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Catalytic Cracking of Palm Oil into Liquid Fuels: Kinetic Study

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ABSTRACT
The kinetics of the catalytic cracking of palm oil into liquid hydrocarbons are investigated and the catalytic cracking of palm oil was performed in a fixed bed microreactor, operated in the temperature range of 673 – 723 K and palm oil feed weight hourly space velocity (WHSV) of $1 – 4$ h^{-1}. Steam treated HZSM-5 zeolite at 1073 K was used as catalyst in the reactor and the catalyst to oil ratio was varied from 0.1 to 0.22 in order to study the deactivation of the catalyst during the reaction. The kinetics of catalytic cracking of palm oil is represented using lumped parameter models based on 3-, 4- and 6- lumps sequentially. The kinetic constants for different models were evaluated and, the yield of products obtained from 6-lump model was compared with the experimental values. The kinetic rate constants showed that gasoline and kerosene fractions did not undergo secondary cracking reactions compared with the diesel fraction. In addition to that, coke mainly formed from the cracking of the gasoline and diesel fractions. The results obtained from 6-lump model were found in agreement with the experimental values within the experimental error.

Keywords: catalytic cracking, HZSM-5, kinetics, lump parameter model, palm oil.

1. INTRODUCTION
The production of biofuels such as bio-diesel and bio-gasoline has attracted the interest of the number of researcher as an alternative or environmental friendly fuels [1]. The catalytic cracking of palm oil to liquid fuels has been studied over acid cracking catalysts [2]. Many complex reactions occur during the palm oil cracking process, but one of primary interest is to crack large molecules into smaller ones and thus reduce their boiling point to the more useful range of gasoline fraction, kerosene fraction, diesel fraction and gaseous products [3]. The description of complex mixtures by lumping large numbers of chemical compounds into smaller number of products of pseudo components has been widely used in petroleum refining industry to provide tractable model useful for the plant design and operation [4]. The lumping of the products into groups depending on their classification made to facilitate the handling of the data obtained from the experimentation. These products can be classified into many groups such as gaseous products, liquid products and coke [5].

The reaction rate for each lump pathway describes the mechanism of the cracking reaction and thus selectivity for the desired products. The complexity of the lump model varies according to the degree of lumping proposed. 3-lump parameter model has been proposed for the catalytic cracking reaction of gasoil [6]. The sum of the lumped parameters incorporated in the model presents the kinetics of the overall cracking reaction [7]. Most of the cracking reaction of pure hydrocarbons followed first order reaction kinetics whereas the feedstocks of petroleum hydrocarbons showed variable order in the range of 1.6 - 1.9 [8]. Incorporating more products in the model could increase the number of lumps. den Hollander et al., [9] and Ancheyta-Juarez et al., [7] applied 5-lump parameter model to heavy cycle oil (HCO) and gasoil cracking respectively. Other higher lump parameter models were also proposed such as 7-lump model in methanol to olefins process [10] and 10 or 12 lumps for gasoil cracking [11].

The catalytic activity decreases with time due to the catalyst decay during the cracking reaction. The deactivation of catalyst may occur during the cracking reaction due to coke formation. A deactivation model is generally proposed to describe the deactivation of the catalyst. The activity depends upon the mechanism of catalytic decay and can be found with an appropriate model. The rate of catalyst deactivation can be incorporated in the catalytic cracking model to account for catalyst deactivation. The catalyst activity ($\varnothing$) is defined as the ratio of the rate of reaction at time t to the rate of reaction over a fresh catalyst (t = *0*) [12].

$$\varnothing(t) = \frac{rate\ of\ reaction\ at\ time\ (t)}{rate\ of\ reaction\ at\ time\ (t = 0)} \qquad (1)$$

Some researchers reported deactivation models based on the coke formed over the catalysts during cracking reaction [13-14]. However, measuring the coke formed on the catalyst and its relation with the catalyst decay is subjected to the experimental errors, and the complex nature of coke does not allow a more mechanistic interrelation of catalyst decay. A deactivation model based on time on stream involves the assumption that catalyst activity ($\varnothing$) is dependent on the time on stream (t) [5] and the rate of deactivation may be presented by Equation (2).

$$-\frac{d\phi}{dt} = k_d \varnothing^{n_d} \qquad (2)$$

Where k_d : deactivation rate constant and n_d : order of catalyst deactivation rate.
Therefore, the time on stream model can be more useful and deactivation parameters can be evaluated from activity against time on stream data.

