

Kinetic Studies of Free Fatty Acid Esterification using Cation Exchange Resins as Catalyst

N. M. Yunus¹, N. A. Roslan¹, S. Y. Chin^{1,2} and S. Z. Abidin^{1,2*}

¹Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

²Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia; sumaiya@ump.edu.my

Abstract

Objective: The aim of this work is to study the kinetics of Free Fatty Acid (FFA) esterification using cation exchange resins with different polymer structure arrangement as catalysts. **Methods/Statistical Analysis:** In this current work, cation exchange resins (i.e. Sulphonated Hypercrosslinked Exchange Resin (SHER), RCP160M and SK104H) were employed as catalysts in free fatty acid (FFA) esterification of Simulated Used Cooking Oil (SUCO). The kinetic models, pseudo-homogenous (PH), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) model were used to correlate the experimental data. The kinetic parameters i.e., the rate constant, adsorption coefficients and activation energy were determined using the non-linear regression analysis in POLYMATH 6.10 program. **Findings:** The kinetic results revealed that the esterification reaction of SUCO using SHER was successfully fitted with LHHW model, whereas for RCP160M and SK104H the experimental data was well fitted by the ER model (Case II) and ER model (Case I) respectively. The activation energy, E_a was observed to be 48.8, 37.2 and 45.3 kJ mol⁻¹ for SHER, RCP160M and SK104H, which the reaction step were governed by chemical step ($E_a > 15$ kJ mol⁻¹) and there is no mass transfer limitation occurred during the reaction. **Application/Improvements:** From the findings, the newly synthesized SHER was found to be a promising catalyst in the esterification of FFA.

Keywords: Cation Exchange Resin, Esterification, Free Fatty Acid, Kinetics, Simulated used Cooking Oil

1. Introduction

Kinetic models are important in understanding mechanism and pathway of the reaction. Currently, there are three types of kinetic models that commonly applied to heterogeneously catalysed esterification reaction which are the pseudo-homogeneous (PH), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER). Numerous researcher claimed that PH model produced good agreement between predicted and experimental concentration profile for the esterification of FFA as the model is comparable to the homogeneous reactions since no adsorption of reactant molecules involved. On the other hand, LHHW model and ER model are the most applicable for heterogeneously catalysed esterification reaction as the rate of reaction for both model are limited by surface reaction. LHHW model

represents the adsorption of both reactants on the surface of the catalyst while ER model describes a competing adsorption phenomenon between the polar (methanol) and non-polar (FFA) molecules onto the catalyst surface¹.

The presents study describes the kinetic models of FFA esterification in simulated used cooking (SUCO) using cation exchange resins (i.e., SHER, RCP160M and SK104H) as catalysts. SHER, hypercrosslinked polystyrene-EGDMA-VBC polymer is an attractive catalyst because it is self-synthesised catalyst and highly porous. RCP160M is also highly porous catalyst with highly crosslinked St-DVB polymer while SK104H is a gelular type catalyst with low crosslinked St-DVB polymer². These catalysts were subjected to the kinetic modelling as these catalyst showed excellent performance in esterification reaction in a batch process. The kinetic models, PH, ER and LHHW was proposed in this work

* Author for correspondence

to correlate the experimental data. The parameters of the kinetic model such as reaction rate constant and adsorption coefficient were determined via the non-linear regression analysis (POLYMATH 6.10). The effect of reaction temperature on the rate constant was investigated. The best fitted model was chosen for further calculation on the activation energy.

2. Materials and Methods

Cooking oil (Saji brand), oleic acid (95%, Sigma-Aldrich) and methanol (99.99 %, Fisher Scientific) were used as reactants for esterification reaction. DIAON™ RCP160M and DIAON™ SK104H were supplied by Mitsubishi Chemical Corporation whereas SHER was synthesised via dispersion polymerization method. A solution of 0.1 M potassium hydroxide in isopropanol and α -naphtholbenzene were acquired from Sigma Aldrich and used as a titrant solution and indicator for acid value analysis. The titration solvents (2-propanol (99.96%) and toluene (99.99%)) were purchased from Fisher Scientific. All these chemicals were used without further purification.

