

Available online at BCREC Website: https://bcrec.undip.ac.id

BCREC

Bulletin of Chemical Reaction Engineering & Catalysis, 13 (2) 2018, 196-203

Research Article

Triglycerides Hydrocracking Reaction of *Nyamplung* Oil with Non-sulfided CoMo/γ-Al₂O₃ Catalysts

Rismawati Rasyid¹, Rahmaniah Malik², Heri Septya Kusuma³, Achmad Roesyadi³, Mahfud Mahfud³*

¹Department of Chemical Engineering, Universitas Muslim Indonesia, Makassar 90231, Indonesia ²Department of Industrial Engineering, Universitas Muslim Indonesia, Makassar 90231, Indonesia ³Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia

Received: 20th October 2017; Revised: 8th September 2017; Accepted: 17th September 2017; Available online: 11st June 2018; Published regularly: 1st August 2018

Abstract

The purpose of this research are to study the temperature influence in hydrocracking process of the nyamplung oil (Calophyllum inophyllum) using a non-sulfided CoMo/ γ -Al $_2$ O $_3$ catalyst and to develop a simple kinetic model in interpreting the data of hydrocracking products. The experiment was carried out in a pressurized batch reactor operated pressure up 30 bar. The CoMo catalyst supported with γ -Al $_2$ O $_3$ was prepared through impregnation method without sulfidation process. The operating temperature varied from 200 to 350 °C. The results show that the non-sulfided CoMo/ γ -Al $_2$ O $_3$ catalysts, nyamplung oil triglycerides can converted into gasoil and gasoline-like hydrocarbons. The triglyceride hydrocracking reaction of nyamplung oil followed a several stages, i.e., hydrogenation, dehydrogenation, and cracking. Based on the compounds contained in liquid product, hydrocracking reaction was dominated by decarboxylation. The products obtained in hydrocracking process of nyamplung oil are classified to gasoil (C_{11} - C_{18}) and gasoline (C_5 - C_{10}). The triglycerides hydrocracking reaction of nyamplung oil was assumed by following a series reaction mechanism and a simple kinetic model used for determined the kinetics constants. The highest reaction conversion is 99.10% obtained at temperature of 350 °C for 160 minutes reaction time. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Calophyllum inophyllum; triglyceride; hydrocracking; gasoil; gasoline

How to Cite: Rasyid, R., Malik, R., Kusuma, H.S., Roesyadi, A., Mahfud, M. (2018). Triglycerides Hydrocracking Reaction of Nyamplung Oil with Non-sulfided CoMo/y-Al₂O₃ Catalysts. Bulletin of Chemical Reaction Engineering & Catalysis, 13 (2): 196-203 (doi:10.9767/bcrec.13.2.734.196-203)

Permalink/DOI: https://doi.org/10.9767/bcrec.13.2.734.196-203

1. Introduction

Liquid fuels such as gasoil and gasoline from petroleum have been still widely used for transportation and industry sector. The advantages of these fuels include storage and distribution easier so it is considered more efficient to use. Along with the development of transportation and industrial activity, the use of fuel continues to rise. Although the alternative fuel sources such as fuel gas has been found, gasoil and gasoline are still favored as fuel. Therefore, the addition of fuel reserves from vegetable oils may help to prevent the emergence of problems due

* Corresponding Author. E-mail: rismawati.rasyid@umi.ac.id (R. Rasyid), mahfud@chem-eng.its.ac.id (M. Mahfud) Telp: +62-31-5946240; Fax: +62-31-5999282 to the depletion of oil reserves. Vegetable oil is one of considerable potential feedstock because of renewable resource. Biofuel derived from vegetable oils produces lower pollutants in application as a fuel even nitrogen and sulfur-free [1].