The objective of the present investigation is to propose a suitable kinetic model for palm oil cracking over HZSM-5 catalyst for the production of liquid hydrocarbons. The reaction parameters of the proposed kinetic model are evaluated and experimental data obtained are compared with the calculated values obtained from proposed model.

2. EXPERIMENTAL

Refined, bleached and deodorized (RBD) palm oil was used for cracking studies in the present investigation. HZSM-5 zeolite (CBU 8070) powder was supplied by P.Q. Corporation, Kansas, USA and used as cracking catalyst. The hydrothermal deactivation of the catalyst was performed by heating the sample in a tubular reactor at 1073 K in the presence of saturated steam. The steam was passed through the catalyst bed for 2 h at a pressure of 3 bar. The catalyst sample was calcined in air at 823 K for 4 h after the steam treatment.

Cracking reaction of palm oil was conducted in a stainless steel fixed bed micro-reactor (155mm length ×10mm I.D.) fitted with a thermocouple placed in the center of the catalyst bed. One gram of steam treated catalyst sample was placed in the micro-reactor. The reactor was heated to the desired reaction temperature using electrical vertical tube furnace. Nitrogen gas was passed at 0.2 l/h through the system for 1 h before the palm oil was fed into the reactor. Palm oil was fed by syringe-metering pump and products were cooled in a condenser at 313 K. The liquid products were collected in a glass trap and the gaseous products separated in the trap were collected in a glass-sampling vessel. The volume of the gaseous products was measured by water displacement technique. In order to estimate the quantity of the residual oil, the liquid product was distilled in a micro-distillation unit (Buchi B580, GKR) at a temperature of 473 K under vacuum of 100 Pa. The distillate fraction was the organic liquid product (OLP) and the pitch was assumed the unconverted palm oil.

The gaseous products were analyzed with a gas chromatograph (GC) (Hewlett Packard, model No. 5890 series II) using a plot Q glass column (30m-length × 0.3mm I.D.). The GC was equipped with both flame ionization detector (FID) and thermal conductivity detector (TCD). After normalizing the components, the molecular weight of the gases was calculated. The FID was used to analyze the organic liquid products (OLP) using a capillary glass column (Petrocol DH 50.2, film thickness 0.5 μm, 50m length and 0.2mm I.D.). The components were defined according to boiling point range of hydrocarbon fuel by injecting commercial samples of gasoline, kerosene and diesel. The spent catalyst was washed with acetone to determine the remaining residual oil over the catalyst. The coke formed on the catalyst during the cracking reaction was determined using a thermal gravimetric analyzer (Perkin-Elmer TGA7).

3. DEACTIVATION MODEL

The catalyst deactivates due to coke formation during the cracking reaction. The deactivation model in the catalytic cracking of palm oil was assumed to be a function of time-on-stream. In order to calculate the deactivation, experiments were performed at three catalyst-to-oil ratios 0.1, 0.14 and 0.22 respectively, and presented in Table 1.

Table 1. Experimental matrix of the palm oil cracking at different ranges of temperature (673 - 723 K), catalyst-to-oil ratio (0.1 – 0.22) and WHSV (1 – 4 h^{-1}).

