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ORIGINAL STUDY

Reaction Pathways, Kinetic Modelling and Parameter Estimation of Heterogeneous Catalytic Trans-esterification Process

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Abstract

The kinetics of heterogeneous catalyzed trans-esterification between castor oil and methanol was studied and modeled. Kinetic data was obtained from a perfectly mixed slurry batch reactor. The modeling was conducted via the modified-hattori mechanism to determine the exact rate controlling step for the reaction. A total of five rate expressions were formed, which were as a result of; methanol adsorption, Triglyceride adsorption, Formation of the complex, Surface reaction and Glycerol desorption. Evaluation of best fitting model and parameter estimation were done using the Neadler simplex least square optimization algorithm with the aid MATLAB software. The result from the regression analysis indicated that a kinetic model based on the modified hattori mechanism gave a good fit for the experimental data when assuming the formation of intermediate as the rate determining step. Visual depiction of the conversion and time values for the experimental and the theoretical procedure were also produced to show visual contrast between the two procedures both for experimental and the theoretical. Other models derived from the other mechanisms were rejected based on statistical analysis, mechanistic considerations and physicochemical interpretation of the parameters. Thus, the study gives exact rate controlling step for heterogeneous catalysis to be used for the reactor design and cost-effective production of biodiesel.

Keywords: Castor oil, Heterogeneous system, Mechanistic modelling, Parameter estimation, Rate controlling step

1. Introduction

Energy plays a vital role in the day to day activities of mankind on earth. As the population grows and industrialization expands, the need for more energy to run daily operations also increases. The drive to develop an alternative source of energy is thus important. Renewable energy which ranges from solar, hydro, biofuels and many more have been adjudged to be an alternative energy source (Rubi et al., 2011). In this research, biodiesel which is a subset of biofuel remains our focus.

According to the International Energy Statistics for the year 2010, Africa and the rest of the world produced a total of 990 barrels and 1.9 million barrels of biofuel; and consumed 3.4 and 85.7 million barrels of petroleum fuel, respectively (1 barrel = 0.159 m^3) (International Energy Agency, 2010; Shereena and Thangaraj, 2009). There are also speculations that the rate of consumption of the petroleum fuel is 2.7% of the reserve. Estimations projected that, the rate will lead to a total exhaustion of the fossils fuel in about 50 years from now (Senthil et al., 2009; Keera et al., 2018). Liquid biofuels consist of biodiesel and bio gasoline. When compared to petroleum hydrocarbons, these renewables do not add to the net carbon dioxide and also decrease the net carbon dioxide from the combustion of the fuels thereby contributing less to environment Pollution and degradation (Senthil

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Application of the Modified-Hattori mechanism for the mechanistic modelling of the trans-esterification process.

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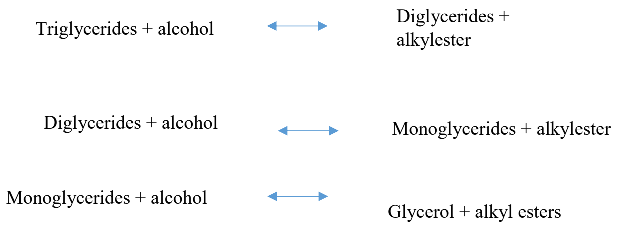
et al., 2009; Keera et al., 2018).There are various methods to produce biodiesel in the energy industry; amongst them are dilution, micro emulsion, pyrolysis, and transesterification (Viraj et al., 2023). Of these methods of preparation, the trans-esterification has been adjudged the best because it produces biodiesel of low viscosity and properties close to petro diesel (Niken and Subhash, 2011). Trans esterification is defined as a chemical reaction between a triglyceride and an alcohol in the presence of catalyst (homogeneous or heterogeneous) to produce FAME (fatty acid methyl esters) (Basavaraje et al., 2005; Ahmia et al., 2014; Amita and Susan, 2014). If methanol is widely used with glycerol as a by-product (Ayhan et al., 2016; Viraj et al., 2023; Basavaraje et al., 2005). The study of the trans-esterification mechanism for the biodiesel production is thus important. The widely and basically accepted reaction mechanism follows that, the triglycerides are converted to diglycerides and then diglycerides are converted to the Monoglycerides before its react with the last of the three methanol to produce glycerol and methyl oleate (Biodiesel) (Sreenivas et al., 2011; Agency, 2021; Abdul Kalam and Rizki PPZY, 2018). The equation of the reaction shown in Scheme 1 is a reaction at chemical equilibrium because the reaction proceeds in two directions where the forward reaction is equal to the backward reaction.

Prior to this period, the study of the production of biodiesel from non-edible oil have been done with the use of homogeneous catalyst. The usage of this catalyst poses a lot of threat to the process because of the formation of soap which is difficult to separate from the biodiesel. The deactivation of the catalyst also poses a threat to the economic extraction of biodiesel (Rubi, Sandra, Reyna).

Similarly, the development of the kinetic models for reactions is a powerful tool for reactor design. The entire process, including the heating and separation processes, must be optimized, which calls for the use of the kinetic model (Ivana et al., 2012). Hence, depending on the kind of reactor being used—CSTR, PFR, or batch reactors, the kinetic model must be incorporated into the reactor model. The choice of the most advantageous circumstances (such as temperature, pressure, and mixing rate) to optimize the creation of desired products is made much easier when considering chemical or biological transformations in reactors or bioreactors. The reaction products, which can vary depending on the conditions, also influence the separation steps. This goes a long way in also determining the cost of the either process (Nuria et al., 2015). This also applies to the different biodiesel production processes, including homogeneous, heterogeneous, enzyme catalysis (Baohua et al., 2023). A kinetic model which is at equilibrium in this case can be applied as strategic tool for obtaining a better understanding of the rates of product formation and the inhibition patterns present in the transformation scheme (Sreenivas et al., 2011). In addition, kinetic models may offer different levels of detail and predictive capabilities, as they can take into account mass and heat transfer phenomena, as well as thermodynamic equilibrium. (Rubi, Sandra, Reyna; Bioenergy, 2023). The level of theory for modelling the reactions can go from the use of quantum chemistry to the individual elementary steps up to a series of encompassed reaction steps between pseudo-components (Lumped models). The catalyst deactivation, the presence of undesired side reactions, the consideration if inhibition processes and a detailed feedstock composition are among factors that can be considered to derive more realistic models and with a higher predictive capacity. A kinetic model can also be applied as a strategic tool for obtaining a better relationship of the rates of product formation and inhibition patterns present in the transformation scheme (Turner, 2005; Rohollah et al., 2021).



Scheme 1. Scheme I showing the Trans-esterification process (Wenlei et al., 2018; Humphrey et al., 2017).

The aim of this research is to develop models for the mathematical representation of a heterogeneous trans-esterification process between castor oil and methanol using the modified Hattori Mechanism. The models formulated will help further reduce the controversy surrounding the most suitable reaction mechanism for the biodiesel production.

The kinetic modelling of the Trans esterification process over the past years either using homogeneous and/or heterogeneous catalyst has arguably been successful via the most widely used sites mechanism which are Eley-Rideal (ER), Langmuir-Hinelshood Hougen—Watson (LHHW) and Hattori (Bioenergy, 2023; Erich et al., 2018). However, some of these mechanisms have certain shortcomings. For example, both the ER and LHHW mechanism don't account for the formation of intermediates during the Trans esterification process which is a very

