

Kinetic Study of Catalytic Cracking of Bio-oil over Silica-alumina Catalyst

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One of the most important aspects in the catalytic cracking of bio-oil is understanding the kinetics of the process. The aim of this paper was to study the kinetics of bio-oil cracking with a silica-alumina catalyst using a continuous fixed-bed reactor. The reaction was studied over the temperature range of 450 to 600 °C with a catalyst bed length of 1 to 4 cm. Three models, Models 1, 2, and 3, were proposed to represent the catalytic cracking kinetics of bio-oil. Model 1 was based on the cracking of bio-oil into the products, while Models 2 and 3 were based on the three- and four-lump models, respectively. The results showed that the rate constants of the catalytic cracking of bio-oil increased with an increasing temperature. The reaction rate constants of the catalytic cracking of bio-oil using Model 1 ranged from 0.221 to 0.416 cm³/g cat-min with an activation energy of 22.3 kJ/mol. It was found that the reaction rate constants from Model 2 can be employed to describe the cracking phenomenon of bio-oil, liquid hydrocarbons, and gas and coke, whereas Model 3 can illustrate the kinetics of bio-oil, kerosene, gasoline, and gas and coke cracking.

Keywords: Bio-oil; Catalytic cracking; Catalyst; Kinetic; Silica-alumina

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INTRODUCTION

The consumption of fossil fuels has increased during the 21st century because of the growth of the global population and the automobile industry. This has led to high levels of depletion of non-renewable fossil fuels (Payormhorm *et al.* 2013; Wang *et al.* 2014). In addition, a continuous use of these fuels as energy source has resulted in the environmental pollution by increasing the concentration of carbon dioxide (CO₂) in the atmosphere (Wang *et al.* 2012; Sudibyo *et al.* 2017a). Therefore, there is an urgent need for the development of alternative renewable and environment friendly alternative energy sources (Sunarno *et al.* 2016).

Lignocellulosic biomass appears to be a potential renewable source of energy. Fuels derived from biomass can be produced in a CO₂ neutral system (Rezaei *et al.* 2014). One of the most abundant sources of biomass in Indonesia, which is an agricultural country, is palm empty fruit bunch (EFB) (Bahri *et al.* 2012; Djuned *et al.* 2014). This type of biomass has a very competitive price because it is produced as a solid waste from the palm oil industry. EFB contains 59.7% cellulose, 22.1% hemicellulose, and 18.1% lignin. These compounds can be converted into bio-oil through pyrolysis (Abdullah and Gerhauser 2008; Pradana and Budiman 2015).

Bio-oils are a complex mixture of water (15 to 30%) and various oxygen-containing compounds (28 to 40%), such as hydroxylketones, hydroxyaldehydes, esters, furans, sugars, phenols, and carboxylic acid. Because of their oxygen-rich composition, bio-oils present low heating values, chemical instability, and immiscibility with hydrocarbon fuels, high viscosity, and corrosiveness (Hew *et al.* 2010; Mortensen *et al.* 2011). As a result, improving their quality is required. This can be achieved by reducing the amount of the oxygenated compounds, which involves various processes, such as catalytic cracking (Saad *et al.* 2015; Sunarno *et al.* 2017).

Several studies on catalytic cracking of bio-oil using silica-alumina and ZSM-5 catalysts have been done in fixed-bed reactors. Adjaye and Bakhshi (1995) investigated the catalytic cracking of bio-oil from 330 to 410 °C and obtained an oil yield of 13.2%. Zhu *et al.* (2013) studied catalytic cracking using ZSM-5 as a catalyst from 500 to 600 °C and obtained an oil yield of 36%. In another study, Graça *et al.* (2009) used a mixture of bio-oil and gas oil as the raw materials for catalytic cracking at 535 °C and obtained an oil yield of 19.6%. However, these studies merely investigated the processing conditions of bio-oil catalytic cracking.

One of the most important aspects in the catalytic cracking of bio-oil is the understanding of its kinetic properties. This is critical to design and simulate the reactor, as well as to predict the reaction behaviours (Mufrodi *et al.* 2014; Pu *et al.* 2015). Because of its complexity, it is difficult to describe the kinetics of bio-oil catalytic cracking at the molecular level (Wicakso *et al.* 2017). The formulation of lumped kinetics is usually utilized to determine the cracking kinetics of petroleum hydrocarbons (Meier *et al.* 2015; Dewajani *et al.* 2016). Most cracking reactions of hydrocarbon follow the first order reaction kinetics (Sedighi *et al.* 2013; Rahimi and Karimzadeh 2015). Therefore, the aim of this paper was to study the kinetics of bio-oil cracking with a silica-alumina catalyst using a continuous a fixed-bed reactor.