2.1 Kinetic Modelling Studies

The FFA esterification in SUCO utilising cation exchange resins, SHER, RCP160M and SK104H was represented as follows:



The kinetic model of this work has been developed under several assumptions; the reaction was a reversible heterogeneous process, there was no existence of esters in the solution mixture at $(t) = 0$ the volume of reaction mixture did not change during the reaction and the catalytic performance of all sites on the catalyst surface was accounted to be identical. The PH, LHHW, ER I, and ER II models in term of concentration based are shown in Eq. (2-5).

$$r_A = k_f (C_A C_B - 1/K_{eq} C_C C_D) \quad (2)$$

$$r_A = \frac{k_f \left(C_A C_B - \frac{1}{K_{eq}} C_C C_D \right)}{1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D} \quad (3)$$

$$r_A = \frac{k_f \left(C_A C_B - \frac{1}{K_{eq}} C_C C_D \right)}{1 + K_B C_B + K_D C_D} \quad (4)$$

$$r_A = \frac{k_f \left(C_A C_B - \frac{1}{K_{eq}} C_C C_D \right)}{1 + K_A C_A + K_C C_C} \quad (5)$$

where C_A , C_B , C_C and C_D denotes the FFA, methanol, esters and water concentrations in the reaction media respectively; k_f is the forward rate constant. The k_p , K_A , K_B , K_C and K_D were calculated by fitting the r_A profile at different temperatures using Levenberg-Marquardt algorithm ($L-M$) method for the non-linear regression analysis in POLYMATH 6.10 program. Using this program, the values of variables were adjusted until the coefficient (R^2) was closest to one. The equilibrium constant, K_{eq} is calculated using the experimental data. The equilibrium constant was calculated by considering it does not depends on methanol concentration (due to its excess) and both esters and water concentrations are equal. Thus, the K_{eq} can be defined as:

$$K_{eq} = \frac{(C_A X)^2}{[C]_A (1 - X)^2} \quad (6)$$

The temperature effect on reaction rate were then used to determine the best model by plotting the rate constant to the Arrhenius equation ($\ln k$ versus $1/T$) and the equation is shown in Eq. (7) below.

$$\ln k_i = \left(\frac{-E_{ai}}{RT} \right) + \ln A \quad (7)$$

where k_i is the rate constant (L/mol.min), A is the pre-exponential factor (L/mol.min), E_{ai} is the activation energy (J/mol), R is ideal gas constant (8.314 J/mol.K) and T is the temperature of reaction (K).

3. Results and Discussion

3.1 Estimation of Reaction Rate Constant

A comprehensive study on esterification kinetics of SUCO with methanol over SHER, RCP160M and SK104H was conducted. The PH, LHHW and ER models were developed to study the kinetic behaviour. The determination of equilibrium constant, K_{eq} was determined using eq. 6 the calculation for kinetic constants and adsorption coefficient for each model were performed by $L-M$ method for non-linear regression in POLYMATH 6.10. The kinetic rate constants obtained were then used at different temperatures to determine the best model. This was done by plotting the rate constant to the Arrhenius equation ($\ln k$ versus t) as shown in Figure 1.

Overall, it was found that that k_f increased with the increase of reaction temperature. The experimental data for SHER, RCP160M and SK104H was highly fitting by the LHHW, ER (Case II) and ER (Case I), respectively. Kinetic parameters obtained from this work are shown in Table 1.