$$* + CH_3OH \Leftrightarrow CH_3OH*$$

$$CH_3OH* + T \Leftrightarrow D* + MeOl$$

$$CH_3OH* + D \Leftrightarrow M* + MeOl$$

$$CH_3OH* + M \Leftrightarrow G* + MeOl$$

$$D* \Leftrightarrow D + *$$

$$M* \Leftrightarrow M + *$$

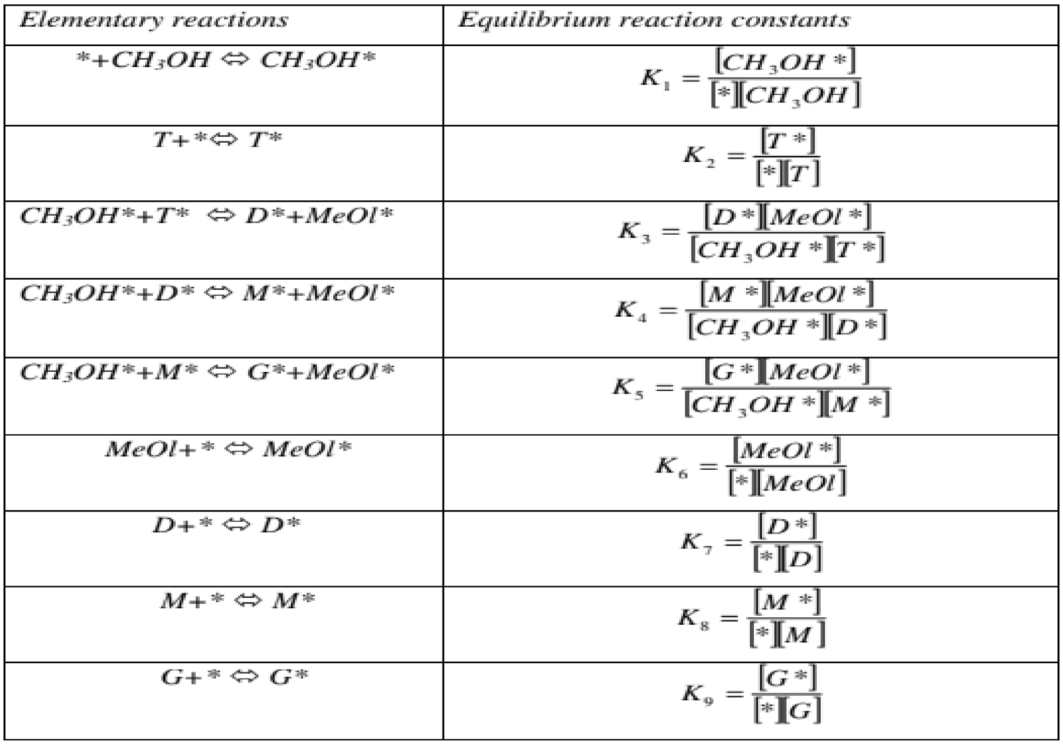
$$G* \Leftrightarrow G + *$$

Scheme 2. Eely rideal reaction mechanism (Ankur Kapil, 2010).

critical step in the process of the synthesis of biodiesel (Bioenergy, 2023). The hattori mechanism however considered the formation of the intermediates but does not put into perspective the stepwise addition of methanol which could have an impact on the yield of biodiesel. To combat these shortcomings a slight adjustment to the hattori mechanism (Modified Hattori) was proposed to put into account the stepwise addition of the methanol and the formation of intermediates (Erich et al., 2018). Hence, to accurately certify this mechanism, a mathematical representation of the process will be developed and also validated using experimental data (Vineet et al., 2015).

Asides from the advancement in the aspect of the reaction mechanism, there has also been technological advancement in the biodiesel market. Major companies in this space now focused on developing technological solutions to strengthen market position because this determines how profitable the industry will be. For instance, in November 2021, according to a report published by the International Energy Agency (IEA), a France-based autonomous intergovernmental organization, biodiesel consumption was 47,867 million litres in 2022, an increase from 43,855 million litres in 2020. Moreover, biodiesel consumption is expected to reach 51,424 million litres in 2026 (Thomas et al., 2013). Therefore, an increase in biofuel demand is driving the biodiesel market's growth. One of the major development by Crown works, a US based supplier of oils seed extraction technology, refining plants and equipment introduced a better form of reaction called the Advanced Catalyst Reduction and Economization (ACRE) (Thomas et al., 2013).

The ACRE mentioned above is a process upgrade to refine its biodiesel process technology. The ACRE uses three transesterification reactor the residence



Elementary reactions	Equilibrium reaction constants
$* + CH_3OH \Leftrightarrow CH_3OH*$	$K_1 = \frac{[CH_3OH*]}{[*][CH_3OH]}$
$T + * \Leftrightarrow T*$	$K_2 = \frac{[T*]}{[*][T]}$
$CH_3OH* + T* \Leftrightarrow D* + MeOl*$	$K_3 = \frac{[D*][MeOl*]}{[CH_3OH*][T*]}$
$CH_3OH* + D* \Leftrightarrow M* + MeOl*$	$K_4 = \frac{[M*][MeOl*]}{[CH_3OH*][D*]}$
$CH_3OH* + M* \Leftrightarrow G* + MeOl*$	$K_5 = \frac{[G*][MeOl*]}{[CH_3OH*][M*]}$
$MeOl + * \Leftrightarrow MeOl*$	$K_6 = \frac{[MeOl*]}{[*][MeOl]}$
$D + * \Leftrightarrow D*$	$K_7 = \frac{[D*]}{[*][D]}$
$M + * \Leftrightarrow M*$	$K_8 = \frac{[M*]}{[*][M]}$
$G + * \Leftrightarrow G*$	$K_9 = \frac{[G*]}{[*][G]}$

Scheme 3. Langmuir-Hinshelwood-Hougen-Watson reaction mechanism (Ankur Kapil, 2010).

time and this will help meet the stoichiometric reactions number. This process also allows for the optimal use of catalyst as it gives a potential for use. This process is also energy-efficient which helps biodiesel producers save money on steam and electricity. This amount of fresh steam injected is limited by using economizers that takes the heats from the flue gases and then ejected back to the heater.

The aim of the research is to establish a kinetic model for the heterogeneous Trans esterification reaction between castor oil and methanol using the Modified hattori reaction mechanism.

A review of the previous reaction mechanism is as described

1) Eely rideal mechanism

The Eely Ideal (ER) mechanistic model assumes that one of the reactants adheres to an active site, proceeding to react with other raw materials in the bulk phase (Baohua et al., 2023). This then proceeds to form products bonded to the active site and then the other products present in the bulk phase. In common terms, the first reaction represents the adsorption of methanol on the active site of catalyst surface. The second step is the surface reaction step which is the rate determining step. Finally, the third step is the desorption of glycerol from the active site of catalyst surface (Baohua et al., 2023). The equation of the reaction is shown in Scheme 2. It also shows scheme for the rate equation for each specie.

1.1. Langmuir-Hinshelwood-Hougen-Watson (LHHW)

The LHHW on the other hand assumes that both the reactants bond to the active sites of the catalyst and these proceeds to reacts to form products still bonded to the active sites. This is why the LHHW site is called the dual site mechanism. The first reaction that adheres to the two active site is called the adsorption step (Rohollah et al., 2021; Canakci and Van Garpen, 1999). The surface reaction that takes place at the active sites on the catalyst is formed from the protonated carbonyl group and alkoxide group. The only other if they are adjacent to produce diglycerides and methyl oleate (Biodiesel) before the further reaction. Besides this difference the LHHW model is preferred when a higher carbon alcohol is used while the ER is used when low carbon alcohol is used. Scheme 3 show the stepwise stoichiometry equation and the rate equation using each step as rate limiting Scheme 3 (Octave, 1999).

1.2. Hattori Mechanism

The hattori site mechanism is an improvement to the other two described above. It is a combination of aspects of the Eely Rideal Mechanism (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW). The reactants are first adsorbed onto an adjacent active site (ER present) and then forms intermediates molecule (LHHW) bonded to only

Table 1. Rate expression for the modified Hattori Mechanism.

Elementary reaction	Rate expression with the elementary reaction as the rate-determining step
$\mathrm{A + S}\ \underset{k'_1}{\overset{k_1\leftrightarrow}{\ }}\ \mathrm{AS}$ (Methanol adsorption)	$r1 = \dfrac{K_1\left[C_A - \dfrac{C_C C_D}{K C_B}\right] C_O}{\dfrac{K_1}{K}\left[\dfrac{C_C C_D}{C_B}\right] + K_2 C_B + K_5 C_D + K_4 K_5 C_C C_D + 1}$
$\mathrm{B + S}\ \underset{k'_2}{\overset{k_2\leftrightarrow}{\ }}\ \mathrm{BS}$ (Triglyceride adsorption)	$r2 = \dfrac{K_2\left[C_B - \dfrac{C_C C_D}{K C_A}\right] C_O}{\dfrac{K_2}{K}\left[\dfrac{C_C C_D}{C_A}\right] + K_1 C_A + K_5 C_D + K_4 K_5 C_C C_D + 1}$
$\mathrm{AS + BS}\ \underset{k'_3}{\overset{k_3\leftrightarrow}{\ }}\ \mathrm{ABS + S}$ (Formation of Intermediate)	$r3 = \dfrac{K_3 K_1 K_2\left[\dfrac{C_A C_B}{1} - \dfrac{C_C C_D}{K}\right]}{\left[k_1 C_A + K_2 C_B + K_5 C_D + K_4 K_5 C_C C_D + 1\right]^2}$
$\mathrm{ABS + AS}\ \underset{k_4}{\overset{k'_4\leftrightarrow}{\ }}\ \mathrm{C + DS}$ (Surface reaction)	$r4 = \dfrac{K_4 K_1 C_A\left[\dfrac{K_1 K_2 K_3 C_A C_B}{K_4} - \dfrac{K K_5 C_A C_B}{1}\right]}{\left[k_1 C_A + K_2 C_B + K_5 C_D + \dfrac{K_3 K_1 K_2 C_A C_B}{1} + 1\right]^2}$
$\mathrm{DS}\ \underset{k_5}{\overset{k'_5\leftrightarrow}{\ }}\ \mathrm{D + S}$ (Glycerol desorption)	$r5 = \dfrac{K_5\left[\dfrac{K C_A C_B}{C_C} - C_D\right] C_O}{\left[\left[k_1 C_A + K_2 C_B + K_5 \dfrac{K C_A C_B}{C_C} + \dfrac{K_3 K_1 K_2 C_A C_B}{1} + 1\right]\right]}$

Table 2. Reaction conditions (Vineet et al., 2015).

