

**STUDY OF SURFACE KINETIC MODELS FOR FATTY ACID  
ESTERIFICATION TO ESTERS USING ACIDIC  
HETEROGENEOUS CATALYST**



By

**Afeeq Shahid**

(NUST201261021MSCEE65112F)

A thesis submitted in partial fulfillment of requirements for the degree of

Master of Science (MS)

In

Environmental Engineering

**Institute of Environmental Sciences and Engineering (IESE)**

**School of Civil and Environmental Engineering (SCEE)**

**National University of Sciences and Technology (NUST)**

**Islamabad, Pakistan**

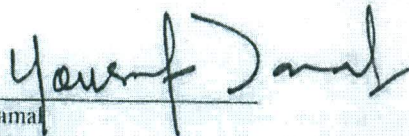
**(2016)**

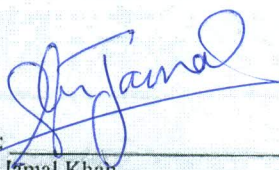
It is certified that the contents and forms of the thesis entitled  
**STUDY OF SURFACE KINETIC MODELS FOR FATTY ACID ESTERIFICATION TO  
ESTERS USING ACIDIC HETEROGENEOUS CATALYST**

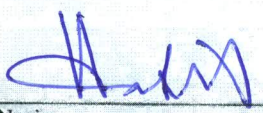
Submitted by

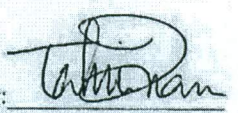
**Afeeq Shahid**

Has been found satisfactory for the requirements of the degree of  
Master of Science in Environmental Engineering

Supervisor:   
Dr. Yousuf Jamal  
Assistant Professor  
IESE, SCEE, NUST

Member:   
Dr. Sher Jamal Khan  
HoD Environmental Engineering  
IESE, SCEE, NUST

Member:   
Dr. Habib Nasir  
Professor  
SNS, NUST

External Member:   
Dr. Tahmina Imam  
Lead Chemical Engineer  
Altex Technologies  
California, USA

It is with my deepest gratitude and warmest affection that **I dedicate this thesis to my Supervisor** who has been a constant source for knowledge and inspiration

## ACKNOWLEDGEMENTS

*Most importantly, I am grateful to thank Almighty Allah, for making all this possible.*

*I also like to show my sincere gratitude to my research supervisor **Dr. Yousuf Jamal** for his continuous patience, suggestions, guidance, and encouragement throughout my research work. Also, I can't forget to mention the honorable faculty members, **Dr. Sher Jamal Khan, Dr. Habib Nasir** and **Dr. Tahmina Imam** of my GEC (Guidance and Examination Committee) who played a pivotal role in completing my research work successfully. The much needed moral and technical support from my fellow colleague **Mr. Jamshed Ali Khan** and my friend **Shahab Nasir**, is deeply acknowledged. My heartiest gratitude covers all the laboratory staff and technicians for their help and support. All the funds for the research work were provided by the Institute of Environmental Sciences and Engineering, SCEE, NUST which is highly appreciated.*

*I also like to acknowledge my heartiest respect and thanks to my parents for their constant encouragement and love during my studies.*

**AFEEQ SHAHID**

## TABLE OF CONTENTS

Dedication	i
Acknowledgements	ii
Table of Contents	iii
List of Tables	iv
List of Figures	v
Abstract	1
<b>Chapter No. 1: Introduction.</b>	2
1.1 Background Information	2
1.2 Objectives	6
<b>Chapter No. 2: Literature Review.</b>	7
<b>Chapter No. 3: Materials and Method.</b>	14
3.1 Materials	14
3.2 Experimental Setup	15
3.3 Methodology	15
3.4 Process Details	17
3.5 Calculation Method for Percent Free Fatty Acid (%FFA).	17
3.6 Determination of Reaction Rate Constants from Kinetic Models	18
<b>Chapter No. 4: Results and Discussion.</b>	20
4.1 Temperature Effect on Esterification	20
4.2 Effect of the Catalyst Concentration	21
4.3 Effect of Molar Ratio	22
4.4 Effect of Fatty Acid Carbon Chain-Length	23
4.5 Values of Surface Reaction Kinetic Rate Constants	24
4.6 Equivalent Comparison of Results	27
<b>Chapter No. 5: Conclusion and Recommendations.</b>	29
5.1 Conclusion	29
5.2 Recommendations and Scope	30
<b>References</b>	31
<b>APPENDIX-1</b>	35
<b>APPENDIX-2</b>	45

## LIST OF TABLES

<b>Table 2.1</b> Literature Review.	7
<b>Table 3.1</b> Properties of Amberlyst 15	14
<b>Table 4.1</b> Reaction rate constant values derived with Eley Rideal (ER) surface reaction kinetic model equations for acetic and oleic acid fatty acid molecules when adsorption of alcohol and surface reaction are the rate limiting steps.	25
<b>Table 4.2</b> Reaction rate constant values derived with Langmuir Hinshelwood Hougen-Watson (LHHW) surface reaction kinetic model equations for acetic and oleic acid fatty acid molecules with adsorption of alcohol and surface reaction as the rate limiting step.	26

## LIST OF FIGURES

<b>Figure 1.1</b> Transesterification Reaction.	3
<b>Figure 1.2</b> Esterification Reaction.	4
<b>Figure 1.3</b> Eley Rideal (ER) Model.	5
<b>Figure 1.4</b> Langmuir Hinshelwood Hougen Watson (LHHW) Model.	6
<b>Figure 3.1</b> Experimental set up schematic diagram	15
<b>Figure 3.2</b> BET surface area analyzer	16
<b>Figure 4.1</b> Temperature effect on the acetic acid esterification to ethyl acetate	21
<b>Figure 4.2</b> Effect of the catalyst concentration on acetic acid esterification	22
<b>Figure 4.3</b> Effect of molar ratio on acetic acid esterification	23
<b>Figure 4.4</b> Carbon chain length effect on fatty acid esterification.	24

