

Kinetic Modeling of Transesterification of Triacetin Using Synthesized Ion Exchange Resin (SIERs)

Hafizuddin W. Yussof, Syamsutajri S. Bahri, Adam P. Harvey

Abstract—Strong anion exchange resins with QN^+OH^- , have the potential to be developed and employed as heterogeneous catalyst for transesterification, as they are chemically stable to leaching of the functional group. Nine different SIERs (SIER1-9) with QN^+OH^- were prepared by suspension polymerization of vinylbenzyl chloride-divinylbenzene (VBC-DVB) copolymers in the presence of n-heptane (pore-forming agent). The amine group was successfully grafted into the polymeric resin beads through functionalization with trimethylamine. These SIERs are then used as a catalyst for the transesterification of triacetin with methanol. A set of differential equations that represents the Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) models for the transesterification reaction were developed. These kinetic models of LHHW and ER were fitted to the experimental data. Overall, the synthesized ion exchange resin-catalyzed reaction were well-described by the Eley-Rideal model compared to LHHW models, with sum of square error (SSE) of 0.742 and 0.996, respectively.

Keywords—Anion exchange resin, Eley-Rideal, Langmuir-Hinshelwood-Hougen-Watson, transesterification.

I. INTRODUCTION

TRANSESTERIFICATION reaction is also known as alcoholysis since it takes place by exchanging the alcohol groups and where the original ester reacts with an alcohol. In transesterification reactions, one mole of triglycerides in the vegetable oil or animal fat reacts with three moles of alcohol in the presence of a base or acid catalyst, producing three moles of the respective fatty acid alkyl esters and one mole of glycerol as a by-product. Since transesterification is an equilibrium reaction, the alcohol to be exchanged is generally added in excess in order to achieve a high yield of the desired ester.

Nearly all the processes use homogeneous base catalysts since they give conversion rates to biodiesel of over 95%. Even though reproduction of biodiesel using homogeneous base-catalysts involves a rapid process resulting in high conversion rates with minimal side reactions, it is still not very commercially competitive compared to petroleum diesel due the factors. Firstly, the catalyst cannot be recovered and secondly, the use of homogeneous catalyst necessitates the neutralization of glycerol at the end of the reaction. Replacing

liquid homogeneous catalysts with solid heterogeneous catalysts is expected to yield a product that does not require neutralization, leading to lower processing costs, because the catalyst will not have to be continually replaced. Several types of heterogeneous base catalysts have been developed for the transesterification of vegetable oils into biodiesel over the past few years. Among these, ion exchange resin with a quaternary ammonium functional group (QN^+OH^-) have been identified as an alternative to homogeneous base catalysts that suitable for transesterification in biodiesel production, due to their physical strength, as they are not easily degraded by oxidation or hydrolysis and the better conversion rates achieved [1], [2].

A number of researchers have modelled the kinetics of the transesterification reaction as many of them use homogeneous rather than heterogeneous alkaline catalysts. Not much information is available regarding the kinetics of heterogeneous base-catalyzed transesterification. Reference [3] studied the kinetics of heterogeneous alkaline earth metal oxides. A five-step mechanism was proposed for the transesterification of ethyl acetate, with different rate-determining steps according to the basicity of the catalyst. The basic strengths of alkaline earth metal oxides are in the order $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$. It was assumed that the surface reaction step is rate-determining step for catalysts of higher basicity, such as BaO, SrO and CaO. However, methanol adsorption was assumed to be the rate-determining step for alkaline earth metal oxide catalysts of the lower basicity, such as MgO [3].

A similar conclusion was reached by [4], who studied the kinetics of heterogeneous MgO-catalyzed transesterification by comparing three different models. The first one had been proposed by [3], while the other two are the Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) models. Based on the satisfactory agreement found with experimental data over the range of conditions investigated, a kinetic model was proposed by [4] based on a three-step mechanism of the Eley-Rideal. It was suggested that the rate-determining step for the lower basicity MgO is methanol adsorption on its active sites [4].