Reaction time	2 h
Catalyst type	Hydrated Lime
Catalyst Concentration	1.6% (in relation to the mass of methanol and oil)
Alcohol type	Methanol
Alcohol to oil ratio	0.42 (volume) 10:1 (molar)
Temperature	60 °C

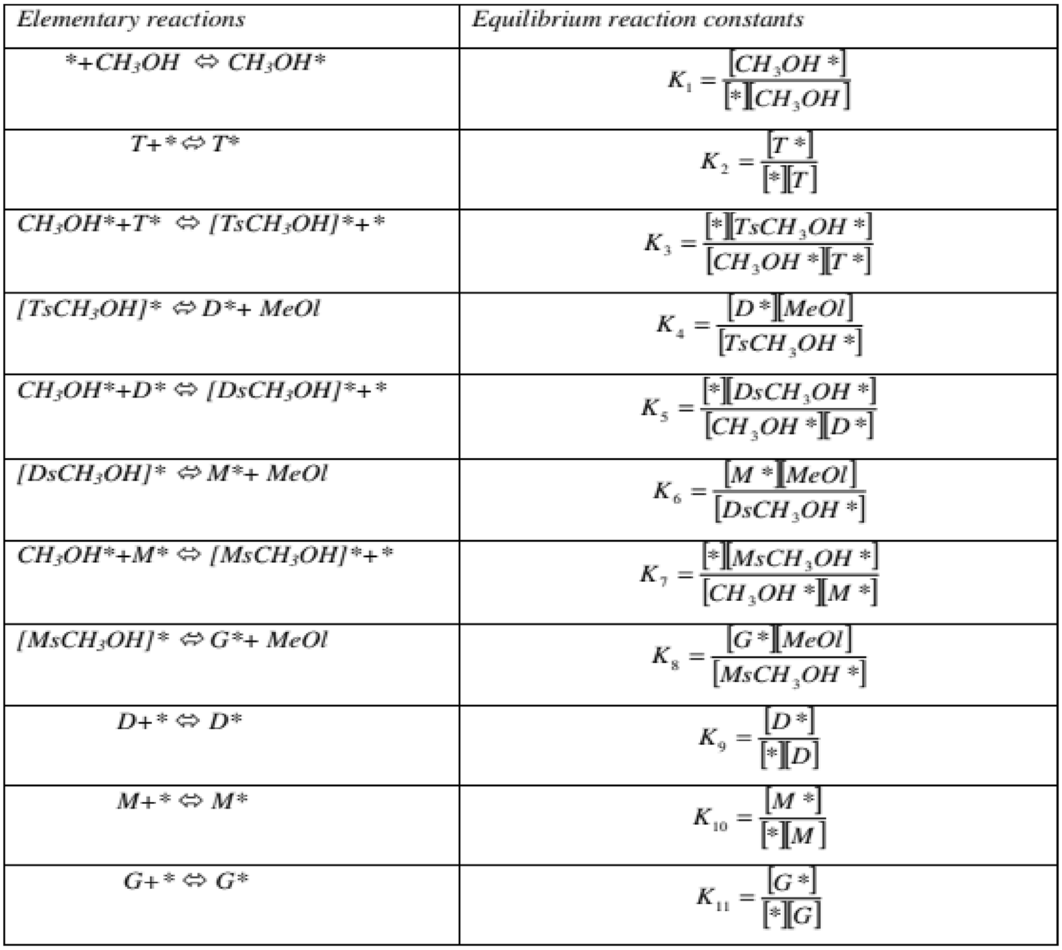
one of the sites. This intermediate then splits to form one of the products adsorbed on the active site and the other products (usually the main product on the bulk phase) (Aashish et al., 2019). Table 2 shows the elementary equations of this mechanism as well as the rate equation taking the surface reaction as the rate determining step Scheme 4.

1.3. Limitation of study

The general purpose of this study is to develop a kinetic model of a Trans-esterification process using the modified hattori mechanism, which are formulated using elementary reaction steps from chemical kinetics. The experimental samples or data used for the model development and validation were based on literature. This research model covers a few topics and theories such as rates of reactions, adsorption sites mechanisms, quasi and/or pseudo steady state reactions. However, the study does not cover kinetic effects such as process economics, atom economy, feedstock quantity, and does not take account of competing reactions. This study also put into perspective the assumptions that each step is the rate-determining step and since the proposed reaction mechanism has 5 elementary steps a total of 5 models were formulated (each step will be rate determining).

2. Materials and methodology

Established reaction mechanism using the Modified Hattori Mechanism was developed and validated using experimental trans-esterification



Elementary reactions	*Equilibrium reaction constants*
$*+CH_3OH \Leftrightarrow CH_3OH*$	$K_1 = \frac{[CH_3OH*]}{[*][CH_3OH]}$
$T+* \Leftrightarrow T*$	$K_2 = \frac{[T*]}{[*][T]}$
$CH_3OH*+T* \Leftrightarrow [TsCH_3OH]*+*$	$K_3 = \frac{[*][TsCH_3OH*]}{[CH_3OH*][T*]}$
$[TsCH_3OH]* \Leftrightarrow D*+MeOl$	$K_4 = \frac{[D*][MeOl]}{[TsCH_3OH*]}$
$CH_3OH*+D* \Leftrightarrow [DsCH_3OH]*+*$	$K_5 = \frac{[*][DsCH_3OH*]}{[CH_3OH*][D*]}$
$[DsCH_3OH]* \Leftrightarrow M*+MeOl$	$K_6 = \frac{[M*][MeOl]}{[DsCH_3OH*]}$
$CH_3OH*+M* \Leftrightarrow [MsCH_3OH]*+*$	$K_7 = \frac{[*][MsCH_3OH*]}{[CH_3OH*][M*]}$
$[MsCH_3OH]* \Leftrightarrow G*+MeOl$	$K_8 = \frac{[G*][MeOl]}{[MsCH_3OH*]}$
$D+* \Leftrightarrow D*$	$K_9 = \frac{[D*]}{[*][D]}$
$M+* \Leftrightarrow M*$	$K_{10} = \frac{[M*]}{[*][M]}$
$G+* \Leftrightarrow G*$	$K_{11} = \frac{[G*]}{[*][G]}$

Scheme 4. Hattori reaction mechanism (Ankur Kapil, 2010).

Table 3. Conversion time data (Vineet et al., 2015).

Time (min)	Conversion (%)
5	20
10	33
30	43
60	74
90	81
120	100

reaction data obtained from (Aashish et al., 2019) for biodiesel synthesis under a heterogeneously catalysed environment.

2.1. *Kinetic models based on pseudo steady state approximation*

The pseudo steady state approximation was done by assuming each of the reaction steps to be the rate determining step.

The overall equation for the green fuel production process can be written as

$$3\,CH_3OH + C_{57}H_{104}O_9 \leftrightarrow 3\,C_{19}H_{36}O_3 + C_3H_8O_3 \qquad (1)$$

$$3\,A + B \leftrightarrow 3\,C + D \qquad (a)$$

The modified hattori mechanism was used to develop the kinetic model of the trans-esterification reaction. It was proposed by Om Tapanes as it is a better modification to both the LHHW (Langmuir-Hinshelwood-Hougen-Watson) and Hattori mechanism respective. The mechanism involves the formation of a chemical intermediate before the reaction of this intermediate with a second alcohol bonded to an adjacent site, forming one of the products in the bulk phase with the other product and the replenished alcohol bound to the active sites. The stepwise reaction for this mechanism include the stepwise addition, the methanol (Vineet et al., 2015).