## ABSTRACT

Fatty acid esterification behavior with varying reaction parameters such as; reaction temperature, alcohol to fatty acid molar ratio, catalyst concentration, and fatty acid carbon chain length have been investigated in a batch reactor system. Compared experimental data of acetic and oleic acid esterification using Langmuir Hinshelwood Hougen-Watson (LHHW) and Eley Rideal (ER) surface reaction kinetic models. Amberlyst 15 dry acidic resin surface considered as standard. Esterification of fatty acids increases with increase in reaction temperature and catalyst concentration. The lower molar ratio in a reaction mixture initially increases conversion but a higher molar ratio gives better reaction conversion over longer reaction time. Carbon chain length of fatty acid has an important effect on esterification, a higher percent conversion was observed with shorter chain length fatty acid in a short reaction time under constant reaction parameters. A maximum esterification of 67.1% and 41.6% was observed for acetic and oleic acids, respectively. Surface reaction was found the rate limiting step for the two fatty acid esterification. ER model for acetic acid with a reaction rate constant  $k = 4.31/\text{min}$ , proved to be applicable ( $R^2 \geq 0.94$ ) more accurately on the experimental data than a LHHW model with  $k = 0.174/\text{min}$  ( $R^2 \geq 0.92$ ). The opposite kinetic pattern was observed for oleic acid esterification with the rate constant  $k = 0.197/\text{min}$  ( $R^2 \geq 0.79$ ) for ER model and  $0.263/\text{min}$  ( $R^2 \geq 0.79$ ) for LHHW model. Determination of reaction rate constants from heterogeneous surface reaction kinetic models should be helpful for designing of scale up esterification reactors.

**Keywords:** Heterogeneous esterification; Fatty acids, Amberlyst 15; Surface reaction;

Reaction rate



## **Introduction.**

### **1.1 Background Information**

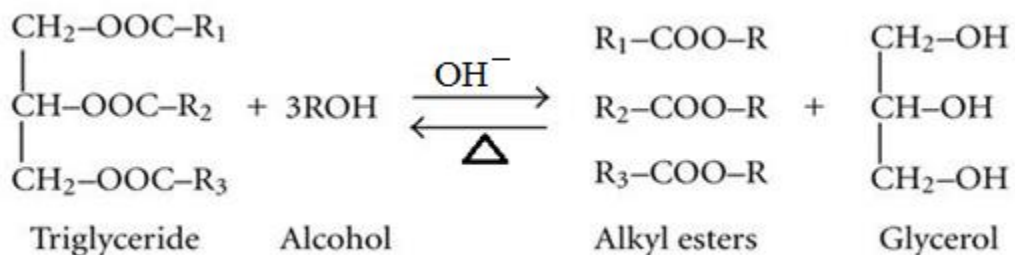
Environmental concerns and challenges can be addressed by promoting renewable energy sources. Due to the dire need for developed renewable alternative energy sources in the current energy deficient era, production and utilization of biofuels is one area which can bridge the gap between demand and supply of energy. Biofuels is the derived energy from the sources of biological origin using different types of feedstock. Among different types of biofuels, biodiesel is gaining more and more importance due to the concerns of petro-diesel unavailability in future, its fluctuating prices and serious impacts on the environment.

Biodiesel is a fuel chemically composed of mono-alkyl esters of long and short chain fatty acids, produced from the reaction of a primary alcohol ( $C_1\sim C_4$ ) with extracted lipids from a feedstock source like edible plants, vegetable seeds, non-edible plants, animal fats, algae, primary and secondary wastewater sludge and waste cooking oil in the presence of a catalyst. Catalyst may be acidic or basic in nature depending on the composition of lipids present in the feedstock. Biodiesel is a non-toxic, biodegradable fuel, that also reduces carbon, sulfur and nitrogen oxide emissions in the environment (Pirola et al., 2014; Liu et al., 2014; Boey et al., 2013) Biodiesel can heavily reduce the load on the utility of traditional petro-diesel fuel and can open a new gateway towards a safer and greener world. Furthermore, biodiesel finds its advantage when blended with petro-diesel up to 20 % in the existing petro-diesel compression ignition engines without any modifications in the engines.

Biodiesel can be used directly or as a blended mixture with petro-diesel. When it is used in blended form with petro-diesel, mixture is denoted as “BXX” where “XX” denotes the percentage of biodiesel in the blend for example B100 means 100% pure biodiesel and B20 shows the 20% presence of biodiesel in the petro-diesel blend. The feedstock lipid for biodiesel mainly consists of fatty acids and triglycerides

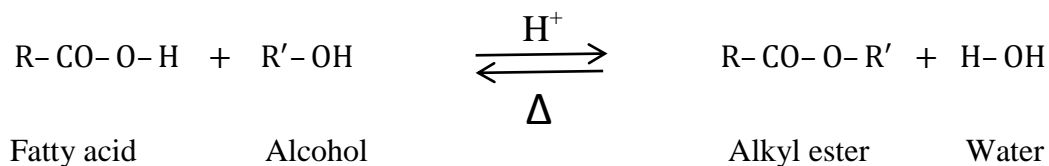
Different methods and techniques have been derived for biodiesel production such as microemulsion, pyrolysis (Marchetti et al., 2007), esterification (Atadashi et al., 2012) and transesterification (Lam et al., 2010) reactions. However, among these techniques esterification and transesterification are gaining more and more attention due to ease of their application. Thus, selection among the two techniques depends on the type of lipid and quality of feedstock.