T	WHSV	CTO	X_P	C_{OLP}	C_{Diesel}	$C_{Kerosene}$	$C_{Gasoline}$	C_{Gas}	C_{Coke}
(K)	(h^{-1})		(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
673	1	0.22	75.27	55.26	6.80	18.51	30.00	5.12	8.22
698	1	0.22	83.43	66.85	7.50	21.42	39.55	7.10	4.63
723	1	0.22	98.22	78.90	8.20	25.20	45.50	11.10	1.56
673	2.5	0.22	67.29	55.59	22.5	10.00	23.60	2.15	6.00
698	2.5	0.22	74.36	57.82	9.80	16.90	34.81	8.20	4.70
723	2.5	0.22	95.14	72.18	3.00	22.66	45.83	17.85	1.56
673	4	0.22	35.23	27.89	7.00	10.57	9.96	1.79	5.56
698	4	0.22	59.30	44.93	6.35	14.23	26.17	7.54	5.32
723	4	0.22	76.70	50.92	1.78	15.89	33.56	18.44	1.78
673	1	0.14	57.27	48.77	10.19	11.07	24.70	2.69	5.40
698	1	0.14	78.30	61.44	9.00	15.55	33.92	7.44	4.82
723	1	0.14	98.34	76.8	4.00	22.50	45.00	16.40	3.46
673	2.5	0.14	50.52	31.26	12.22	9.44	22.72	3.79	4.33
698	2.5	0.14	69.15	52.41	10.31	14.11	32.18	8.47	3.81
723	2.5	0.14	92.17	69.58	5.57	20.87	43.55	16.20	2.86
673	4	0.14	46.45	28.75	9.43	8.42	20.03	3.34	3.10
698	4	0.14	66.00	39.52	8.86	13.37	30.54	8.80	2.95
723	4	0.14	88.72	52.32	1.83	18.06	42.43	16.78	1.75
673	1	0.10	66.49	53.12	3.88	14.08	34.20	2.77	4.55
698	1	0.10	79.28	59.39	5.45	17.65	35.71	7.37	2.77
723	1	0.10	97.70	76.80	3.90	25.70	48.50	13.90	0.91
673	2.5	0.10	35.61	25.80	6.81	3.74	13.80	1.63	2.12
698	2.5	0.10	66.04	50.36	7.76	13.21	30.97	8.40	2.86
723	2.5	0.10	96.86	69.70	2.02	20.56	46.56	20.29	0.81
673	4	0.10	15.15	11.99	0.64	3.50	6.52	1.14	2.02
698	4	0.10	83.42	66.85	7.49	21.41	39.55	7.18	4.63
723	4	0.10	70.88	46.59	2.47	14.67	30.33	15.81	3.43
723	2.5	0.22	96.12	71.23	2.21	20.51	47.51	16.66	1.56
723	2.5	0.22	96.51	72.21	3.73	24.89	45.32	15.08	1.51
723	2.5	0.22	97.85	73.32	3.78	24.2	45.79	14.96	1.68
723	2.5	0.22	94.15	69.91	3.50	24.55	42.86	15.87	1.52
723	2.5	0.22	96.57	73.60	2.94	20.24	49.68	14.68	1.60

The conversion, X_P and concentration of desired product, $C_{Product}$ such as organic liquid products (C_{OLP}), diesel fraction (C_{Diesel}), kerosene fraction ($C_{Kerosene}$), gasoline fraction ($C_{Gasoline}$), gaseous products (C_{Gas}) and coke (C_{Coke}) are defined as follows:

$$X_P(\text{wt.\%}) = \frac{\text{Palm oil fed (wt.) - Residual oil (wt.)}}{\text{Palm oil fed (wt.)}} \times 100\% \tag{3}$$

$$C_{Prodeuct}(\text{wt.\%}) = \frac{\text{Product (wt.)}}{\text{Palm oil fed (wt.)}} \times 100\% \tag{4}$$

Time-on-stream was adjusted by changing the total weight of oil injected into the reactor at selected feed rate. Five experiments were repeated to check the reproducibility of the experimental data. The data were reproducible within ±5%.

