Production of biofuel by low temperature Fischer-Tropsch using Co-K/γ-Al_2O_3

I.G.B.N Makertiahtha, Fadhli, Zaki Al Fathoni, Subagjo

Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132 Indonesia

E-mail: makertia@che.itb.ac.id, fadhli@che.itb.ac.id

Abstract. Fischer Tropsch is a heterogeneous catalytic chemical reaction which converts a mixture of hydrogen and carbon monoxide (syngas) into a hydrocarbon product with varying chain length by polymerization reaction on the surface of the catalyst. The hydrocarbon produced from Fischer Tropsch reaction using bio-syngas is biofuel (diesel, kerosene, gasoline) that can replace petroleum-based fuels. Cobalt catalyst with potassium promoter and γ-Al_2O_3 support has been successfully synthesized in Catalysis and Reaction Engineering (CaRE) laboratory, Institut Teknologi Bandung (ITB). Co-K/γ-Al_2O_3 catalyst was prepared by dry impregnation method on the γ-Al_2O_3 support under alkaline conditions. Catalysts were characterized using X-Ray Diffraction (XRD), temperature program reduction (TPR), and N_2 physisorption measurements such as Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods. Co-K/γ-Al_2O_3 catalyst activity was evaluated using fixed bed reactor with various flow rates and temperatures which is still classified as Low-Temperature Fischer Tropsch (LTFT) process. The best results were obtained at minimum syngas flow rate and highest reaction temperature with a total pressure of 20 bar. The results show CO and H_2 conversion were 96.6% and 82.31% respectively. Selectivity value of the hydrocarbon product was calculated using the Anderson Shultz Flurry (ASF) equation. The greatest selectivity value was obtained for C_5+ product with selectivity value was 86.07 % wt.

1. Introduction
Dependence on fuel derived from fossil becomes a serious problem in the next few decades. It is estimated that the total world energy consumption is 13,864.9 Mtoe (Million tons of oil equivalent) in 2018, the percentage of fossil fuel use reaches 84.7% [1]. This led the researchers to be able to find synthetic liquid fuels that could be used generally and commercially. Several fuel synthesis technologies based on conversion technology XTL (X to Liquid) began to be developed, one of which is the Fischer Tropsch process.

The Fischer Tropsch process is a syngas conversion process (CO + H_2) derived from natural gas, coal, or biomass into long chain hydrocarbons that can be upgraded to diesel or kerosene fractions [2]. Processing of Fischer Tropsch synthesis products can be done by hydrocracking reactions to form fuel products according to what is needed, such as jetfuel, diesel or gasoline [3]. Fischer Tropsch process has become an important key in XTL technology producing fuel, chemical compounds, and other hydrocarbon products [4].
Fischer Tropsch reaction is a catalytic reaction by metals such as Fe, Co, Ru, Rh and Ni. The choice of catalyst in this process will determine the condition of the process and the type of hydrocarbon of the resulting product. Currently, only Fe and Co catalysts are already used in industrial-scale [5]. The resulting product is a wide variety of organic compounds, especially n-paraffins and 1-olefins depending on the type of catalyst and operating conditions. Other products that may be formed are branched hydrocarbons, 2-olefins, and various oxygenate compounds (alcohols, aldehydes, ketones, etc.). The resulting product may comprise one carbon atom up to hundreds of carbon atoms in long-chain hydrocarbons [6,7]. Fischer Tropsch synthesis is a polymerization reaction on the surface of the catalyst with a CHx monomer. The CHx monomer is formed from the hydrogenation process of CO adsorbed on the surface of the catalyst to produce hydrocarbons with a wide chain range and wide function [8]. In this polymerization, the main carbon chain will increase with the addition of monomers one by one carbon atom. Every single addition step, the termination process can occur and will determine the product produced and is desorbed from the surface of the catalyst [9,10]. Reactions that may occur during the Fischer Tropsch process are presented in Table 1 [11].

| Table 1. Fischer Tropsch Reaction |
|-----------------------------------|
| **Main Reaction**                 |
| Paraffin Formation                | nCO + (2n+1)H₂ → CₙH₂ₙ₊₂ + nH₂O |
| Olefin Formation                  | nCO + 2nH₂ → CₙH₂ₙ + nH₂O        |
| WGSR                              | CO + H₂O → CO₂ + H₂              |
| **Side Reaction**                 |
| Alcohol Formation                 | nCO + 2nH₂ → CₙH₂ₙ₊₁O + (n+1)H₂O |
| Boudard Reaction                  | 2CO → C + CO₂                    |