Conventionally biodiesel is produced from edible plant oils containing mainly tri-, di-, and mono- glycerides in the presence of a basic catalyst. Plant oils or any lipid oil cannot be applied directly to engines because of their higher viscosity (Ilgen et al., 2014). Therefore, the transesterification or esterification reaction is used to convert them into esters (less viscous fluid). 100% pure esters have viscosities around 5.6-5.8 centipoise in comparison to plant oils having 40-50 centipoise whereas No. 2 diesel fuel has viscosity of 3.0 centipoise. Blending of esters (biodiesel) with petro-diesel helps to keep the mixture viscosity near the diesel fuel. Figure 1.1 illustrates the basic transesterification reaction.



**Figure 1.1** Transesterification Reaction.

However, different oils such as non-edible oil like jatropha oil, animal fats, algae oil and waste cooking oil have greater percentage of free fatty acids (FFA). Due to higher concentrations of FFA in these oils, esterification reaction is the desired method to produce esters (Veljkovic et al., 2014). Esterification reaction progresses slowly than transesterification reaction and requires an acidic catalyst to speed up the reaction. Figure 1.2 shows the basics of esterification reaction. In contrast to transesterification reaction where every mole of triglyceride give 3 mole of esters and 1 mole of glycerol in esterification reaction for every mole of free fatty acid esterified with alcohol only one mole of ester and one mole of water are produced respectively.



Where R & R' are the alkyl groups.

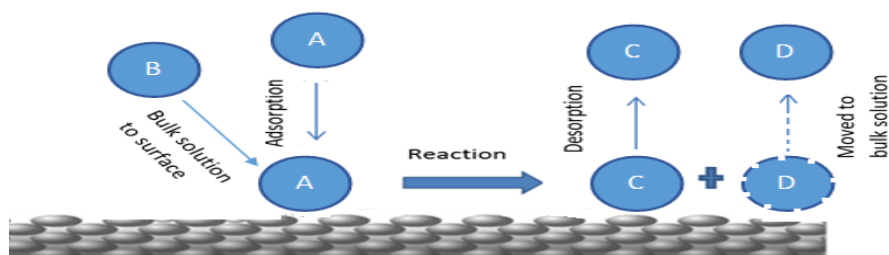
**Figure 1.2** Esterification Reaction.

For biodiesel production two catalysis reaction approaches, homogeneous and heterogeneous catalysis, are mainly adopted. Homogeneous catalysis is characterized by the catalyst and reactants being in the same liquid phase while in heterogeneous catalysis the catalyst is in the solid phase and reactants are in liquid phase. The homogeneous catalysis is of short reaction time and simple to proceed but it also has some disadvantages like no recovery of the catalyst, side reactions of the catalyst, requires cleaning of the reaction product from unreacted catalyst, disposal of the contaminated effluent and this cause's equipment corrosion. (Huang et al., 2010; Boro et al., 2011). These disadvantages can be neutralized by the use of heterogeneous catalysts that can be regenerated and reused several times (Jamal et al.,2014). The esterification of free fatty acids is carried out by numerous heterogeneous acidic catalysts (Hayyan et al., 2010; Giri et al., 2005). Some of them include hetero-polyacids (HPAs) (Lam et al., 2010; Brahmkhatri

et al., 2010), metal oxides and acidic ion exchange resins (Park et al., 2010; Son et al., 2011). Esterification reaction can be performed in an acidic catalytic column (Khan et al., 2016) or in a batch reactor (Jamal et al., 2014). In heterogeneous catalysis conversion reaction mainly take place at the surface of the catalyst (Jamal et al., 2015).

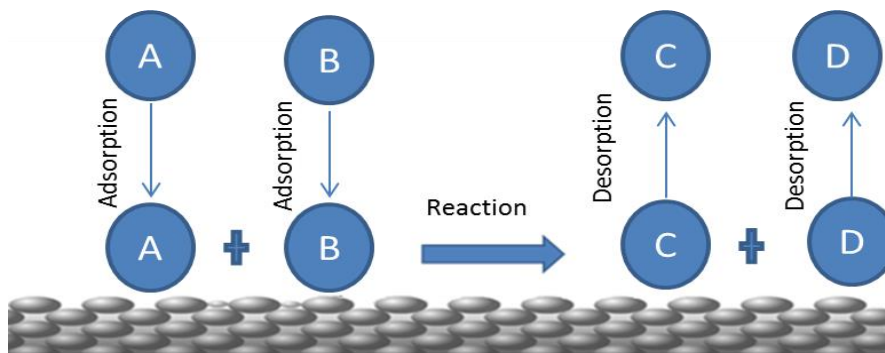
Research works have been published on the quantification and qualification of esters produced from transesterification and esterification reaction of lipids. This work mainly focuses on how esterification reaction actually take place at the surface of an acidic catalyst namely Amberlyst 15 and to calculate the kinetic rate constants for esterification reaction using two different kinetic surface reaction models and two different chain length fatty acids (Acetic and Oleic Acid). Amberlyst 15 is a polystyrene based acidic resin with macro porous structure having strong sulfonic acid groups. For kinetic study, some models have been proposed including power-law model, the pseudo-homogeneous model, the Langmuir Hinshelwood Houghton Watson (LHHW) model, the Eley Rideal (ER) model (Borges et al., 2012). Among these, Eley Rideal model and Langmuir Hinshelwood Houghton Watson kinetic models are studied in this work. The ER model proposes that one of the reacting species gets absorbed at the surface of the catalyst while the other moves from the bulk of the solution and then reaction takes place at the surface of the catalyst (Sharma et al., 2014). Figure 1.3 illustrates the reaction mechanism for Eley Rideal

Model.



