Kinetic Study of Palm Oil Catalytic Cracking Over A Zeolite-Based Catalyst

(Study Kinetika Perengkahan Katalitik Minyak Sawit Pada Katalis Berbasis Zeolite)

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ABSTRACT

A study on catalytic cracking of palm oil (RBDPO) over an equilibrium zeolite-based catalyst to produce gasoline fraction was carried out. The effect of contact times between the feed and catalyst was studied by experimenting with WHSV in the range of 6 h^{-1} to 25 h^{-1}, and the effect of catalytic reaction temperatures was observed at 490 °C, 510 °C, and 530 °C. The results show that yields of gasoline fraction tend to decrease with the decrease of WHSV, due to "over-cracking" of gasoline fraction into gaseous products. A four-lump kinetic model consisting of gasoline fraction, gaseous products, and coke was applied to derive sets of reaction rate equations. A numerical method was used to estimate the kinetic parameters.

Keywords: palm oil, biogasoline, catalytic cracking, kinetic model

ABSTRAK

Suatu studi mengenai perengkahan katalitik minyak sawit (RBDPO) pada katalis berbasis zeolit untuk menghasilkan fraksi bensin telah dilakukan. Pengaruh waktu kontak antara umpan dan katalis dipelajari melalui eksperimen dengan variasi WHSV dalam kisaran 6 $^{h-1}$ hingga 25 $^{h-1}$, dan pengaruh temperature reaksi katalitik diamati pada 490°C, 510 °C, dan 530 °C. Hasil penelitian menunjukkan rendemen fraksi bensin cenderung menurun seiring dengan penurunan WHSV, mengindikasikan terjadinya perengkahan lanjutan fraksi bensin menjadi produk gas. Model kinetika empat gumpalan yang terdiri dari fraksi bensin, produk gas, dan kokas diterapkan untuk memperoleh serangkaian persamaan laju reaksi. Metode numerik digunakan untuk memperkirakan parameter kinetika.

Kata kunci: minyak sawit, biogasoline, perengkahan katalitik, model kinetika

INTRODUCTION

Palm oil has been well known as a good source for liquid fuel substitutions; however, up to now, its commercial application is still limited to Fatty Acid Methyl Ester (FAME) as a diesel oil substitute. One of the routes to convert vegetable oil into biogasoline is *via* catalytic cracking, where the vapor of vegetable oils catalytically cracks into lighter hydrocarbon fractions, including gasoline fractions Catalytic cracking of vegetable oils has been studied using various

reactors over many catalysts. Sang et al., (2003) conducted an experimental study on the catalytic cracking of crude palm oil in a fixed-bed reactor over zeolite-based catalysts with various acidity and pore size, which gave a significant effect on the conversion and product distributions in the catalytic cracking of palm oil. It showed that the conversion increases with the surface area, while the increase in acidity gave higher selectivity toward the gasoline fraction that reached up to 48%. The operational conditions in catalytic

cracking of palm oil using a fixed-bed reactor over MCM-41 catalyst showed an optimum value of the weighted hourly space velocity (WHSV) at 19 h^{-1} to obtain 43 % yield of gasoline fraction (Siswanto, Salim, & Wibisono, 2008). Further, many studies in catalytic cracking of vegetable oil using mini pilot plant of Fluid Catalytic Cracking (FCC) reactor have been reported. Bielansky et al. (2011) performed a study on the production of biogasoline from pure vegetable oils and the blend of petroleum derivative, vacuum gas oil (VGO), and vegetable oils using a pilot plant with the flowrate of 3 liters per hour feed. It suggested that the mixtures of VGO and vegetable oils and pure vegetable oils could be performed in an FCC small-scale pilot plant without any difficulties. Further, Ibarra et al. (2019) studied the effect of catalyst type on the catalytic cracking process of bio-oil produced from the pyrolysis process in a small FCC simulator unit. It was found that the acidity of zeolite-based catalysts has a significant impact on the activity and selectivity of the catalyst.

