fuel products while the naphtha can be further refined into gasoline or used as a thermal cracking feedstock for olefins production.

Catalysts for FTS were first developed in the early 1900s. Following the discovery by Sabatier and Senderens in 1902 that CO could be hydrogenated over Co, Fe, and Ni catalysts to methane, BASF reported the production of liquids over Co catalysts in 1913. Fischer and Tropsch later reported production of hydrocarbons over alkalized iron in 1923. Much of the early catalyst and process development continued in Germany during the 1930s and 1940s. During World War II, coal based FT production played an important role providing the transportation fuel requirements of the German war effort because of insufficient access to crude oil resources. This production was discontinued when the war ended.

Cobalt catalysts as used in the FTS(Fischer-Tropsch Synthesis) are relatively expensive and need to have a high metal dispersion and long life to be able to offer a good balance between cost and performance. The oxidation of nano-sized metallic cobalt oxide during FTS has long been postulated as a major deactivation mechanism.

Supported cobalt catalysts are receiving widespread attention as the preferred FTS catalyst for the GTL process[1-4]. The development of economically attractive cobalt based FTS catalysts with a high stability requires detailed fundamental understanding of the deactivation mechanisms at play for supported nano-sized cobalt crystallites.

In this study, ATR based synthesis gas process and slurry bed reactor based on cobalt

catalyst FTS process is considered. A process simulation with Aspen HYSYS software is conducted to demonstrate the possibly available effects of temperature, H_2/CO ratio, etc. The results will be the baseline for the design and operation of GTL pilot scale process.

2. Technical approach and process simulation

A GTL plant consists of three main process units: a reforming unit where syngas is produced, a FT unit where syngas is converted into liquids(syncrude), and a product upgrading unit where syncrude is upgraded into synthetic fuel. Product upgrading unit is not included in this study. ATR is applied to reforming unit and slurry bed reactor is used for FT synthesis process simulation. A schematic process flowsheets of ATR unit and FTS unit are shown in Figure 1, 2.

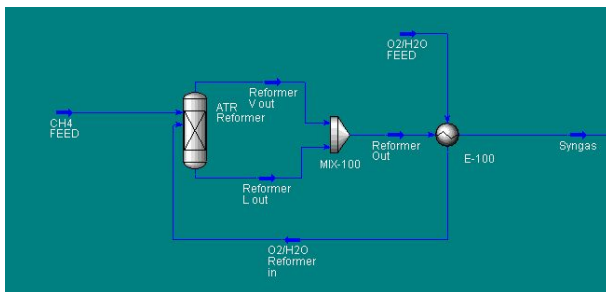


Fig.1. ATR Syngas Production unit simulation PFD

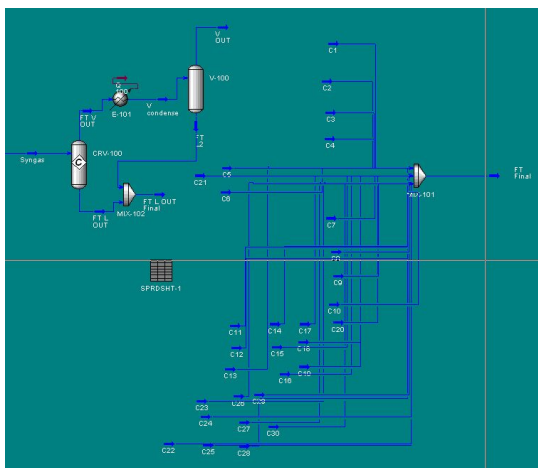


Fig.2. FT FBR Reaction unit simulation PFD

There are some kinds of methods for producing syngas. As a general flow, there is a move toward ATR that uses oxygen. However, because it requires an oxygen plant, thus incurring enormous costs, the issue of excess equipment costs becomes a problem.

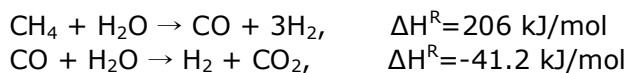
Slurry bed is more efficient in removing the heat of the reaction in the FT synthesis, and because the equipment can be more compact. However, this method still has many unanswered technical issues, such as establishing a method for designing scaled-up systems.