**Figure 1.3** Eley Rideal (ER) Model.

LHHW model proposes that both reactants adsorb on the surface of catalyst and the adsorbed molecules undergo a bimolecular reaction on the surface (Ahmedzeki et al., 2013, Jamal et al., 2015)



**Figure 1.4** Langmuir Hinshelwood Hougen Watson (LHHW) Model.

Both ER and LHHW models show esterification reaction completes in three major steps i.e. adsorption, surface reaction and desorption. Mathematical model expression can be derived by determining the rate limiting step for the esterification reaction.

## 1.2 Objectives

Therefore objectives of this research work are to study surface catalysis at low temperatures for esterification reaction below the boiling point of alcohol using different chain length fatty acids ( acetic and oleic acid), acidic resin catalyst (amberlyst 15) and alcohol (ethanol) in a batch reactor. To study

- The effect of temperature, catalyst concentration and molar ratio of alcohol to free fatty acids on esters production.
- The esterification rate constants through surface reaction kinetic models for heterogeneous esterification considering different rate limiting steps, under two different reaction models (ER and LHHW) studied.

**Literature Review.**

A number of published articles were read and their findings with article title and author details are matrix in the following table 2.1.

**Table 2.1** Literature Review.

	<b>Title</b>	<b>Author</b>	<b>Findings</b>
1	Esterification of acetic and oleic acids within an Amberlyst 15 packed catalytic column	Khan et al., 2016	Percentage conversion of fatty acids into esters in a packed heterogeneous column was studied. Produced esters were analyzed with FTIR for conversion over amberlyst 15 acidic resin surface. Impact of different parameters like flow rate through packed column and structural impact of different fatty acids and carbon chain length was studied along with reuse of heterogeneous catalytic column surfaces after regeneration.
2	Determination of methanolysis rate constants for low and high fatty acid oils using heterogeneous surface reaction kinetic models	Jamal et al., 2015	Heterogeneous surface reaction kinetics was shown for the transesterification reaction of a mixture of triglycerides in presence and absence of fatty acids on a basic resin catalyst. Reaction kinetics on resin surface was explained by the surface reaction kinetic models. Author concluded that fatty

			acid in a triglyceride feed mixture reduces the hydrophilic nature of the basic catalyst surface resulting in higher reaction rates and the adsorption of alcohol at the basic catalyst surface is highly important for the reaction to proceed.
3	Investigation of reaction parameters, kinetics and mechanism of oleic acid esterification with methanol by using Amberlyst 46 as a catalyst	Ilgen et al., 2014	Studied impact of reaction parameters like molar ratio (fatty acid/alcohol), catalyst concentration, reaction time and temperature on oleic acid yield conversion into esters. It is reported that conversion into esters increases with increase in reaction temperature and this conversion is more in initial reaction time. Therefore concluded that reaction rate reduces by increased reaction beyond a certain time limit. Finally surface kinetics is performed for reaction over amberlyst 46 resin catalyst. Also noted that the reaction efficiency remains same after successive re-run of the acidic resin catalyst.
4	Heterogeneously Catalyzed Esterification	Ahmedzeki et al., 2013	Reaction reaches equilibrium faster with increase in catalyst concentration.

	Reaction: Experimental and Modeling Using Langmuir-Hinshelwood Approach		Increase of temperature and free fatty acid to alcohol molar ratio also results in increase conversion of esters.
5	Heterogeneous catalyzed esterification of acetic acid with isoamyl alcohol: kinetic studies	Teo et al., 2004	At a fixed contact time higher reaction temperature yields greater conversion of free fatty acids.  LHHW model assumes that the reactants are first adsorbed on catalytic surface and then reaction takes place on the surface. Kinetic behavior of reaction is better presented by LHHW model when compared to ER model. Rate limiting step is the surface reaction
6	Kinetic study of catalyzed and uncatalyzed esterification reaction of acetic acid with methanol	Mandake et al., 2013	Beyond 1000rpm no significant change in rate of reaction was observed. At 1000 rpm no resistance to mass transfer rate at solid – liquid and liquid – liquid interface was observed
7	A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin	Feng et al., 2010	A significant increase in free fatty acid conversion from 17.1% to 94.0% when temperature was increased from 25 °C to 65 °C. After further increase in temperature



	as heterogeneous catalyst		beyond 65 °C, there was no increase in the conversion and no flow of oil as an effluent was observed as the vaporized methanol (boiling point 64.5 °C) blocked the flow of oil from the outlet.
8	Kinetic study of catalytic esterification of butyric acid and ethanol over amberlyst 15	Singh et al., 2013	Amberlyst 15 was found out to be suitable catalyst for esterification  The reaction parameters were optimized and esterification was found influenced with high temperature and molar ratio. Reaction was found to take place in the between an adsorbed alcohol molecule and molecule of free fatty acid from the bulk phase (Eley-Rideal model). It was also observed that water has inhibiting effect on reaction.
9	Oleic acid esterification with ethanol under continuous water removal conditions	Lucena et al., 2011	Increasing alcohol (ethanol) to fatty acids molar ratio decreased the ethyl esters production. The increased amount of ethanol pushed the reaction in forward direction but the water molecules produced as a result of increased alcohol concentration rendered the fatty acids

			conversion process.
10	Biodiesel production from esterification of free fatty acid over PA/NaY solid catalyst	Liu et al., 2014	Higher temperature accelerates the reaction rate. Molecular motion and mass transfer speed is enhanced at elevated temperatures resulting in higher conversion of free fatty acids to esters.
11	Kinetics of the esterification reaction between pentanoic acid and methanol catalyzed by noncorrosive cation exchange resin	Sharma et al., 2014	Reaction temperature has a favorable impact on forward reaction. Ester conversion increased at higher temperatures.
12	Esterification of oleic acid with ethanol catalyzed by ssulfonated cation exchange resin: Experimental and kinetic studies	Jiang et al.,2013	Higher catalyst loading results in higher conversion of fatty acids into esters. Increase in reaction rate by increasing catalyst loading is due to the fact that more active acid sites are available. Without using catalyst sites reaction proceeds very slowly.
13	Factors affecting biodiesel production	Mathiyazhagan et al., 2011	Reviewed transesterification reaction and impact of various reaction parameters including role of moisture in feed stock on reduction in reaction yield. Emphasized that