2.2. *Modified hattori mechanism*

The elementary reactions in Modified Hattori kinetic mechanism are written below as eqns (2) − (6)

$$\mathbf{A + S \underset{k'_1}{\overset{k_1}{\leftrightarrow}} AS} \qquad (2)$$

$$\mathbf{B + S \underset{k'_2}{\overset{k_2}{\leftrightarrow}} BS} \qquad (3)$$

$$\mathbf{AS + BS \underset{k'_3}{\overset{k_3}{\leftrightarrow}} ABS + S} \qquad (4)$$

$$\mathbf{ABS + AS \underset{k_4}{\overset{k'_4}{\leftrightarrow}} C + DS + AS} \qquad (5)$$

$$\mathbf{DS \underset{k_5}{\overset{k'_5}{\leftrightarrow}} D + S} \qquad (6)$$

The modified Hattori mechanism proposed is a better modification to both the LHHW and Hattori mechanism respectively. The mechanism involves the formation of a chemical intermediate before the reaction of this intermediate with a second alcohol bonded to an adjacent site, forming one of the products in the bulk phase with the other product and the replenished alcohol bound to the active sites. Subsequently, the adsorbed intermediate decomposes into the production of adsorbed glycerol and bulk FAME respectively.

For classical transesterification processes, the following equations hold

$$3\,A + B \leftrightarrow 3\,C + DC_A = C_{BO}\left(\frac{C_{AO}}{C_{BO}} - 3\,x\right) \qquad (b)$$

$$C_B = C_{BO}(1 - x) \qquad (c)$$

$$C_C = 3\,x\,C_{BO} \qquad (d)$$

$$C_D = x\,C_{BO} \qquad (e)$$

$$\mathbf{r = C_{Bo}\frac{dx}{dt}} \qquad (f)$$

Where x represents the conversion of the limiting reactant and is the rate of reaction for each of the models presented above.

2.3. *Model validation*

The concentration time data for this study was adapted from (Aashish et al., 2019). In this research, the influence of the catalyst amount, methanol: oil ratio, reaction time, and reaction temperature were studied using hydrated lime as a catalyst for the transesterification of castor oil with methanol. The particular result of interest is the conversion time data which is presented in Table 4.

To establish the mechanism followed by the reaction, the obtained concentration time data were fitted into the 5 rate equations (Table 1) for the estimation of their respective reaction rate constants. Before proceeding to the next calculation, the Van't Hoff equation was used to calculate the overall

Table 4. The fourth order rate constants for the specific heat capacity (C O et al., 2013).

Components	A	B	C	D	$\Delta H^{o}_{f,298K}$ (J/mol)	$\Delta G^{o}_{f,298K}$ (J/mol)
CH_4O	21.152	7.0924×10^{-2}	25.870×10^{-6}	-2.852×10^{-8}	-201.30×10^{3}	-162.62×10^{3}
$C_3H_8O_3$	8.424	**444.22×10^{-3}**	31.59×10^{-5}	**9.3784×10^{-8}**	**-585.310×10^{3}**	-438.520×10^{3}
$C_{18}H_{33}O_3$	41.6476	**25.66×10^{-5}**	-85.92×10^{-5}	1.6529×10^{-6}	-719.95×10^{3}	**-224.1×10^{3}**
$C_{19}H_{36}O_3$	10.6	14.99×10^{-3}	66.889×10^{-5}	**-1.537×10^{-6}**	-781.148×10^{3}	-278.4655×10^{3}

thermodynamic equilibrium (Roman et al., 2013). The parameter estimation and best fitting of the model equation was done using MATLAB software environment while MATLAB was employed in solving the resulting ordinary differential equations via the Runge–Kutta method. The nealder-simplex (SSE) algorithm was used for minimizing the sum of squared errors (Turner, 2005). The regression coefficient and sum of squared error were used to evaluate the best kinetic model that adequately describes the transesterification pathway. The statistical test was further applied in describing the mechanism of biodiesel production. The model with the smallest sums of squares (variance) and with good and realistic positive physical parameters (rates and rate constants) was selected based on the 95% confidence level.

2.4. Parameter estimation

Parameter estimation is a very key step in the modelling of a chemical reaction because through this the results of the models can coincide with the experimental results and when this happens the theoretical approach can be used in place of the experimental (Rohollah et al., 2021). The parameter estimation which is used in this process makes use of the optimization tool called the least square method optimization. This aims to reduce the square of the difference between the experimental and the calculated rate of reaction. Hence, parameter estimation imposes a constrained optimization problem where the objectives is to minimize the sum of the square error (SSE) between the predicted and observed values of the component. Therefore, in respect to this research work, the parameters to be estimated are the rate reaction constants (K1, K2, K3, K4, K5) which will help to get our objective of minimization (Canakci and Van Garpen, 1999). However, to proceed with this optimization some experimental data was are Conversion(X) and the rate of reaction(R) at those conversions are given. The initial concentration of both the triglyceride and the alcohol was also gotten from experiment. Finally, the overall equilibrium constant K was also calculated using the Van't Hoff equation and tabulated. With all these data given we proceeded to get our constants using the MATLAB software package (Gabriel et al., 2016).

2.5. Fitting the non-linear kinetic model

The adoption of the least square estimation was to calculate the values of the coefficients in a model from experimental data. Here the number of the data sets or the experimental data must be equal to or greater than the coefficients in the model i.e. the degree of freedom must be positive and greater than zero (AICHE Academy, 2006). This is necessary to compensate for errors involved in experimental data. Presently, there are many software packages used in fitting the models e.g. MATLAB, SCILAB. Nonlinear parameter estimation can also be done using Microsoft excel depending on the complexity of the model. The ordinary least square estimation was used to fit this model and thus use to determine the different rate constant (k1, k2, k3, k4, k5) respectively.

2.6. Choosing starting value

This is one of the most critical part of parameter estimation and its significance is not overlooked regardless of the procedure being adopted. The choice of initial values has significant influence on the convergence of estimation algorithm, in the worst case yielding no convergence and in the best case convergence in a few iterations (Thomas et al., 2013). There are so many methods of picking the starting value for the rate constants e.g. using the grid search, random jump and random walk. However, in this result a random jump method was used and this values gave convergence at a high speed using few iterations.

2.7. Algorithm convergence

Convergence is achieved when relative offset or maximum change among parameter estimates is below a certain threshold value 10^{-6} (Neyda et al., 2008). This implies that the algorithm has found a best solution. Following, convergence, the parameter estimates are evaluated to determine if they fall within a reasonable range. This requires evaluating the point estimates and their standard errors. Unusually large standard errors are indicators of poor model fitting.

2.8. Model validation adopting the experimental data

The experimental data obtained was fitted to obtain the precise reaction steps and subsequent rate expression for surface reaction on the active sites of the catalyst. The obtained results from each of the mechanisms are presented in full in the appendix. The validation and selection of the actual model that describes the transesterification process, where certain statistical parameters for each of the elementary steps considered are presented in this section. The model discrimination and subsequent selection was based on the physical significance of the estimated parameters and on the comparison between the experimental reaction rates and the calculated rate obtainable from the proposed models. Models were rejected if a large deviation from the experimental data is observed or when kinetic parameters with exaggerated values are obtained, such as negative values, too high values or not significantly different from zero at the 95% confidence level (International Energy Agency, 2021).

3. Results and discussion

3.1. Computation of overall thermodynamic equilibrium constant (Van't Hoff equation)

The variation of the thermodynamic equilibrium constant, K_{AT}, in the rate expressions with temperature was calculated using the expression:

$$\ln K_{AT} = \frac{1}{R_u}\left[\Delta a \ln T + \left(\frac{\Delta b}{2}\right)T + \left(\frac{\Delta c}{6}\right)T^2 + \left(\frac{\Delta d}{12}\right)T^3 - \frac{c_2}{T}\right] + c_1 \tag{g}$$

But

$$dH^o_{f,298K} = c_p dT \Rightarrow \Delta H^o_{f,298K} = \int \Delta c_p dT + c_2 \tag{h}$$

Where

$$\Delta c_p = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3 \tag{i}$$

The values of various constants in equation (12), as well as the standard heats of formation, $\Delta H^o_{f,298K}$ and standard Gibbs free energy, $\Delta G^o_{f,298K}$ for the components participating in the triglyceride esterification reaction are presented in Table 4 (Newswire, 2023).