Cobalt catalyst in the Fischer Tropsch reaction is known to provide good performance, high activity, high degree of polymerization, and the formation of byproducts such as small oxygenate compounds (<5%) when compared with iron catalysts. The cobalt-based catalyst is also not selective to WGSR reactions as well as iron catalysts. The suitable Cobalt catalyst used for the production of the target product is diesel. Diesel is obtained from hydrocracking/isomerization of a long chain of paraffin compounds [12].

Fischer Tropsch process is very sensitive to operating conditions. Temperature has an effect on desorption effect and speed of hydrogenation process. This may affect the chain polymerization process and the degree of hydrogenation of the product [13]. In the industry are known 3 operating conditions of Fischer Tropsch reaction based on reaction temperature. High-Temperature Fischer Tropsch (HTFT) is operated at temperatures above 320°C, usually using an iron-based (Fe) catalyst producing a straight chain of olefin with a low molecular mass. Medium Temperature Fischer Tropsch (MTFT) at temperature 270°C and Low Temperature Fischer Tropsch (LTFT) at temperature less than 250°C [14]. In LTFT process used Cobalt (Co) catalyst producing a hydrocarbon with big molecular mass (wax). The resulting wax will be cracking with hydrogenation process to produce fuel [15]. Therefore the aim of this study was to synthesize the Co-Kγ-Al₂O₃ catalyst for the Fischer Tropsch reaction and study the influence of condition operation on the conversion and selectivity of the Fischer Tropsch reaction.
2. Experimental Section

2.1. Synthesis of Co-K/γ-Al₂O₃ catalyst
Catalyst Co-K/γ-Al₂O₃ synthesized by alkaline impregnation method using an ammonia solution. The support used is γ-Al₂O₃, Co(NO₃)₂.6H₂O was used as a precursor of Co and KNO₃ was used as a metal precursor of K. The impregnant solution was prepared by dissolving the precursor compound into the ammonia solution. The impregnant solution was impregnated on a γ-Al₂O₃ support with stirring for ±15 minutes. Impregnation process was carried out in stages for a total of 15% metal loading. Impregnated support was dried at 120°C for 3 hours and continued with calcination at 400°C for 6 hours. Co-K/γ-Al₂O₃ catalysts were characterized using XRD, BET and TPR methods.

2.2. Activity test of Co-K/γ-Al₂O₃ catalyst
The catalyst activity test was performed on the fixed bed reactor by using syngas as feed. Testing of catalyst activity was carried out under various operating conditions which are still included in LTFT category. An analysis of gas composition in inlet and outlet of the reactor was carried out by using gas chromatography with Thermal Conductivity Detector (TCD) detector. The product formed was analyzed with GC equipment with FID detector. Gas carrier was used He and H₂. The activity testing tool scheme is described in Figure 1.

![Fixed bed reactor scheme](source)

The catalyst activity testing process begins with an activation process of catalyst using H₂ gas with a flow rate of 90 mL/ min at a 5 bar reactor pressure. Activation of the catalyst was carried out at 450°C for 8 hours. The catalyst activity test was carried out at 20 bar syngas pressure and varying syngas flow rate. Temperature reactions used were 230°C, 240°C, and 250°C to determine the effect of temperature on the Fischer Tropsch process. Catalyst activity test carried out until it reaches a steady-state condition. Gas sampling was taken every hour and analyzed by GC-TCD. The liquid product was taken at the end of the testing process and analyzed by GC FID. CO and H₂ conversions were calculated based on the area ration of CO and H₂ peaks in gas chromatograph.
3. Results and Discussion

3.1 Catalyst characterization

The XRD diffractogram pattern of the Co-K/γ-Al₂O₃ catalyst is shown in Figure 2. Referring to the crystallographic open data, the specific peak of Co appears on the 2θ = 36.559 with the highest intensity. This peak represents the crystal phase [311] of Co₃O₄ crystals [16]. Conaro et al, 2012, explained that K₂O crystals have a specific peak at 2θ = 39.59 with the highest intensity [17]. At the Co-K/γ-Al₂O₃ catalyst diffractogram the K₂O peak was not seen due to the small concentration of K promoter and low sample crystallinity. The catalyst particle size Co was calculated using the debye scherer equation at the highest peak that appears on the diffractogram. Co particle size obtained is 8.45 nm. According to Shimura et al. (2014), Co particle size that has good performance for the Fischer Tropsch reaction is 8-12 nm [18].

