Conversion Enhancement of Pilot Scale Fixed Bed Reactor for Fischer-Tropsch Synthesis

Phavanee Narataruksa\textsuperscript{a,c}, Sabaithip Tungkamani\textsuperscript{b,c}, Karn Pana-Suppmassadu\textsuperscript{a,c},
Monrudee Phongaksorn\textsuperscript{b,c}, Siriluck Nivitchanyong\textsuperscript{d}, Piyapong Hunpinyo\textsuperscript{a,c},
Prayut Jiumrittiwong\textsuperscript{a,c}, Hussanai Sukkathanyawat\textsuperscript{b,c}

\textsuperscript{a}Department of Chemical Engineering (ChE), Faculty of Engineering, King Mongkut’s University of Technology North Bangkok, 10800
\textsuperscript{b}Department of Industrial Chemistry (IC), Faculty of Applied Science, King Mongkut’s University of Technology North Bangkok, 10800
\textsuperscript{c}Research and Development Center for Chemical Engineering Unit Operation and Catalyst Design (RCC),
King Mongkut’s University of Technology North Bangkok, 10800
\textsuperscript{d}National Science and Technology Development Agency (NSTDA), Pathumthani, 12120

*Corresponding Author. 1518 Pibulsongkram Road, Wongsawang, Bang-Sue, Bangkok 10800, Thailand.
Tel: (+662)-913-2500#8230, Mobile phone: (+6689)-002-7027
E-mail: phn@kmutnb.co.th or lookmeawoun@hotmail.co.th

Abstract: The fluctuation of crude oil prices is presently reaching a crisis. The root of this problem has emerged from the fact that a petroleum resource has been continuously depleted and couldn’t meet the demand. A renewable energy derived from biomass has become one of the very promising resources in Thailand. Biomass alteration through gasification has gained more attentions recently. The biomass derived syngas mainly comprises CO (g) and H\(_2\) (g), which is suitable for being the feed reactant for the Fischer-Tropsch (FT) process to produce liquid fuel. The present research aims to investigate a continuous FT fixed-bed reactor, which is an essential component of a liquid-fuel production process from biomass. The pilot scale fixed bed reactor (diameter of 10 cm, height 90 cm) was adopted in this study. Three steady-state experiments were performed for finding optimum operating conditions. Continuous feeds of modeled syngas of 6, 18, and 29 slpm (H\(_2\)/CO molar ratio 2/1) were passed onto a fixed Ru supported alumina catalyst bed. The reactions were carried out at 180-220°C and 1-3 bars. The experimental results revealed that the CO conversion for the case using the syngas of 6 slpm gave the highest conversion of 66.7% and the highest overall selectivity of 67.29% (C5+).

Keywords: Pilot Scale, Fixed Bed Reactor, Fischer-Tropsch Synthesis

1. Introduction
The demand for transportation oil continues to increase in Thailand. The Thai government has tried to solve this energy issue via supporting various routes of alteration fuels such as biodiesel and bioethanol. However, most of raw materials used for those bio-fuels productions can be very limited since they have to be shared with the food markets. Therefore, in the near, middle and long term, Thailand’s energy policy was written in the way to support other sustainable energy technologies using non-food bio-materials (15 yrs from 2009 to 2014). One of possible technology routes is the Biomass-to-Liquids (BTL). BTL is the integrated process of syngas production between biomass gasification, and hydrocarbon production from Fischer-Tropsch process.

Gasification is primarily a thermo-chemical process, converting biomass into combustible gases or syngas (a mixture of CO, H\(_2\) and CH\(_4\)) at elevated temperatures. The syngas can proceed to be the reactants for Fischer-Tropsch reactions in order to produce various ranges of hydrocarbons such as synthetic kerosene, diesel, and wax. Raw materials of BTL process can be many kinds of biomass such as chaff, rice straw, trash and palm shell, which are available in Thailand. These materials are currently used to provide the nation as a direct thermal
energy, power, and electricity [2]. Recently in Germany, CHOREN’s Carbo-V® gasification process has been developed in its ability to overcome many drawbacks has arose from adopting biomass with alternative of synthetic liquid fuels [3]. Also in Thailand, many organizations have discussed about research and development of gasification technologies for more than 20 years. Among many agricultural countries, Thailand was mentioned as the suitable location for the commercial biomass gasification projects. Then, to further develop the BTL process to produce a wide spectrum of hydrocarbons has become the major focus R&D projects to represent the conversion of biomass to liquid transportation fuels. With this reason, an interest in the study of the Fischer-Tropsch synthesis (FTS) has regained the attentions. Fuels from FTS such as FT diesel have been proven to be used as a transportation fuel directly or partially blended to improve the performance of the conventional diesels. Besides, it has no sulphur and aromatic compounds and therefore it can burn more efficiently and cleanlier [4].

