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Kinetics of Palm Oil Cracking in Batch Reactor

Farouq Twaiq, Ishaq Al-Anbari, and Mustafa Nasser

***Abstract*—**The kinetics of palm oil catalytic cracking over aluminum containing mesoporous silica Al-MCM-41 (5% Al) was investigated in a batch autoclave reactor at the temperatures range of 573 – 673 K. The catalyst was prepared by using sol-gel technique and has been characterized by nitrogen adsorption and x-ray diffraction methods. Surface area of 1276 m^2/g with average pore diameter of 2.54 nm and pore volume of 0.811 cm^3/g was obtained. The experimental catalytic cracking runs were conducted using 50 g of oil and 1 g of catalyst. The reaction pressure was recorded at different time intervals and the data were analyzed using Levenberg-Marquardt (LM) algorithm using polymath software. The results show that the reaction order was found to be −1.5 and activation energy of 3200 J/gmol.

***Keywords*—**Batch Reactor, Catalytic Cracking, Kinetics, Palm Oil.

I. Introduction

THE increment of environmental awareness and depletion of fossil fuels are driving research to develop possible alternative fuels from renewable resources that are economical and feasible. Alternative fuel can be made from natural, renewable sources such as vegetable oils and fats [1]. Vegetable oils are water-insoluble that consist of one mole of glycerol and three moles of fatty acids known as triglycerides. The carbon chain length of fatty acids varies and could be saturated or unsaturated bonds [2]. Various methods have been reported for the production of biofuel from vegetable oil and fats such as direct use and blending, microemulsification, transesterification and pyrolysis [3]. The biofuels are slightly better exhaust gas emissions and they are non – toxic biodegradable with the ability to reduce carbon dioxide emissions upon combustion [4]. The main argument and considerable discussion were regarding the concept of using of vegetable oil which is food as fuel [5]. In the past, vegetable oil fuels have not been acceptable because they were more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels.

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst in the absence of oxygen or in the reductive environment, e.g. using molecular hydrogen. Pyrolysis chemistry is difficult to characterize because of the variety of reaction path ways and the variety of products that may be obtained. The advantages of using pyrolysis are that, the products are chemically similar to petroleum-derived fuels. The production of biofuels, by thermal pyrolysis of vegetable oils has been studied by many researchers. Many complex reactions occur during the pyrolysis process [6]. The description of complex mixtures could be one of the most difficult analyses. Therefore lumping large numbers of chemical compounds of pseudo components has been used in such complicated case. Different types of catalysts were used in the catalytic conversion of vegetable oil into fuel [7]. As the bio-fuels production technologies improve, the need to design production processes is desirable. It has wide scope for further improvements in the reactor and process design [8]. And therefore, the need for kinetic data representing the mechanism of such process is highly desirable.

The study of the kinetics of heterogeneous catalyzed reactions consists of three different aspects: kinetics studies for design purposes, kinetics studies of mechanistic details and kinetics as a consequence of a reaction mechanism [9]. The scatter in the reported kinetic data of vegetable oil pyrolysis is significant as shown in Table I. Most researchers prefer the use pseudo first-order kinetic models to interpret the experimental data because they are simple with solving lumped models [10]. There is probability that more than one model fit the data within the experimental error [11]. Most of the cracking reaction of pure hydrocarbons follow first order reaction kinetics whereas the feedstocks of petroleum hydrocarbons showed variable order in the range of 1.6 - 1.9 [12]. So far there is no model proposed a path way for the cracking reaction of vegetable oil that meets with the proposed mechanisms. In addition, the experimental errors in cracking reactions are always subjected to many assumptions that will increase the errors of the model fitting. The special role of the catalyst as a key to efficient technology is never been addressed together with the composition of vegetable oil used [13]. Many complex reactions occur during the vegetable oil cracking process, but one of primary interest is the crack of large molecules into smaller ones and thus reduce their boiling point to the more useful range of gasoline, kerosene, diesel and gaseous products [6, 14-17].

The current research aims to study the kinetics of catalytic cracking of palm oil to hydrocarbons as a new alternative for the replacement of fossil fuels. The kinetic study was defined to determine the reaction order, activation energy and the pre-exponential factor from Arrhenius relationship. The approach used for data collection is by collecting the pressure of the reaction against the reaction time, then analyzing the data to

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Farouq Twaiq is lecturer and assistant dean for research with College of Engineering and Architecture at University of Nizwa, 616 Brikat Al Mouz, Nizwa, Oman. (phone: 968-25446200, Ext. 200; fax: 968-25446245; e-mail: farouq.twaiq@unizwa.edu.om).