			increase in reaction temperature increases ester yield. However increase in reaction temperature beyond the boiling point of alcohol in an open system reduces ester production due to escape of alcohol from the reaction mixture and to fast saponification of triglycerides.
14	Kinetic study of esterification of acetic acid with n-butanol and iso-butanol. Catalyzed by ion exchange resin	Toor et al., 2011	LHHW model gives the best fitting results for esterification of acetic acid. Surface reaction found to be the rate limiting step controlling overall rate of the reaction
15	Technologies for biodiesel production from used cooking oil – a review	Math et al., 2010	Biodiesel, mono-alkyl esters are considered as substitute diesel fuel derived from renewable biomass. These mono-alkyl esters can be obtained from a catalyst assisted (an acid, base, or an enzyme) reaction of fatty acids or triglycerides with alcohols in esterification or transesterification mechanism respectively
16	Esterification of fatty acids to biodiesel over polymers with sulfonic acid groups.	Caetano et al., 2009	Two different alcohols methanol and ethanol were used for reaction. Increasing temperature from 60 – 80 °C in the presence

			of ethanol resulted in increased conversion of Palmitic acid. Increase in the molar ratio results in higher equilibrium conversion of Palmitic acid and reaction shifted from 30% (1:3) to 90% (1:63) whereas as ethanol was observed to resist the conversion compared to methanol
17	Kinetics Study of Propyl Acetate Catalyzed by Amberlyst 15 Synthesis Reaction	Huang et al., 2006	Reaction rate increases in proportion to the amount of catalyst added. Best fitting result was given by LHHW model when compared with other kinetic models.
18	kinetics of catalytic esterification of Acetic acid and amyl alcohol over dowex	Lee et al., 2000	Esterification rate increases with increase in alcohol to free fatty acid ratio. Kinetic behavior of catalyzed esterification reaction was studied best with LHHW model at different temperatures and catalyst concentrations

## Materials and Method.

### 3.1 Materials

Following chemicals were purchased from authorized dealers of Sigma Aldrich and Merck (Germany) in Pakistan.

- Acetic acid (99.8% pure)
- Sodium hydroxide in pellet form (99.9% pure)
- Phenolphthalein
- Amberlyst 15 resin in dry hydrogen form
- Ethanol in purest available form (99.9% pure)
- Oleic acid with purity greater than 99%

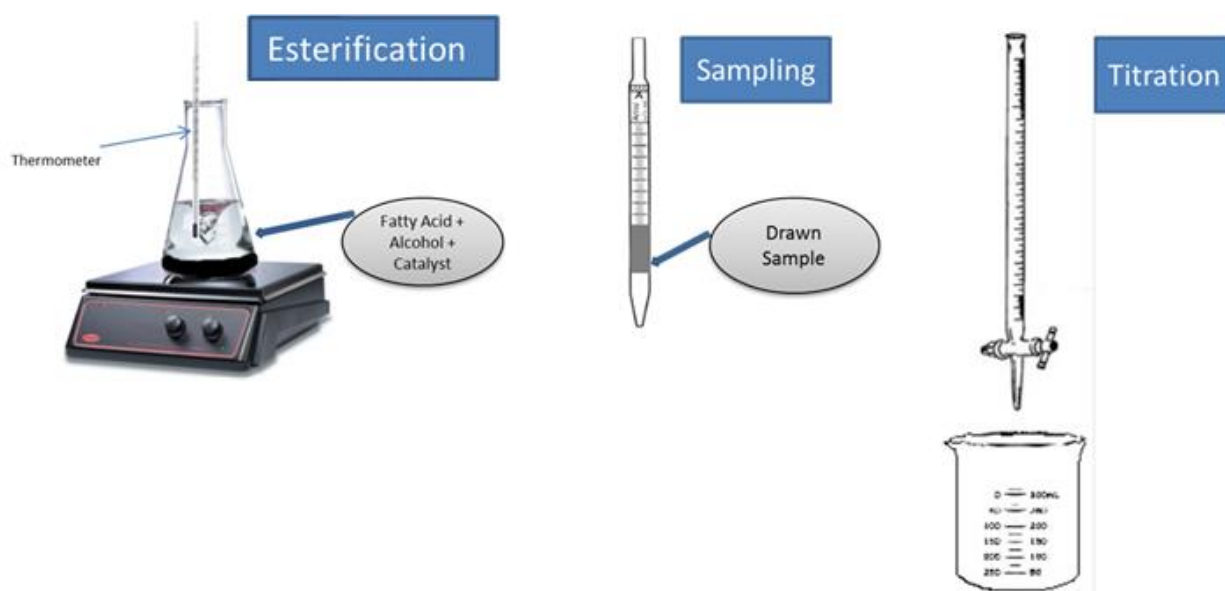
Properties of Amberlyst 15 resin given in table 3.1 are adopted from (Yu et al., 2004).