EXPERIMENTAL

Materials

Bio-oil, which was the raw material used in this study, was produced by the pyrolysis of oil palm EFB (PTPN V Sei Galuh, Riau, Indonesia) in a fixed-bed reactor at 500 °C. The pyrolysis product consisted of solid bio-char, liquid bio-oil, and non-condensable gases. The liquid bio-oil (the top phase fraction and the aqueous product) was separated by decantation. The top phase fraction and aqueous product contained 3% and 36% water, respectively. The top phase fraction of the bio-oil was used as a raw material for catalytic cracking. The properties of the raw material were as follows: density of 0.997 g/mL, viscosity of 17.9 centipoises (cP), and a heating value of 27.6 MJ/kg. The raw material was analyzed using GC-MS and was composed of 4.02% acetone, 5.24% acetic acid, 2.69% gasoline (C₅-C₁₁), 6.53% kerosene (C₁₂-C₁₈), 23.89% phenol, and 57.54% oxygenated organic compounds. The chromatogram of the analysis result is shown in Fig. 1.

Catalyst Preparation

The silica-alumina catalyst was obtained from PT. Pertamina (Balongan, Indonesia). The powder-form catalyst was converted into a granular form to facilitate the cracking process. Granulation was done manually with the addition of the clay (5 wt.%)

to form pellets that had the same size (0.4 cm x 0.6 cm). Furthermore, the catalyst was activated in a furnace at 500 °C for 2 h. The catalyst had a SiO₂/Al₂O₃ ratio of 1.167, surface area of 240.553 m²/g, and average pore diameter of 3.3 x 10⁻⁶ mm.

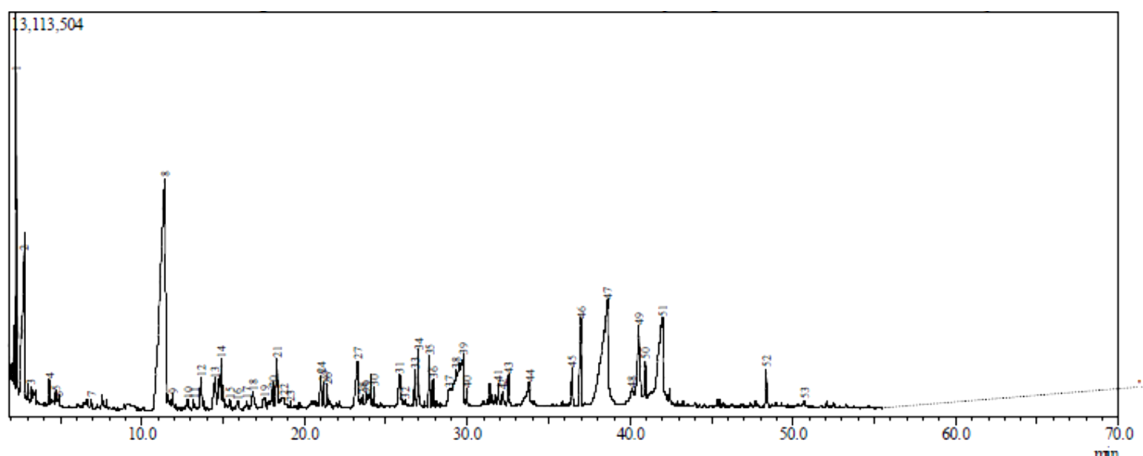


Fig. 1. The GC-MS chromatogram of bio-oil composition profile

Catalytic Cracking Reaction

The experiments were performed under atmospheric pressure from 450 to 600 °C in a tubular reactor packed with a silica-alumina catalyst bed that had a length of 1 to 4 cm. The scheme of the experimental equipment is presented in Fig. 2.