Ni catalyst and Co catalyst are often used in FTS. Due to the high selectivity of Co-based catalysts, a lot of effort has been spent on developing and improving catalysts for use in industrial applications.

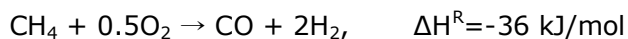
2.1 Reaction Mechanism of GTL Synthesis

2.1.1 ATR process

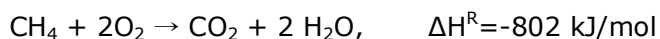
ATR consists of steam methane reforming and partial oxidation. Steam methane reforming, the most commonly used process to produce hydrogen and syngas, can be represented as[13]:



The partial oxidation of methane consists of sub-stoichiometric oxidation written as[14] :



The active catalysts for this process are the same as those used for steam reforming and for total oxidation of methane written as[15] :



ATR technology is the preferred and most cost effective technology for natural gas conversion into synthesis gas to GTL plants. The Oryx GTL plant in Qatar is based on ATR technology at low steam/carbon ratio (S/C=0.6). ATR process produces a synthesis gas with a H₂/CO ratio equal to 2, which is suitable for the subsequent use in the FTS[16].

2.1.2 FT Synthesis process

The FTS is a catalytic process that converts CO and H₂ into a mixture of linear gaseous, liquid and solid hydrocarbons. The FTS is in principle a carbon chain building process, where CH₂ groups are attached to the carbon chain. Which reactions exactly taking place and how, is a matter of controversy, as it has been the last century since 1930's [9]. The main reaction involved in this process can be schematically written as [10]:



There is also other reactions taking place in the reactor, but the detailed behavior of the reactions is not known. The reactions reported are [11]:

Table 1: Reactions taking place in the FT reactor [11]

| Reaction | Reaction enthalpy $\Delta H_{300\text{K}}$ [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 |

These reactions are highly exothermic, and to avoid an increase in temperature, which results in lighter hydrocarbons, it is important to have sufficient cooling, to secure stable reaction conditions [10]. The total heat of reaction amounts to 25 % of the heat of combustion of the synthesis gas [11], and lays thereby a theoretical limit on the maximal efficiency of the FT process.

The reaction is dependent of a catalyst, mostly an iron or cobalt catalyst where the reaction takes place. There is either a low or high temperature process (LTFT, HTFT), with temperatures ranging between 200-240 °C for LTFT and 300-350 °C for HTFT [12]. The HTFT uses an iron catalyst, and the LTFT either an iron or a cobalt catalyst.

The different catalysts include also nickel and Ru based catalysts, which also have enough activity for commercial use of FT. But the availability of Ru is limited, thus forcing a high price. The nickel based catalyst has high activity but produces too much methane, and additionally the performance at high pressure is poor, due to production of volatile carbonyls. This leaves only cobalt and iron as practical catalysts, and this study will only consider these two. Iron is cheap, but cobalt has the advantage of higher activity and longer life, though it is on a metal basis 1000 times more expensive than iron catalyst [9].

Cobalt-based catalysts have been successfully applied in the industrial processes due to their high FT activity and their low oxygenates selectivity, which makes this catalysts suitable for the H₂-rich syngas obtained from natural gas.

2.2 Reaction Kinetics of GTL Process

The Aspen HYSYS reactor was used to simulate the ATR process. In this step, methane is converted to syngas, CO and H₂.

Dry [6] and Huff and Statterfield [7] showed that when hydrogen conversion is below 60% the first-order FT kinetics is a good approximation. Except in a few more detailed approaches [8] linear kinetics is used in most of the previous FT slurry models. Given the small solids particle size (50µm and smaller) usually encountered in industrial

slurry systems, intra-particle temperature and concentration profiles are most often negligible. Therefore, solids intra-particle mass and heat transfer resistances are presently neglected.

There are a lot of efforts that have been made on FT reaction mechanism and kinetics, which is undoubtedly complex. Table 2 shows the studies about Co catalyst based FT kinetic model.