Ishaq Al Anbari was Chemical Engineering Student at Department of Chemical Engineering and research assistant for Research Project: ORG/EI/10/005, (e-mail: alanbari@hotmail.com).

Mustafa Nasser is lecturer and head of chemical engineering department, University of Nizwa, College of Engineering and Architecture, University of Nizwa, 616 Brikat Al Mouz, Nizwa, Oman (e-mail: Mustafa.nasser@unizwa.edu.om).

estimate the reaction parameters.

TABLE I
COMPARISON OF REPORTED KINETIC PARAMETERS FOR CRACKING OF SEVERAL OILS IN THE LITERATURE

Feed	Catalyst/ Thermal	Reaction order (n)	Frequency factor (A) (1/s)	Activation Energy (E) kJ/mole	Reference
Palm oil	HZSM-5	1	9×10^{10}–2×10^{12}	132 – 137	[6]
Palm oil	MCM-41	1	1.8×10^{3} –1.1×10^{4}	37 – 42	[16]
Sawdust oil	Thermal	1	2.2×10^{4} – 6×10^{4}	55 – 60	[14]
Oleic acid	HZSM-5	1	7×10^{2}	62	[15]
Used cook oil	Zirconia Sulfide	1	9×10^{2}	83	[17]

II. EXPERIMENTAL

A. Catalyst Synthesis and Characterization

Aluminosilicate mesoporous material Al-MCM-41 with 5% alumina content was synthesized using sol-gel technique following a method reported in reference [1]. Tetraethylorthosilicate (TOES, 98%, Merck) was used as the silica source and aluminum isopropoxide (97%, Fluka) was used as an aluminum source. Fourteen grams of TEOS was dissolved in 30mL water and 40mL ethanol, and the mixture was refluxed under vigorous stirring for 4 h at 343 K. Appropriate amount of aluminum isopropoxide was refluxed in 35mL isopropyl alcohol overnight at 343 K and then added to the TEOS solution. Amount of aluminum isopropoxide was added to maintain the alumina to silica ratio in the gel at 5%. A solution of 10g of dodecylamine (99%, Fluka) in 40 mL ethanol and 5 mL of HCl was added as a structure-directing template to the resulting mixture with vigorous mixing. The mixture was allowed to react at room temperature for 24h, and then the product was filtered, washed with ethanol followed by deionized water. The solid was kept to dry overnight at room temperature and calcined at 873 K for 6h.

The produced calcined powder was characterized using X-ray diffraction and N_2-adsorption. X-ray diffraction patterns of all the calcined powder was obtained on a D8 Advanced diffractometer Bruker AXS using Cu-Kα radiation at 2θ in the range of 2 – 10º and step of 0.02/10sec. The N_2 adsorption-desorption isotherm of vacuum degasses powder at 523 K was obtained at P/P_0 in the range of 0 – 1 using the Quantachrome Autosorb-6B. The BET surface area is calculated in the P/P_0 of 0 – 0.1, and average pore size (APS) measurement of the sample were calculated using BJH method.

B. Catalytic Cracking Experiments

Refined, bleached and deodorized (RBD) palm oil was used for cracking studies in the present investigation. Cracking reaction of palm oil was conducted in a well mixed 400 mL stainless steel autoclave Parr reactor fitted with a thermocouple placed in the center of the reactor and water cooling coil as shown in Fig. 1. A 50 mL of oil was used in each experimental run. The reactor is heated to the desired reaction temperature using electrical heating mantle and the temperature was controlled using PID controller. Nitrogen gas is passed at 0.2 L/min through the system for 1 h before the palm oil and catalyst were charged into the reactor. The reaction was conducted in the temperature range of 573 – 673 K. The reactor temperature was maintained at the desired temperature for 1 h. At the end of the experiment, the reactor was cooled to ambient room temperature, using cooling water circulation. During the experimental run, the reactor pressure was recorded every 10 min at constant temperature.