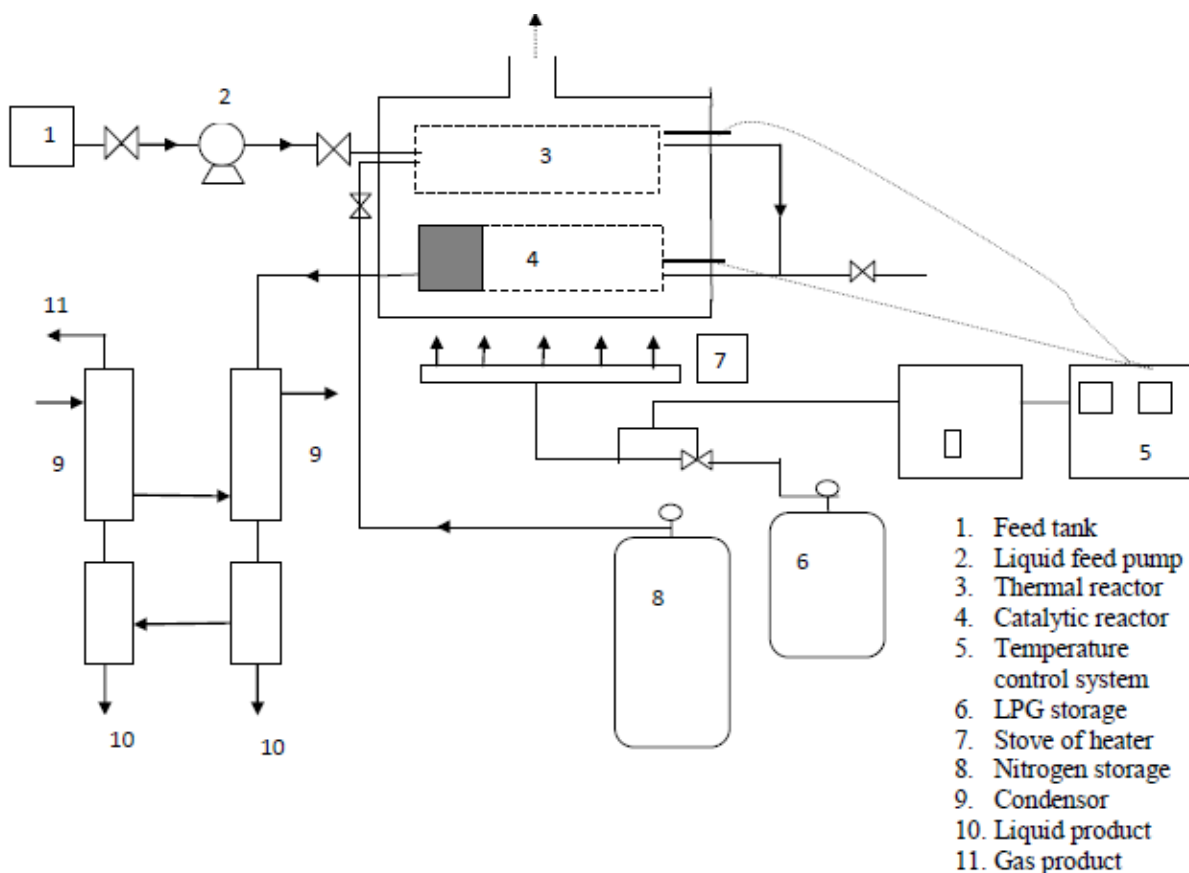


Fig. 2. Schematic diagram of the cracking reaction experiment

The system consisted of a tubular reactor (inner diameter = 70 mm), vaporizer, a liquid feed system, a liquid feed pump, furnace, stove, liquefied petroleum gas (LPG) system, a condenser, and a cooling water pump. The reactor was heated with the LPG fuel system to the desired temperature.

Nitrogen was used at a flow rate of 400 mL/min to completely remove the air completely throughout the reactor system, and then bio-oil was pumped in at a volumetric rate of 8 mL/min until there was a volume of 50 mL.

The vapor produced was condensed in the water-cooled condenser and the liquid product was collected in an Erlenmeyer flask. The compositions of the liquid and gas products were analyzed using gas chromatography-mass spectroscopy (GC-MS) (QP2010S Shimadzu, Kyoto, Japan) and gas chromatography (GC) (Shimadzu series GC 8A, Kyoto, Japan), respectively.

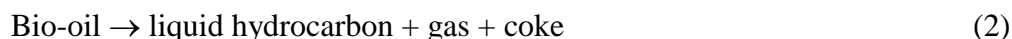
Kinetic Model 1

The Model 1 was developed with the following assumptions: (1) the fixed-bed reactor is in a steady-state operation, (2) the reaction takes place under isothermal conditions, and (3) the reactions are all catalytic, where the thermal conversion and diffusion in the axial direction are not taken into account.

Based on the above assumptions, the mass balance equation for bio-oil cracking in a fixed-bed reactor with an incremental catalyst bed length was written as follows:

$$v_z \frac{dC_A}{dz} = -(-r_A \cdot \rho_B) \quad (1)$$

The cracking products consisted of a liquid, gas, and coke. From the GC-MS analysis results, it was found that the main contents of the liquid product were oxygenated compounds, phenols, and hydrocarbons. The oxygenated compounds and phenols can be deoxygenated into hydrocarbons through catalytic cracking. The reaction of bio-oil cracking was modelled as a single reaction (Model 1; Eq. 2).



By assuming that bio-oil cracking is a first-order reaction, its reaction rate (r_A) was written as Eq. 3. Substituting Eq. 3 into Eq. 1 resulted in Eq. 4,

$$r_A = -k \cdot C_A \quad (3)$$

$$v_z \frac{dC_A}{dz} = -(k \cdot C_A \cdot \rho_B) \quad (4)$$

where C_A is the concentration of gravimetric bio-oil, expressed as mass per mass of the total product, v_z is the superficial velocity (cm/min), ρ_B is the bulk density of the catalyst (g/cm^3), and k is the reaction rate constant ($\text{cm}^3/\text{g cat} \cdot \text{min}$).