The non-linear regression analysis method based on Levenberg-Marquard's algorithm was used to estimate the values of the deactivation order n_d from Equation (2). The integral form of Equation (2) resulted in Equation (5).

$$\varnothing(t) = 0.59 k_d t^{-0.59} \tag{5}$$

The deactivation rates constant k_d at different reaction temperatures were found to be 0.0372, 0.0415 and 0.0459 at 673K, 698K and 723K respectively. The dependency of k_d with temperature is given as:

$$k_d = k_{do} e^{-E_d / RT} \tag{6}$$

The frequency factor (k_{do}) was found as $k_{do} = 0.777$ and the activation energy (E_d) was found 17.00 kJ/mol. The deactivation function $\varnothing$ was incorporated in the kinetic model.

4. KINETIC MODELING

In order to calculate the cracking reaction parameters, lump parameter model was used in this study. The sequential method proposed for gasoil cracking by Archeyta-Juarez et al., [7] was used. The sequential strategy containing 3 steps is shown in Figure 1; step (1) 3-lump model, step (2) 4-lump model and step (3) 6-lump model. The rate of reaction data based on palm oil conversion and products formation for the cracking reaction were obtained using differential method of calculation at catalyst/oil ratio of 0.14 and variation of the residence time ($\tau = 1/WHSV$).

Figure 1(a) shows 3-lump parameter model for palm oil cracking. The lumps of cracking products were based on the weight fraction. The 3-lump model resulted in two rate equations. The rate of palm oil cracking is represented in Equation (7) and the formation of the organic liquid product (OLP) containing hydrocarbon fractions is presented in Equation (8). The reaction order n was assumed to be same for all the reaction and the unknown reaction constants (k_1, k_2, and k_3) were estimated.

$$\frac{dC_P}{d\tau} = -\varnothing (k_1 + k_2) C_P^n \tag{7}$$

$$\frac{dC_{OLP}}{d\tau} = \varnothing (k_1 C_P^n - k_3 C_{OLP}^n) \tag{8}$$

The reaction parameters (k_1, k_2 and k_3) were estimated using the least square method by minimizing the sum of squares of the error which was the difference between the values obtained from model and from the experimental values. The sum of squares of the errors was minimized using an iterative method based on Levenberg-Marquard's algorithm using Polymath software package [15].

The first step was finding the values of the reaction constant ($k_1 + k_2$) and the reaction order n from Equation (7). The reaction order (n) of palm oil cracking was found to be 1 and the kinetic constants obtained are presented in Table 2. The values of the reaction order found in the 3-lump model were used in further lump models to obtain reaction parameters.

The second step was parameters estimation from 4-lump model presented in Figure 1(b), using the parameter values obtained from the 3-lump model. The rate of formation of the gaseous and coke products was incorporated separately into 4-lump parameters model by splitting of the (gaseous+coke) lump into two lumps gas and coke [16]. The kinetic constant k_1 of palm oil cracking remains unchanged and the reaction rate equations for gas and coke formation are presented in Equations (9) and (10) respectively. The reaction constants (k_{21}, k_{22}, k_{31}, k_{32} and k_4) were estimated by solving Equations 9 to 12, and the estimated kinetic constants for 4-lump model are presented in Table 2.

$$\frac{dC_{Gas}}{d\tau} = \varnothing (k_{21} C_P^n + k_{31} C_{OLP}^n - k_4 C_{Gas}^n) \tag{9}$$

$$\frac{dC_{Coke}}{d\tau} = \varnothing (k_{22} C_P^n + k_{32} C_{OLP}^n + k_4 C_{Gas}^n) \tag{10}$$