Where $\Delta = 3.0\times C_{19}H_{36}O_3 + 1.0\times C_3H_8O_3 - [3.0\times C_{18}H_{33}O_3 + 3.0\times CH_3OH)]$

Hence, $\Delta a =$ -148.1748, $\Delta b = 2.756602\times 10^{-1}$, $\Delta c = -96.44 \times 10^{-5}$, $\Delta d =$ -9.38893 $\times 10^{-6}$

$\Delta H^o_{f,298K} = -16.5\times 10^4$ J/mol, $\Delta G^o_{f,298K} = -11.38 \times 10^4$ J/mol and $\Delta S^o_{f,298K} = -171.8$ J/mol

Using equation (I) in equation (h), the constant of integration, c_2, in equation (j) can be determined for T = 333 K. Multiplication of equation (i) by (−RT) and substitution of known values from Table 2 into the resulting expression gives the value of another constant of integration, c_1 for T = 333 K. Hence, using equation (i), the general expression for the variation of the overall thermodynamic equilibrium constant, K_{AT} , with temperature was found to be:

$$\ln K_{AT} = \frac{12274}{T} - 17.822\ln T + 0.016578T - 1.9332 \times 10^{-5}T^2 - 9.4108\times 10^{-8}T^3 + 107.84 \tag{j}$$

The variation of the equilibrium constant, K_{AT}, with temperature is presented in Table 5.

The other values shown in the Table 5 such as Change in Enthalpy ΔH_{AT} are gotten from the equation h above. The equation for the change in Gibbs free energy and the change in Entropy is shown below.

$$\Delta G_{AT} = -RT\text{In}K_{AT} \tag{k}$$

$$\Delta G_{AT} = \Delta H_{AT} - T\nabla S_{AT} \tag{l}$$

Hence making the ∇S_{AT} the subject of the formula in equation l above we have: Tables 5 and 6.

$$\nabla S_{AT} = -\frac{\Delta G_{AT} - \Delta H_{AT}}{T} \tag{m}$$

A tabular form of the results is now formulated for easier comparison. To further show the deviation of the three reaction rate i.e. R1, R2 and R3 from the

Table 5. The overall thermodynamic constant, entropy, Gibbs free Energy and the enthalpy for different Temperature.

Reaction parameters	Temperature				
	298.15 K	303 K	313 K	323 K	333 K
ΔH_{AT}/J mol^{-1}	-16.5×10^4	−143,225	−144772.0081	−146351.6483	−147965.9888
ΔG_{AT}/J mol^{-1}	− 118411	−118,772	−117243.2425	−115574.67	−113751.8944
ΔS_{AT}/J mol^{-1}K^{-1}	− 156.27	−80.703	−87.9513	−95.2847	−102.745
K_{AT}	5.572×10^{20}	2.993×10^{20}	3.6873×10^{19}	4.91×10^{18}	6.98×10^{17}

Table 6. Results on Parameter Estimation using Modified Hattori Mechanism.

Modified Hattori Mechanism							
	K	k1	k2	k3	k4	k5	fmin
Alcohol adsorption	6.98E+17	0.00083287	0.2172028		1.340854	1.601034	0.00000159
Triglyceride adsorption	6.98E+17	1.35454182	0.0556212		1.234802	1.119507	6.93568E-13
Formation of intermediate	6.98E+17	0.53998831	0.2623333	1.36977	0.81307	0.737278	1.22574E-14
Surface Reaction	6.98E+17	1.59381858	0.2193294	1.10324	0	1.101974	0.00003065
Glycerol desorption	6.98E+17	1.00066308	0.2001003	1.00048		1.000778	2940

experimental procedure, the visualization of the data is more effective and shown in both Fig. 1. and Table 7.

From the Table 7, a statistically based test was conducted on the conversion and see which of the three is the least far from the experimental conversion by conducting a standard deviation or variance analysis. The least far of the three i.e. the rate reaction that shows the smallest deviation was chosen as the rate controlling reaction.

Table 8 shows the standard deviation of various rates of reactions i.e. the deviation from the experimental values. From the results of the standard deviation, the rate reaction three (R3) has the least value and thus chosen as the rate controlling step for the modified hattori mechanism for the transesterification reaction. This implies that out of the three reaction rates, the one that most suitably matches that of the experimental rate from literature is the reaction rate 3 which then shows that the formation of the intermediate is the rate limiting/controlling step and can be used for initially gauging the reaction instead of using the experimental procedure. This has always been found to be more cost-effective.

Table 7. Conversion using the theoretical models.

Time	R1	R2	R3
5	0.2783	0.0362	0.1746
10	0.4855	0.3578	0.38
30	0.9876	0.7234	0.47
60	1.3224	0.8251	0.8207
90	1.5	0.8604	0.855
120	2.1348	0.9332	0.9284

Table 8. Statistical Test using the theoretical models through standard deviation.

Time	R2	R3	R1	Expt. Rate	S.D R1	S.D R3	S.D R2
5	0.0362	0.1746	0.2783	0.2	0.006131	0.000645	0.02683
10	0.3578	0.38	0.4855	0.33	0.02418	0.0025	0.000773
30	0.7234	0.47	0.9876	0.43	0.310918	0.0016	0.086084
60	0.8251	0.8207	1.3224	0.74	0.33919	0.006512	0.007242
90	0.8604	0.855	1.5	0.81	0.4761	0.002025	0.00254
120	0.9332	0.9284	2.1348	1	1.287771	0.005127	0.004462
					0.638265	**0.055391**	**0.14602**

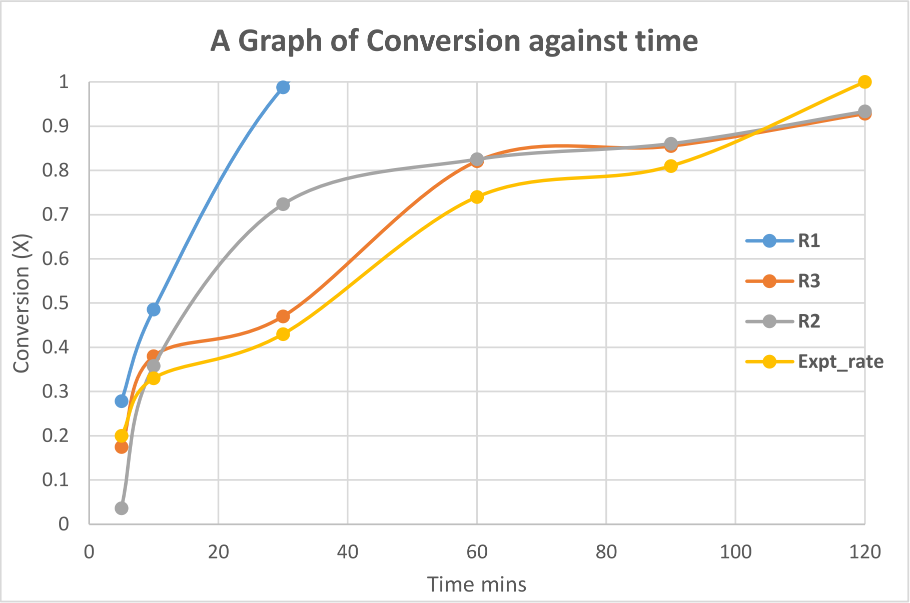


Fig. 1. A graph of Conversion against time showing the different reaction rates and their deviations.

From the statistical test using the standard deviation, it has shown significantly that the reaction 1 cannot be used for the theoretical procedure because it shows a large departure from the

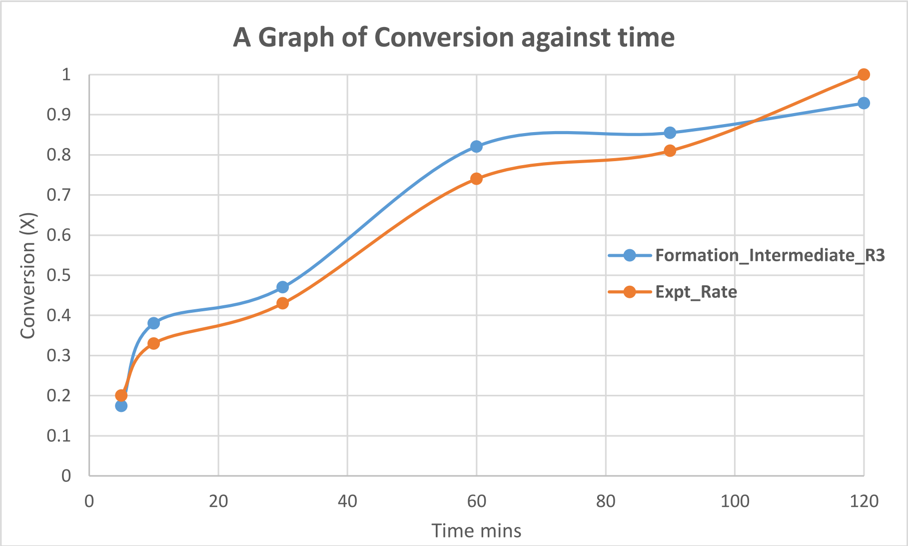


Fig. 2. Figure showing the experimental and theoretical conversions with time.

experimental and also overshoots the maximum conversion of 100%. No conversion of this form can be more than 100%. Thus, it was discarded. This also goes for the reaction rate 2 but it is a much better form of the experimental that R1. However, for the purpose of high accuracy and minimization of errors the reaction rate 3 is chosen.