Many vegetable oils have a molecular structure which can be converted into fuel. In general, the vegetable oil triglycerides consist of saturated and unsaturated fatty acids such as lauric acid ($C_{12}H_{24}O_2$), myristic acid ($C_{14}H_{28}O_2$), acid $(C_{16}H_{32}O_2),$ palmitic stearic $(C_{18}H_{36}O_2)$, oleic acid $(C_{18}H_{34}O_2)$, linoleic acid (C₁₈H₃₂O₂), linolenic acid (C₁₈H₃₀O₂), arachidic $acid\quad (C_{20}H_{40}O_2),\quad gadoleic\quad acid\quad (C_{20}H_{38}O_2),$ behenic acid (C22H44O2), and erucle acid $(C_{20}H_{42}O_2)$, lignoceric acid $(C_{24}H_{48}O_2)$ [2]. These triglycerides can be converted into gasoline, kerosene and diesel. At the beginning of the process, triglycerides are converted into nparaffins as the main hydrocarbon product and release CO_2 and H_2O as by-products. To convert triglycerides into hydrocarbon, the chemical reactions (including hydrodeoxygenation, decarboxylation, and decarbonylation) took place at a temperature of 300-450 °C and a hydrogen pressure of 3 MPa [3].

Several operating units have been applied in the petroleum refining process, that is, hydrocracking, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), catalytic cracking, Currently, hydrocracking process can be used to produce vegetable oil based-fuel. Catalyst and hydrogen are used in hydrocracking so that this process is categorized in the process of hydrogenation and catalytic cracking. Hydrogen plays a role in the hydrogenation process and catalyst supports cracking reactions. This process may present several advantages namely: oxygen removal, olefins saturation, sulfur removal, etc. Additionally, hydrocracking can also convert heavy fractions of crude oil into the environmentally friendly fuels [4].

The catalyst used in the hydrocracking consists of two functions, i.e. acid function and metal function, so that it can be called as bifunctional catalyst. This type of catalyst has a role in the hydrogenation process and the formation of carbonium ion. Several previous studies have used bifunctional catalyst to produce fuel. The activity of the CoMo/y-Al₂O₃ catalyst increased after tungsten (W) added. The CoMoW/y-Al₂O₃ catalyst activity resulted in a reaction conversion of 93% at temperature of 350 °C, pressure of 40 bar for 2 h [5]. With CsxH_{3-x}PW₁₂O₄₀ catalyst, n-decane was

converted into the main reaction product (C_4 - C_6), C_2 , and C_8 hydrocarbon. Meanwhile, C_1 and C_9 were produced in cracking and hydogenolysis reaction with the presence of acid site and metal site [6].

According to previous study, the reaction kinetic occurred in hydrocracking varied greatly and depended on the reaction mechanism obtained. The kinetic model of heavy oil hydrocracking in CSTR had seven stages to generate ten reaction rate constants. In the first stage, the product obtained by the order were vacuum residue (VR), vacuum gas oil (VGO), middle distillates (MD), naphtha (N), the final product gases (G). Furthermore, the second stage of reaction process was VR → MD \rightarrow N \rightarrow G, the third stage: VR \rightarrow N \rightarrow G, was proceeded with the next stage of the reaction, that is, $VR \rightarrow G$, the fifth stage: $VR \rightarrow VGO \rightarrow$ N, then $VR \rightarrow VGO \rightarrow MD \rightarrow G$ and $VR \rightarrow$ $VGO \rightarrow G$ [7].

Before used, metal catalysts, like cobalt (Co) and molybdenum (Mo) or NiMo, are subjected to sulfidation using gas mixtures H₂S/H₂ or S/H₂, for activating the metal sites on the surface of catalysts [8,9]. The use of catalysts sulfidation process may vield non environmentally friendly products as a result of sulfur contamination [10]. One of the unfavorable impacts for the catalysts (deactivation) is sulfur where the sources are derived from gases, H₂S [11]. Therefore, it is necessary to develop a catalyst to obtain products that are environmentally friendly.

This study used nyamplung oil as triglycerides source and applied hydrocracking process with non-sulfided CoMo/y-Al₂O₃ catalyst as bifunctional catalyst. The use of this type catalyst without sulfidation process can prevent the use of toxic substances like H₂S and more economical. The hydrocracking using nonsulfidation catalyst produced environmentally friendly liquid fuel [12]. Therefore, the aims of this research are to study the temperature effect in hydrocracking process of the nyamplung oil (Calophyllum inophyllum) using a non-sulfided CoMo/y-Al₂O₃ catalyst and to develop a simple kinetic model in interpreting the data of hydrocracking products in a highpressure batch reactor.