**Table 3.1** Properties of Amberlyst 15

Appearance	Distributions of resin size retained from standard US screens (%)	Resin density in bulk (kg/m <sup>3</sup> )	Moisture (wt%)	Concentration of hydrogen ion (meq./g dry)	Surface area of Resin (m <sup>2</sup> /g)	Porosity of resin (pore,ml/ bead,ml)	Pore diameter (Å)
Hard, dry, spherical particles	16 mesh, 02–05% 16–20 mesh, 20–30% 20–30 mesh, 45–55% 30–40 mesh, 15–25% 40–50 mesh, 5–10% Through 50 mesh, 1.0%	608	Less than 1%	4.7	50	0.36	240

### 3.2 Experimental Setup

The esterification reaction was performed in a laboratory batch reactor. The experimental setup consisted of three magnetic stirrers with hot plates (auto temperature controlled), three thermometers, Erlenmeyer flasks measuring cylinder, burette, pipette, and weighing balance. The experimental assembly is shown in the figure 3.1.



**Figure 3.1** Experimental set up schematic diagram

### 3.3 Methodology

Fatty acid and ethanol were added in a known molar ratio in an Erlenmeyer flask. The mixture was heated to the desired temperature on a hot-stirring plate. Mixture contents were stirred with a magnetic bar in the flask at a fixed speed of 900 rpm. Starting time of the reaction was noted when acidic resin catalyst Amberlyst 15 was added to the mixture. Amberlyst 15 was used for its effective catalytic activity and mechanical strength. Temperature of reaction mixture

was continuously monitored using thermometers. At time intervals of 0, 20, 40, 60, 90, 120, 150, 180, 240, 300 and 360 minutes, 2g samples were drawn out from the reaction mixture. The drawn sample was then mixed with ethanol in a titration flask and two drops of phenolphthalein were added. The mixture was then titrated against 0.5N Sodium hydroxide (NaOH) solution. Experiments were performed at temperatures (50, 60, 70 and 75 °C). All the experiments were repeated three times to minimize errors.

Experiments for BET surface area and porosity of amberlyst 15 were determined at a relative pressure (P/P<sub>0</sub>) range of 0.00–0.30 using a Micrometrics Gemini VII apparatus available at SCME lab shown in figure 3.2. The sample was initially degassed at 100 °C for 5 hours. The BET surface area calculated was 29.68 m<sup>2</sup>/g and BJH Adsorption average pore width (4V/A) came out to be 20.340 Å.



**Figure 3.2** BET surface area analyzer

### **3.4 Process Details:**

Different cited research work depicted that conversion of free fatty acids to esters increases with the increase in temperature, increase in molar ratio and increase in catalyst

concentration (Ilgen et al., 2014). In this research experimental work was performed at temperatures (50, 60, 70 and 75 °C). Catalyst concentration was varied from 2% to 3% and 4%, and molar ratios used were 1:1, 1:3 and 1:5. Mixing was kept constant throughout the experiments at 900rpm.

Initially the reaction of acetic acid with ethanol was performed at 50°C having a molar ratio of 1:1 and catalyst concentration of 2% by weight of free fatty acid. Temperature effect on reaction efficiency, was studied by varying temperature to other pre-selected values and was optimized. The next step was increasing catalyst concentration values to get better reaction conversion and finally molar ratio effect was studied by using different molar ratios.

Multiple runs for each parameter were evaluated to enable meaningful post-hoc analysis statistically. Each experiment was 6 hours in duration with a total of 11 samples taken at fixed time intervals to evaluate reaction conversion. The samples were drawn from the mixture by using pipettes.

To check the effect of fatty acid molecular structure and chain length on esterification reaction two different fatty acids i.e. acetic and oleic acid were used. Initially the experiments were carried out with acetic acid at different values of temperature, catalyst concentration and molar ratio. The optimum values of all the three variables for acetic acid esterification were then selected for oleic acid esterification reaction.

### **3.5 Calculation Method for Percent Free Fatty Acid (%FFA):**

Esters formation was determined by measuring the change in acid value at different time intervals. The percentage of free fatty acids in 2 g samples of the reacted product stream and



unreacted feedstock was calculated on the basis of American Oil Chemist Society (AOCS) Method Ca 5a-40 (Food chemicals codex 2003).

Briefly, 2 grams of reaction samples were added into 50 mL of alcohol solution stored in a beaker. 2 mL of phenolphthalein was added to beaker and the beaker contents were titrated with 0.5 N solution of sodium hydroxide drop by drop until endpoint light pink in color is achieved. The volume of sodium hydroxide solution used was noted down and the percentage of free fatty acids was calculated as per following equation 3.1.

$$\% \text{ FFA} = \frac{\text{Volume of NaOH solution used (mL)} \times N \times 28.2}{\text{Weight of sample}} \quad (\text{Eq. 3.1})$$

Where N is the normality of sodium hydroxide solution.

Decrease in %FFA in solution, or conversion to esters was then reported over the reaction time.

### **3.6 Determination of Reaction Rate Constants from Kinetic Models:**

Experimental data recorded was correlated with different kinetic models. Namely Eley Rideal (ER) and Langmuir Hinshelwood Hougen Watson (LHHW). These surface reaction models were selected for ease of their application and understanding. Both models were applied on acetic and oleic acid esterification data obtained at the best reaction conditions of acetic acid studied. In both of these models rate of reaction is controlled by a limiting step. Slowest step of esterification reaction is called rate limiting step and it controls overall rate of reaction. For both models adsorption of alcohol at resin catalyst surface and surface reaction steps were considered as rate limiting step. Disappearance rate of alcohol from the reaction mixture was used to calculate reactant and product molecule concentrations, stoichiometrically.

The derivation of equations for each model considering different rate limiting steps for esterification reaction rate constants determination are given in Appendix 1 for LHHW model and Appendix 2 for ER model.