$$k_2 = k_{21} + k_{22} \tag{11}$$

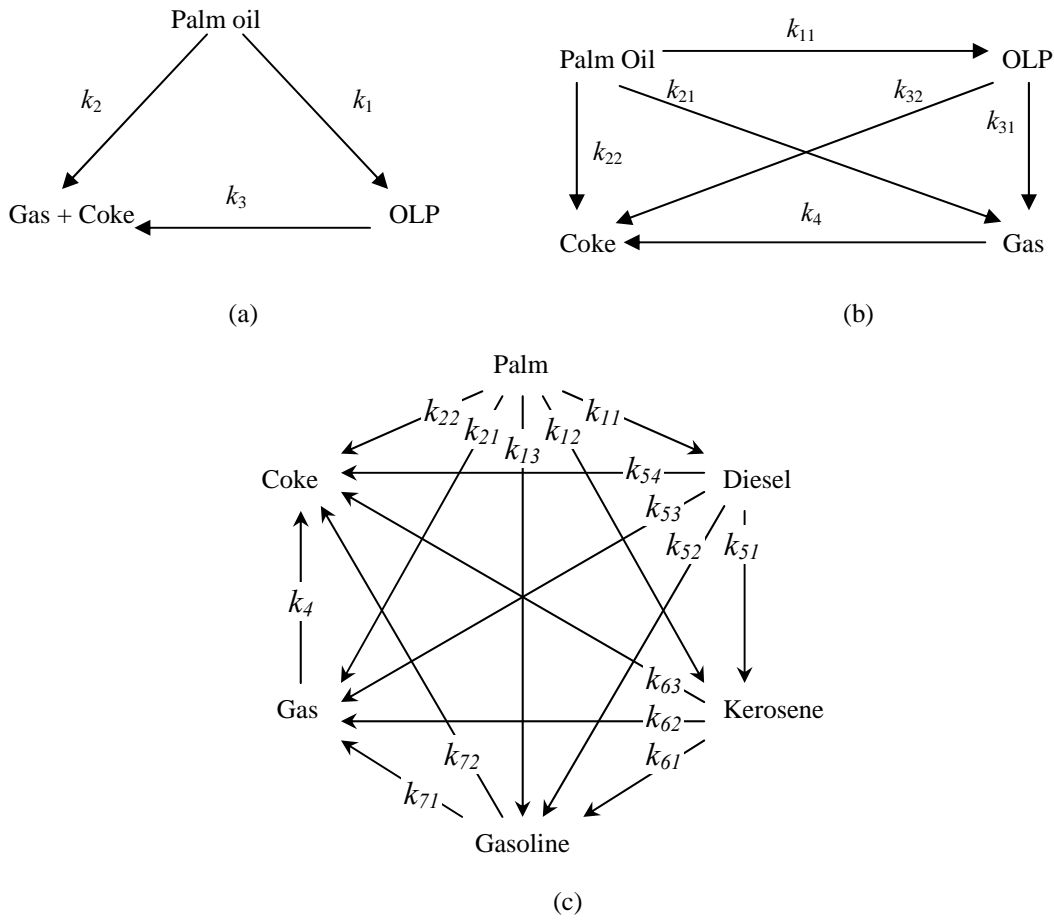$$k_3 = k_{31} + k_{32} \tag{12}$$

(a)

(b)

(c)

Figure 1: (a) 3-lump model, (b) 4-lump model and (c) 6-lump model

The third step was application of 6-lump model and estimation of reaction parameters using the parameters obtained from 4-lump model. Figure 1(c) shows the reaction network based on 6-lump model derived from 4-lump parameters model. In this model, the organic liquid product lump is divided into three lumps are gasoline fraction, kerosene fraction and diesel fraction respectively. The network of the reaction covers all the possibilities, assuming higher hydrocarbons will crack into lower hydrocarbons. The procedure developed for determination of reaction parameters of 4-lump model was applied to 6-lump parameters model. The reaction order found in the 3-lump and 4-lump models were used for further calculations in the network of 6-lump model and the reaction rates for the lumps are presented in Equations 13 to 17.

