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KINETIC STUDY OF CATALYTIC CRACKING OF INDONESIAN NYAMPLUNG OILS (*Calophyllum inophyllum*) OVER ZSM-5 CATALYST

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ABSTRACT

Catalytic cracking of nyamplung oils was performed over ZSM-5 catalyst. This process is carried out in a packed bed reactor which is equipped with two-stage preheater to convert the nyamplung oil into vapor form. The reaction was studied in the temperature range of 350-450°C and reactor length of 2-5 cm. The kinetic study of catalytic cracking of nyamplung oil is represented using lumped parameter model based on 5-lumps modelwhich is modified from 4 and 6 model. This model was developed by classified the reactant and product into five-lumps, namely C_4-C_{11}, C_{12}-C_{15}, C_{16}-C_{18}, gas and coke. The simulated data which obtained from the model gave satisfactory results with the experimental data.

Keywords: catalytic cracking; nyamplung oil, ZSM-5.

INTRODUCTION

Over the past few decades, the issue of developing alternative energy has been an area research. Alternative and renewable energy includes wide range technologies including wind power, solar power, hydrogen production, fuel cells, biofuel and biomass [1]. Biomass is the only renewable energy source that yields solid, gaseous and liquid fuels. Gasification is one of the thermo-chemical conversion techniques which most common and convenient methods of harnessing energy from biomass [1]. The products of gasification called bio-syngas. The gasification process with the raw material of sugarcane bagasse [2] and oil palm empty fruit bunches [3] showed promising results for bio-syngas production. However there are several problems about bio-syngas production including expensive set-up, costly storage and transport of the product [1]. Compared to other biomass resources, triglycerides present a relatively high energy density due to their low oxygen content [4]. However they also possess certain properties, such as high viscosity and low volatility, which prevent their direct use as transportation fuels. Therefore triglycerides must be processed to yield valuable fuels or raw chemicals [5].

Among the various biofuel types, the production of biodiesel is widely studied by adopting transesterification reaction [6]. There are several studies reported on the biodiesel production from crude palm oil (CPO), second used cooking oil [7], and palm fatty acid distillate [8] performed in batch-stirred reactor and recently the continuous process of reactive distillation column which is more popular due to low energy cost [9-10]. However, biodiesel exhibit poor cold-flow properties, which can be problem for engine performance and the oxygen content in the biodiesel is responsible for the low quality of heating value and the weakness of stability [5,11]. Compared to transesterification, catalytic cracking presents some advantages which can be converted into hydrocarbons in the absence of oxygen at atmospheric pressure and at a relatively low temperature 400-600 ^{0}C. The hydrocarbon product distribution obtained ranging from gaseous compounds to gasoline, depending on the operating conditions and type of catalyst employed [12]. There are several studies reported on the production of biofuels from catalytic cracking. But most of the research work on vegetable oil cracking concentrated on edible oils such as palm oil [12-13]. Due to competition which its utilization as a food product, it is required to carry out cracking of non-edible vegetable oils to generate biofuel [13]. Nyamplung oilsis one of the Indonesian non-edible vegetable oils with 57.6% oleic acid (C18:1) content, is used to produce biofuels as a promising route by many different reasons: easy conversion to liquid bio fuels, high oil production at a low price, ease of establishing, widely cultivated and maintain nyamplung plantation [14].

In most of the studies reported in the literature regarding triglyceride catalytic cracking, molecular-sieve catalysts, including ZSM-5, MCM-41 and Y zeolite were used [11].When considering hydrocarbon cracking, an important zeolite catalyst is the ZSM-5. Compared to other zeolite ZSM-5 shows a high resistance to deactivation [5]. It is a synthetic and has a basic structure consists of layers of silica alumina pentagon chains liked by oxygen atoms. ZSM-5 also have the ability to convert a remarkable range materials to high octane, aromatic, gasoline like products [1, 5]. ZSM-5 has been used for the conversion of vegetable oils to gasoline range compounds [15]. And it has been proven that ZSM-5 catalyst can convert crude nyamplung oils with high levels fatty acids into gasoline, kerosene and diesel fractions [16].