2. Materials and Methods

2.1 Materials and chemicals

 $Co(NO_3)_2$ $6H_2O$ and $(NH_4)_6Mo_7O_{24}$ $\cdot 4H_2O$ were provided by Merck with purity of 99%, while the γ - Al_2O_3 catalyst as support material was also obtained from Merck (p.a.).

2.2 Preparation of catalyst

The catalyst used in this study was prepared by the wet impregnation method or incipient wetness impregnation. The catalyst consisted of Co and Mo as catalyst active element and promoter and y-Al₂O₃ as a support. The CoMo catalyst was made from cobalt(II) nitrate hexahydrate [Co(NO₃)₂6H₂O] and ammonium molvbdenum(VI) tetrahvdrate [(NH₄)₆Mo₇O₂₄·4H₂O]. After the suspension of $Co(NO_3)_26H_2O$ was added to the $(NH_4)_6M_{07}O_{24} \cdot 4H_2O$, the suspension stirred until solid phase formed, then was dried at a temperature of 110 °C for 8 h, and was further calcined at a temperature of 500 °C for 3 h. Furthermore, the CoMo catalyst was impregnated on γ-Al₂O₃. This mixture was stirred until a solid phase was formed, then was dried at a temperature of 110 °C for 8 h. Afterward, this catalyst was calcined at a temperature of 500 °C for 5 h to produce the CoMo/y-Al₂O₃ catalyst.

2.3 Characterization of catalyst

The BET surface area of CoMo/γ-Al₂O₃ catalyst was measured by N₂ adsorption-desorption technique (NOVA instrument 1994-2007, Quantachrome Instruments version 10.01). The following Brunauer-Emmett-Teller (BET) analysis method was used to identify the catalyst volume surface. Samples were added to the sample cells with 3 hours of outgas time and 573 K from outgas temperature. Nitrogen gas has been used and bath temperature of 77.3 K. Pressure tolerance for adsorption / desorption was 0.100/0.100 with equil time of 180/180 sec (ad/des), equil timeout of 360/360 sec (ad/des), and the approximation of time analysis of 67.4 min.

The characterization of the catalyst was also conducted by using X-ray diffraction (XRD) to identify the catalyst composition and the small-entrepreneur Latine form of the catalyst crystal. The catalyst sample was placed on the sample container, using Philips PN-1830 with CuKa radiation 1,5406 Å at 40 kV and 30 mA. Samples are scanned in 20 range of 5-90° with step size of 0.017 and time step 10.15 s.

2.4 Hydrocracking of nyamplung oil

Hydrocracking of *nyamplung* oil was conducted using an autoclave at a reaction temperature of 350 °C and pressure of 30 bar. The type of reactor used was a 600 mL pressure batch reactor (model 4563 series) with system specifications, that is, moveable vessel with a height of 36 in, a width of 12 in and a depth of

18 in), magnetic stirrer (models No. A1120HC6), and heating mantle. The catalyst materials used as promoter of Co(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O with 10 % loading, were provided by Merck with purity of 99%, while the γ-Al₂O₃ catalyst as a support material was also obtained from Merck (p.a). The hydrocracking product was analyzed by GC-MS (gas chromatography-mass spectrometry). It analytically qualitative quantitative. The component will be detected by means of the instrument with the model of the capillary number column of Agilent 19,091 S-493, HP-5MS 5% Phenyl Methyl siloxane, nominal length: 30.0 m, nominal diameter: 250 um, nominal thickness of film: 0.25 um, and a nominal initial pressure of 10.5 psi.

3. Result and Discussion

3.1 The characterization of catalyst

Before BET surface area analysis, the catalyst was degassed at 300 °C for 3 h and nitrogen isotherms of catalyst were obtained at 77.3 K, adsorption/desorption pressure ratio of 0.100/0.100, equil time of 180/180 sec, equil time out of 360/360 sec for 126.1 min. Based on BET summary, the CoMo/y-Al₂O₃ catalyst surface area of 197.350 m²/g is obtained at slope of 17.409, intercept of 2.370E-1, constants of 74.453 with correlation coefficient of 0.999994, as shown in Table 1.