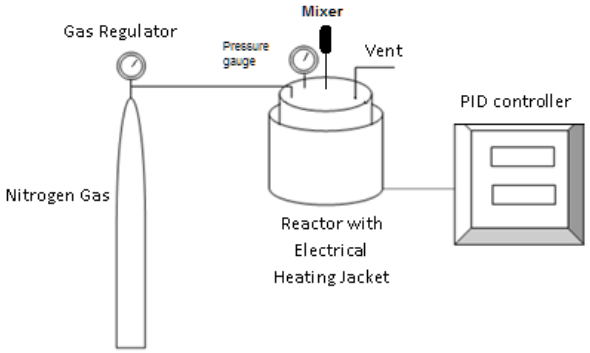

Fig. 1 Autoclave reactor setup used for catalytic cracking of palm oil

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

Calcined mesoporous aluminosilicate Al-MCM-41 was prepared and characterized to confirm the formation of the mesoporous structure. Nitrogen adsorption-desorption isotherms characterizes the quality of the pore structure of the catalyst. The adsorption-desorption data was collected at P/P_0 in the range of 0 to 1 as shown in Fig. 2. The isotherm shows that the major nitrogen intake is found in the P/P_0 range above 0.4. The result also indicates that a very high external surface area is formed. The BET surface area of the material is measured using 5 points in the P/P_0 range of 0 to 0.1. The surface area was found to be 1276 m^2/g. BJH method was used to calculate the average pore size distribution and pore volume. The average pore size was found equal to 2.54nm and the pore volume is 0.811 cm^3/g.

The aim of the mesoporous material characterization using X-ray diffraction (XRD) is to identify the properties of the material crystalinity as shown in Fig. 3. The x-ray scan was obtained for 2-theta in the range of 2 – 10°. The patterns are in agreement with reported data for MCM-41 mesoporous materials. Crystallinity with hexagonal pore structure is found as indicated by the number of peaks in the spectrum. The first peak is narrow indicating a uniform pore structure however a thick wall is formed.

B. Catalytic Cracking

The experimental results of the catalytic cracking runs are presented in Table II. The results show that cracking reaction is not taking place at temperature below 623 K. Only the data obtained at temperature range 623 – 673 K will be used for kinetic study. It is reported [18] that the first reaction occurs during the catalytic cracking is the deoxygenation and the oxygen is removed as CO_2, CO or H_2O. The catalytic cracking reaction is selective C-C scission of the carbonyl carbon and

adjacent alpha-carbon to it in a triglyceride molecule [19]. It is a direct route to the hydrocarbon chains of the fatty components of the triglycerides. Hence, it is most ideal and also the shortest route at arriving to short chain hydrocarbon [20]. Uncontrollable side reactions such as cracking reactions or polymerisation reactions of the hydrocarbons result in poor selectivity of desired degree of reactions. The selectivity can be enhanced by using an acid of the catalyst.

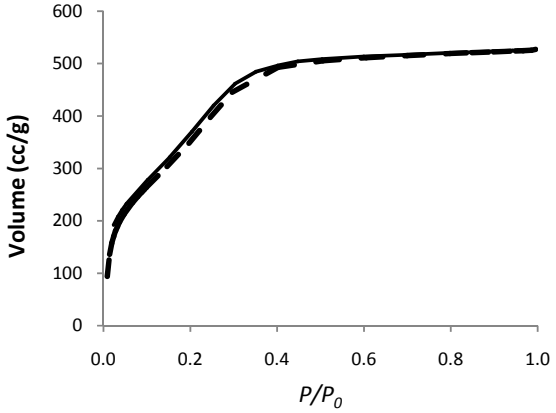

Fig. 2 Nitrogen adsorption desorption isotherms of 5% alumina containing Al-MCM-41

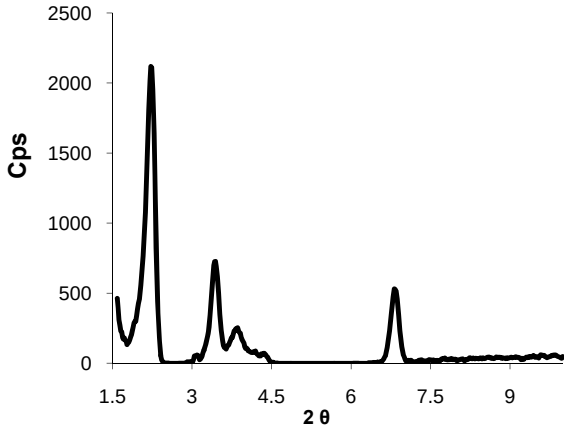

Fig. 3 X-ray diffraction of 5% alumina containing Al-MCM-41

C. Kinetics Study

In order to determine the reaction kinetics of the catalytic cracking of palm oil over Al-MCM-41 as a catalyst, palm oil was cracked in a batch autoclave reactor. The experiments were conducted at reaction temperature of 623, 648 and 673 K. As the time proceeds, the reaction pressure increase and the reactor pressure is recorded every ten minutes. After 60 minutes of reaction time, the reaction is stopped by stop heating and cooling the reactor through a water circulation.