The physisorption test of nitrogen on the catalyst was carried out to determine the surface area, volume and pore diameter of the catalyst. The volume and pore diameter of the catalyst were calculated using Brunauer-Emmet Teller (BET) and Barret-Joyner-Halenda (BJH) isotherm methods. Measurement results are presented in table 2. The measurement results show a decrease in values on surface area, pore volume and pore diameter. This is due to the impregnation process which causes the filling of the support pore by metal Co.

![Figure 2. X-Ray diffraction patterns of the catalyst](image)

| Conc. | BET surface area (m²/g) | Pore Volume (cm³/g) | Pore Diameter (nm) |
|-------|-------------------------|---------------------|-------------------|
| γ-Al₂O₃ | 227.3                   | 0.46                | 8.40              |
| Co-K/γ-Al₂O₃ | 176.5                   | 0.36                | 8.20              |

TPR analysis was used to determine the characteristics of the reduction of Co₃O₄ to Co⁰ which is the active phase in the Fischer Tropsch reaction. Cordoba, et al 2017, explained that the reduction of Co₃O₄ compounds through 2 stages in different temperatures. Co₃O₄ was reduced to CoO at temperatures of 250-300⁰C and CoO reduced to Co⁰ at temperatures of 400-500⁰C [19]. TPR Analysis of catalyst Co-K/γ-Al₂O₃ showed a double peak at temperatures of 250-480⁰C and 500-800⁰C. The first peak is interpreted as a reduction process from Co₃O₄ to Co⁰ in 2 stages. In contrast to the study of Cordoba et al 2017, the peak that appears is only one but wide enough. Wide peak models were
interpreted that the reduction peak of \( \text{Co}_3\text{O}_4 \) to CoO shifted and merged with the second peak which described the reduction of CoO to Co. TPR peaks at temperatures of 500-800°C represent the reduction of Cobalt aluminate compounds formed during the calcination process. Aluminate compounds have a stronger bond with metals and require a much higher reduction temperature.

![Graph](Co-K/\gamma\text{-Al}_2\text{O}_3)

**Figure 3.** \( \text{H}_2\)-TPR profile of the catalyst

3.2 *Activity test of Co-K/\gamma\text{-Al}_2\text{O}_3*

Testing of the catalytic activity of the Co-K/\gamma-Al\text{2}O\text{3} catalyst was carried out in a variety of operating conditions to determine its effect on catalyst performance. All experiments were carried out at a pressure of 20 bar and a CO: \( \text{H}_2 \) ratio of 1:2. Conversion of CO and \( \text{H}_2 \) is based on the ratio of the area of CO and \( \text{H}_2 \) to the area of the \( \text{N}_2 \) inert gas. The selectivity value of the hydrocarbon product formed is calculated using the Anderson Shultz Fluhr equation to obtain the probability value of the extension of the hydrocarbon chain (\( \alpha \)). Test results of catalytic activity and calculation of alpha values are shown in Table 3.