Diffraction patterns of catalyst samples were analyzed with a X-ray diffractometer using Cu-Ka radiation (λ = 1.54056 Å). The sample was measured in the 2 θ range from 0 to 90°. Figure 1 presents the diffraction pattern showing the metal oxide component, i.e. alumina oxide with three different types (reference code: 00-013-0373; 00-016-0394; 00-001-1303; 00-001-1307). The difference in crystal shape of three different types of alumina oxide deposited on the CoMo/ γ -Al₂O₃ catalyst was observed at 2 θ = 67.034° (h k l = 2 1 4), 66.98° (h k l = 3 1 4), and 66.7° (h k l = 2 1 1), which

Table 1. Isoterm data for catalyst CoMo/γ-Al₂O₃

Relative pressure (P/P_{θ})	Volume @ STP (cc/g)	$1/[W((P_0/P)-1)]$
9.72480e-02	44.6719	1.9294e+00
1.53130e-01	49.7475	2.9082e+00
1.99936e-01	53.8269	3.7146e+00
2.48077e-01	58.0204	4.5497e+00
3.02847e-01	63.0336	5.5141e+00

are attributed to the hexagonal, tetragonal, and cubic, respectively. The existence of MoO_2 phase (reference code: 00-032-0671) were observed at $2\theta = 26$ (h k l = -1 1 1) with monoclinic crystal system. Beside that, Co_3O_4 phase (reference code: 00-042-1467) was observed at $2\theta = 36,853^\circ$ (h k l = 3 1 1) and CoO phase (reference code: 00-042-1300) was also observed at $2\theta = 34.149$ (h k l = 1 1 1). Both Co_3O_4 and CoO phasees are detected in cubic crystal system.

In this present research, metal oxides existing in the surface of the catalysts function to bond hydrogen so that nyamplung oil undergo hydrogenation to form saturated bonds. Hydrocracking process is able to yield better quality products than those usual cracking process. Hydrogenation is one of the existing processes in hydrocracking that enhances higher quality product. The support of the catalyst functions to elucidate ion carbenium for cutting off long bonds of carbon chains.

Hydrocracking reactions require good catalysts, indicated by the wide of the surface area; thus, in the present study it is figured out

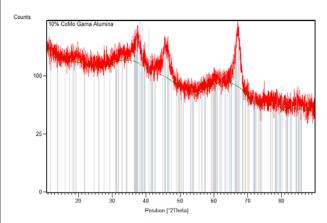


Figure 1. XRD patterns of CoMo/γ-Al₂O₃ catalyst

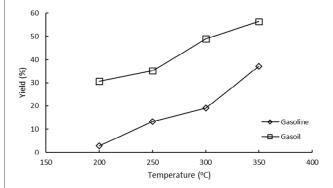


Figure 2. The yield of product obtained by hydrocracking of nyamplung oil at the various temperatures of 200, 250, 300, and 350 °C

that the wide of the surface areas range from $\text{CoMo/}\gamma\text{-Al}_2\text{O}_3$ (Table 1). Hence, based on the analysis using XRD and BET method, the surface area required to employ cracking process is 100 m²/g minimum [13]. The research is conducted by making $\text{CoMo/}\gamma\text{-Al}_2\text{O}_3$ going with the criteria of catalysts cracking.

3.2. Effects of temperature

The hydrocracking reaction of *nyamplung* oil is affected by temperature and reaction time. Figure 2 shows that according to the catalytic activity test of $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst at the various temperatures of 200, 250, 300, and 350 °C, the highest gasoil yield was obtained.

Gasoil and gasoline yields increased with the increasing reaction temperature. The gasoline yield increased significantly at reaction temperature from 300 to 350 °C. This phenomenon occurred because the resulting carbenium ion was longer formed in the hydrocracking reaction with high temperature so that the many long-chain hydrocarbon molecules were cleaved into the short-chain hydrocarbon molecules. As a result, the reaction conversion also increased with the increasing temperature. It can be seen in Figure 3 that shows the effect of reaction temperature on conversion of nyamplung oil. From Figure 3, it can be seen that the highest conversion was achieved at a temperature of 350 °C.