The Fischer-Tropsch reactions have been considered as the polymerization type of chemical reactions. To carry on the FTS, the mixture of carbon monoxide (CO) and hydrogen (H₂) have to stay within the catalytic bed under the suitable physical and thermodynamic conditions in order to obtain a designed range of hydrocarbons at a specific conversion. In this research work, the pilot scale fixed bed with ruthenium supported alumina oxide catalyst was used as the FT reactor to investigate the reaction performance focusing on the once through conversion together with the product selectivity. The major aim of this research is to find out the feed conditions that can give the highest conversion and selectivity at specified temperature, pressure, and feed ratio of H₂/CO. The results in terms of the hydrocarbon product distribution obtained from the pilot scale operations would be also compared with that obtained from the related lab scale experiments and reasonably explained.

2. Methodology

2.1 Small scale fixed bed reactor

In the early 2008, KMUTNB by Research and Development center for Chemical Unit Operation and Catalyst Design (RCC) was granted from The National Science and Technology Development Agency (NSTDA) to carry out a research project focusing on the design, synthesis and analysis of Fischer-Tropsch catalysts. Two years later, the scope of work was extended to scaling-up the catalyst production to meet adequacy for a larger scale reactor. Ruthenium (Ru) was again chosen as the active metal for providing high selectivity in the range of C9-C24 meaning a high yield of diesel.

Laboratory implementations of the FT catalysts were initially conducted in a small scale fixed bed reactor. This reactor had an internal diameter of approximately 10 mm and fitted with 2.5 mm thermo-well. Catalyst pellets were formed as 355-600 micron in particle size. The reaction set consisted of a feed section, reactor module and product analysis/product collection section, which were shown in Fig. 1. The reactor module was a metal tube surrounded by an electric furnace with a single-zone temperature controller. Temperature was measured by a K-type thermo-well located inside and outside of the catalytic bed. For product analysis, samples of gas and liquid products were collected over a period of time and analyzed by gas chromatography. The volume of gas at the outlet was measured by a bubble gas rota-meter.
2.2 Pilot scale fixed bed reactor

In 2010, RCC was supported by NSTDA to construct a pilot plant of FTS. The aim of this project was to design and commissioning a catalytic rig, which can be used to test the reaction and system performance of the pilot scale fixed bed reactor. A larger loading tested in the pilot reactor was expected to give useful insights concerning the limitations of heat and mass transfer, catalyst deactivation, and system controllability all of which a small loading tested in the small scale reactor impossible to provide. The pilot reactor was a 10-cm external diameter reactor fitted with a three-zone thermo-well inside the catalytic bed. A single-zone electric heating system was exploited to provide the thermal energy needed. The design of the pilot scale fixed bed reactor and supporting systems followed the development of the reactor design, efficient catalyst regeneration methods and the integrated reactive system in order to achieve the optimum efficiency i.e., simple structure, ability to be fabricated within the country, controllability, easy maintenance and operation, detachability and endurance [6].

Design of the pilot system was different from the small scale system in such a way that the expanded pre-heater section, product separation/product collection section and more precise devices for manipulating process variables were integrated. The pilot system was designed to overcome operability problems, and to be operated continuously with the use of system monitoring and safety devices. Diameters of tube (D) and particle (D_p) used for the pilot reactor module were in accorded with the value of D/D_p applied in the small scale reactor units. Apart from the temperature control equipments, a pressure control device was installed after the reactor. All pressures and pressure difference across the bed were monitored and controlled. These installations enabled successful operation of the reactive system. The schematic of the pilot reactor was exhibited in Figure-2.

To monitor and control the pilot reacting system, the commercial software LabVIEW™ was adopted to communicate between an operator with a personal computer and all of monitoring and control equipments. Control screens interface were utilized to adjust and/or monitor process parameters such as temperatures, gas flow rates, pressures, and on/off status of certain valves. Important operating parameters were recorded and trended on data logging screens. History data can also be viewed via data logging functions.
Fig. 2. (a) Photographs of a FTS pilot scale apparatus, (b) Control screens interface of pilot reacting system

3. Results and discussion

Three experimental runs were performed using the FTS pilot scale apparatus in order to find the run that could provide the highest conversion. Three different continuous feeds of syngas (H₂/CO molar ratio 2/1) were passed onto a fixed Ru supported alumina bed (details as shown in Table-2). The reactions were carried out by trying to maintain the reaction temperature at 180-220 °C and pressure at 1-3 bars. The first experimental run (Run 1) had the inlet syngas flow of CO : H₂ : N₂ at 3 : 6 : 4-9 slpm. The reaction temperature and pressure were successfully controlled between 180-220°C and at 1 bar respectively. The testing period for this run was 20 hours and the thermodynamics equilibrium and steady state was approached within the first operating hour. Reaction conversion and the overall selectivity were calculated using equations (1) and (2) to be 21.05 % and 52.65 %, respectively. To increase reaction conversion, the second experimental run (Run 2) was initiated. The underline principle was to increase the operating pressure in order to overcome mass transfer limitation in the heterogeneous system. Run 2 had the inlet syngas flow of CO : H₂ : N₂ at 3 : 6 : 15-20 slpm and the controlled pressures between 1.5 to 3.5 bars. More N₂ was needed for this Run to maintain the reaction temperature at 180-220 °C. The total run time was 5 hours. As a result, the higher conversion of 37.73 % was obtained but the overall selectivity was reduced to 12.18 %. The reason should be that the increase of reaction pressure affected directly the initiation step of FTS so that CO conversion was higher than that of the first run. However, with the higher conversion, a larger amount of heat must be removed and more N₂ was fed into the reactor as mentioned. This suppressed the partial pressures of the reactants (CO and H₂) and possibly caused the chain propagation step of the FTS to slow down as shown by the smaller value of the overall selectivity.