### Table 3. A slightly more complex table with a narrow caption.

| T (°C) | Q (mL/min) | XCO (%) | X\( \text{H}_2 \) (%) | \( \alpha^a \) | SC\textsubscript{1} (%wt) | SC\textsubscript{2} (%wt) | SC\textsubscript{3} (%wt) | SC\textsubscript{4} (%wt) | SC\textsubscript{5+} (%wt) |
|--------|------------|---------|----------------|-------------|----------------|----------------|----------------|----------------|----------------|
| 230    | 25         | 75.33   | 69.99         | 0.85        | 2.12           | 3.63           | 4.65           | 5.30           | 84.30          |
|        | 30         | 60.19   | 58.87         | 0.84        | 2.53           | 4.25           | 5.36           | 6.01           | 81.84          |
|        | 35         | 45.70   | 43.12         | 0.81        | 3.57           | 5.80           | 7.05           | 7.62           | 75.96          |
|        | 40         | 32.61   | 31.88         | 0.77        | 4.92           | 7.66           | 8.94           | 9.27           | 69.21          |
| 240    | 25         | 87.71   | 77.52         | 0.83        | 2.76           | 4.60           | 5.76           | 6.40           | 80.48          |
|        | 30         | 67.01   | 65.15         | 0.80        | 3.78           | 6.08           | 7.35           | 7.90           | 74.89          |
|        | 35         | 57.93   | 57.3          | 0.76        | 5.49           | 8.40           | 9.65           | 9.85           | 66.60          |
|        | 40         | 44.41   | 42.64         | 0.74        | 6.60           | 9.80           | 10.93          | 10.83          | 61.85          |
| 250    | 25         | 95.19   | 81.83         | 0.82        | 2.95           | 4.88           | 6.07           | 6.70           | 79.40          |
|        | 26.7       | 91.36   | 78.72         | 0.80        | 3.77           | 6.07           | 7.34           | 7.89           | 74.93          |
|        | 35         | 81.48   | 74.76         | 0.80        | 3.78           | 6.08           | 7.35           | 7.90           | 74.89          |
|        | 40         | 100     | 100           |           |                |                |                |                |                |

\( a \) probability value of the extension of the hydrocarbon chain.
3.2.1 Effect of temperature reaction. The effect of reaction temperature on conversion and selectivity is presented in Table 3. The increase in reaction temperature causes the conversion values of CO and H2 to increase. This is because the increase in reaction temperature will increase the kinetics aspect of the Fischer Tropsch reaction so that it will increase the reaction rate and conversion value of the two reactants.

In the Fischer Tropsch process, the increase of temperature reaction will be followed by a change in selectivity towards a lighter product [20]. The product selectivity of the Fischer Tropsch reaction is determined by the propagation and termination process that occurs on the catalyst surface during the Fischer Tropsch reaction. The effect of the reaction temperature on the selectivity will be significant if the rate of termination of the product is greater than the propagation rate, so that the increase in temperature will cause the termination process in shorter hydrocarbon products.

3.2.2 Effect of syngas flowrate. The effect of syngas flow rate on CO and H2 conversion can be seen from Table 2. The best catalytic activity of Co-K/γ-Al2O3 catalyst was obtained at the lowest linear flow rate and the minimum at the highest flow rate at all temperatures. The linear flow rate is inversely proportional to the residence time which is the time for the reactants to react on the catalyst surface. In general, a high flow rate will cause a small residence time for the reactants to react with the catalyst, thereby reducing the final conversion value. Product selectivity with short hydrocarbon chains or light hydrocarbon compounds (C1 - C4) increases with increasing linear flow rate, while for long-chain hydrocarbon products (C5+) decreases. The effect of flow rate on product selectivity is related to the removal process of hydrocarbon products on the catalyst surface [21].

From all experimental data, data anomalies were shown in conditions with flow rates 35 and 40mL/min at reaction temperatures 250 °C. In this condition, the conversion value is very high, reaching 100% for CO and H2. This is caused by the influence of the flow rate and temperature which can cause the reaction shift towards the formation of short-chain hydrocarbon compounds. In this condition, the influence of the two factors appears very dominantly, so that the Fischer Tropsch reaction which should undergo a polymerization reaction to form long-chain hydrocarbon compounds no longer occurs. The product selectivity value in this condition cannot be estimated because no long-chain hydrocarbon products are formed and can be analyzed at the end of the reaction.

4. Conclusion
The catalytic activity of the Co-K/γ-Al2O3 catalyst in the Fischer Tropsch reaction is strongly influenced by operating conditions. Conversion of CO and H2 is influenced by temperature and flow rate of syngas feed. Temperature affects the reaction kinetics aspect of the Fischer Tropsch reaction which accelerates and enlarges reactant conversion. The selectivity of the product depends on the rate of termination of the Fischer Tropsch reaction. Temperatures that are too high speeding up the termination process and cause the shorter the chain elongation process. Likewise, with a linear flow rate, a linear flow rate that is too high will make it easier for hydrocarbon products on the catalyst surface to be removed before propagation process occurs on the catalyst surface.

5. References
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