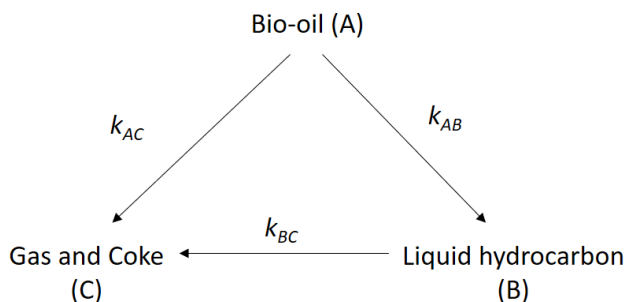


Fig. 3. Reaction kinetics of three-lump model (Model 2)

Kinetic Model 2

Based on Eq. 1, gas and coke are only produced from bio-oil cracking. However, gas and coke can also be produced from the cracking of hydrocarbons. Therefore, a kinetic model of bio-oil cracking can be formulated from the three-lump model, which is shown in Fig. 3.

The three-lump model is described by the following rate equations,

$$\frac{dC_A}{dz} = [-k_{AB} \cdot C_A - k_{AC} C_A] \frac{\rho_B}{v_z} \quad (5)$$

$$\frac{dC_B}{dz} = [k_{AB} \cdot C_A - k_{BC} C_B] \frac{\rho_B}{v_z} \quad (6)$$

$$\frac{dC_c}{dz} = [k_{AC} \cdot C_A + k_{BC} C_B] \frac{\rho_B}{v_z} \quad (7)$$

The C_A , C_B , and C_C terms are the concentrations (wt.%) of gravimetric bio-oil, liquid hydrocarbons, and gas and coke, respectively. The rate constants (k_{AB} , k_{AC} , k_{BC}) were optimized by using a non-linear program (Matlab R2008a, version 7.6.0.324, USA).

Kinetic Model 3

Model 3 was based on kinetic Model 2, and the liquid hydrocarbons were classified as kerosene and gasoline. With this model, bio-oil can be cracked into gas and coke, kerosene, and gasoline. Kerosene can subsequently be converted into gasoline and gas and coke, whereas gasoline can also be cracked into gas and coke. The reaction mechanism of kinetic Model 3 is represented in Fig. 4.

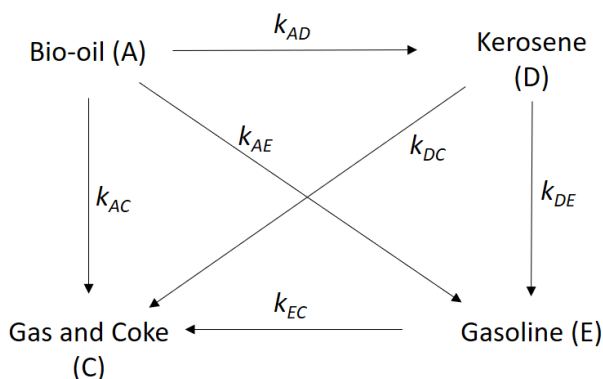


Fig. 4. Reaction kinetics of four-lump model (Model 3)

The four-lump model is described by the following rate equations which are based on Eq. 4.

$$\frac{dC_A}{dz} = [-k_{AD} \cdot C_A - k_{AC} \cdot C_A - k_{AE} \cdot C_A] \frac{\rho_B}{v_z} \quad (8)$$

$$\frac{dC_D}{dz} = [k_{AD} \cdot C_A - k_{DC} \cdot C_D - k_{DE} \cdot C_D] \frac{\rho_B}{v_z} \quad (9)$$

$$\frac{dC_c}{dz} = [k_{AC} \cdot C_A + k_{DC} \cdot C_D + k_{EC} \cdot C_E] \frac{\rho_B}{v_z} \quad (10)$$

$$\frac{dC_E}{dz} = [k_{AE} \cdot C_A + k_{DE} \cdot C_D - k_{EC} \cdot C_E] \frac{\rho_B}{v_z} \quad (11)$$

The C_A , C_D , C_C , and C_E quantities are the concentrations (wt.%) of the gravimetric bio-oil, kerosene, gas and coke, and gasoline, respectively. The rate of reaction constants k_{AD} , k_{AC} , k_{DC} , k_{DE} , and k_{EC} were directly stated in the form of an Arrhenius equation as shown by Eq. 12. The symbols A , R , T , and E represent the frequency factor, gas constant (8.314 J/mol.K), absolute temperature (K), and activation energy (J/mol) respectively. Thus, the calculation to find the constants would focus on finding the Arrhenius constants of each reaction constants above (Sudibyo *et al.* 2017b). To do so, the optimization was conducted by minimizing the sum of squares of errors (SSE) using an iterative method. The SSE was defined by Eq. 13.

$$k = A \cdot \exp\left(\frac{-E}{RT}\right) \quad (12)$$

$$SSE = \sum [(C_i)_{simulation} - (C_i)_{data}]^2 \quad (13)$$

RESULTS AND DISCUSSION

Effect of the Temperature and Catalyst Bed Length on the Yield

The catalytic cracking of bio-oil was performed in a continuous fixed-bed reactor with silica-alumina catalyst from 450 to 600 °C with a catalyst bed length of 1 to 4 cm. The products from the catalytic cracking process consist of oil, gases, and coke. Product of oil contained bio-oil (phenol, oxygenate compounds) and hydrocarbons. Figure 5 shows the yields of the bio-oil, liquid hydrocarbons, and gas & coke at different temperatures and catalyst bed lengths.