In the present paper, it was propose to investigate the kinetics model of nine different synthesized ion exchange resins (SIERs) in the transesterification of triacetin with methanol. Triacetin is used as model triglyceride in this study, due to its structural simplicity, which makes the identification and quantification of reaction products easier.

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II. EXPERIMENTAL

A. Synthesis of Ion Exchange Resins

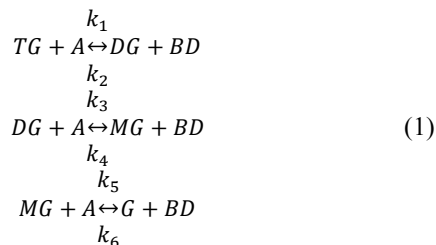
Suspension polymerization was carried out by adding the organic phase solutions to the three-necked round-bottomed flask containing the aqueous phase solutions in a nitrogen environment and at room temperature. Then, 1 wt. % of 2,2'-azobis(2-methylpropionitrile) or AIBN was added to the reactor. Next, the temperature was raised to 80°C at a stirring speed of 350 rpm and polymerization was allowed to continue for 24h. The polymer beads were then washed with hot distilled water to remove the suspending agent (PVOH), and hot ethanol to remove any traces of monomers and diluents. Next, the beads were filtered and dried, and sieved to the range of 150-300 microns. The resins were further washed with methanol and dried at 60°C for 48h in the oven. Amination of resin beads was carried out using trimethylamine solution in ethanol. The final product was washed with distilled water, methanol, and a 1M NaCl solution and dried.

B. Transesterification of SIERs with Triacetin

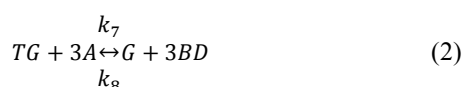
The experimental method was performed using the three-necked round-bottomed flask. 45 mL of reagent grade methanol (Fisher Scientific, UK) was mixed with 35 mL of triacetin at 99 wt. % (Sigma-Aldrich, UK). The molar ratio of methanol to triacetin was maintained at 6:1 (mol/mol). Then, the reaction mixture was heated to 60°C in a water bath. Transesterification was then initiated by charging with 5.5 mmol/g of the SIER. This SIER catalyst was mixed using an overhead stirrer at 450 rpm for 4h. 1 mL samples were taken initially and then at specified time intervals, before being filtered and analyzed.

C. Kinetic Modeling

The transesterification reaction can be presented by the following stoichiometric equation. The stoichiometric equation contains three reversible steps, forming the intermediate di- and monoglycerides, and then glycerol. Each equilibrium is described by its respective constant, K_i (where $K_i = \frac{k_i}{k_{i+1}}$), where $i = 1, 3$ and 5



with the overall reaction :



where triglyceride is TG , diglyceride is DG , monoglyceride is MG , methanol is A , glycerine is G and fatty acid methyl ester (biodiesel) is BD .

In order to model the transesterification kinetics of the SIERs reaction, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal models have been applied in the present study, in sets of differential equations, in line with the work by [4].

1. Langmuir-Hinshelwood-Hougen-Watson (LHHW) Model

Two special cases of LHHW are presented in this study from models developed from [5]. The first LHHW model is based on the surface reaction as the rate-determining step, and the second on the adsorption of methanol as the rate determining step. The rate equations with the assumption that surface reaction is the rate-determining step (RDS) and adsorption of A (methanol) is the rate-determining step (RDS) are shown below, respectively obtained from [5] and [6]:

$$(-r_A) = \frac{k_s K_A K_B ([A][B] - \frac{1}{K} [C][D])}{(1 + K_A [A] + K_B [B] + K_C [C] + K_D [D])^2} \quad (3)$$

$$(-r_A) = \frac{k_{s(A)} ([A] - \frac{1}{K} \frac{[C][D]}{[B]})}{(1 + \frac{K_A [C][D]}{K [B]} + K_B [B] + K_C [C] + K_D [D])} \quad (4)$$

where K_i is the equilibrium adsorption constant for each component.