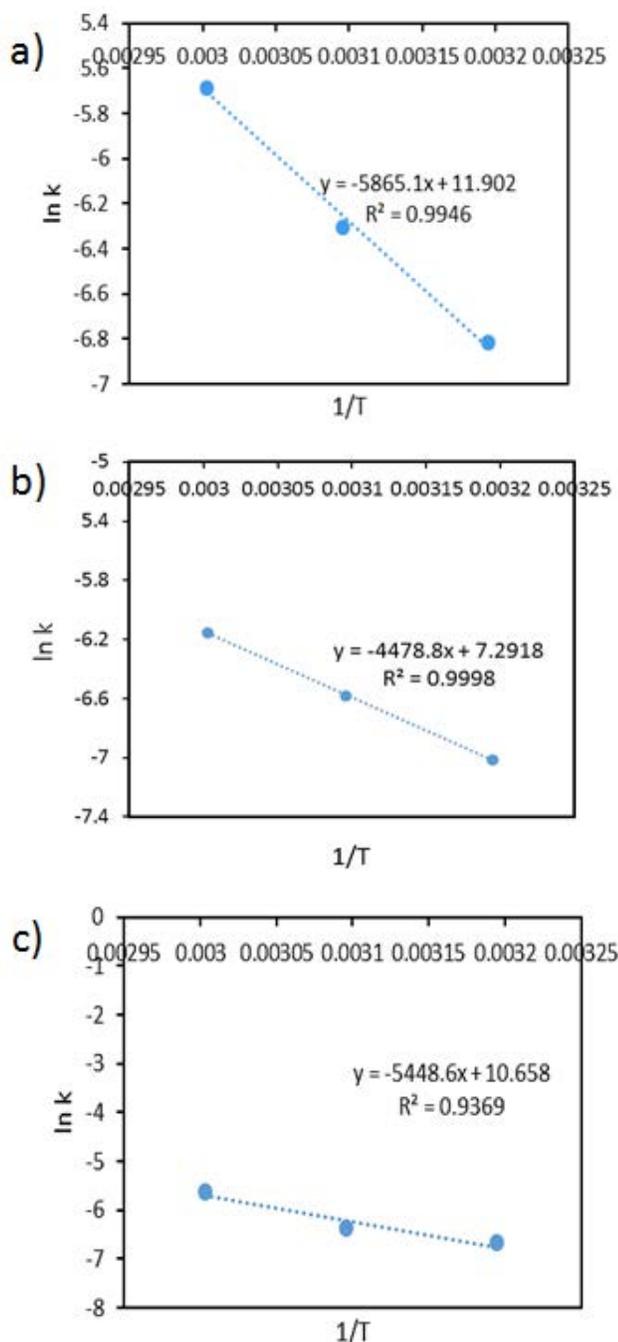


Figure 1. The Arrhenius plot for the SUCO esterification using a. SHER b. RCP160M and c. SK104H as catalysts.

Table 1. Kinetic parameters for esterification of SUCO

Temp (K)	k_f	K_{eq}	Adsorption Coefficient			
			K_B	K_C	K_D	K_A
SHER (LHHW)						
313	0.0011	85.56	0.99	6.76×10^{-5}	7.35	12.35
323	0.0018	380.25	0.99	5.04×10^{-5}	9.48	12.48
333	0.0034	1600	11.10	2.57×10^{-5}	136.67	146.67
RCP160M (ER Case II)						
313	0.0009	34.03	2.73		101.99	
323	0.0014	85.56	26.64		102.00	
333	0.0021	237.16	31.30		270.58	
SK104H (ER Case I)						
313	0.0013	23.59		0.04		12.53
323	0.0017	25.20		0.08		148.15
333	0.0036	28.17		0.08		810.54