To scale up the catalytic cracking reactor it is necessary to provide useful information for the design of reactor which presented as a reaction model. Because the complexity of the reaction and the large number of components involved in the cracking process, it is difficult to describe the kinetics of bio-fuels at the molecular level [17]. The formulation of lumped kinetic schemes is one approach to dealing with multi component mixtures. Hence, lumping the products into groups depending on their classification made to facilitate the handling data obtained from the experimental [18]. The reaction rate for each lump pathway describes the mechanism of the cracking reactionand selectivity for the desired products. The complexity of the lump model varies according to the degree of lumping. 3-lump parameter model has been proposed for the catalytic cracking reaction of gas oil [19]. The sum of lumped parameters incorporated in the model presents the kinetics of the overall cracking reaction [19].

Most of the cracking reaction of pure hydrocarbon followed first order reaction kinetics whereas the feedstocks of petroleum hydrocarbons showed variable in the range of 1.6-1.8 [20]. Incorporating more products in the model could increase the number of lumps [21]. Juarez *et al*. [21] reported a four-lump kinetic model for hydrotreated gas oil catalytic cracking, based on three main cracking products (gasoline, gas and coke). The kinetic study of catalytic cracking of palm oil, used palm oil and palm oil fatty acid mixture have been reported by several research [17, 18, 22].

The objective of this study is to develop the kinetic study of catalytic cracking of nyamplung oil over ZSM-5 catalyst. A modification of six lump model namely five lump model is proposed for representing nyamplung oil cracking. The reliable model kinetics will provide the appropriate fitting data between the experimental and prediction data.

EXPERIMENTAL

Materials

Crude nyamplung oils asaraw material used in this study was obtained from Mirit, Kutoarjo,Central Java, Indonesia without further purification. The compositions of nyamplung oil are 17.56% of palmitic acid, 57.61% of oleic acid and 18.90% of stearic acid and free fatty acid (FFA) 29%.

Catalyst preparation

Catalyst ZSM 5 which obtained from Wish Chemicals Yueyang Factory, China with a powder form must be made in granular form to facilitate the process of calcination and cracking. Granulation is done manually by adding the adhesive agent in the form of kaolin (5 wt. %) to form pellets of the same size 0.3 x 0.5 cm. Furthermore, catalyst was activated in the furnace with a heating temperature of 600 ^{0}C for 2 hours and followed by calcination by flowing nitrogen gas for 2 hours at a temperature of 600 ^{0}C. After being activation and calcination, the catalyst is cooled and to be analyzed its characteristics.

Catalytic cracking reaction

The experiments were carried out in the temperature range of 350-450 ^{0}C in a stainless steel tubular reactor (1 cm internal diameter) filled with catalysts with the length of 2-5 cm and equipped with 2 stages preheater to ensure the oil enters the reactor in the vapor phase. The reactor dan preheater are also equipped with a temperature control device to ensure the temperature remain constant. The incoming feed to the reactor is vapor oils resulted from thermal cracking of the preheater which consist of hydrocarbon compound which have number of carbon ranging from 1 up to 18.The explanation of the catalytic cracking reaction and the equipment used to experimental has been presented in previous paper [16].

Product analysis

The product which comes from the catalytic cracking reaction consists of organic liquid product (OLP), gas and solid phase as coke which attached in the surface of catalyst. The organic liquid product contains a large number of components of liquid hydrocarbons. The OLP product is analyzed using GC and GCMS and grouped into 3 categories based on the number of atom carbon: C_4-C_{11}, C_{12}-C_{15} and C_{16}-C_{18}. The specification of GC and GCMS has been reported in previous paper [16].