The reaction scheme for LHHW in the transesterification of triglycerides is given as follows [7], where the concentration of the bulk species is in square brackets and θ_i is the fraction of component vacant sites:

$$\begin{aligned} \frac{d[TG]}{dt} &= -k_1 \theta_{TG} \theta_A + k_2 \theta_{DG} \theta_{BD} \\ \frac{d[DG]}{dt} &= k_1 \theta_{TG} \theta_A - k_2 \theta_{DG} \theta_{BD} - k_3 \theta_{DG} \theta_A + k_4 \theta_{MG} \theta_{BD} \\ \frac{d[MG]}{dt} &= k_3 \theta_{DG} \theta_A - k_4 \theta_{MG} \theta_{BD} - k_5 \theta_{MG} \theta_A + k_6 \theta_G \theta_{BD} \\ \frac{d[BD]}{dt} &= k_1 \theta_{TG} \theta_A - k_2 \theta_{DG} \theta_{BD} + k_3 \theta_{DG} \theta_A - k_4 \theta_{MG} \theta_{BD} + k_5 \theta_{MG} \theta_A \\ &\quad - k_6 \theta_G \theta_{BD} \\ \frac{d[A]}{dt} &= -k_1 \theta_{TG} \theta_A + k_2 \theta_{DG} \theta_{BD} - k_3 \theta_{DG} \theta_A + k_4 \theta_{MG} \theta_{BD} - k_5 \theta_{MG} \theta_A \\ &\quad + k_6 \theta_G \theta_{BD} \\ \frac{d[G]}{dt} &= k_5 \theta_{MG} \theta_A - k_6 \theta_G \theta_{BD} \end{aligned} \quad (5)$$

2. Eley-Rideal (ER) Model

The derivation of Eley-Rideal reaction kinetics is similar to that for LHHW. The only difference is that it is assumed that only some of the molecules involved in the reaction are adsorbed onto the catalyst [8]. Reference [4] derived equations to describe the ER mechanism. When the rate-determining step is methanol adsorption, the rate of reaction is given by:

$$(-r) = \frac{k_1 ([A] - \frac{1}{K} \frac{[C][D]}{[B]})}{1 + \frac{K_1}{K} ([C][D]/[B]) + K_3 [D]} \quad (6)$$

However, when the rate-determining step is the surface reaction, the rate of reaction becomes:

$$(-r) = \frac{k_{sr}K_1([A][B] - \frac{1}{K}([C][D]))}{1 + K_1[A] + K_3[D]} \quad (7)$$

The reaction scheme for ER in the transesterification of triglycerides is given as follows [7], where the concentration of the bulk species is in square brackets and θ_i is the fraction of component vacant sites:

$$\begin{aligned} \frac{d[TG]}{dt} &= -k_1[TG]\theta_A + k_2\theta_{DG}[BD] \\ \frac{d[DG]}{dt} &= k_1[TG]\theta_A - k_2\theta_{DG}[BD] - k_3[DG]\theta_A + k_4\theta_{MG}[BD] \\ \frac{d[MG]}{dt} &= k_3[DG]\theta_A - k_4\theta_{MG}[BD] - k_5[MG]\theta_A + k_6\theta_G[BD] \\ \frac{d[BD]}{dt} &= k_1[TG]\theta_A - k_2\theta_{DG}[BD] + k_3[DG]\theta_A - k_4\theta_{MG}[BD] + k_5[MG]\theta_A \\ &\quad - k_6\theta_G[BD] \\ \frac{d[A]}{dt} &= -k_1[TG]\theta_A + k_2\theta_{DG}[BD] - k_3[DG]\theta_A + k_4\theta_{MG}[BD] - k_5[MG]\theta_A \\ &\quad + k_6\theta_G[BD] \\ \frac{d[G]}{dt} &= k_5[MG]\theta_A - k_6\theta_G[BD] \end{aligned} \quad (8)$$