The relevance of this aspect is in deriving the kinetic model of the Trans esterification reaction between castor oil and methanol for the production of bio diesel in the optimum way attainable. It will also contribute a significant quota to having a full grab of the reaction mechanism, which is essential for reactor design and reaction engineering for large scale production.

3.2. Model validation

The selected model is given thus:

$$r_3 = \frac{K_3K_1K_2\left[\frac{C_AC_B}{1} - \frac{C_CC_D}{K}\right]}{\left[k_1C_A + K_2C_B + K_5C_D + K_4K_5C_CC_D + 1\right]^2} \tag{k}$$

By substituting for the parameter estimates, we obtain

$$r_3 = \frac{1.369774 * 0.53 * 0.2623\left[\frac{C_AC_B}{1} - \frac{C_CC_D}{6.98*10^{17}}\right]}{\left[0.539988 * C_A + 0.26233 * C_B + 0.73728 * C_D + 0.8131 * 0.73728 * C_CC_D + 1\right]^2} \tag{l}$$

Where

$$C_B = C_{BO}(1 - X) \tag{m}$$

$$C_c = 3 * X * C_{BO} \tag{n}$$

$$C_D = X * C_{BO} \tag{o}$$

$$C_A = C_{BO}\left(\frac{C_{AO}}{C_{BO}} - X\right) \tag{p}$$

$$r = C_{Bo}\frac{dX}{dt} \tag{q}$$

X = conversion, C_{AO} = 8.24 M and C_{BO} = 0.824 M.

C_{AO} and C_{BO} are initial concentrations of oil and methanol respectively.

The resulting ordinary differential equation was solved using the MATLAB software and the obtained result is presented in Fig. 2. From the graph, it can be observed that model describes the experimental data very well and the selection of the modified Hattori mechanism with formation of intermediate as rate determining step is in order Fig. 2.

4. Conclusion

The objective of the current work was to examine the precise kinetics to determine the rate-regulating step in the heterogeneous transesterification of castor oil for the production of biodiesel. By determining the appropriate rate expression, the kinetic modeling for each possible reaction step was therefore derived. The results of kinetic modeling indicate that, a kinetic model of the modified Hattori mechanism using the formation of intermediate as the rate-controlling step provided a good description of the experimental data over the investigated range of experimental conditions. To produce a better estimate for the response numbers, a better model that has less restrictions can be utilized.

The methanol adsorption, triglyceride adsorption, surface reaction, and glycerol desorption were all assumed to be quasi-equilibrated whereas the production of the intermediate is assumed to be the rate-determining phase. By computing the sum of square errors (nealder simplex) and performing statistical tests, the appropriateness, reliability, and accuracy of the model in predicting the concentration and conversion with respect to time were examined and validated. The studies revealed that the suggested model accurately captured the kinetics of the biodiesel synthesis with an appreciable accuracy. Due to the intricacy of the process, the creation of the intermediate controls the kinetics of the biodiesel synthesis from castor oil employing a heterogeneous catalyst.

The conclusion herein are that various input parameters, including concentration, volume, and the like, can be changed as frequently as feasible without requiring an experiment to obtain the conversion rates of the reaction. In addition to being cost-effective, the outcomes will be useful in reaction engineering and reactor design for large-scale production.

The research goals, which were to create and solve models based on a mathematical representation of the Modified-Hattori mechanism, were achieved. MATLAB was used to evaluate the models using experimental data. Aside from the heterogeneous catalyst, the use of reusable magnetic solid catalysts with a conversion rate of about 99.2% has been a new advance in the manufacturing of biodiesel. The process has the benefit that magnetic decantation makes it simple to separate the biodiesel from the by-product (Ankur Kapil, 2010). The use of magnetically reusable Brønsted acid catalyst for biodiesel synthesis is another recent advance in the industry.

This worked well for low-quality oils, which produced more oil and were simple to separate using magnetic methods (Al-Sakkari et al., 2017).

In addition, by strengthening the reaction mechanism, the project's results might be more precise. Triglyceride addition can be done in steps, and the addition of alcohol and triglyceride in the same reaction mechanism can also be done in steps. The results will undoubtedly vary as a result of these modifications, which will also provide a more precise model for the transesterification reaction's use in the production of biodiesel.

Author contribution/Author credit statement

This is to confirm that there is no conflict of interest among the authors. All authors have contributed to the manuscript as stated below:

Rasheed Owolabi: Study conception or design of the work, Visualization, Data collection and tools, Data analysis and interpretation, Funding acquisition, Methodology, Project administration, Resources, Supervision, Critical revision of the article, Final approval of the version to be published.

Aderinsola Aliu: Investigation, Statistical analysis, Software, Drafting the article, Final approval of the version to be published.

Conflicts of interest

There is no conflict of interest among the authors. All authors have agreed to publish the manuscript in Mansoura Engineering Journal.

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APPENDIX.

The derivations for the rate expressions displayed in Table 1 are presented below for clarification purposes. The step by step rate reactions were used to process the overall rate reaction by taking each rate as the rate determing step. Some of the results of the kinetic modelling are shown below.

Modified Hattori mechanism

$$\mathbf{A + S \underset{k'_1}{\overset{k_1}{\leftrightarrow}} AS} \tag{1}$$

$$\mathbf{B + S \underset{k'_2}{\overset{k_2}{\leftrightarrow}} BS} \tag{2}$$

$$\mathbf{AS + BS \underset{k'_3}{\overset{k_3}{\leftrightarrow}} ABS + S} \tag{3}$$

$$\mathbf{ABS + AS \underset{k_4}{\overset{k'_4}{\leftrightarrow}} C + DS + AS} \tag{4}$$

$$\mathbf{DS \underset{k_5}{\overset{k'_5}{\leftrightarrow}} D + S} \tag{5}$$

Taking methanol adsorption as rate determining step

$$\mathbf{A + S \underset{k'_1}{\overset{k_1}{\leftrightarrow}} AS}$$

$$\mathbf{r = k_1 C_A C_S - k'_1 C_{AS}} \tag{i}$$

$$\mathbf{r = k_1 C_S \left(C_A - \frac{C_{AS}}{K_1 C_S} \right)} \tag{ii}$$

To derive the rate expression, the site balance of the active sites is necessary. Hence, by considering all five elementary steps for the mechanism, the total number of sites can be summed up as addition of number of sites occupied by methanol, triglyceride, methanol–triglyceride complex, glycerol, and number of vacant sites. The site balance is expressed below,

$$\mathbf{C_O = C_{AS} + C_{BS} + C_S + C_{DS} + C_{ABS}} \tag{iii}$$

Where C_{XS} is the number of sites occupied (concentration) by specie x on the catalyst's surface.

Because they are intermediates, the expressions were derived using pseudo steady state approximation (PSSA) and quasi-equilibrating, hence the expressions for each intermediate is expressed in terms of measurable quantities. Also since it is a reversible reaction, the forward reaction is equal to the backward reaction. This forms the basis of our solution.