Kinetic model

The modification of 6-lump model which proposed by Twaiq *et al*. [18] is used in order to estimate the kinetic parameter in the catalytic cracking of nyamplung oils and called as 5-lump model. The following assumptions are considered to develop this model: (1) The reactions take place on isothermal condition. (2) The reactions are all catalytic, the thermal conversion and diffusion to the axial direction is not taken into account. (3) The cracking reaction of nyamplung oil is follow first order reaction based on cracking of palm oil done by Twaiq *et al*. [18]. Based on the assumptions, the differential equation for nyamplung oil cracking for the incremental length of reactor can be written:

$$V_z \frac{dC_a}{dz} = -(k_a C_a . \rho_b) \quad (1)$$

Where C_a denotes as the concentration of the component (mol ratio), V_z is superficial velocity ($cm^3/cm^2.s$), k_a is reaction rate constants and ρ_b is bulk density of the catalyst (g/cm^3).

The estimated parameter from 5-lump model is presented in Figure-1. This figure shows the reaction network which OLP divided into three lump C_4-C_{11}, C_{12}-C_{15} and C_{16}-C_{18} respectively. The network of the reaction covers all the possibilities, assuming higher hydrocarbons will crack into lower hydrocarbons.

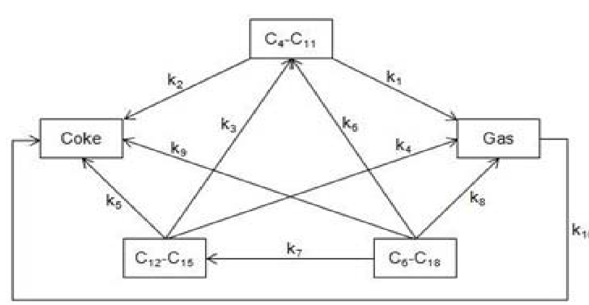

Figure-1. Kinetic scheme for the 5-lump model.

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The five-lump model is described by the following rate equation according to equation (1):

$$\frac{v_z}{\rho_b}\frac{dC_{C16\text{-}C18}}{dz} = (-k_6\text{-}k_7\text{-}k_8\text{-}k_9).(C_{C16\text{-}C18}) \quad (2)$$

$$\frac{v_z}{\rho_b}\frac{dC_{C12-C15}}{dz} = (-k_3 - k_4 - k_5).(C_{C12-C15}) + k_7 C_{C16-C18} \quad (3)$$

$$\frac{v_z}{\rho_b}\frac{dC_{C4-C11}}{dz} = (-k_1 - k_2)\, C_{C4-C11} + (k_3.C_{C12-C15} + k_6.C_{C16-C18}) \quad (4)$$

$$\frac{v_z}{\rho_b}\frac{dC_{gas}}{dz} = (k_1.C_{C4-C11} + k_4.C_{C12-C15} + k_8 C_{C16-C18} - k_{10}.C_{gas}) \quad (5)$$

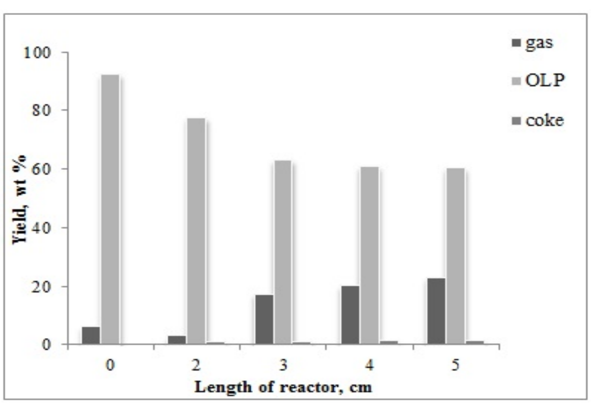
$$\frac{v_z}{\rho_b}\frac{dC_{coke}}{dz} = (k_2.C_{C4-C11} + k_5.C_{C12-C15} + k_9 C_{C16-C18} + k_{10} C_{gas}) \quad (6)$$