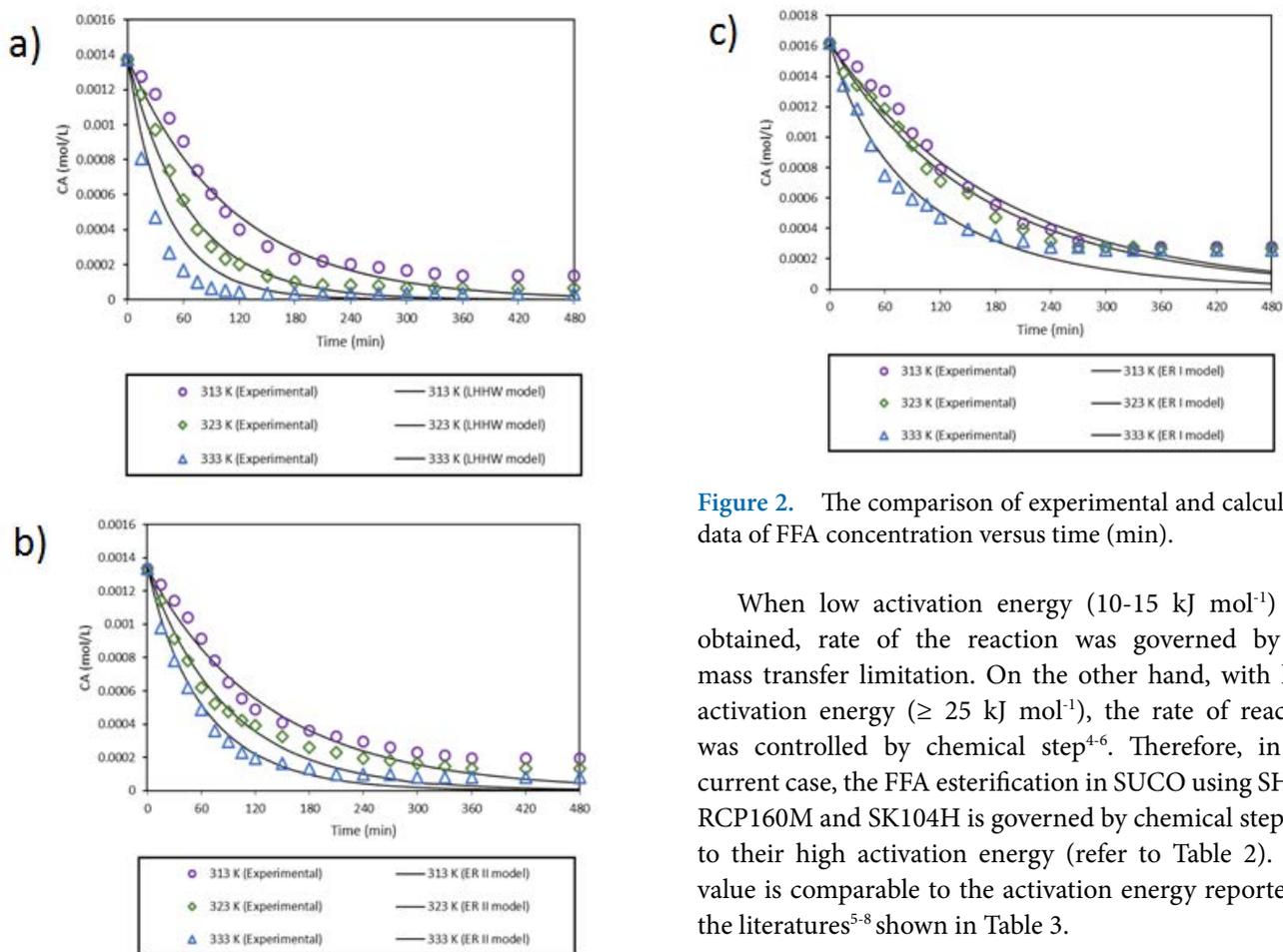
As shown in Figure 2, the predicted values from the selected model correlated well with the experimental data. This results have proven that all the catalyst is limited by surface reaction where the reaction is assumed to happen on the catalyst surface³. LHHW model describes the adsorption behaviour of reactants molecules onto the surface of catalyst while ER model describes the adsorption of either one of the reactant molecule onto the catalyst surfaces and other reactant molecule remains in the bulk fluid.

3.2 Evaluation of activation energy and pre-exponential factor

The slope of $\ln k$ versus $1/T$ in Figure 1 were used to determine the activation energy, E_a and pre-exponential factor, A of the reaction. The calculation was done using the Arrhenius equation (eq. 7). The values for the activation energy, E_a and pre-exponential factor, A for each model are listed in Table 2. Nandiwale and Bokade³ claimed that the value of activation energy was significantly influenced by the reaction rate. The higher the E_a , the slower the reaction rate. Additionally, mass transfer resistance is also important in esterification reaction as it is connected to the interaction between the molecules of reactants and products to the surface of catalyst. Thus, it is necessary to understand whether the rate of reaction is limited by mass transfer or controlled by chemical step when the resin is utilized up to its limit⁴.

Table 2. Activation energy and pre-exponential values for SHER, RCP160M and SK104H

Catalyst	Models	Activation energy (kJ mol ⁻¹)	Pre-exponential factor (L mol ⁻¹ min ⁻¹)
SHER	LHHW	48.8	149614.80
RCP160M	ER (Case II)	37.2	1468.21
SK104H	ER (Case 1)	45.3	42531.49


Figure 2. The comparison of experimental and calculated data of FFA concentration versus time (min).

When low activation energy (10-15 kJ mol⁻¹) was obtained, rate of the reaction was governed by the mass transfer limitation. On the other hand, with high activation energy (≥ 25 kJ mol⁻¹), the rate of reaction was controlled by chemical step^{4,6}. Therefore, in the current case, the FFA esterification in SUCO using SHER, RCP160M and SK104H is governed by chemical step due to their high activation energy (refer to Table 2). This value is comparable to the activation energy reported in the literatures⁵⁻⁸ shown in Table 3.