Table 2: Co catalyst based FT kinetic model

| Reactor Type | Kinetic expression | Study |
|----------------------|--|-------|
| Fixed Bed Reactor | $-r_{CO} = \frac{aP_{H_2}P_{CO}^{0.5}}{(1+bP_{CO}^{0.5})^3}$ | [18] |
| Fixed Bed Reactor | $-r_{CO} = \frac{aP_{H_2}^{0.6}P_{CO}^{0.65}}{(1+bP_{CO})}$ | [19] |
| Slurry Phase Reactor | $-r_{CO} = \frac{aP_{H_2}P_{CO}}{(1+bP_{CO})^2}$ | [20] |

This 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 validate the models using the experimental data[21].

Slurry phase kinetic study was applied to simulate FT reaction. It was used for calculating CO conversion.

Modeling FT-product distributions

There have been many attempts to model the product distributions of the FT process. The hydrocarbon synthesis reactions involved in FTS may be regarded as analogous to a polymerization reaction. An essential characteristic of catalysts applied to FT diesel production therefore is the ability to catalyze chain propagation versus chain termination steps. The specific selectivity for a particular hydrocarbon and the overall product distribution may generally be described by a chain polymerization kinetics model involving the stepwise addition of one carbon to another on the growing chain.

There are deviations between inspected product distributions and the different models when the conditions are changed. But there is an agreement in literature that the distributions follow some sort of exponential function, with the probability of chain growth as an important factor. The methodology is mainly divided into a kinetic approach and a thermodynamic approach. The best known model of the latter kind was developed in the early years of FT-synthesis, where a constant probability of chain growth was assumed. This model has been ascribed to Anderson, Schultz, and Flory and is commonly referred to as the Anderson-Schultz-Flory (ASF) model.

$$W_n / n = (1 - \alpha)^2 \alpha^{(n-1)}$$

(The W_n is equal the weight fraction)

Chain growth probability(α) is calculated by experiment based on Co catalyst[21].

2.3 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. Many equations of state of varying complexity have been developed. No equation is sufficiently accurate to represent all real gases under all conditions. In this simulation study, RKS (Redlich Kwong Soave) equation is utilized for calculating thermodynamic parameters in the model. RK (Redlich-Kwong) equation of state is an extension of the more familiar van der Waal's equation. The RK equation is not suitable for use near the critical pressure, or for liquids. The RK equation is widely applied to binary components.

It has good accuracy in volumetric and thermal properties between pure components and mixture, but it is tend to lower accuracy of VLE (Vapor Liquid Equilibrium) calculation in multi-components. Giorgio Soave (1972) modified the RK equation to extend its usefulness to the critical region and for use with liquids in order to make up for the weak point of RK state equation. This equation is written as[17] :

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

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

Because GTL process is composed of multi-components accompanied with vapor-liquid phase, RKS equation is selected as governing equation for simulating of GTL process.

2.4 Simulation Assumptions

The following assumptions were considered in modeling GTL process:

- Process is steady state and isothermal
- Constant input flow rate of natural gas
- GTL synthesis catalyst is composed of homogeneous catalyst and charged with constant void fraction of catalyst bed in the GTL reactor
- Catalytic poisoning effected by H₂S neglected

3. Results and discussion

Simulation RESULTS

3.1 Comparison of experimental and simulation results in FT product distribution

The experimental carbon distribution with Co based alumina support catalyst and simulation results are shown in Fig.3. As non-linear form, $\text{Log}(W_n/n)$ decreases while carbon number increases. In simulation study, $\text{Log}(W_n/n)$ increases linearly while carbon number increases.

Mass fraction FT product distribution by simulation study is shown in Fig.4. Mass fraction reached maximum for carbon number region around 10.

There is a slight difference in FT product distribution between simulation output and actual FT product behavior. The difference between experimental value and simulation value is explained by actual discrepancy of ASF distribution in FTS. But the heavier the carbon is, the smaller the difference between actual distribution and simulation output. Therefore, in heavy carbon region, FT product distribution can be predicted by this simulation model.