Initial and boundary conditions for the proposed 5-lump model are: at z=0; $C_i=C_{i0}$ and at z=L; $C_i=C_i$. Where i denotes as group of compounds (C_4-C_{11}, C_{12}-C_{15}, C_{16}-C_{18}, gas and coke). The rate constants (k_1, k_2, ... k_{10}) are optimized by non-linier regression program. The sum of squares of the errors was minimized using iterative method

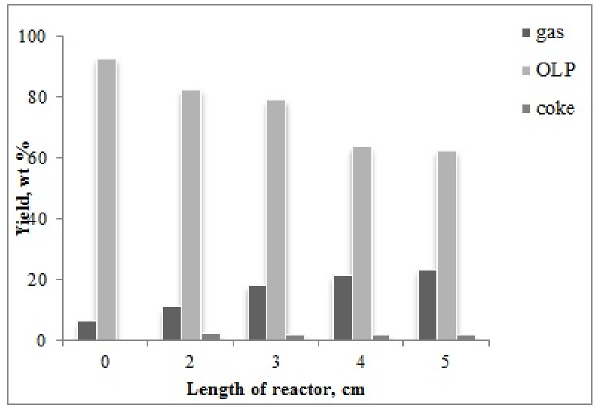
RESULT AND DISCUSSION

Effect of temperature and length of reactor

The experimental results were obtained from nyamplung oil cracking in a fixed bed reator. In this study, the cracking of nyamplung oil gave liquid products, gas and coke formation. The amount of water formation in liquid products was insignificant so is not listed as parameter to calculate yield. Figure-2 presents the yield of organic liquid product (OLP), coke and gas fraction in wt. % at different temperature and length of reactor over ZSM-5 catalyst.



(a)



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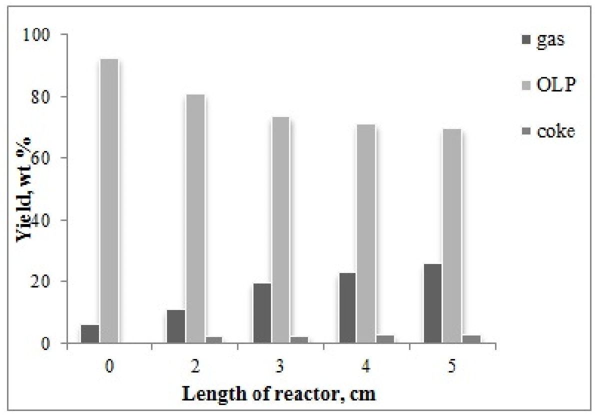

(c)

Figure-2. Yield of products from nyamplung oil cracking over ZSM-5 catalyst at temperature of (a) 350, (b) 400 and (c) 450 ^{0}C.

Figure-2 shows that the maximum yield of OLP at temperature of 400 ^{0}C at the length of reactor 2 cm. The yield of OLP decreases with the length of reactor and temperature. These results are the opposite of the yield of gas. This is due to at the higher temperature occurs secondary and over-cracking of liquid product form gas products. Despite having a lower liquid yield but at temperature of 450 ^{0}C resulted higher selectivity at the C_4-C_{11} fraction. The same phenomena happened on increasing the length of the reactor and it will produce a high selectivity of C_4-C_{11}

Kinetics of catalytic cracking

From GC and GC MS analysis showed that nyamplung oil as a reactor feed in the vapor phase which undergone thermal cracking from preheater in the form of hydrocarbons compounds, some oxygenated

This analysis results showed that the product from thermal cracking consist of hydrocarbon compounds ranging from 1 up to 18 of carbon atoms. During the catalytic cracking with the use of ZSM-5 catalysts the oxygen from carboxylic acids is eliminated either as water, CO or CO_2 through the decarboxylation and