Table 3. A comparative analysis of Ea for reported heterogeneous esterification of FFA

Free fatty acid	Catalyst	Activation energy (kJ mol ⁻¹)	References
Oleic acid	TPA ₃ /SBA-15	44.6	Brahmkhatri and Patel ⁵
Oleic acid	TPA ₃ /H β	45.2	Patel and Narkhede ⁶
Oleic acid	Mesoporous SnO ₂ /WO ₃	39.5	Sarkar et al. ⁷
Oleic acid	Amberlyst 15	74.4	Tesser et al. ⁸

4. Conclusion

The kinetic of SUCO esterification with methanol using the types of catalysts; SHER, RCP160M and SK104H have successfully studied. Three kinetic models (PH, LHHW and ER models) were used to correlate with the results of experimental and the parameters of kinetic were determined using non-linear regression analysis in POLYMATH 6.10 program. It was discovered that the experimental data for SHER was best fitted with LHHW model whereas the RCP160M and SK104H the experimental data was best fitted by the ER model (Case II) and ER model (Case I) respectively. The results also revealed that as the temperature increase, the forward rate constant increases. The activation energy of the reaction was found to be 48.8, 37.2 and 45.3 kJ mol⁻¹ for SHER, RCP160M and SK104H, respectively. This results concluded that the reaction step were governed by chemical step ($E_a > 15$ kJ mol⁻¹). The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website⁹ and organized by The Centre of Excellence for Advanced Research in Fluid Flow (CARIFF)¹⁰. The publications on chemical engineering allied fields have been published as a special note in volume 3¹¹. Host being University Malaysia Pahang¹² is the parent governing body for this conference.

5. Acknowledgement

We would like to thank Mitsubishi Chemical Corporation for generously supplying the catalysts for this work. We would also like to thank to the TWAS-COMSTECH and Universiti Malaysia Pahang for the financial assistance through research grants with vot no. 14-337, RDU140357 and RDU130311.

6. References

1. Tesser R, Di Serio M, Guida M, Nastasi M, Santacesar-ia E. Kinetics of oleic acid esterification with methanol in the presence of triglycerides. *Industrial and Engineering Chemistry Research*. 2005 Sep; 44(21):7978–82. Available from: Crossref
2. Yunus NM, Roslan NA, Chin SY, Abidin SZ. Esterification of free fatty acid in used cooking oil using gelular exchange resin as catalysts. *Procedia Engineering*. 2016;7978–82. Available from: Crossref
3. Nandiwale KY, Bokade VV. Process optimization by response surface methodology and kinetic modelling for synthesis of methyl oleate biodiesel over H3PW12O40 Anchored Montmorillonite K10. *Industrial and Engineering Chemistry Research*. 2014 March; 53(49):18690–8. Crossref
4. Narkhede N, Patel A. Biodiesel production by esterification of oleic acid and transesterification of soybean oil using a new solid acid catalyst comprising 12-Tungstosilicic acid and zeolite H β . *Industrial and Engineering Chemistry Research*. 2013; 52(38):13637–44. Available from: Crossref
5. Brahmkhatri V, Patel A. 12-Tungstophosphoric acid anchored to SBA-15: An efficient, environmentally benign reusable catalysts for biodiesel production by esterification of free fatty acids. *Applied Catalysis A: General*. 2011; 403(1-2):161–72. Available from: Crossref
6. Patel A, Narkhede N. 12-Tungstophosphoric acid anchored to zeolite H β : Synthesis, characterization, and biodiesel production by esterification of oleic acid with methanol. *Energy and Fuels*. 2012; 26(9):6025–32. Crossref
7. Sarkar A, Ghosh SK, Pramanik P. Investigation of the catalytic efficiency of a new mesoporous catalyst SnO₂/WO₃ towards oleic acid esterification. *Journal of Molecular Catalysis A: Chemical*. 2010; 327(1-2):73–9. Available from: Crossref
8. Tesser R, Casale L, Verde D, Di Serio M, Santacesaria E. Kinetics of free fatty acids esterification: Batch and loop reactor modelling. *The chemical Engineering Journal*. 2009; 154(1):25–33. Available from: Crossref
9. FluidChe 2017 official website. Crossref
10. The Center of Excellence for Advanced Research in Fluid Flow (CARIFF) Crossref
11. Chemical Engineering Allied Fields - International Conference on Fluids and Chemical Engineering FluidsChE 2017 Malaysia, Special Issue, Vol: 3. *Indian Journal of science and technology*. 2017; 10.
12. University Malaysia Pahang. www.ump.edu.my