\[
\text{CO Conversion} \, (\%) = \frac{\text{Moles of CO Consumed}}{\text{Moles of CO Fed into Reactor}} \quad (1)
\]

\[
\text{Overall Selectivity} \, (\%) = \frac{\text{Moles of C - atom found in Liquid Product}}{\text{Moles of C - atom Consumed}} \quad (2)
\]

where CO is the carbon monoxide reactant and C is the carbon atom.
Table-1. Experimental results for different reaction conditions in a prototype reactor

<table>
<thead>
<tr>
<th>Runs</th>
<th>Ratio (slpm)</th>
<th>Temperature °C</th>
<th>Pressure (atm)</th>
<th>Temperature °C</th>
<th>Pressure (atm)</th>
<th>Time on stream (hr)</th>
<th>Diesel : Water (ml)</th>
<th>Diesel : Water (ml/hr)</th>
<th>Conversion (%)</th>
<th>Overall Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO: H₂ : N₂</td>
<td>3 : 6 : 4-9</td>
<td>180-220</td>
<td>(1)</td>
<td>20</td>
<td>38.5 : 558</td>
<td>1.9 : 27.9</td>
<td>21.05</td>
<td>52.65</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CO: H₂ : N₂</td>
<td>3 : 6 : 15-20</td>
<td>180-220</td>
<td>(1.5-3.5)</td>
<td>5</td>
<td>3 : 250</td>
<td>0.6 : 50</td>
<td>37.73</td>
<td>12.18</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CO : H₂</td>
<td>2 : 4</td>
<td>180-220</td>
<td>(1)</td>
<td>3</td>
<td>10.5 : 177</td>
<td>3.5 : 59</td>
<td>66.70</td>
<td>67.29</td>
<td></td>
</tr>
</tbody>
</table>

Due to the main products of this work should be liquid hydrocarbons (C5+), the third experimental run (Run 3) was then conducted. The objective of the third run was to enhance the reaction conversion as well as the overall selectivity. The idea was not to add N₂ with the gas reactants, so the partial pressures of CO and H₂ were occupied the total feed in. However, the system without N₂ faced to the problem of the largest amount of heat release from the exothermic FTS. Reducing of the CO and H₂ from 3 : 6 to 2 : 4 slpm was necessary in order to maintain the reaction temperatures between 180-220 °C at 1 bar. The total run time of this run was 3 hours. The results showed the highest conversion of 66.70% and the highest overall selectivity of 67.29%. Although, the results cannot properly be compared with the first two runs due to the difference in the value of Gas Hour Space Velocity (GHSV: presentation of reactant fed rate per gram catalyst usage). The increases in both reaction conversion and selectivity found from this run can lead us to the significant ideas of how to improve the system performance. To utilize the effective cooling system was then agreed to be the next approach in order to process the syngas without or with low N₂ containment, in which high conversion and selectivity can be expected.

The results in terms of the hydrocarbon product distribution obtained from the pilot scale operations were also compared with that obtained from the lab scale experiments as shown in Figure-3. All of the distribution curves show the same pattern whereas the product peak appeared between hydrocarbon C5 and C24 (diesel range). Therefore, it is a good sign that all proposed techniques used to promote for higher conversion did not significantly interrupt the process of termination step of the FTS. However, future works need to be done to find the most appropriate technique to compromise between the reaction conversion and selectivity.
Fig. 3. Liquid sample (C5+) accumulated over different reaction conditions in a pilot scale reactor (a) represents the chromatographic peak of CO : H₂ : N₂ as 3 : 6 : 9 slpm under atmospheric pressure, (b) represents the chromatographic peak of CO : H₂ : N₂ as 3 : 6 : 15-20 slpm under pressurized condition, (c) represents the chromatographic peak of CO : H₂ as 2 : 4 slpm under atmospheric pressure, and liquid sample approximately accumulated over a further 36 hr in a small scale reactor (d) represents the chromatographic peak of 180°C, 1.5 atm, and H₂/CO = 2.

4. Conclusions

Improvement of the overall efficiency of the pilot scale FTS reactor is still a big challenge. The works appeared in this paper were considered as the first group of experiments which can be very useful results to do further study on investigation of optimum FTS conditions to produce transportation fuels. Also, the information will further be used as the primary operating conditions for kinetic study as future works. However, it must be kept in mind that catalyst design and reactor type are the significant effects on FT reaction conversion and product distribution. Applying the results from this works should be careful on the system
characteristics which should not be far from those proposed in the methodology section. Otherwise, reproducible results may not be obtained.

5. Acknowledgments
The authors are gratefully appreciated for the project financial granted by The National Science and Technology Development Agency (NSTDA), Thailand.

6. References
[1] www.eppo.go.th