III. RESULTS AND DISCUSSION

To ensure that the observed kinetics were attributable to those of the transesterification reaction and not the result of external or internal mass transfer limitations, reaction studies were conducted with varying degrees of agitation and for a range of catalyst particle sizes. It was determined in these present studies, that for agitation speeds above 600 rpm ($Re = 23227$) was sufficient to eliminate external mass transfer limitations in initial period for SIERs (150 μm). Meanwhile, reducing the catalyst particle to $\leq 150 \mu\text{m}$ was sufficient to overcome internal diffusion limitations.

Evaluations on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) models, in the set of differential equations were solved using the explicit Runge-Kutta 4th order method in MATLAB7.9.0 version R2009b software (Math Works, Natick, MA). The simulation was initiated by fitting the initial reaction rate constants from the literatures to produce the model data of concentration-time profile. The kinetic models of Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (ER) were fitted to the experimental data for SIER-6. A set of differential equations that represents the LHHW and ER models for the transesterification reaction are previously given in (5) and (8), respectively. SIER-6 was chosen since this ion exchange resin catalyst allowed transesterification of triacetin to reach completion within a practical time frame. In developing these models, it was assumed that the adsorption coefficient of all species was equal to $K = 3 \text{ Lmol}^{-1}$, which was estimated by [4] on the methanol absorbing onto MgO. In addition, this value has been successfully used to evaluate the ER kinetics for metal oxide catalysts by [7].

The ER fitted kinetics are shown in Figs. 1 and 2, while the LHHW fitted kinetics are shown in Figs. 3 and 4. Their sum of square errors (SSEs) is displayed in Table I, along with their rate constant values. It can be seen that there are closer fits between the model and experimental data, when fitted with ER compared to LHHW kinetic models. In ER plots, the

model data for MeOH, MeAc, MoAc, and Gly are fit the experimental data well, while the TAc differs significantly, and DAc is the weakest fitted. In contrast, LHHW plots exhibit close fits for only MoAc and Gly, while the other component are poorly fitted. SSEs for the individual compound are given in Table II.

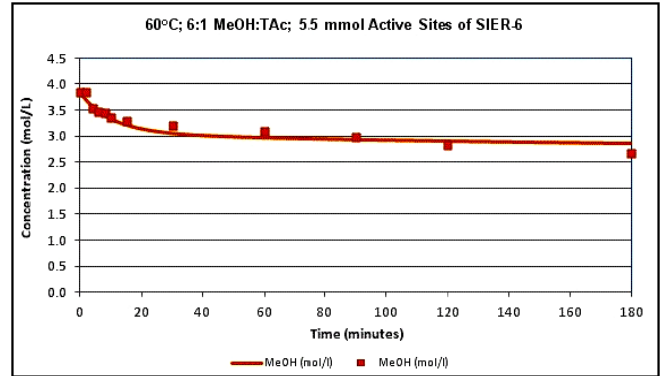


Fig. 1 ER Model Fitted to 5.5 mmol Active Sites of SIER-6 (Methanol) (Line = Model Data; Symbol = Experimental Data)

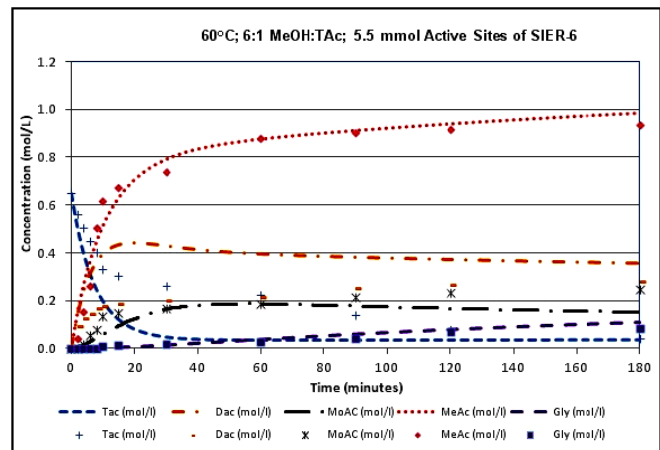


Fig. 2 ER Model Fitted to 5.5 mmol Active Sites of SIER-6 (All Compounds Except Methanol) (Lines = Model Data; Symbols = Experimental Data)