$$\frac{dC_{Diesel}}{d\tau} = \varnothing(k_{11}C_P^n - k_5C_{Diesel}^n) \tag{13}$$

$$\frac{dC_{Kerosene}}{d\tau} = \varnothing(k_{12}C_P^n + k_{51}C_{Diesel}^n - k_6C_{Kerosene}^n) \tag{14}$$

$$\frac{dC_{Gasoline}}{d\tau} = \varnothing(k_{13}C_P^n + k_{52}C_{Diesel}^n + k_{61}C_{Kerosene}^n - k_7C_{Gasoline}^n) \tag{15}$$

$$\frac{dC_{Gas}}{d\tau} = \varnothing(k_{21}C_P^n + k_{53}C_{Diesel}^n + k_{62}C_{Kerosene}^n + k_{71}C_{Gasoline}^n - k_4C_{Gas}^n) \tag{16}$$

$$\frac{dC_{Coke}}{d\tau} = \varnothing(k_{22}C_P^n + k_{54}C_{Diesel}^n + k_{63}C_{Kerosene}^n + k_{72}C_{Gasoline}^n + k_4C_{Gas}^n) \tag{17}$$

Table 2. Reaction constants, activation energies and frequency factors values estimated from 3-lump, 4-lump and 6-lump models in the temperature range of (673 – 723).

Reaction	Rate Constant				Activation energy (E) (kJ/mol)	Frequency factor, α
	Parameter	673 K	698 K	723 K		
3-lump model						
Palm oil $\rightarrow$ OLP	k_1	0.3080	0.9400	1.5673	132.19	5.91E+09
Palm oil $\rightarrow$ gas+coke	k_2	0.0620	0.1890	0.3161	132.19	1.25E+09
OLP $\rightarrow$ gas+coke	k_3	0.0025	0.0780	0.0131	137.01	2.53E+08
4-lump model						
Palm oil $\rightarrow$ gas	k_{21}	0.0072	0.0500	0.2500	287.16	1.46E+20
Palm oil $\rightarrow$ coke	k_{22}	0.0226	0.0690	0.1150	132.19	4.39E+08
OLP $\rightarrow$ gas	k_{31}	0.0000	0.0000	0.0000	0.00	1.00E+00
OLP $\rightarrow$ coke	k_{32}	0.0025	0.0079	0.0131	132.19	5.22E+07
Gas $\rightarrow$ coke	k_4	0.2500	0.0840	0.0606	-115.23	2.52E-10
6-lump model						
Palm oil $\rightarrow$ diesel	k_{11}	0.2000	0.3000	1.5220	162.95	7.18E+11
Palm oil $\rightarrow$ kerosene	k_{12}	0.0700	0.1000	0.6250	175.59	2.38E+12
Palm oil $\rightarrow$ gasoline	k_{13}	0.1000	0.1000	0.9388	178.75	5.31E+12
Diesel $\rightarrow$ kerosene	k_{51}	0.3200	0.6000	1.5220	125.79	1.78E+09
Diesel $\rightarrow$ gasoline	k_{52}	0.0260	0.0790	0.1328	132.44	5.36E+08
Diesel $\rightarrow$ gas	k_{53}	0.10000	0.5460	0.9105	179.58	1.07E+13
Diesel $\rightarrow$ coke	k_{54}	0.0400	0.0800	0.3600	176.92	1.86E+12
Kerosene $\rightarrow$ gasoline	k_{61}	0.0000	0.0000	0.0000	0.00	1.00E+00
Kerosene $\rightarrow$ gas	k_{62}	0.0000	0.0000	0.0000	0.00	1.00E+00
Kerosene $\rightarrow$ coke	k_{63}	0.0000	0.0000	0.0000	0.00	1.00E+00
Gasoline $\rightarrow$ gas	k_{71}	0.0000	0.0000	0.0000	0.00	1.00E+00
Gasoline $\rightarrow$ coke	k_{72}	0.0045	0.0100	0.2000	304.70	1.39E+21

The parameters in Equations 13 to 17 are evaluated using the relations given in Equations 18 – 23.