The optimum process condition was achieved under 500 °C reaction temperature and 1 cm of the length of the catalyst. At the other conditions, the yield of gas and coke formation was greater. It preferred to have high yield of hydrocarbon formation and low yield of gas and coke formation because the purpose of increasing the calorific value of oil product was realized by converting it into high calorific value hydrocarbon.

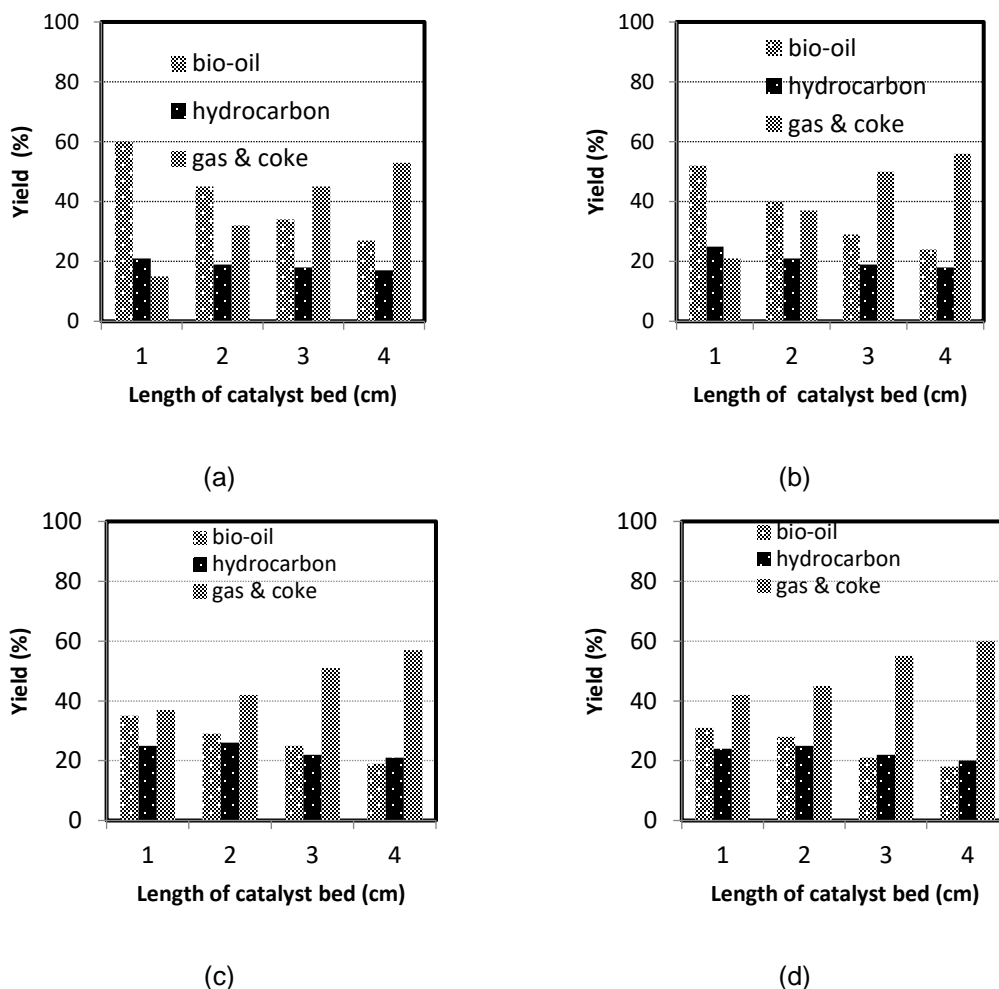


Fig. 5. Yield of products from bio-oil cracking with a silica-alumina catalyst at various temperatures : (a) 450 °C, (b) 500 °C, (c) 550 °C, and (d) 600 °C

Kinetic Model 1

Figure 6 shows the catalytic cracking of bio-oil at different catalyst bed lengths (0 to 4 cm) and temperatures (450 to 600 °C).

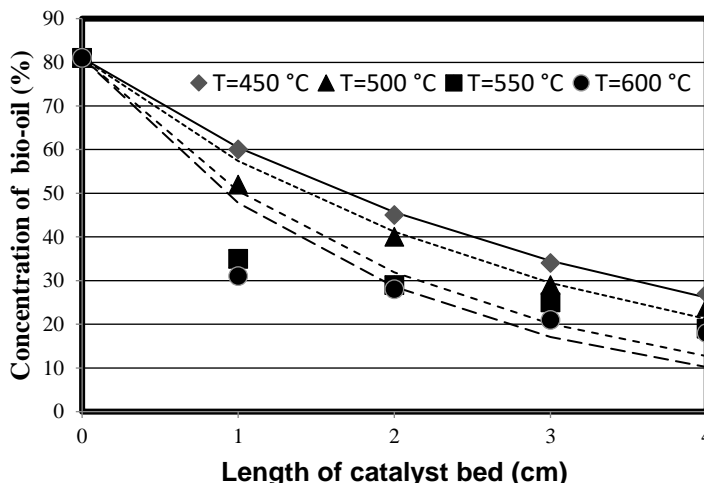


Fig. 6. Experimental (points) and simulated (lines) data of Model 1 for bio-oil cracking