The ER model data fitted the experimental data better than the LHHW model. The smaller value of SSE suggests that ER kinetics may be considered as the most appropriate model to use, when describing the ion exchange resin catalyzed reaction, with the surface reaction is believed to be the rate-determining step (RDS).

TABLE I
RATE CONSTANT VALUES FOR 5.5 MMOL ACTIVE SITES OF SIER-6

Rate Constant Values	k_1	k_2	k_3	k_4	k_5	k_6	SSE
ER (Lmin^{-1})	0.145	0.0409	0.0296	0.197	0.0062	0.0095	0.742
LHHW ($\text{mol L}^{-1} \text{min}^{-1}$)	0.625	0.0179	0.0454	0.159	0.0062	0.0310	0.996

* k_1 , k_3 and k_5 are forward rate constants for the reactions of TAc to DAc, DAc to MoAc, and MoAc to Gly, respectively.

** k_2 , k_4 and k_6 are backward rate constants for the reactions of TAc to DAc, DAc to MoAc, and MoAc to Gly, respectively.

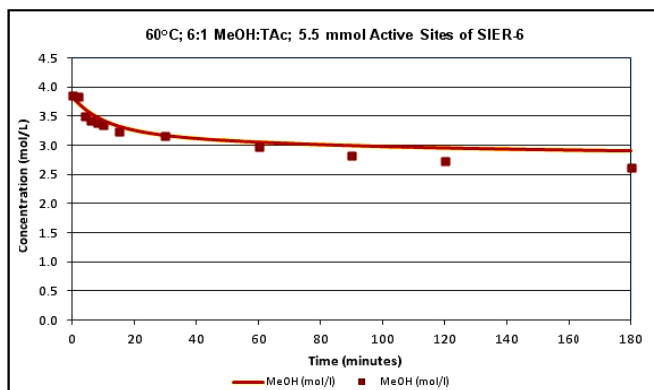


Fig. 3 LHHW Model Fitted to 5.5 mmol Active Sites of SIER-6 (Methanol) (Line = Model Data; Symbol = Experimental Data)

Nevertheless, this could be overcome by employing an excess amount of methanol, to drive this reaction forward.

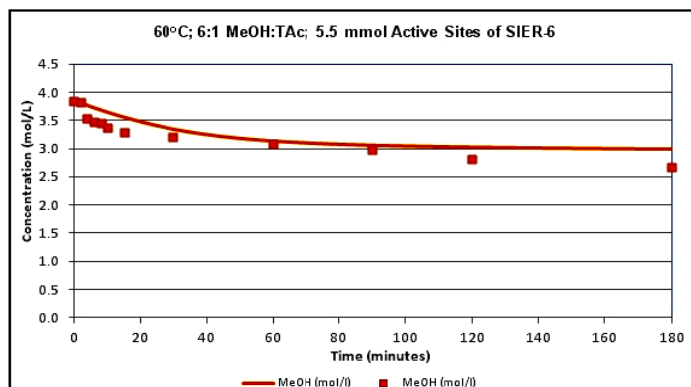


Fig. 5 ER Model Fitted to 5.5 mmol Active Sites of SIER-6 (Methanol) using $K = 30 \text{ Lmol}^{-1}$ for Glycerol (Line = Model Data; Symbol = Experimental Data)