$$k_1 = k_{11} + k_{12} + k_{13} \tag{18}$$

$$k_{31} = k_{53} + k_{62} + k_{71} \tag{19}$$

$$k_{32} = k_{54} + k_{63} + k_{72} \tag{20}$$

$$k_5 = k_{51} + k_{52} + k_{53} + k_{54} \tag{21}$$

$$k_6 = k_{61} + k_{62} + k_{63} \tag{22}$$

$$k_7 = k_{71} + k_{72} \tag{23}$$

The estimated kinetic parameters for 6-lump model are presented in Table 2 at the temperatures of 673, 698 and 723 K respectively. It is important to include the temperature effect on the kinetic parameters using the

Arrhenius law ($k = \alpha \, e^{-E/RT}$) and calculating the activation energies for each reaction in the network by plotting logarithematic kinetic constant against reciprocal temperature. Table 2 shows the activation energies and frequency factors calculated for the reaction parameters obtained in the 6-lump model. The activation energies were compared with the reported values for gas oil cracking and found to be lower [7]. Equations 13 – 17 were integrated simultaneously using Runge-Kutta-Fehlberg (RKF) algorithm and Polymath software in the residence time range of 0.25 – 1h to predict the conversion and yield of products. The model can predict values in the range of variables studied. The concentration of palm oil and products were predicted from the 6-lump model are presented in Figure 2 at 673, 698 and 723 K, respectively.

5. DISCUSSION

The results in Figure 2 shows the concentrations of palm oil against the residence time. It is clearly seen that the concentration of palm oil linearly decreased with residence time at different temperatures. The reaction constants for palm oil cracking presented in Table 2 show that the reaction rate increased significantly with the reaction temperature and the activation energy required for the cracking was compared and found higher than those reported with the cracking of gasoil [7]. However, the values of activation energies for the intermediate reactions were similar to the reported values for gasoil.
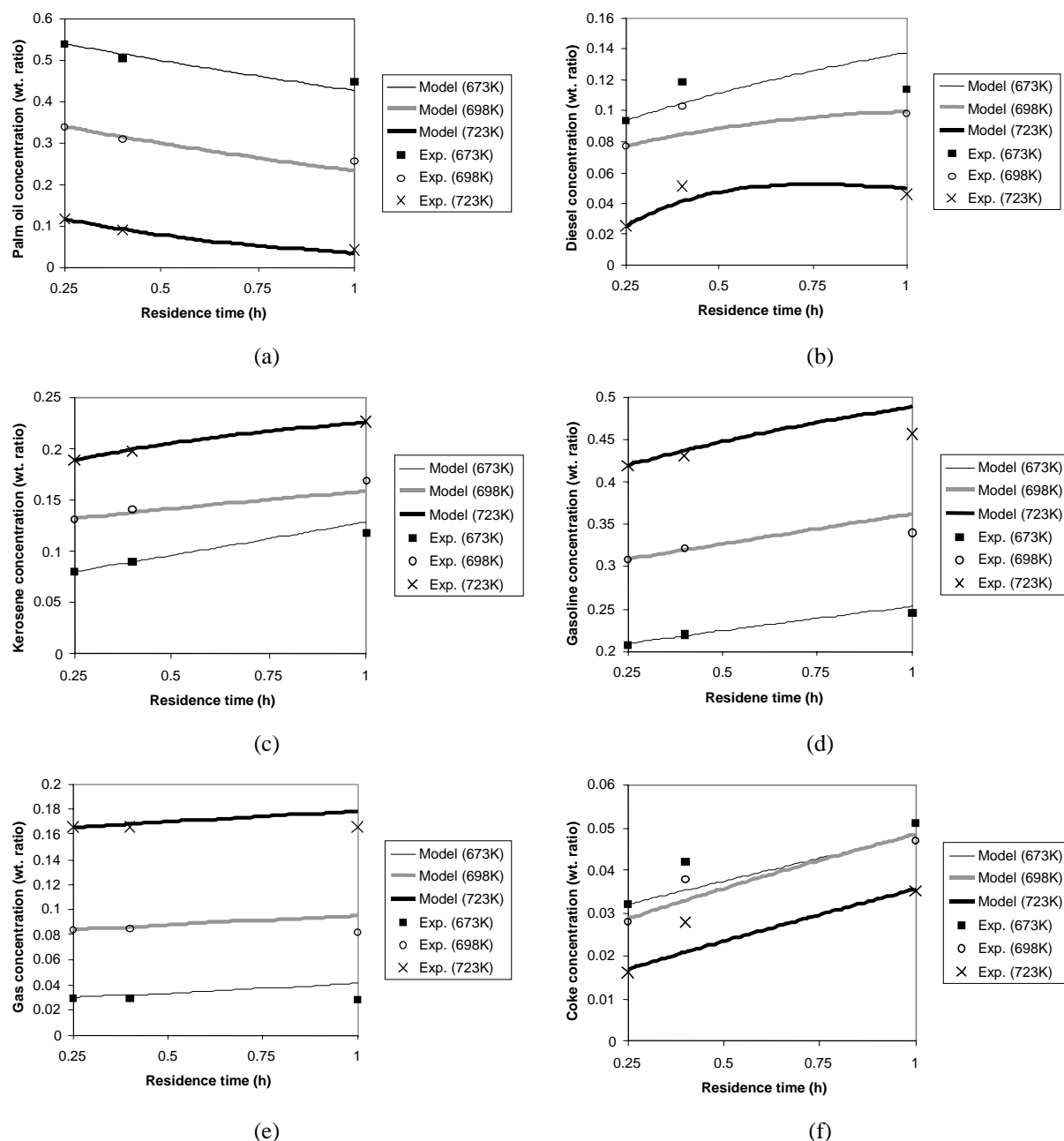