TABLE II
REACTION PRESSURE OBTAINED FROM CATALYTIC CRACKING OF PALM OIL IN AUTOCLAVE BATCH REACTOR AT DIFFERENT REACTION TIME USING 5 DIFFERENT REACTION TEMPERATURES IN THE RANGE OF 573 – 673 K

Time	Temperature (K)				
(minutes)	573	598	623	648	673
0	1	1	1	2	31
10	1	1	1	7	38
20	1	1	2	10	44
30	1	1	4	16	50
40	1	1	5	20	54
50	1	1	7	24	58
60	1	1	8	27	62

In order to model for the batch reactor, the general material balance equation for batch reactor is used shown in equation (1).

$$-r_A = dC_A/dt \quad (1)$$

where $-r_A$ is the reaction rate (gmol·L^{-1}·min^{-1}); C_A is the reactants concentration (gmol·L^{-1}); t is the time (min).

As the mechanism of the reaction will not be considered and black box approach is adopted. The rate of reaction is written in the form as in Equation (2)

$$-r_A = k \cdot C_A^n \quad (2)$$

where k is the specific reaction rate and n is the reaction order.

As the reaction occurred in constant volume reactor, the concentration is written in the form as in equation (3)

$$C_A = C_{A0}(1 - X) \quad (3)$$

where C_{A0} is the initial concentration and X is defined as the reaction conversion.

In gaseous reaction phase and assuming ideal gas, the concentration C_A is written as in Equation (4)

$$C_A = P/RT \quad (4)$$

where P is the reaction pressure (bar), R is the universal gas constant (0.083)

Rearranging Equation (4) to get X and substituting in Equation (2) will result in Equation (5)

$$-r_A = kP^n/(RT)^n \quad (5)$$

Differentiating Equation (4) will get equation (6)

$$dC_A = dP/RT \quad (6)$$

then substitute Equation (5) and (6) in Equation (1) will result in the kinetic model equation (7) which will be used further for the evaluation of the reaction parameters.

$$dP/dt = k \cdot P^n \cdot R^{1-n} \cdot T^{1-n} \quad (7)$$

The experimental data presented in Table II will be used to fit this equation in order to estimate the reaction parameters. The results presented in Table III shows that there is no reaction take place at low temperatures 573 and 598 K

respectively. Only results at temperatures of 623, 648 and 673K will be analyzed accordingly. The data in the time range of 0 – 10 minutes were excluded from the calculations as the process was at unsteady state operation and temperature not reaches the final steady operation temperature. The reaction pressure were plot against the time and 2nd order polynomial equations were fitted using excel spreadsheet as shown in Fig. 3. The polynomial equation is differentiated in order to calculate (*dP/dt*) as shown in Fig. 4. The results of the differential data were treated in polymath 5.1 non-linear regression analyses in order to estimate the values of the reaction constants and the order of reaction. Equation (7) was introduced as the model equation and the parameters values *k* and *n* were identified as initial guess values. The program uses Levenberg-Marquardt (LM) algorithm for finding the parameter values, which minimize the sum of squares of the errors. The data for each experimental runs were treated separately in which the reaction temperature is considered constant for that run. The *k* values at three different temperatures are presented in Table III

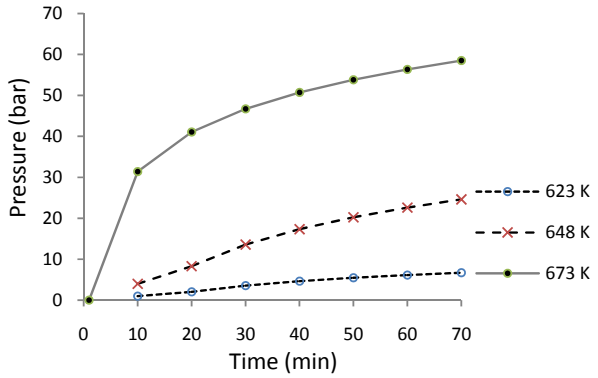

Fig. 3 Catalytic cracking reaction pressure vs time of palm oil over Al-MCM-41 in autoclave batch reactor at three different temperatures 623, 648 and 673 K respectively