For all data gathered from experimental work, model fitting was performed. Values for reaction rate constants were calculated using excel solver based on minimum error values of root mean square error (RMSE) and normalized root mean square error (NRMSE) (Jamal et al., 2015). Finally correlation linear coefficient ( $R^2$ ) were determined to show the linearity of the results. Root mean square error (RMSE) and normalized root mean square error (NRMSE) in this work is explained as

$$\text{RMSE} = \sqrt{\frac{\sum(\text{Exp values} - \text{Model values})^2}{N_t}} \quad (\text{Eq. 3.2})$$

$$\text{NRMSE} = \frac{\text{RMSE}}{\text{Experimental value (max)} - \text{Experimental value (min)}} \quad (\text{Eq. 3.3})$$

Here

Experimental value represent ester concentration from experimental work and Model values shows ester concentration from model calculation

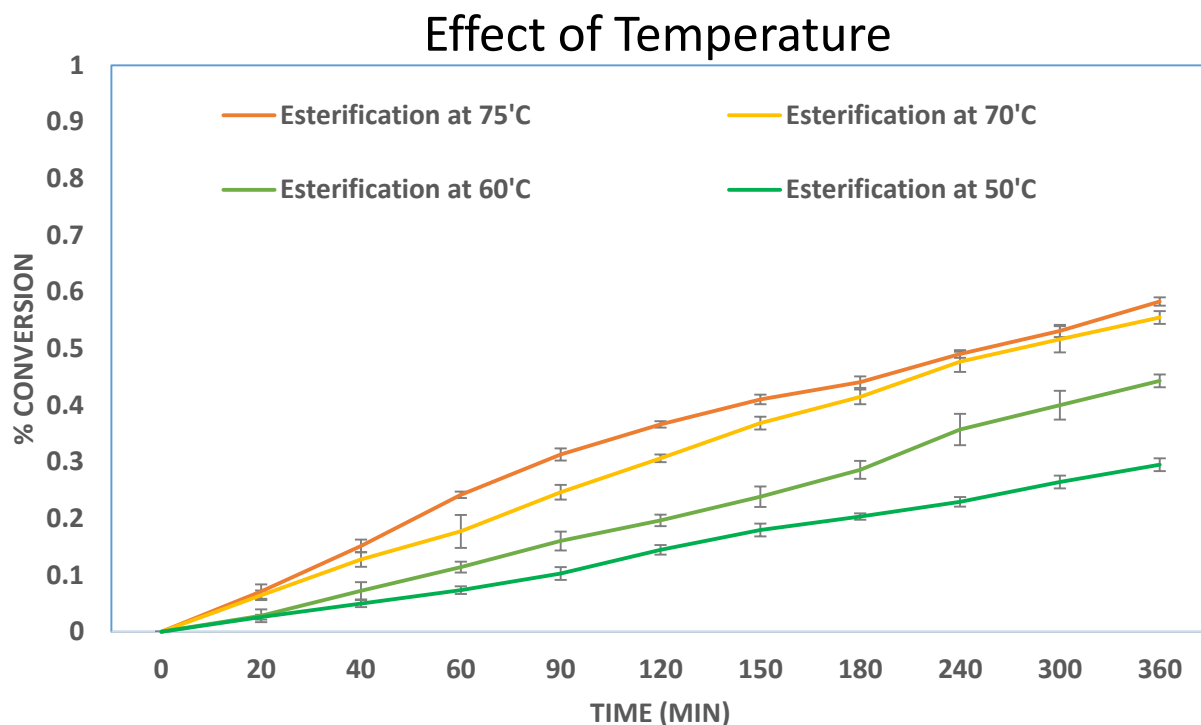
Experimental value (max and min) represent ester concentration at time t.

$N_t$  is the total data points used for calculation.

## **Results and Discussion.**

### **4.1 Temperature Effect on Esterification**

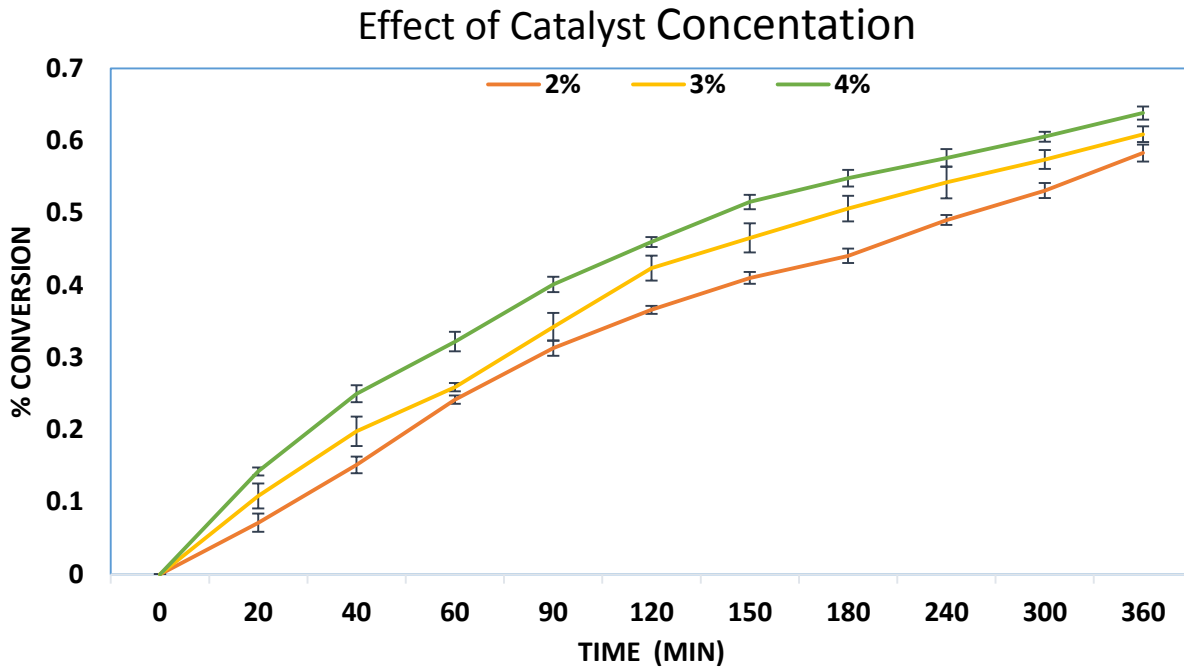
All esterification experiments were carried out at 900 rpm and atmospheric pressure in the batch reactor as explained in the experimental set up section. In first stage, acetic acid was used as a fatty acid for esterification reaction at fixed acidic resin catalyst concentration of 2% by weight of fatty acid in reactor, acetic acid to ethanol molar ratio was kept 1:1 at four different esterification temperatures i.e. 50, 60, 70 and 75 °C. Figure 4.1 illustrates temperature effect on acetic acid esterification conversion in the batch reactor at the stated conditions. Esterification was found to increase as the temperature of the reaction mixture was increased. The maximum conversion measured (58.3%) was observed at the maximum applied temperature (75 °C) after 6 hours of reaction. Maximum applied temperature was kept 75 °C because it was the maximum possible temperature manageable below the boiling point (78.37 °C) of ethanol at atmospheric conditions. However increase in ester yield with increase in temperature was noted. This is due to the fact that increase of temperature decreases the viscosity of fatty acid that helps its approach to the catalyst surface resulting in more conversion to esters.