(a)

(b)

(c)

(d)

(e)

(f)

Figure 2: Yield of products obtained from 6-lump model at 673 K, 698 K and 723 K at catalyst to oil ratio of 0.14. (a) Palm oil, (b) Diesel, (c) Kerosene, (d) Gasoline, (e) gaseous products and (f) Coke

The gasoline and kerosene fractions increased with the increase in the residence time. It is observed that the reaction constants for the decomposition of kerosene and gasoline fractions were almost neglected with the exception of the formation of coke from gasoline decomposition. The coke formation from gasoline was inline that ZSM-5 catalyst is selective for the formation of aromatic hydrocarbons which may undergo further polymerization reactions to form the coke, showing high energy consumption compared to the other cracking reactions [2]. The rate constant values showed that gasoline and kerosene fractions did not undergo secondary cracking reactions compared with the *k* values for the decomposition of diesel fraction indicating that secondary cracking reactions occurred. Moreover, the coke did not form from the cracking of the kerosene fraction probably due to the diffusional effects in the zeolite pores. The rate constant for kerosene fraction formation was lower as compare to the rate constant of the palm oil cracking, however it was observed that most of the kerosene fraction was formed from the decomposition of the diesel fraction. The diesel fraction concentrations were higher at the low residence time and remained almost constant with further increase in residence time. In addition, the gaseous products showed constant values along the reaction time, whereas the gas production was mainly from palm oil and diesel fraction cracking, respectively. The gaseous product undergoes to form coke, however this reaction showed a decrease in the reaction constant with the temperature indicating energy released through the reaction. The coke and diesel fraction both showed low concentration at higher temperatures. At lower temperature, the coke deposited in the pores offered more diffusional resistance.

6. CONCLUSION

The strategy for using 3-, 4- and 6-lumps models was useful in the estimation of the kinetic parameters in sequence and testing the confidence of the model in the earlier stage of calculations. However, the diffusion process could affect the selectivity of the product formation as well as the kinetics of the reaction. In the present model, the effect of diffusional resistance was not accounted. The 6-lump model predicted palm oil and products concentrations within the experimental error at different residence time in the range of study.

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