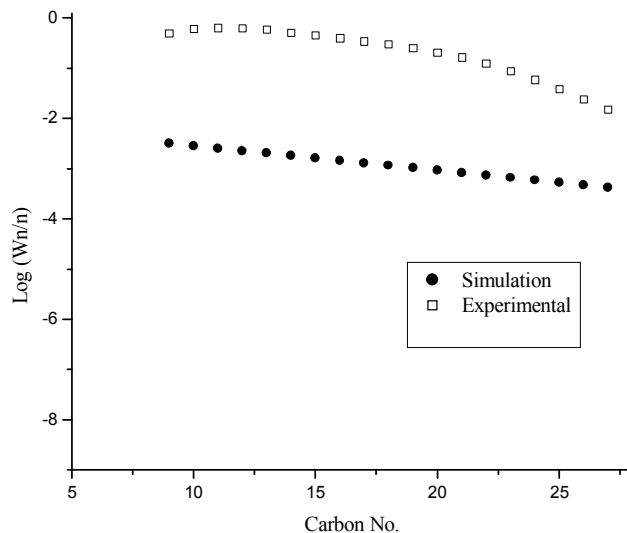


Fig.3. Co based catalyst FT Product carbon number distribution

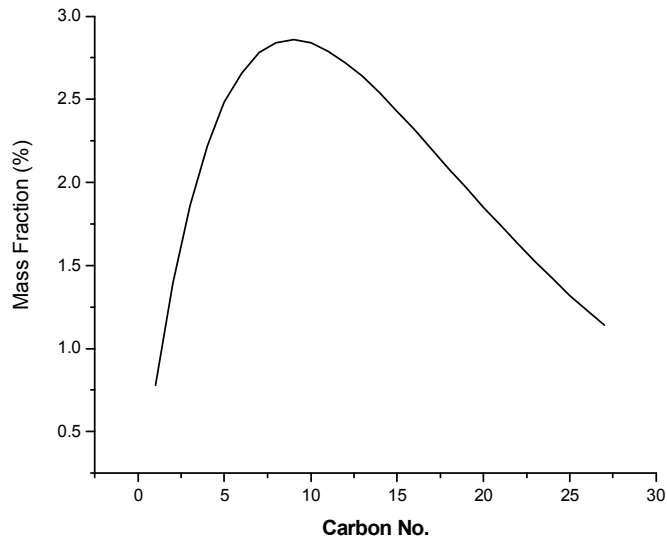


Fig.4. Product distribution by simulation

3.2 Effect of H₂/CO ratio

The influence of the H₂/CO ratio on CO conversion was also studied. The effect of the H₂/CO ratio on CO conversion is shown in Fig.4. CO conversion reached maximum for a H₂/CO ratio of 2.0 as indicated in Fig.4.

Simulation shows good agreement with experimental data. Fig.4 demonstrates good prediction of FTS reaction condition in H₂/CO ratio.

In syngas process, H₂/CO ratio produces 3:1 in SMR (Steam Methane Reforming). In ATR process, H₂/CO ratio is around the desired level of about 2:1. So, ATR has advantage for FTS in H₂/CO ratio.

In actual plant, for the low-temperature FT (LTFT, 200-240°C) process, the H₂/CO ratio is about 1.8 and so is suitable as feed gas to the wax producing LTFR reactors.

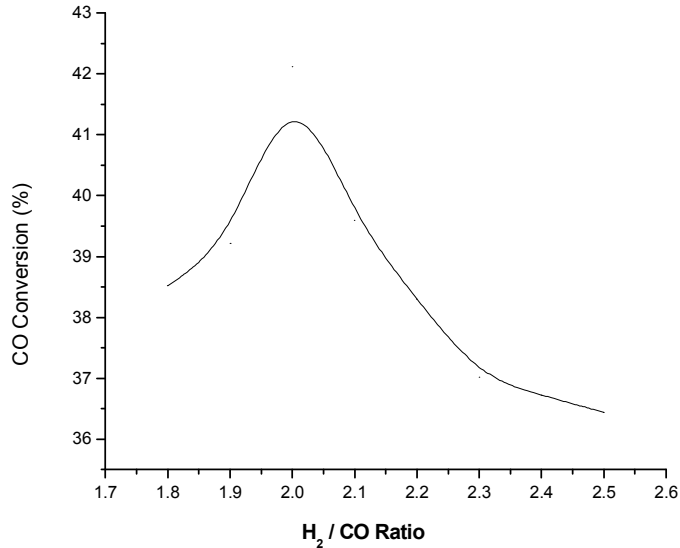


Fig.5. Effect of H₂/CO ratio on CO conversion

3.3 Effect of Temperature on CO conversion and C5+ selectivity simulation case vs experimental case

The simulation results varying reaction temperature of FTS are shown in Fig.6. CO conversion reached maximum for 255°C of reaction temperature both experimental case and simulation case.