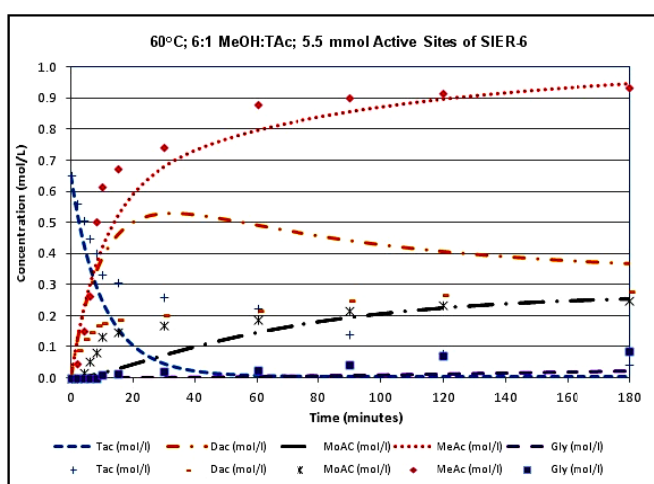


Fig. 4 LHHW Model Fitted to 5.5 mmol Active Sites of SIER-6 (All Compounds Except Methanol) (Lines = Model Data; Symbols = Experimental Data)

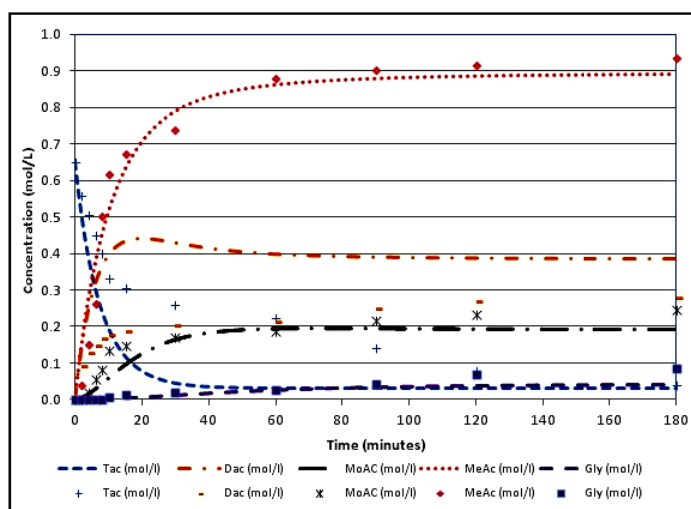


Fig. 6 ER Model Fitted to 5.5 mmol Active Sites of SIER-6 (All Compounds Except Methanol) using $K = 30 \text{ Lmol}^{-1}$ for Glycerol (Lines = Model Data; Symbols = Experimental Data)

TABLE II

INDIVIDUAL SSE FOR 5.5 MMOL ACTIVE SITES OF SIER-6

SSE	TAc	DAc	MoAc	MeAc	Gly	MeOH	Total
ER	0.211	0.311	0.026	0.048	0.001	0.145	0.742
LHHW	0.172	0.427	0.046	0.101	0.009	0.240	0.996

Initially, it was assumed that the adsorption coefficient, K of all species was equal to 3 Lmol^{-1} [4]. However, it is unlikely that the adsorption coefficient of all species will be the same, as glycerol that is highly polar would absorb more strongly onto the catalyst active sites [7]. When the adsorption coefficient, K of glycerol was increased to 30 Lmol^{-1} , it increased the SSEs to 0.833. It can be observed in Figs. 5 and 6 that there are marginal increases in the conversion to diacetin and monoacetin intermediates; along with the conversion to methanol; and slight decreases in the conversion of triacetin. Conversely, significant decreases can be observed in the conversion to methyl acetate and glycerol. This suggests that an increase in the adsorption coefficient, K of glycerol increases the backward rate of reaction, as the equilibrium composition is slightly closer to the reactant side [7].

IV. CONCLUSIONS

In conclusion, the ion exchange resin-catalyzed reaction were well-described by the Eley-Rideal model. Significantly, the ER model data fitted the experimental data for all ion exchange resins studied in this work.

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