Decarboxylation, decarbonization, and deoxygenation took place more effectively with increasing temperature. The cracking process will also increased with increasing temperature. Metal oxide found on catalyst surface can break hydrogen into hydrogen radical so that the hydrogenation, dehydrogenation, and

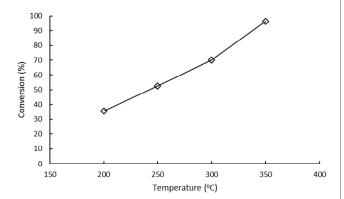


Figure 3. The effect of reaction temperature on conversion in the presence of $CoMo/\gamma$ - Al_2O_3 catalyst

cracking process occur. If hydrocracking was compared with the catalytic cracking, the hydrogenation process occurred only in hydrocracking to produce a quality product. In hydrotreating of sunflower oil, the reaction conversion increased with the increasing temperature with $\text{CoMo/}\gamma\text{-Al}_2\text{O}_3$ catalyst [14]. The same thing was found in petroleum refinery. Gasoil and kerosene yields increased at temperatures from 400 to 420 °C in hydrocracking process [15].

With CoMo/y-Al₂O₃ catalyst, gasoil yield produced from hydrocracking of *nyamplung* oil was greater than the other products. As shown in Figure 4, gasoil yield increased significantly with the increasing reaction time from 20 to 120 min and decreased with the increasing reaction time from 140 to 160 min at temperature of 350 °C. It can be assumed that when the reaction time was greater than 120 min, gasoil was converted into gasoline.

3.3 The hydrocracking products

Table 2 presents the fatty acids composition in *nyamplung* oil which analyzed by gas cromatography-mass spectrometry (GC-MS) and consisted of saturated and unsaturated fatty acids. The oleic and linoleic acids were identified as monounsaturated and polyunsaturated fatty acids, respectively, while palmitic

Table 2. The fatty acids composition in *nyamplung* oil

Chemical formula	% wt	Fatty acids
$\begin{array}{c} C_{18}H_{34}O_2 \\ C_{16}H_{32}O_2 \\ C_{18}H_{30}O_2 \\ C_{18}H_{36}O_2 \end{array}$	58.13 18.46 12.26 11.14	Oleic acid Palmitic acid Linoleic acid Stearic acid

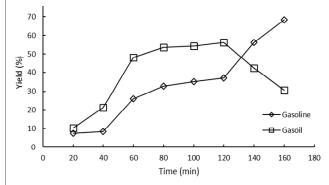


Figure 4. The product distribution of gasoline and gasoil as function of time at 350 °C and in the presence of $CoMo/\gamma$ - Al_2O_3 catalyst

acid was identified as saturated fatty acid. The hydrogenation process was applied to convert triglycerides to obtain fatty acid.

The products of hydrocracking nyamplung oil were grouped into gasoline range (C₅-C₁₁) and gasoil range (C₁₂-C₁₈). Hydrocarbon components contained in gasoil range (C₁₁-C₁₈) and gasoline range (C5-C10) may be identified as aliphatic and aromatic compounds. Some of the compounds have isomers with the same number of C and H atoms but have a different bond structure. Hydrocarbon compounds found in gasoil range consisted of alkanes and alkenes. These long-chain hydrocarbon compounds can be converted into short-chain hydrocarbon compounds found in gasoline range product. Aromatic and aliphatic were also found in gasoline range, as presented in Table 3. The existence of aromatic compounds in gasoline increases the octane number so that the high quality biofuel is obtained.

3.4 The mechanism of hydrocracking reaction

The presence of hydrogen and high pressure in hydrocracking process can support triglycerides conversion to fatty acids. At first, triglycerides were converted into trioleins. Furthermore, the trioleins was cracked into saturated and unsaturated fatty acids through hydrogenation and dehydrogenation reactions (1).

$$Trigliceride \rightarrow Triolein \rightarrow Fatty Acid (A)$$
 (1)

After the formation of fatty acids, oxygen removal may be done through decarboxylation

Tabel 3. Hydrocarbon compounds contained in gasoil and gasoline

Bulletin of Chemical Reaction Engineering & Catalysis, 13 (2), 2018, 201

(2), decarbonylation (3), and hydrodeoxygenation reactions (4) [16,17]. In this work, reactions of (2), (3), and (4) were assumed to occur.