The reaction kinetic studies of catalytic cracking of petroleum derivatives have been extensively conducted for predicting the distribution of products and activity of catalysts under various operating conditions. In the earlier study, the lump kinetic model of VGO cracking consists of three numbers of lump, i.e.: oil feed, gasoline fraction, and other components such as dry gases and coke (Weekman & Nace, 1970). Then, the model is developed into 4-lump models, separating coke into an additional lump (Lee, Yu, Cheng, & Pan, 1989). Further, a 5-lump model is proposed for VGO cracking and HCO (heavy cycle oil) cracking (Ancheyta-Juárez, López-Isunza, Aguilar-Rodríguez, & Moreno-Mayorga, 1997). The reaction kinetic model is also developed into several 6-lump kinetic models (John, Mustafa, Patel, & Mujtaba, 2019). Yield of catalytic cracking in FCC can be estimated using the lumping technique with the reaction kinetic model (Das, Murthy, & Ghosh, 1992).

Although many lump kinetic models of catalytic cracking reactions have been developed, a palm oil cracking reaction model still needs to be studied. Bhatia, Leng & Tamunaidu (2007) have developed a kinetic model of palm oil by proposing a three-lump, four-lump, and six-lump kinetic model. The proposed model was developed by combining data from the experiments using a model compound of fatty acids mixtures and palm olein running in a plug-flow microreactor.

In this work, catalytic cracking of refined, bleached, and deodorized palm oil (RBDPO) using an equilibrium zeolite-based catalyst commercially available was carried out in a micro-activity test (MAT). A 4-lumps kinetic model is developed to estimate the conversion of RBDPO catalytic cracking into gasoline fraction, gaseous products, and coke, and the kinetic model was simulated and compared to the experimental data.

Table 1. Properties of RBDPO and catalyst

RBDPO		Katalis esetimbangan FCC berbasis zeolit *(Eq. zeolite-based FCC Catalyst)*	
ALB - Palmitat (FFA as Palmitic) (%)	7.9	Ukuran pertikel rata-rata *(Particle size avg.)* (μm)	87
Angka Yod *(Iodine Value)* (gI$_2$/100g)	49.3	Luas permukaan rata-rata *(Surface area avg.)* (m2/g)	217
Densitas pada 50ºC *(Density at 50ºC)* (g/cm^3)	0.9	Densitas massal rata-rata *(Bulk density avg.)* (g/cc)	0.84
Viskositas *(Viscosity at 50ºC (cPs)*	30.7		
Kandungan uap *(Moisture content)* (%)	0.03		

Keterangan (*Remark*): *ALB-palmitat = asam lemak bebas sebagai Palmitat (*FFA =free fatty acid as Palmitic*)

MATERIALS AND METHODS

Material

RBDPO, palm oil that had undergone a refining process to eliminate the origin of free fat and purification to remove color and odor, obtained from Buditama Agri Ltd, was used as the feed. The equilibrium zeolite-based FCC catalyst was obtained from Pertamina Refinery Unit-III Plaju. The properties of the materials are listed in Table 1.

Methods

The Experiments

The experiments were carried out at the laboratory of P3TKEBTKE, Ministry of Energy and Mineral Resources. Data were obtained by performing RBDPO catalytic cracking process on eq. zeolite-based catalyst in micro activity test unit (MAT) as shown in Figure 1. The MAT unit was provided by PID Engineering & Technology, Spain, which complies with ASTM D-3907-92 to reflect the reaction conditions in FCC. The feeding system and the operation of the MAT were carried out according to Mansur et.al. (2020).

The CO_2 detector Servopro 4000 series was connected with the regenerator that contained CuO catalyst, which converts CO gas into CO_2, and as part of the MAT unit that can operate continuously. The weight of coke was determined by the total amount of CO_2 released during the regeneration of the used catalyst. The flow rate of gaseous products was measured at the outlet of the reactor by deducting total outflow gas with N_2 carrier gas flow rate. The organic liquid products (OLP) were analyzed by a SimDis Gas Chromatography Agilent 7890 series, and gasoline fraction (bp. < 215°C) was separated from the rest of the organics liquid.