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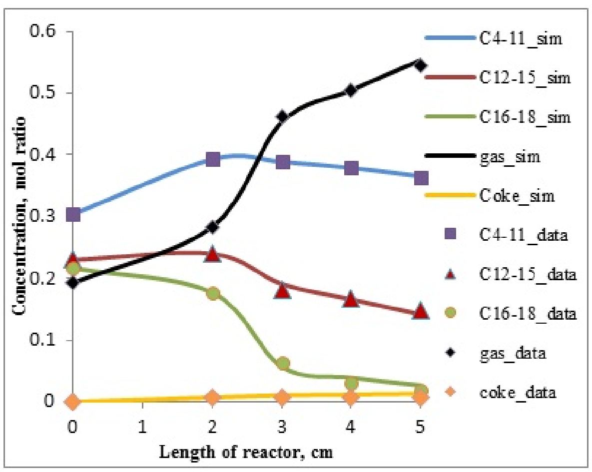
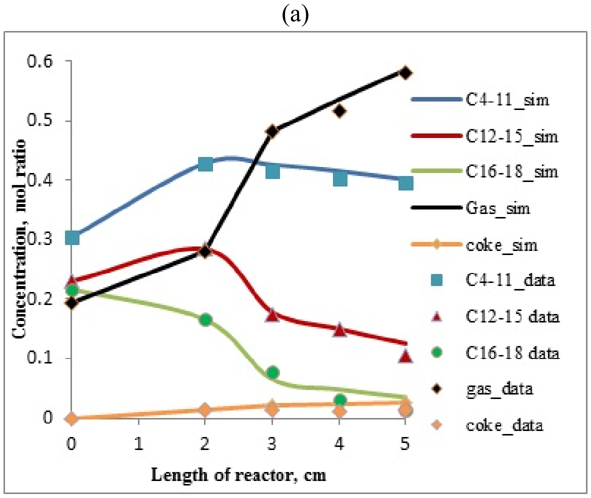
decarbonylation reaction. Figure-3 presents the model prediction on product yields and the experimental result which grouped into compound with the certain number of atom carbon, gas and coke fraction.

From Figure-3 can be seen that for the temperature reation reaction, the fractions of C_{12}-C_{15} and C_{16}-C_{18} have the same trend which decreases with increasing the length of the reactor. This trend shows that C_{12}-C_{15} and C_{16}-C_{18} undergo cracking process form another fraction.The yield of C_4-C_{11} fraction increase at the reactor length of 2 cm and tend to decline, which indicates the catalyst used lead the C_4-C_{11} fraction decomposes into gas and coke. Gas yield from decomposition of fractions C_4-C_{11}, C_{12}-C_{15} and C_{16}-C_{18} increase liniearly with the increase in length of reactor and the temperature reaction. This shows that catalyst used along the length of reactor lead to more active sites which can play a role in the cracking reaction. This is suitable with the characteristic of catalyst ZSM-5 which has the properties tend to produce gas [1]. The coke and C_{16}-C_{18} showed low concentration at higher temperature. At lower temperature (350 ^{0}C), coke deposited in the pores offered more diffusional resistance.



(a)



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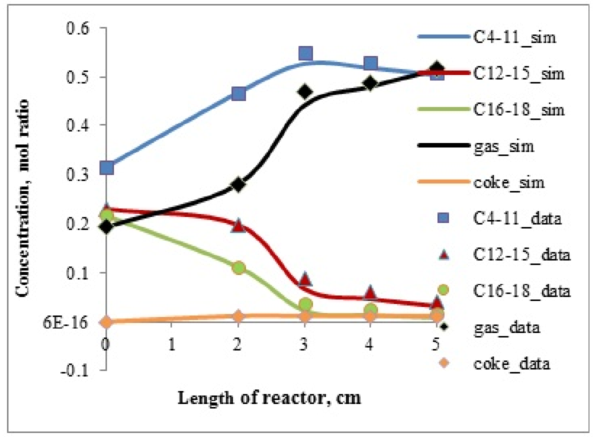

(c)

Figure-3. Experimental and simulated data for cracking over ZSM-5 catalyst at (a) 350, (b) 400 and (c) 450 ^{0}C.