Decarboxylation :
$$RCOOH \rightarrow R_1 + CO_2$$
 (2)

Decarbonylation :
$$RCOOH + H_2 \rightarrow R_1 + H_2O + CO$$
 (3)

Hydrodeoxygenation :
$$RCOOH + 3H_2 \rightarrow R_2CH_3 + 2H_2O$$
 (4)

The oxygen removal process through the above reactions will be followed by the cracking process in the presence of metal active site and acid site on catalyst. In principle, the long-chain hydrocarbons were cleaved into shorter-chain hydrocarbons because these active sites were the driving force of reactions. After the formation of carbenium ions, the short-chain hydrocarbons were obtained by cracking process (eqs. 5,6,7). As a result, gasoil was obtained and furthermore converted into gasoline.

$$R\text{-}CH_2\text{-}CH_2\text{-}CH^+\text{-}CH_2\text{-}CH_3 \rightarrow R\text{-}CH^+ + CH_2\text{-}CH_2\text{-}CH_3$$
 (5)

$$R-CH_2-CH_2-CH_2-CH_2^+ \to R-CH_2-CH_2-CH_2^+-CH_3$$
(6)

$$R-CH_2-CH_2-CH_2^+-CH_3 \rightarrow R-CH_2^+ + CH_2=CH-CH_3$$
 (7)

The carbenium ion is a positively charged C atom due to lack of electron in the outer orbital. The stability of ion is tertiary > secondary > primary > methyl. The carbenium ion is formed in the presence of acid catalyst (Al_2O_3) as a Lewis acid and Brönsted acid. The Lewis acid sites accept electron and Brönsted acid sites donate proton. Furthermore, the carbenium ion cracks to accept and/or donate proton (H^+) so that reaction proceeds. This reaction process was began with the initiation followed by propagation and termination steps.

Initiation:

$$R_2\text{-}CH = CH\text{-}R_2 + H\text{-}Al_2O_3 \stackrel{H^+}{\leftrightarrow} R_1\text{-}CH_2\text{-}CH^+\text{-}R_2 + Al_2O_3 \qquad Carbenium ion}$$
(8)

Propagation:

$$H^{+}$$

$$R_{1}\text{-}CH_{2}\text{-}CH^{+}\text{-}R_{2} + R_{3}\text{-}CH_{2}\text{-}CH_{2}\text{-}R_{4} \leftrightarrow$$

$$R_{1}\text{-}CH_{2}\text{-}CH_{2}\text{-}R_{2} + R_{3}\text{-}CH_{2}\text{-}CH^{+}\text{-}R_{4}$$
Alkane product
$$(9)$$

Termination:
$$R_3$$
-CH₂-CH⁺ -R₄ \rightarrow R_3 -CH₂-CH⁺ -R₄ + H⁺ (10)
Alkane product

Initiation step is the early stapes of the formation of carbenium ions derived from alkenes and alkanes. Brönsted acid site donate proton to alkenes, while Lewis acid site accept electron. After the reactions release proton to produce alkanes, termination step occurs to produce alkenes. This condition will continue until it reaches a state of equilibrium reaction. The resulting product can be classed as gasoline.

Hydrocarbon compounds contained in liquid product does not contain water so that the triglycerides conversion is dominated by decarboxylation reaction. The decarbonylation and dehydrogenation reactions release CO and H₂O. The hydrocracking reaction mechanism of triglycerides to gasoil and gasoline range hydrocarbons as described previously, the reaction kinetics model can be predicted. Three types of reactions can occur with following the irreversible-type first-order reaction, the firstorder reaction in series, and the first-order reaction in parallel. Based on these results in this work, the first assumption stated that the reaction occurred with following the first order irreversible reaction and gasoil was converted into gasoline as the main reaction.

$$Gasoil(G) \rightarrow Gasoline(N)$$
 (11)

The next assumption was the first-order reaction in series, whereas the triglyceride was converted into gasoil and then cracked into gasoline, with the following reaction:

Trigliseride (A)
$$\xrightarrow{k_1}$$
 Gasoil (R) $\xrightarrow{k_2}$ Gasoline (S) (12)

Furthermore, it is predicted that this type of reaction is parallel reaction, i.e. the triglyceride was converted directly into gasoil and gasoline.