Seven sets of experimental conditions were carried out (Table 2). At a constant temperature of 510⁰C and 1.4 CTO, five experiments with different weight hourly space velocities, WHSV (mass flow rate of feed per hour divided by mass of catalyst), were performed. The other two sets of experiments were carried out at 490⁰C and 530⁰C at a constant CTO of 1.4 and WHSV of 6.9. Each set of experiments was repeated twice with reproducible yield data with a deviation of less than 5%. Since the MAT operation needs to keep complying with the standard, such as the catalyst loading ranging between 4-8 grams, the given CTO was selected to enable enough wide range of WHSV variables. The industrial operating conditions of FCC usually set a higher CTO value to obtain higher conversions.
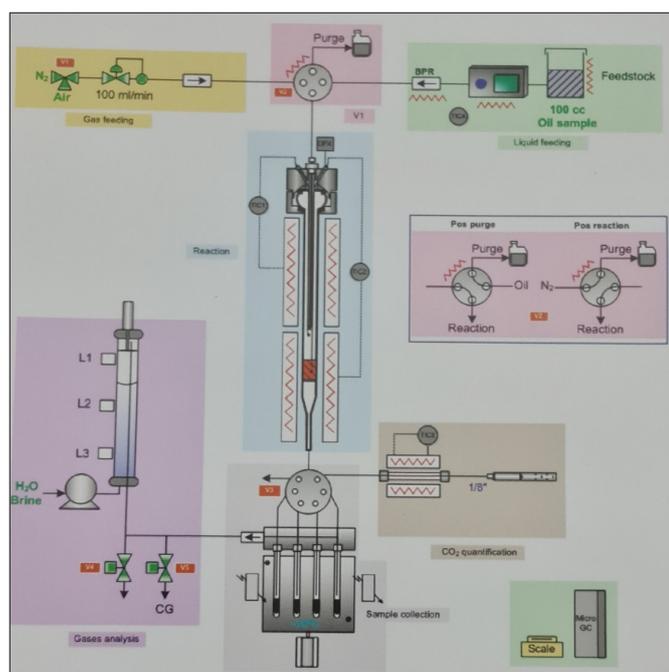
Figure 1. Micro activity test unit (MAT)

Table 2. Experimental operating conditions

Nomor Eks (*Exp. Set*)	1	2	3	4	5	6	7
T (*T*) , °C	490	530	510	510	510	510	510
Rasio katalis-mikyak (*CTO*)	1.4	1.4	1.4	1.4	1.4	1.4	1.4
*LRBJ, jam^{-1} (*WHSV, h^{-1}*)	6.9	6.9	6.9	9.9	14.8	19.8	24.7

Keterangan (*Remark*): *LRBJ= laju alir berat minyak per berat katalis (*WHSV=mass flowrate of oil per weight of catalyst*)

The conversion of RBDPO is defined as:

$$X_{RBDPO} (wt.\%) = \frac{total\ mass\ of\ (gas+gasoline+water+coke)}{mass\ of\ RBDPO_{feed}} \times 100\% \qquad (1)$$

Since the experimental data will be used to build the kinetic model to estimate the yield of gasoline, the organic liquid non-gasoline is defined as unconverted RBDPO into gasoline with gas, water and coke as sides product. The yield of product is defined as:

$$Yield (wt.\%) = \frac{mass\ of\ desired\ product}{mass\ of\ RBDPO_{feed}} \times 100\% \qquad (2)$$

Kinetic Study

Catalytic cracking of RBDPO into gasoline is modeled by the 4-lump reaction kinetics model as shown in Figure. 2. The 4-lump kinetic model is developed in regard to the conversion of RBDPO (as lump-1) into three main products, i.e. gasoline (as lump-2), gaseous products (as lump-3) and coke (as lump-4).

Palm oil triglycerides typically contain no more than 10 wt.% oxygen, and will go under decarbonylation, decarboxylation and dehydration reactions to form CO, CO_2, and water. Some water, which is usually incorporated in OLP during the condensation process, may be observed but is insignificant. In this model, those oxygenate compounds were lumped into a gaseous product. The rate constants of k12, k13, and k14 are assigned to the conversion of RBDPO into gasoline, gaseous product, and coke, while k23 and k24 are the rate constants of gasoline cracking into gas and coke, which may be occurred due to "over cracked". The reaction rate equations used in the model are as follows:

$$\frac{dY_1}{dt} = -(k12 + k13 + k14).(Y_1)^2.\varnothing \qquad (3)$$

$$\frac{dY_2}{dt} = (k12.Y_1^2 - k23.Y_2).\varnothing \qquad (4)$$

$$\frac{dY_3}{dt} = (k13.Y_1^2 + k23.Y_2).\varnothing \qquad (5)$$

$$\frac{dY_4}{dt} = (k14.Y_1^2) + (k24.Y_2).\varnothing \qquad (6)$$

$$\varnothing = e^{(-kd.t)} \qquad (7)$$
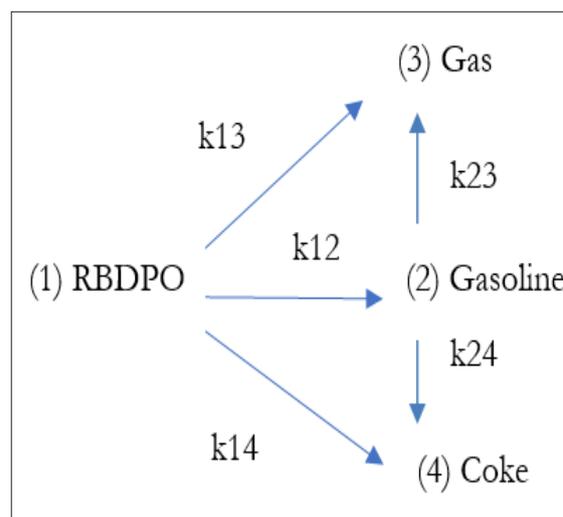
Figure 2. Reaction scheme for the 4-lump model

Y1, Y2, Y3, and Y4 are weight fractions of RBDPO, gasoline, gaseous product, and coke, respectively, and k12, k13, k14, k23, and k24 are the reaction rate constants. A function of catalyst decay (Ø) represents the catalyst activity loss due to coke formation on the catalyst surface. Deactivation constant kd is stated in time on-stream. As it has widely been adopted, these model equations assume that the catalytic cracking of RBDPO occurred as a second-order reaction and gasoline cracking is the first-order reaction. The reactions are assumed to occur in

an isothermal plug flow reactor model, and axial dispersion is neglected.

The kinetics constant value of the reaction is sought through experimental approaches and numerical calculations using the combined Runge-Kutta Algorithm and Levenberg-Marquardt optimization. The differential equations of the four lumps are solved using the 4th-order Runge-Kutta numerical method. The estimated mass fraction of the four lumps at the end of the reaction is determined by the objective function of the optimization, where the sum of squares error between estimated and experimental values of the mass fractions is set to be the minimum value to obtain the best set of kinetic parameters.

RESULTS AND DISCUSSION

The experimental data of RBDPO catalytic cracking performed in the microreactor is presented in Table 3. At a constant WHSV of 6.9, the yield of gasoline tends to decrease with the temperature rise in the range of 490 °C to 530 °C, while the yield of gas products increases. It shows that gasoline cracking into gas is taking place more substantially at higher temperatures.

In his previous works, Hussain (2015) investigated the catalytic cracking of VGO within the temperature range of 500 °C to 600 °C, and it is reported that at higher conversions (above 75%), with the temperature increase, the catalytic cracking promotes more gaseous product than gasoline. However, (Bhatia et al., 2007) studied the catalytic cracking of palm oil and fatty acid mixture in the temperature range of 400°-500°C. They reported that the yield of gasoline increased with temperatures within that range. Thus, it can be understood that the optimum temperature to obtain a high gasoline yield at the higher conversion of RBDPO catalytic cracking lies around 490°C -510 °C.

Further, at 510 °C, the increase of WHSV results in the rise of gasoline yields, the decrease of gas products, and the conversion of RBDPO. It means that the shorter the catalyst contact time, the least the cracking occurs on either RBDPO into gasoline or gasoline into gas, and the product

Table 3. Yield of RBDPO catalytic cracking in MAT reactor

No. Eksp. (Exp. set)	1		2		3		4		5		6		7	
Temp, °C (Temp, °C)	490		530		510		510		510		510		510	
Katalis/minyak (CTO)	1.4		1.4		1.4		1.4		1.4		1.4		1.4	
LRBJ, jam $^{-1}$ (WHSV, h $^{-1}$)	6.9		6.9		6.9		9.9		14.8		19.8		24.7	
Rendemen (Yield), wt.%														
Bensin (Gasoline)	22.12	20.29	14.76	15.91	15.58	15.34	18.14	16.26	19.94	21.02	23.05	24.59	21.91	24.00
Gas (Gas)	56.91	59.37	63.64	70.12	57.66	60.44	50.22	54.32	43.19	42.41	31.28	34.60	32.46	33.82
Kokas (Coke)	1.27	1.25	1.31	1.39	1.07	5.11	7.73	4.85	4.59	3.29	3.99	2.34	2.97	2.29
*POC lain (other OLP)	19.71	19.09	20.29	12.58	25.70	19.02	23.91	24.57	32.29	33.14	41.68	38.48	42.67	39.90
Conv. (%)	80.29	80.91	79.71	87.42	74.3	80.98	76.09	74.43	67.71	66.86	58.3	61.52	57.33	60.1

Keterangan (Remark): *POC lain = Produk Organic Cair lain (other OLP = other Organic Liquid Product)

k14

distributions tend to have higher selectivity of gasoline.