From equation (2),

$$k_2 C_B C_S = k'_2 C_{BS} \tag{iv}$$

$$C_{BS} = K_2 C_B C_S \tag{v}$$

From equation (3)

$$k_3 C_{AS} C_{BS} = k'_3 C_{ABS} C_S \tag{vi}$$

Recall that

$$K_3 = \frac{k_3}{k'_3} \tag{vii}$$

This equation (g) is substituted into equation (f) to give equation (i)

$$K_3 = \frac{C_{ABS} C_S}{C_{AS} C_{BS}} \tag{viii}$$

From equation (4)

$$k_4 C_C C_{AS} C_{DS} = k'_4 C_{ABS} C_{AS} \tag{ix}$$

Making C_{ABS} subject of the formula and insert equation g we have:

$$C_{ABS} = K_4 C_C C_{DS} \tag{x}$$

From equation (5)

$$k_5 C_D C_S = k'_5 C_{DS} \tag{xi}$$

Making C_{DS} subject of the formula and insert equation g we have:

$$C_{DS} = K_5 C_D C_S \tag{xii}$$

Inserting equation h into equation k we have,

$$C_{ABS} = K_4 C_C K_5 C_D C_S \tag{xiii}$$

Lastly we calculate the equation for C_{AS}

Recall that equation (viii) $C_{AS} = \frac{C_{ABS} C_S}{K_3 C_{BS}}$

Recall that equation (xiii) $C_{ABS} = K_4 C_C K_5 C_D C_S$

Substitute equation (xiii) into equation (viii) we have

$$C_{AS} = \frac{K_4 C_C C_S K_5 C_D C_S}{K_3 K_2 C_B C_S} \tag{xix}$$

From overall reaction

$$A+B\overset{k}{\underset{k'}{\leftrightarrow}}C+D$$

$$kC_AC_B=k'C_CC_D$$

$$K=\frac{C_CC_D}{C_AC_B}$$

Recall from equation (i) $\mathbf{k_1C_AC_S-k_1'C_{AS}}$

At equilibrium $\mathbf{k_1C_AC_S=k_1'C_{AS}}$ (xx)

Making $\mathbf{C_A}$ subject of the formula we have;

$$C_A=\frac{C_{AS}}{K_1C_S}\tag{xxi}$$

Recall from equation (v) $C_{BS}=K_2C_BC_S$

Making C_B the subject of the formula we have

$$C_B=\frac{C_{BS}}{K_2C_S}\tag{xxii}$$

Recall that equation (xiii) $C_{ABS}=K_4C_CK_5C_DC_S$

Making C_C subject of the formula we have:

$$C_C=\frac{C_{ABS}}{K_4K_5C_DC_S}\tag{xxiii}$$

Recall that

Substitute equation (viii) equation (xxii), equation (xxi) and equation (xxiii)

$$K=\frac{C_CC_D}{C_AC_B}=\frac{C_{AS}C_{BS}K_3}{K_4K_5C_DC_S}\times C_D\times\frac{K_1C_S}{C_{AS}}\times\frac{K_2C_S}{C_{BS}}$$

Substituting for each concentration term, we obtain

$$\mathbf{K=\frac{K_1K_2K_3}{K_4K_5}}\tag{xxiv}$$

Therefore,

$$C_{AS}=\frac{K_1C_CC_DC_S}{K\,C_B}\tag{xxv}$$

Therefore substituting equation(xii), equation (xiii), equation (v), equation (xxi) into equation iii and making C_S subject of the formula we have;

$$\mathbf{C_S=\frac{C_O}{1+\frac{K_1C_cC_D}{K\ C_B}+K_2C_B+K_4K_5C_CC_D+K_5C_D}}\tag{xxvi}$$

Therefore, to find the expression of the rate of reaction 1 in terms of measurable quantities, substitute equation (xxvi), equation (xxv) into equation (ii).

The rate expression becomes

$$\mathbf{r=\frac{k_1\left(C_A-\frac{C_CC_D}{K\ C_B}\right)}{1+\frac{K_1C_cC_D}{K\ C_B}+K_2C_B+K_4K_5C_CC_D+K_5C_D}}\tag{xxvii}$$

Triglyceride adsorption as rate determining step

$$\mathbf{B+S\overset{k_2}{\underset{k'_2}{\leftrightarrow}}BS}$$

$$\mathbf{r=k_2C_BC_S-k_2'C_{BS}}$$

$$\mathbf{r=k_2C_S\left(C_B-\frac{C_{BS}}{K_2C_S}\right)}\tag{xxviii}$$

Applying PSSA and quasi-equilibrating to determine the intermediates in measurable terms gives; From (1),

$$\mathbf{k_1C_BC_S=k'_1C_{BS}}\tag{xxix}$$

$$\mathbf{C_{AS}=K_1C_AC_S}\tag{xxx}$$

Equation for CBs becomes

$$\mathbf{C_{BS}=\frac{C_{CS}C_{DS}}{K_{11}C_{AS}}}\tag{xxxi}$$

Therefore,

$$\mathbf{C_{BS}=\frac{K_2C_CC_DC_S}{KC_A}}\tag{xxxii}$$

Therefore, site balance (equation vii) is rearranged to give the number of vacant sites on the surface.

$$\mathbf{C_S=\frac{C_O}{1+\frac{K_2C_cC_D}{K\ C_A}+K_1C_A+K_4K_5C_CC_D+K_5C_D}}\tag{xxxiii}$$

The rate expression for triglyceride adsorption can be modified by substituting C_s and C_{BS} into equation 11

$$\mathbf{r=\frac{k_2\left(C_B-\frac{C_CC_D}{K\ C_A}\right)}{1+\frac{K_2C_cC_D}{K\ C_A}+K_1C_A+K_4K_5C_CC_D+K_5C_D}}\tag{xxxiv}$$

Surface reaction as rate determining step

$$AS+BS\overset{k_3}{\underset{k'_3}{\leftrightarrow}}ABS+S$$

$$r=k_3C_{AS}C_{BS}-k_3'C_{ABS}C_S$$

$$\mathbf{r = k_3\left(C_{AS}C_{BS} - \frac{C_{ABS}C_S}{K_3}\right)} \quad \text{(xxxv)}$$

Site Balance

$$C_O = C_{AS} + C_{BS} + C_S + C_{DS} + C_{ABS}$$

Applying PSSA and quasi-equilibrating to determine the intermediates in measurable terms gives the site balance to be,

$$\mathbf{C_S = \frac{C_O}{1 + K_2C_B + K_1C_A + K_4K_5C_CC_D + K_{13}C_D}} \quad \text{(xxxvi)}$$

The rate expression for surface reaction can be modified by substituting into equation (15)

$$\mathbf{r = \frac{k_1K_2K_3\left(C_AC_B - \frac{C_CC_D}{K}\right)}{\left(1 + K_2C_B + K_1C_A + K_4K_5C_CC_D + K_5C_D\right)^2}} \quad \text{(xxxvii)}$$

Methanol-triglyceride complex desorption as rate determining step

$$ABS + AS \underset{k_4}{\overset{k'_4}{\leftrightarrow}} C + DS + AS$$

$$r = k'_4C_{ABS}C_{AS} - k_{12}C_CC_{DS}C_{AS}$$

$$\mathbf{r = k_4C_{AS}\left(\frac{C_{ABS}}{K_4} - \frac{C_{DS}C_C}{1}\right)} \quad \text{(xxxviii)}$$

Applying PSSA and quasi-equilibrating to determine the intermediates in measurable terms gives;

$$C_{ABS} = \frac{K_3C_{AS}C_{BS}}{C_S} \quad \text{(xxxix)}$$

Therefore,

$$C_{ABS} = K_3K_1K_2C_AC_BC_S \quad \text{(xL)}$$

Therefore, site balance (equation 7) is rearranged to give the number of vacant sites on the surface.

$$\mathbf{C_S = \frac{C_O}{1 + K_1K_2K_3C_AC_B + K_2C_B + K_1C_A + K_5C_D}} \quad \text{(xLi)}$$

The rate expression becomes

$$\mathbf{r4 = \frac{K_4K_1C_A\left[\frac{K_1K_2K_3C_AC_B}{K_4} - \frac{KK_5C_AC_B}{1}\right]}{\left[k_1C_A + K_2C_B + K_5C_D + \frac{K_3K_1K_2C_AC_B}{1} + 1\right]^2}} \quad \text{(xLii)}$$

Glycerol desorption as rate determining step

$$\mathbf{DS \underset{k_5}{\overset{k'_5}{\leftrightarrow}} D + S}$$

$$\mathbf{r = k'_5C_{DS} - k_5C_DC_S}$$

$$\mathbf{r = k_5C_S\left(\frac{C_{DS}}{K_5C_S} - C_D\right)} \quad \text{(xLiii)}$$

Applying PSSA and quasi-equilibrating to determine the intermediates in measurable terms gives;

$$\mathbf{C_{DS} = \frac{KK_5C_AC_BC_S}{C_C}} \quad \text{(xLiv)}$$

Therefore, site balance is rearranged to give the number of vacant sites on the surface.