Solving the equation of reaction kinetics was proposed from a lump models used non-linear regression program as described in equation (2) - (6). As input data are the concentration of the product along the length of the catalyst in reactor and the estimated value of the reaction constant. By adjusting the kinetic parameters, calculated concentrations of the product will be compared with experimental data. From the input data, the results of calculation concentration compared with experimental data. The output of program depicted in the form of a plot between the data predictions versus experimental data. The reliable model kinetics will provide the appropriate fitting data between the experimental and prediction data as presented in Figure-3. The proposed kinetic model gave accurate predictions on nyamplung oil with an minimum sum of square error (SSE) yields. The calculated results for the reaction kinetic parameter including the reaction constant are presented Table-1.

Table-1. Kinetic constants calculation.

k (cm^3/sec.g cat)	Temperature, ^{0}C		
	350	400	450
k1	1.05E-01	7.15E-02	5.52E-02
k2	9.22E-04	1.13E-03	1.98E-08
k3	1.59E-01	8.35E-02	2.95E-01
k4	6.51E-02	1.44E-01	1.08E-01
k5	9.14E-09	2.52E-14	3.85E-06
k6	4.68E-02	1.05E-01	2.14E-01
k7	3.15E-01	1.57E-01	9.85E-02
k8	1.56E-02	4.66E-02	2.16E-01
k9	9.32E-13	1.80E-05	2.94E-06
k10	2.12E-03	3.81E-03	2.44E-05

From the reaction kinetics calculation which presented in Table-1 shows that k_1 at temperature of 350 ^{0}C was higher thanat temperature of 400 and 450 ^{0}C. This suggests gas formation was dominated from the decomposition C_4-C_{11} fraction. But at a temperature of 400 ^{0}C shows that gas formation dominated from C_{12}-C_{15} fraction and at a temperature of 450 ^{0}C is derived from the decomposition of C_{16}-C_{18} fraction. This indicates formation of hydrocarbon gas at the higher fraction requires higher energy. The gaseous product under goes decomposition to form coke as shown from value of k_{10}. However this reaction showed a decrease in the reaction constant with temperature indicating there was energy released through the reaction. Formation of coke from C_4-C_{11} fractions is suitable with the characteristic of the ZSM-5 catalyst which has a selectivity to the formation of aromatic compounds. Subsequently it undergo polymerization formed non-volatile polyaromatic and covered the surface of the catalyst in the form of coke. The amount of C_4-C_{11}which formed from fraction of C_{12}-C_{15} and C_{16}-C_{18} shows a higher value with increasing the temperature as shown from the values of k_3 and k_6. This is due to an endothermic reaction which occurs in nyamplung oil cracking. The value of k_5 reaction rate constants for the decomposition of C_{12}-C_{15} fraction at temperature of 400 ^{0}C is very low, it means that almost negligible to coke formation, it is probably due to the diffusional effects in the zeolite pores.

CONCLUSIONS

Indonesian nyamplung oil is one of the potential raw material which can be direct converted into biofuels production without previous treatment and addition of chemicals. The maximum yield of OLP (82%) is resulted at temperature of 400 ^{0}C and reactor length of 2 cm, but the higher selectivity of light fraction (C_4-C_{11}) is achieved at temperature of 450 ^{0}C and reactor length 5 cm at the value of 67%. In this study, a five-lump model for the catalytic cracking of nyamplung oil is developed. In this model the reactant and product were classified into five-lumps, namely C_4-C_{11}, C_{12}-C_{15}, C_{16}-C_{18}, gas and coke. The simulated data obtained from the model gave satisfactory result with the experimental data. For detailed calculation the effect of diffusional resistance should be taken into account.

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