As the catalyst bed length and temperature increased, the concentration of bio-oil decreased. This was ascribed to the presence of oxygenated compounds in the bio-oil, which were deoxygenated and cracked into liquid hydrocarbons and non-condensable gases, such as CH₄, CO₂, and CO. Figure 6 also shows a comparison of the experimental bio-oil concentrations (points) and the Model 1 predicted bio-oil concentrations (lines). The predicted concentrations of the bio-oil were close to the experimental ones. This indicates that the kinetic Model 1 can sufficiently fit the experimental data well, and the predicted results are reliable. The proposed kinetic Model 1 offered accurate predictions of the bio-oil yield with a minimum SSE values. The kinetic parameters obtained by fitting the experimental data are presented in Table 1.

Table 1. Effect of the Temperature on the Reaction Rate Constant from Model 1

Temperature (°C)	SSE	$k(\text{cm}^3/\text{g cat}/\text{min})$
450	0.001	$k = 8.9710 \exp\left(-\frac{22281.52}{8.314T}\right)$
500	0.009	
550	0.102	
600	0.132	

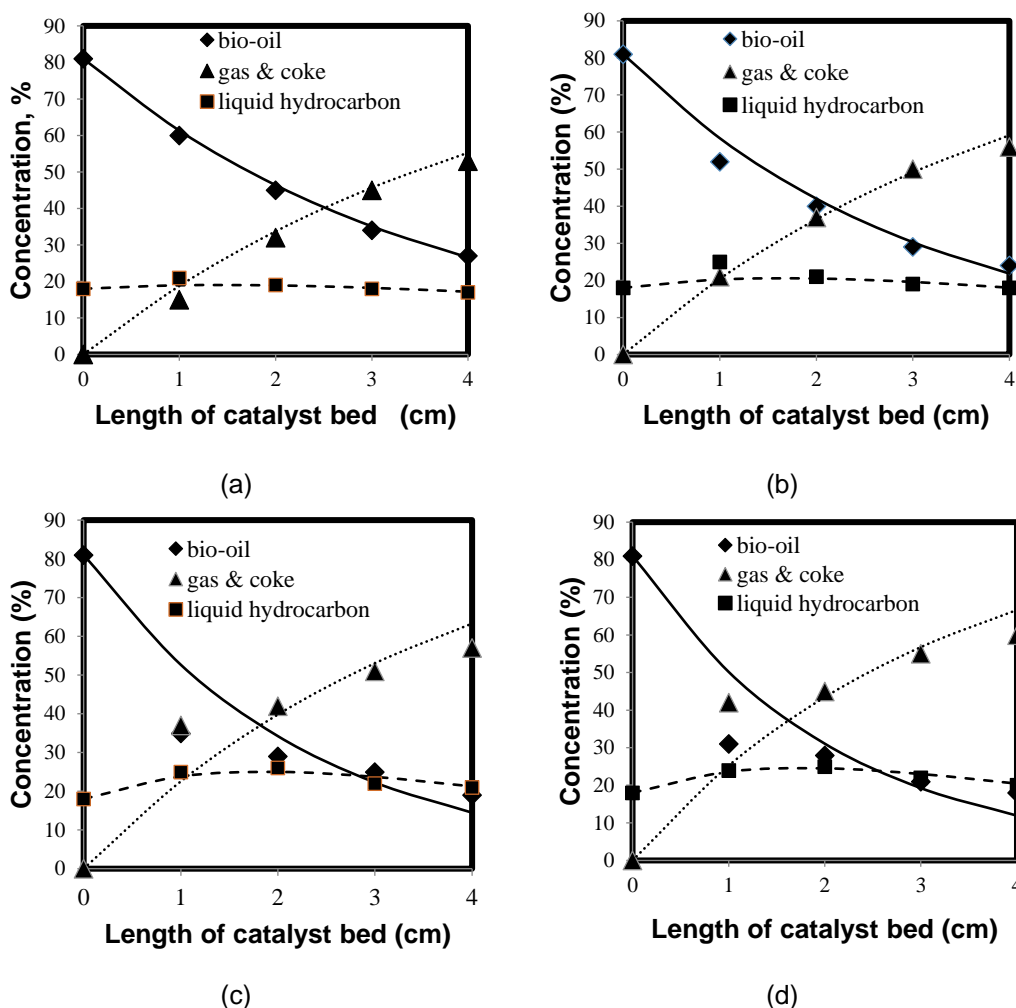


Fig. 7. Experimental (points) and simulated (lines) data from Model 2 for bio-oil cracking over silica-alumina catalyst at (a) 450 °C, (b) 500 °C, (c) 550 °C, and (d) 600 °C

From Table 1, an E of 22.28 kJ/mol was obtained. This value was lower than the activation energy at cracking of palm oil fatty acid with HZSM-5 catalyst, which was 30 kJ /gmol (Ooi *et al.* 2004). This indicated that the bio-oil cracking was easier to perform than palm oil fatty acid cracking.