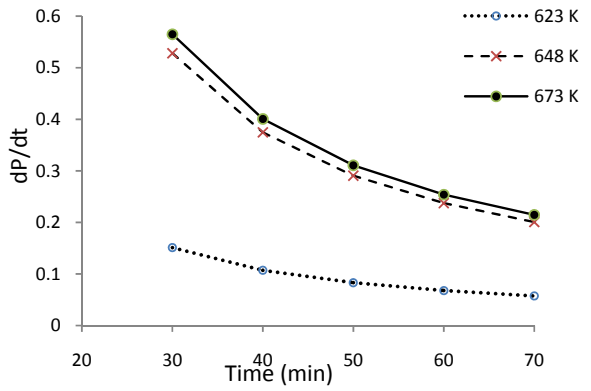

Fig. 4 Calculated catalytic cracking rate of palm oil over Al-MCM-41 catalyst at three different temperatures 623, 648 and 673 K respectively

TABLE III
K VALUES OF THE CRACKING OF PALM OIL IN AUTOCLAVE BATCH REACTOR IN THE TEMPERATURE RANGE OF 623 – 673 K

Temperature (*K*)	623	648	673
k ($gmol^{2.5}$·$^{-2.5}$·min^{-1})	0.000053	0.0021	0.0060

The reaction order was found to be equal (–1.5). The negative value of the reaction order is due to that the cracking reaction which is chain reaction. In chain reactions, the products are becoming reactants and therefore the concentration is increases as the reaction proceeds. In the reported studies of the catalytic cracking of vegetable oils, the oil was always considered as the only reactant which is in fact not true. The conversion is only calculated for the initial feed to the reactor. In most of the reported studies, flow reactors are used with integral interpretations of the conversion. In flow reactors, the volumetric flow rate increases as products increase in several multiple times, however, only the initial flow are used in the calculations. With chain reactions, the increase of the products in the 1st chain indicating an increase of reactants in the following chain which leads to an increase of reaction rate. This behavior is different than in the case when the reaction order is positive and therefore as the reactants decrease, the reaction rate decrease accordingly.

The activation energy is calculated using Arrhenius equation as shown in Fig. 5.

$$k = 6.86 \times 10^{22} \cdot \exp\left(-3200/(0.08314 \cdot T)\right) \qquad (8)$$

The activation energy level is depends on the type of the feedstock and catalyst used. For example the cracking of gas oil needs higher activation energy because the molecular structure of the compounds in the gas oil different than the palm oil. The palm oil contains triglycerides, which very reactive in the pore surface of catalyst. The data of Table III were fitted to Arrhenius equation for the evaluation of activation energy and frequency factor *A*. The activation energy was found to be equal 3200 J/mole and the frequency factor to be 6.86×10^{22}. The activation energy is much lower than reported activation energy of different types of oil.

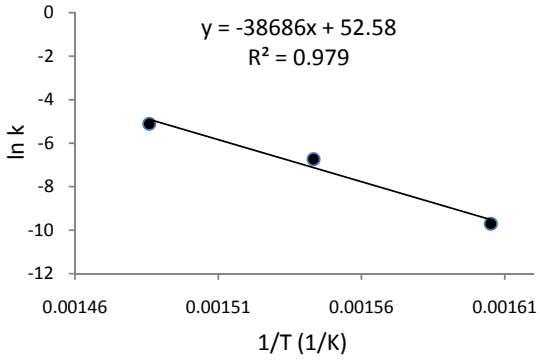

Fig. 5 Natural logarithm of catalytic cracking reactions of palm oil at three temperatures 623, 648 and 673 K respectively

IV. Conclusion

Aluminum containing MCM-41 (5% alumina) was synthesized using sol-gel technique. The surface area of the catalyst was found to be 1276m^2/g and pore diameter of 2.54 nm. The catalyst was used for cracking of palm oil in batch autoclave reactor of a catalyst to oil ratio of 1:50. The kinetics parameters of the reaction were evaluated. The reaction order was found to be (–1.5) and activation energy of 3200 J/gmol of oil.

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