The estimated rate constants at 490°C and 510°C from the 4-lump reaction model are presented in Table 4. The estimation values of the rate constants show that the rate cracking of RBDPO into gasoline and gaseous product are comparable and predominant compared to the cracking route into coke formation. The rate of gasoline cracking into coke is negligible, especially at T=490°C. Hence, it is understood that coke is mainly produced by the cracking process of RBDPO.

Table 4. Estimated kinetic parameter of RBDPO catalytic cracking at 490°C and 510°C

Parameter (Parameters)		Konstanta laju reaksi (Rate constant)	
Reaksi [satuan] (Reaction [unit])		490°C	510°C
RBDPO →Bensin, k12 (RBDPO →Gasoline, k12)	[berat.%⁻¹jam⁻¹] [wt.% ⁻¹h⁻¹]	4.99	14.45
RBDPO → Gas, k13 (RBDPO → Gas, k13)	[berat.%⁻¹jam⁻¹] [wt.%⁻¹h⁻¹]	4.99	13.45
RBDPO → Kokas, k14 RBDPO → Coke, k14	[berat.%⁻¹jam⁻¹] [wt.%⁻¹h⁻¹]	0.30	3.34
Bensin → Gas, k23 Gasoline → Gas, k23	[jam⁻¹] [h⁻¹]	2.38	8.99
Bensin → Kokas, k24 Gasoline → Coke, k24	[jam⁻¹] [h⁻¹]	2.77 e⁻¹⁶	0.73
Penyimpangan total Total error	[%] [%]	8.1	9.5

The total error to obtain the best sets of kinetic parameters is below 10%. Although the fitting is expected to reach a satisfactory level, the error value below 10% is still within the acceptable range to estimate the relative yield distribution of RBDPO catalytic cracking. The comparison of the estimated yield of RBDPO catalytic cracking at 510°C and experimental data are shown in Figure 3. It shows that the highest yield of gasoline obtains at shorter contact times with the catalyst, while gasoline yields tend to decrease at longer contact times. The yield of gaseous product and coke consistently increases with the contact time.
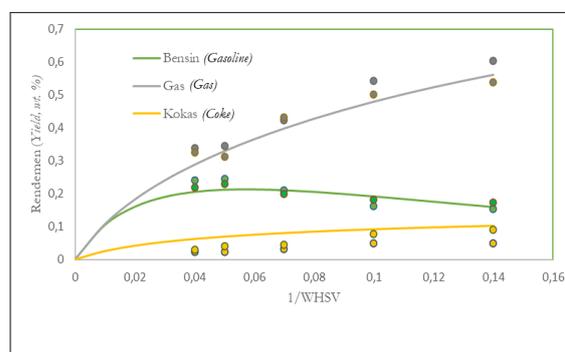
Figure 3. Yields of RBDPO catalytic cracking's product at various space velocities (1/WHSV) at 510°C

CONCLUSION

RBDPO catalytic cracking over commercial FCC catalyst has been performed in the microreactor unit. The obtained experimental data was used to develop sets of kinetic parameters, and the 4-lump model was applied and solved by numerical methods. The model is fit well with the experimental data and can predict the yield distributions of RBDPO at specific operating conditions. The rate of RBDPO cracking into gasoline and gaseous products is found to be predominant compared to other reactions. Hence, a commercial FCC catalyst is likely suitable for RBDPO catalytic cracking to produce gasoline and light hydrocarbon gases, such as LPG.

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AUTHOR'S CONTRIBUTION

The authors contributed equally to this work

Verina Januati Wargadalam: prepared detailed experimental designs and reaction kinetic schemes for the model, analyzing the data and writing the full manuscript

Aminuddin: conducting the experiments, processing and analyzing the data

Vetri Nurliyanti: preparing material and conducting the experiments

Muhammad H.G. Syafei: translate the reactions schemes into OD equations and solve numerically

Josiah Enrico: translate the reactions schemes into OD equations and solve numerically

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