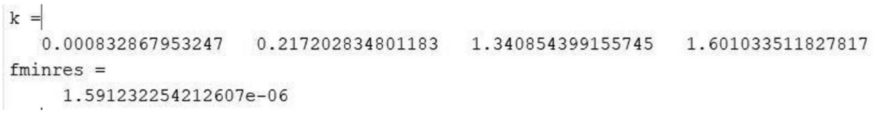
$$\mathbf{C_S = \frac{C_O}{1 + \frac{K_5KC_AC_B}{C_C} + K_3K_2K_1C_AC_B + K_2C_B + K_1C_A}} \quad \text{(xLv)}$$

The rate expression becomes

$$\mathbf{r = \frac{k_5\left(\frac{KC_AC_B}{C_C} - \frac{C_D}{1}\right)}{1 + \frac{K_5K\ C_AC_B}{C_C} + K_2K_3K_1C_AC_B + K_2C_B + K_1C_A}} \quad \text{(xLvi)}$$

```
r1
format compact
format long
xdata = [0.2,0.33,0.43,0.74,0.81,1]
ydata = [0.03296,0.021424,0.00412,0.008514,0
001923,0.00522]
%Function to calculate the sum of residuals for a
given k1, k2, k4, k5
Ca0 = 8.24
Cb0 = 0.824
K = 6.98*10ˆ17
C0=Ca0+Cb0
Cb = Cb0*(1 - xdata)
Cc = 3*xdata*Cb0
Cd = xdata*Cb0
Ca = Cb0*((Ca0/Cb0) - xdata)
fun = @(k) sum (ydata - ((k(1).*C0.*(Ca -
((Cc.*Cd)/(K.*Cb))))/(((k(1).*Cc.*Cd)/(K.*Cb)) + k(2)
.*Cb + k(4).*Cd + k(3).*k(4).*Cc.*Cd +1))).ˆ2;
%starting guess
kguess = [1,0.2,1,1];
```

```
%optimise
```



```
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fminres =
     1.591232254212607e-06
```
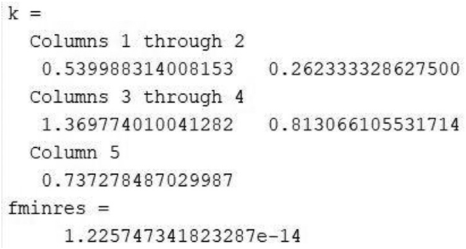
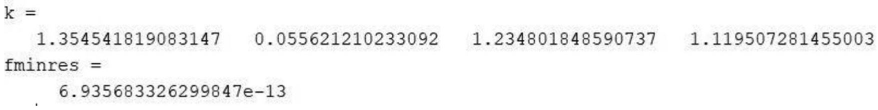

```
[k, fminres] = fminsearch (fun, kguess)
r2
format compact
format long
xdata = [0.2,0.33,0.43,0.74,0.81,1]
ydata = [0.03296,0.021424,0.00412,0.0085
14,0.001923,0.00522]
%Function to calculate the sum of residuals for a
given k1, k2, k3, k4, k5
Ca0 = 8.24
Cb0 = 0.824
K = 6.98*10ˆ17
C0=Ca0+Cb0
Cb = Cb0*(1 - xdata)
Cc = 3*xdata*Cb0
Cd = xdata*Cb0
Ca = Cb0*((Ca0/Cb0) - xdata)
fun = @(k) sum (ydata - ((k(2).*C0.*(Cb -
(Cc.*Cd)/(K.*Ca)))/(((k(2).*Cc.*Cd)/(K.*Ca)) +
k(1).*Ca + k(4).*Cd + k(3).*k(4).*Cc.*Cd + 1))).ˆ2;
%starting guess
kguess = [1,0.2,1,1];
%optimise
[k, fminres] = fminsearch (fun, kguess)
```

```
fun = @(k) sum (ydata - ((k(3). *k(1).
*k(2).*((Ca.*Cb/1) - (Cc.*Cd/K)))/((k(1).*Ca +
k(2).*Cb + k(5).*Cd + k(4).*k(5).*Cc.*Cd + 1).ˆ2))).ˆ2;
%starting guess
kguess = [1,0.2,1,1,1];

%optimise
[k, fminres] = fminsearch (fun, kguess)
```



```
k =
  Columns 1 through 2
   0.539988314008153   0.262333328627500
  Columns 3 through 4
   1.369774010041282   0.813066105531714
  Column 5
   0.737278487029987
fminres =
     1.225747341823287e-14
```

```
R4
format compact
format long
xdata = [0.2,0.33,0.43,0.74,0.81,1]
ydata = [0.03296,0.021424,0.00412,
0.008514,0.001923,0.00522]
%Function to calculate the sum of residuals for a
given k1, k2, k3, k4, k5
```

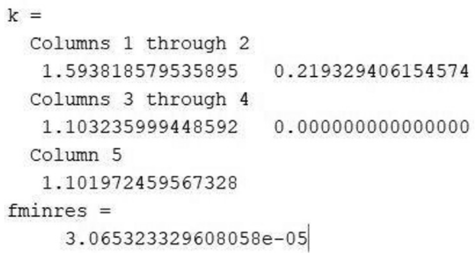


```
k =
   1.354541819083147   0.055621210233092   1.234801848590737   1.119507281455003
fminres =
     6.935683326299847e-13
```

```
R3
format compact
format long
xdata = [0.2,0.33,0.43,0.74,0.81,1]
ydata = [0.03296,0.021424,0.00412,0
008514,0.001923,0.00522]
%Function to calculate the sum of residuals for a
given k1, k2, k3, k4, k5
Ca0 = 8.24
Cb0 = 0.824
K = 6.98*10ˆ17
C0=Ca0+Cb0
Cb = Cb0*(1 - xdata)
Cc = 3*xdata*Cb0
Cd = xdata*Cb0
Ca = Cb0*((Ca0/Cb0) - xdata)
```

```
Ca0 = 8.24
Cb0 = 0.824
K = 6.98*10ˆ17
C0=Ca0+Cb0
Cb = Cb0*(1 - xdata)
Cc = 3*xdata*Cb0
Cd = xdata*Cb0
Ca = Cb0*((Ca0/Cb0) - xdata)
fun = @(k) sum (ydata - ((k(4).*k(1).*Ca.*((k(1).*
k(2).*k(3).*Ca.*Cb/k(4)) - (K.*k(5).*Ca.*Cb/1)))/
((k(1).*Ca + k(2).*Cb + k(5).*Cd + (k(3).*k(1).*k(2).
*Ca.*Cb)+1).ˆ2))).ˆ2;
%starting guess
kguess = [1,0.2,1,1,1];
%optimise
```

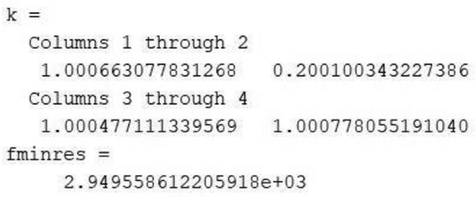
```
[k, fminres] = fminsearch (fun, kguess)
```



```
k =
  Columns 1 through 2
   1.593818579535895   0.219329406154574
  Columns 3 through 4
   1.103235999448592   0.000000000000000
  Column 5
   1.101972459567328
fminres =
     3.065323329608058e-05
```

R5

```
format compact
format long
xdata = [0.2,0.33,0.43,0.74,0.81,1]
ydata = [0.03296,0.021424,0.00412,0.008514,0.001923,0.00522]
%Function to calculate the sum of residuals for a given k1, k2, k3, k4, k5
Ca0 = 8.24
Cb0 = 0.824
K = 6.98*10^17
C0=Ca0+Cb0
Cb = Cb0*(1 - xdata)
Cc = 3*xdata*Cb0
Cd = xdata*Cb0
Ca = Cb0*((Ca0/Cb0) - xdata)
fun = @(k) sum (ydata - ((k(4).*C0.*((K.*Ca.*Cb./Cc) - Cd))/(k(1).*Ca + k(2).*Cb + (k(4).*K.*Ca.*Cb./Cc)+(k(3).*k(1).*k(2).*Ca.*Cb./1)+1))).^2;
%starting guess
kguess = [1,0.2,1,1];
%optimise
[k, fminres] = fminsearch (fun, kguess)
```



```
k =
  Columns 1 through 2
   1.000663077831268   0.200100343227386
  Columns 3 through 4
   1.000477111339569   1.000778055191040
fminres =
     2.949558612205918e+03
```

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