Trigliseride (A)
$$\rightarrow$$
 Gasoil (R)
 k_4 (13)
Trigliseride (A) \rightarrow Gasoline (S)

With the sulfided $CoMo/\gamma$ - Al_2O_3 catalyst, a kinetic model obtained in the hydrocracking of jatropa oil was related to parallel reaction. Triglyceride was converted into lights (C_5 - C_8), middle (C_9 - C_{14}), heavy (C_{15} - C_{18}), and

Bulletin of Chemical Reaction Engineering & Catalysis, 13 (2), 2018, 202

oligomerized ($>C_{18}$) hydrocarbons [18]. The type of heavy oil hydrocracking reaction in CSTR produced ten reaction rate constants. It's assumed that these reactions were a single reaction, series reactions, parallel reaction, and series-parallel reaction [19]. Three kinetic models in the previous study can be defined as a type of reaction that can occur in the triglyceride hydrocracking process nyamplung oil using the non-sulfided $CoMo/\gamma$ - Al_2O_3 catalysts. But according to Figure 4 that illustrate the product distribution of gasoline and gasoil in function of time, the product of gasoil initially increase with time, but then decreases. However, the products of gasoline always increase time. The reduction of gasoline will result in an increase in gasoline. These suggest that the series reaction mechanism, such as equation (13), is most probably to occur. Thus the calculation of kinetic data is based on this mechanism.

The reaction rate constants obtained for series reaction as equation (13) can be calculated from experimental data. The reaction rate constants for the triglyceride conversion of *nyamplung* to gasoil and gasoline with $k_1 = 0.0076$ and $k_2 = 0.0063$.

4. Conclusions

With the non-sulfided CoMo/y-Al₂O₃ catalysts, nyamplung oil triglycerides can be converted into gasoil and gasoline-like hydrocarbons. The triglyceride hydrocracking reaction of *nyamplung* oil was proceeded by several stages, i.e. hydrogenation, dehydrogenation, and cracking. Based on the compounds contained in liquid product, the hydrocracking reaction was dominated by decarboxylation mechanism. The temperature of 350 °C was the optimum temperature in this study. Gasoil (C₁₁-C₁₈) and gasoline (C₅-C₁₀) were products obtained in hydrocracking process of nyamplung oil with following three kinetic models of reaction, i.e. the irreversible-type first-order reaction, the firstorder reaction in series, and the first-order reaction in parallel.

The reaction mechanism followed to produce product had several stages based on the performance of metal site and acid site on the catalyst. The composition of fatty acids in vegetable oil have also a role in the determining of hydrocarbon product. The most predominant fatty acid in *nyamplung* oil was oleic acid of 58.13%, while the other fatty acids were identified in small quantities, i.e. palmitic acid of 18.46%, linoleic acid of 12.26%, and stearic acid of 11.14%.

Acknowledgment

This work was supported by research grant, number: 5058/H.25/UMI/VII/2016.