Kinetic Model 2

Model 2 is based on a three-lump model of bio-oil cracking that produces liquid hydrocarbons, and gas and coke. In this model, it was assumed that the cracked bio-oil contains the oxygenated compounds and phenols. Gas and coke can be produced from hydrocarbons and are also produced directly from bio-oil cracking. The reaction kinetics equation proposed from the lump model was solved by using the non-linear regression program as described in Eqs. 5, 6, and 7. The required input data were the concentration of the product, length of the catalyst bed in the reactor, and the estimated value of the reaction rate constant. By adjusting the kinetic parameters, the concentrations of the products were calculated. The results of the calculated concentration were compared with the experimental data. The output of the program was depicted in the form of a plot between the data predictions and experimental data. The reliable model kinetics provided an appropriate fitting data between the experimental and prediction data, which is shown in Fig. 7.

Figure 7 shows that as the length of the catalyst bed increased, the concentration of bio-oil decreased, while the concentration of gas and coke increased. The concentration of liquid hydrocarbons increased until a catalyst bed length of 2 cm, and then it began to decline as the bed length further increased. This was because when the catalyst bed was longer, there was more bio-oil cracked into gas and coke, and more liquid hydrocarbons produced. However, for a catalyst bed length of more than 2 cm, the amount of liquid hydrocarbons cracked into gas and coke was more than the amount that was produced.

The proposed kinetic Model 2 offered accurate predictions for bio-oil cracking with minimum SSE values. The kinetic parameters obtained by fitting the experimental data are listed in Table 2. It was found that with an increasing operating temperature, the value of the reaction rate constants tended to increase. Additionally, by using Arrhenius's equation, the E values of the three-lump model were calculated, which are presented in Table 2. The E for bio-oil cracking into gas and coke was lower than bio-oil cracking into liquid hydrocarbons. This suggested that the chain breaking reaction between carbon occurs more easily than the termination of oxygen bonds.

Table 2. Kinetic Constants Estimated from Model 2 for Bio-oil Cracking with a Silica-alumina Catalyst

Temperature (°C)	SSE	k_{AB} (cm ³ /g cat/min)	k_{AC} (cm ³ /g cat/min)	k_{BC} (cm ³ /g cat/min)
450	0.005	$6.0439 \exp\left(-\frac{4823}{8.314T}\right)$	$0.6378 \exp\left(-\frac{18315}{8.314T}\right)$	$0.8049 \exp\left(-\frac{6831}{8.314T}\right)$
500	0.033			
550	0.377			
600	0.531			

Kinetic Model 3

In Model 3, the liquid hydrocarbons were divided into groups of gasoline and kerosene. Furthermore, the residual concentrations of the bio-oil, kerosene, gas and coke, and gasoline formed in the catalyst bed with different lengths were calculated using Eqs. 8, 9, 10, and 11, respectively. The simulation results of the model and the experimental data with the model are shown in Fig. 8.

Figures 8a and 8b show that the kerosene concentration decreased with an increasing catalyst bed length, but the concentration of gasoline increased until the length of the catalyst bed reached 2 cm. Figures 8c and 8d show that the concentration of kerosene and gasoline increased until a 2 cm catalyst bed length, and after which it decreased. Additionally, it was concluded from Figs. 8a and 8b that at 450 and 500 °C the calculated concentrations were similar to the experimental data concentrations with average percent errors of 6.71% and 6.18%, respectively. In contrast, Figs. 8c and 8d show that the experimental and simulated data had a larger deviation, *i.e.* 17.06% and 12.33%, respectively. Larger deviation was probably caused by the possibility of intermediate product formation, which was not covered by the model during reaction. This large deviation also indicated that at very high temperature, new kinetics model (outside the three models proposed in this study) must be synthesized.