In low temperature region (below 240°C), CO conversion is relatively lower. Therefore, the optimum operating temperature for high CO conversion is 255°C in this study by experimental and simulation output.

The C5+ selectivity drops rather sharply in experiment case than in simulation case. These results are shown in Fig.7. The C5+ selectivity decreases slightly while temperature is increased in simulation study. In experiment, The C5+ selectivity decreases remarkably while temperature is increased.

In simulation study, optimum temperature considering CO conversion and C5+ selectivity is around 250°C because of the slight decrease of C5+ selectivity in this temperature region. But actual optimum temperature considering both CO conversion and C5+ selectivity is around 220~230°C.

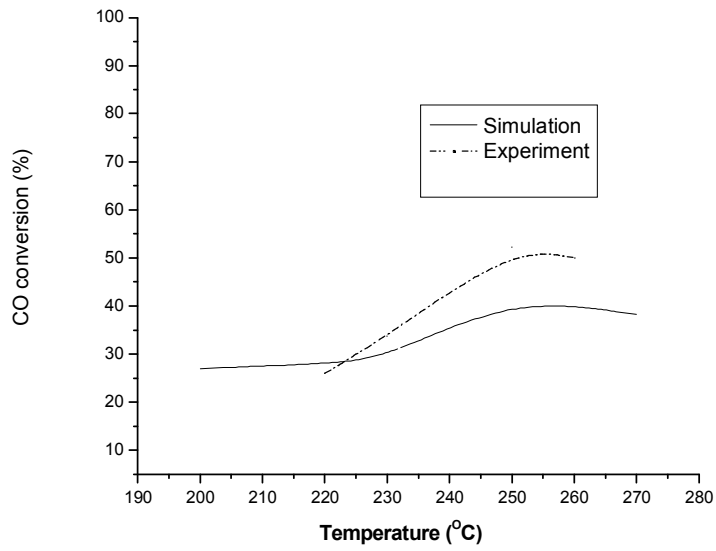


Fig.6. Effect of Temperature on CO conversion simulation case vs experimental case

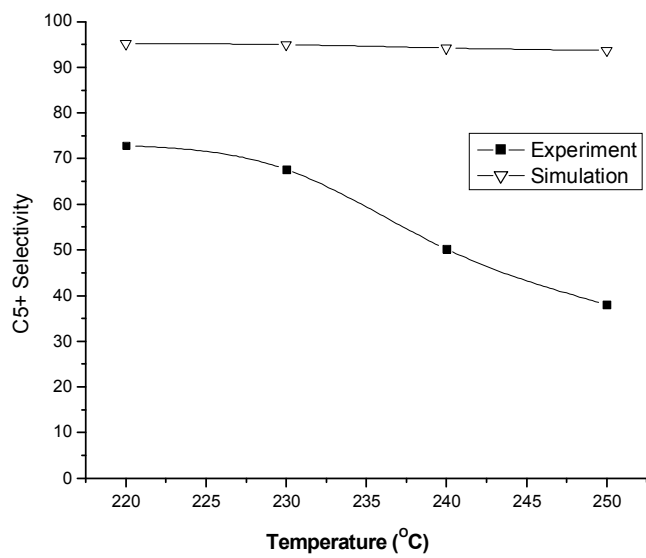


Fig.7. Effect of Temperature on C5+ Selectivity

5. Conclusions

The GTL process simulation can be simulated by the flow sheeting program in Aspen HYSYS. The results of this simulation and the actual results obtained in experiment are practically in reasonable agreement with each other.