References

- [1] Nam, L.T.H., Vinh, T.Q., Loan, N.T.T., Tho, V.D.S., Yang, X.-Y., Su, B.-L. (2011). Preparation of bio-fuels by catalytic cracking reaction of vegetable oil sludge. *Fuel*, 90(3): 1069-1075.
- [2] Ong, H.C., Mahlia, T.M.I., Masjuki, H.H., Norhasyima R.S. (2011). Comparison of palm oil, Jatropha curcas and Calophyllum inophyllum for biodiesel: A review. Renewable and Sustainable Energy Reviews, 15(8): 3501-3515.
- [3] Sotelo-Boyás, R., Trejo-Zárraga, F., Hernández-Loyo F.J. (2012). Hydroconversion of Triglycerides into Green Liquid Fuels, Hydrogenation, Prof. Iyad Karamé (Ed.), InTech. DOI:10.5772/48710.
- [4] Ghosh, U., Kulkarni, K., Kulkarni, A.D., Chaudhari, P.L. (2015). Review – Hydrocracking using different catalysts. Chemical and Process Engineering Research, 34: 51-55.
- [5] Jantharak, P., Kiatkittipong, W., Wongsakulphasatch, S., Laosiripojana, N., Assabumrungrat, S. (2012). Green diesel production from hydrotreating of oleic acid over CoMo/y-Al₂O₃ and CoMoW/y-Al₂O₃ catalyst. In Proceedings 19th Regional Symposium on Chemical Engineering (RSCE 2012), A-62.
- [6] Jin, H., Yi, X., Sun, S., Liu, J., Yang, G., Zhu, H., Fang, W. (2012). Hydrocracking of ndecane over non-sulfided Ni-Cs_xH_{3-x}PW₁₂O₄₀/Al₂O₃ catalysts. Fuel Processing Technology, 97: 52-59.
- [7] Martínez, J., Ancheyta, J. (2012). Kinetic model for hydrocracking of heavy oil in a CSTR involving short term catalyst deactivation. *Fuel*, 100: 193–199.
- [8] Echard, M., Leglise, J. (2000). Sulphidation of an oxidic CoMo/γ-Al₂O₃ catalyst under practical conditions: different kinds of sulphur species. *Catalysis Letters*, 72: 83-89.
- [9] Turaga, T.U., Song, C. (2002). MCM-41-Supported Co-Mo Catalysts for Deep Hydrodesulfurization of Light cycle oil-based real feedstock. Fuel Chemistry Division, 47(2): 457-459.
- [10] Mohammad, M, Hari, K.T, Yakob, Z, Sharima, Y.C, Sopian, K. (2013). Overview on the production of paraffin based biofuels via catalytic hydrodeoxygenation. *Renewable and Sustanable Energy Reviews*, 22: 121-132.

Bulletin of Chemical Reaction Engineering & Catalysis, 13 (2), 2018, 203

- [11] Bartholomew, H.C. (2001). Mechanisms of catalyst deactivation. *Applied Catalysis A: General*, 212: 17-60.
- [12] Rasyid, R., Prihartantyo, A., Mahfud, M., Roesyadi, A. (2015). Hydrocracking of Calophyllum inophyllum oil with non-sulfide CoMo catalysts. Bulletin of Chemical Reaction Engineering & Catalysis, 10(1): 61-69.
- [13] Bekkum, H.V., Flainigen, E.M., Jansen, J.C. (1991). Introduction to Zeolite Science and Practice. Vol. 58, New York.
- [14] Krár, M., Kovács, S., Kalló, D., Hancsók, J. (2010). Fuel purpose hydrotreating of sunflower oil on CoMo/Al₂O₃ catalyst. *Bioresource Technology*, 101(23): 9287-9293.
- [15] Šimáček, P., Kubička, D. (2010). Hydrocracking of petroleum vacuum distillate containing rapeseed oil: Evaluation of diesel fuel. Fuel, 89(7): 1508-1513.

- [16] Mikulec, J., Cvengroš, J., Joríkova, Ĺ., Banič, M., Kleinovà, A. (2010). Second generation diesel fuel from renewable sources. *Journal of Cleaner Production*, 18(9): 917-926.
- [17] Ishihara, A., Fukui, N., Nasu, H., Hashimoto, T. (2014). Hydrocracking of soybean oil using zeolite-alumina composite supported NiMo catalysts. Fuel, 134: 611-617.
- [18] Anand, M., Sinha, A.K. (2012). Temperature-dependent reaction pathways for the anomalous hydrocracking of triglycerides in the presence of sulfided Co–Mo-catalyst. *Bioresource Technology*, 126: 148-155.
- [19] Martínez, J., Ancheyta, J. (2012). Kinetic model for hydrocracking of heavy oil in a CSTR involving short term catalyst deactivation. *Fuel*, 100: 193-199.