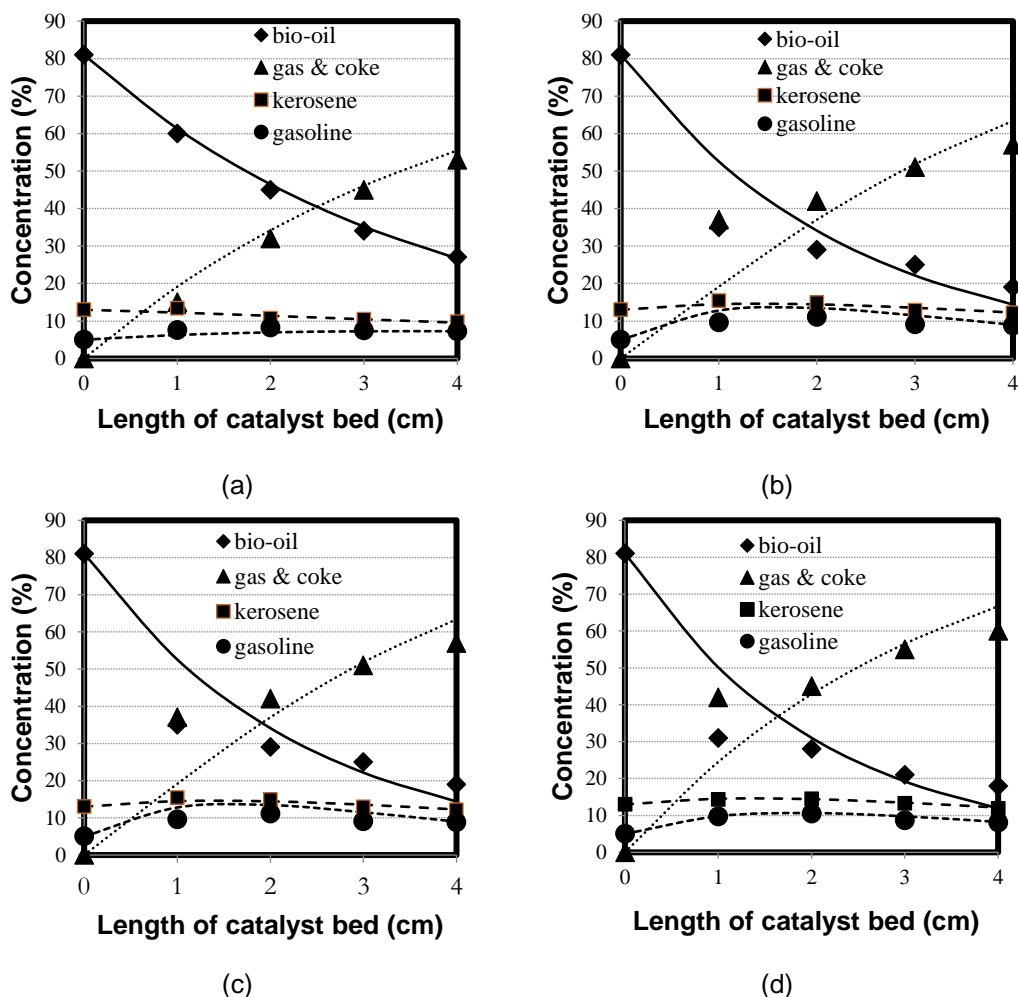


Fig. 8. Experimental (points) and simulated (lines) data of Model 3 for bio-oil cracking with a silica-alumina catalyst at (a) 450 °C, (b) 500 °C, (c) 550 °C, and (d) 600 °C

Table 3. Kinetic Constants Estimated from Model 3 for Bio-oil Cracking with a Silica-alumina Catalyst

Constants	Temperature (°C)			
	450	500	550	600
SSE	0.0106	0.0310	0.3723	0.5296
k_{AD} (cm ³ /g cat/min)	$10.869 \exp\left(-\frac{25890}{8.314T}\right)$			
k_{AC} (cm ³ /g cat/min)	$0.2074 \exp\left(-\frac{390}{8.314T}\right)$			
k_{DE} (cm ³ /g cat/min)	$0.27 \exp\left(-\frac{4429}{8.314T}\right)$			
k_{AE} (cm ³ /g cat/min)	$45.396 \exp\left(-\frac{28816}{8.314T}\right)$			
k_{DE} (cm ³ /g cat/min)	$0.2176 \exp\left(-\frac{9187}{8.314T}\right)$			
k_{EC} (cm ³ /g cat/min)	$33.067 \exp\left(-\frac{21034}{8.314T}\right)$			

The kinetics parameters obtained from Model 3 are listed in Table 3. With an increasing operating temperature, the value of the reaction rate constants tended to increase. The E values of the four-lump model were calculated using Arrhenius's equation. The results presented in Table 3 show that the E for bio-oil cracking into kerosene was lower than for bio-oil cracking into gasoline, which indicated that bio-oil cracking into kerosene formation is easier than gasoline formation. Hence, Model 3 can be employed to describe the phenomena of bio-oil, kerosene, and gasoline cracking.

CONCLUSIONS

1. The temperature and catalyst bed length affected the product yield and kinetics of bio-oil catalytic cracking.
2. With an increase in the catalyst bed length and temperature, the oil yield decreased, while the gas yield increased. The reaction rate constants of bio-oil cracking were calculated by using kinetic Model 1, which satisfied the Arrhenius's equation.
3. Kinetic Models 2 and 3 can be employed to determine the dominant reaction step in bio-oil catalytic cracking.
4. Overall, the developed Models 1, 2, and 3 were found to be suitable for determining the kinetics of continuous bio-oil catalytic cracking.

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