Simulation of the processes, including chemical reactions and heat/mass balance, was carried out with Aspen HYSYS software. The effects of temperature on CO conversion, C5+ selectivity and the effects of H₂/CO ratio on CO conversion were discussed. According to simulation results, optimum operating parameters of GTL process are temperature of 255°C and H₂/CO ratio of 2.

Acknowledgement

The authors express their gratitude to Korea GTL Research Consortium (SK energy, Daelim Cor., KNOC, Doosan Mecatec). Special thanks are also extended to Dr.Bae for his valuable comments provided toward accomplishing this study.

Nomenclature

- ω : acentric factor
 W_n : weight fraction
 α : chain growth probability
 T_r : reduced temperature

References

- [1] P. van Berge, S. Barradas, J. van de Loosdrecht, J.L Visagie, Erdol Erdgas Kohle 117 (3) (2001) 138.
- [2] The Catalyst Review Newsletter, Gas-to-Liquids : Peering into the Crystal Ball, 2005, p. 4.
- [3] M.M.G. Senden, A.D. Punt, A. Hoek, Stud. Surf. Sci. Catal. 199 (1998) 943.
- [4] A.P. Steynberg, M.E. Dry, Fischer-Tropsch technology, Stud. Surf. Sci. Catal. 152 (2004) 441.
- [5] The Catalyst Review Newsletter, Gas-to-Liquids : Peering into the Crystal Ball, 2005, p. 4.
- [6] M.E. Dry, Advances in Fischer-Tropsch chemistry, Ind. Eng. Chem. Prod. Res. Dev. 15 (1976) 282.
- [7] G.A. Huff Jr., C.N. Satterfield, Intrinsic kinetics of the Fischer-Tropsch synthesis on a reduced fused-magnetite catalyst, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 696.
- [8] G.P. van der Laan, A.A.C.M. Beenackers, R. Krishna, Multicomponent reaction engineering model for Fe-catalyzed Fischer-Tropsch synthesis in commercial scale slurry bubble column reactors, Chem. Eng. Sci. 54 (1999) 5013.

- [9] Dry, Mark E, High quality diesel via the FS process - a review, *Journal of Chemical Technology and Biotechnology*, 77/2001, 43-50.
- [10] Fürnsinn, Stefan, Ripfel, Karl, Rauch, Reinhard, Hofbauer, Hermann, Diesel aus Holz - Die FS Synthese als zukunftsweisende Technologie zur Gewinnung flüssiger Brennstoffe aus Biomasse, 4. Internationale Energiewirtschaftstagung an der TU Wien, 2005.
- [11] Rauch, Reinhard, Biomass Gasification to produce Synthesis Gas for Fuel Cells, Liquid Fuels and Chemicals, IEA Bioenergy Agreement, Task 33: Thermal Gasification of Biomass (2001-2003)
- [12] Dry, Mark E., The Fischer-Tropsch process: 1950-2000, *Catalyst today*, 71/2002, 227-241.
- [13] J. Sehested, *Catalyst today* 111 (2006), 103.
- [14] Y.S Seo, A. Shirley, S.T. Kovalaczkowski, *J. Power Sources* 108 (2002), 213-225
- [15] T.S.Christensen, I.I.Primdahl, *Hydrogen Processing*, March 1994, p39-46
- [16] K. Aasberg-Petersen, T.S. Christensen, C.S. Nielsen, I. Dybkjaer, *Fuel Process. Technol.* 83 (2003), 253
- [17] Giorgio Soave, *Chemical Engineering Science*, 27, 1197 (1972)
- [18] A.O.I. Rautavuoma, H.S. van der Baan, *Apply Catalysis*, 1 (1981), 247-272
- [19] E. Iglesia, S.C. Reyes, S.L. Soled, in: E.R Becker, C.J. Pereira (Eds.), *Computer-Aided Design of Catalysts*, Dekker, New York, 1993
- [20] I.C. Yates, C.N. Satterfield, *Energy and Fuels* 5 (1991), 168-173
- [21] S-H Song, S-B Lee, J-W Bae, P.S Sai Prasad, K-W Jun, *Catalysis Communications* (2008), 2284