**Figure 4.1** Temperature effect on the acetic acid esterification to ethyl acetate

#### 4.2 Effect of the Catalyst Concentration

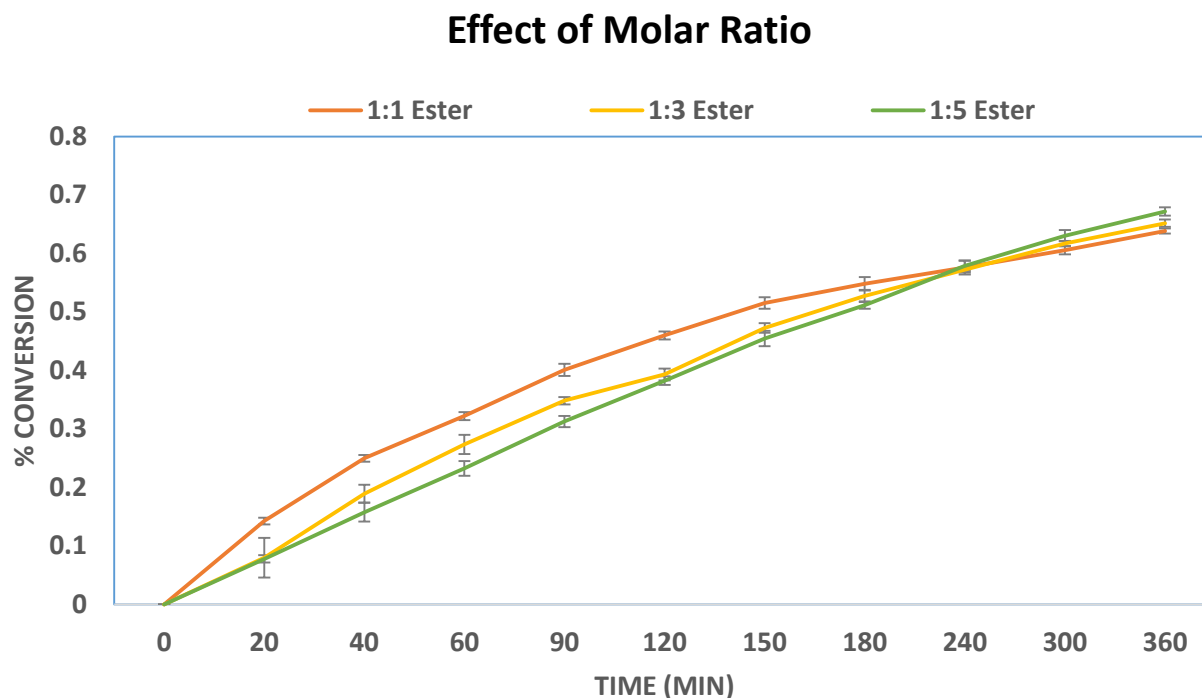
Catalyst concentration effect on esters formation is illustrated in Figure 4.2. Three different catalyst concentrations (2%, 3%, and 4%) were studied for acetic acid esterification reaction over the catalyst surface. Reaction performed at optimized temperatures of 75 °C, and molar ratio of 1:1 showed that catalyst concentration has a significant impact on conversion of free fatty acids in to esters. Percentage conversion increases with increase in catalyst concentration. The lowest conversion (58.3 %) occurred at the lowest evaluated catalyst concentration of 2%. This means that sufficient amount of catalyst surface must be present for the reaction to proceed as reducing catalyst concentration decreases the reaction sites for esters formation. Maximum fatty acid conversion of 63.8% was noted at catalyst concentration of 4% at the stated conditions.



**Figure 4.2** Effect of the catalyst concentration on acetic acid esterification

### 4.3 Effect of Molar Ratio

To examine the effect of fatty acid to alcohol molar ratio on conversion reaction, three molar ratios (1:1, 1:3, and 1:5) were selected as illustrated in figure 4.3. The esterification of acetic acid at temperature of 75 °C and catalyst concentration of 4% by weight of fatty acid in reactor showed that reaction conversion initially increases at lower molar ratios but conversion increases more at high molar ratios on long reaction times. This is because more alcohol is present in the reactor increases the conversion of the reactants. So high fatty acid to alcohol molar ratio in a batch can increase the overall conversion of fatty acids in to esters. A maximum conversion of acetic acid into esters was thus achieved at 75 °C, catalyst concentration of 4% and molar ratio of 1:5.

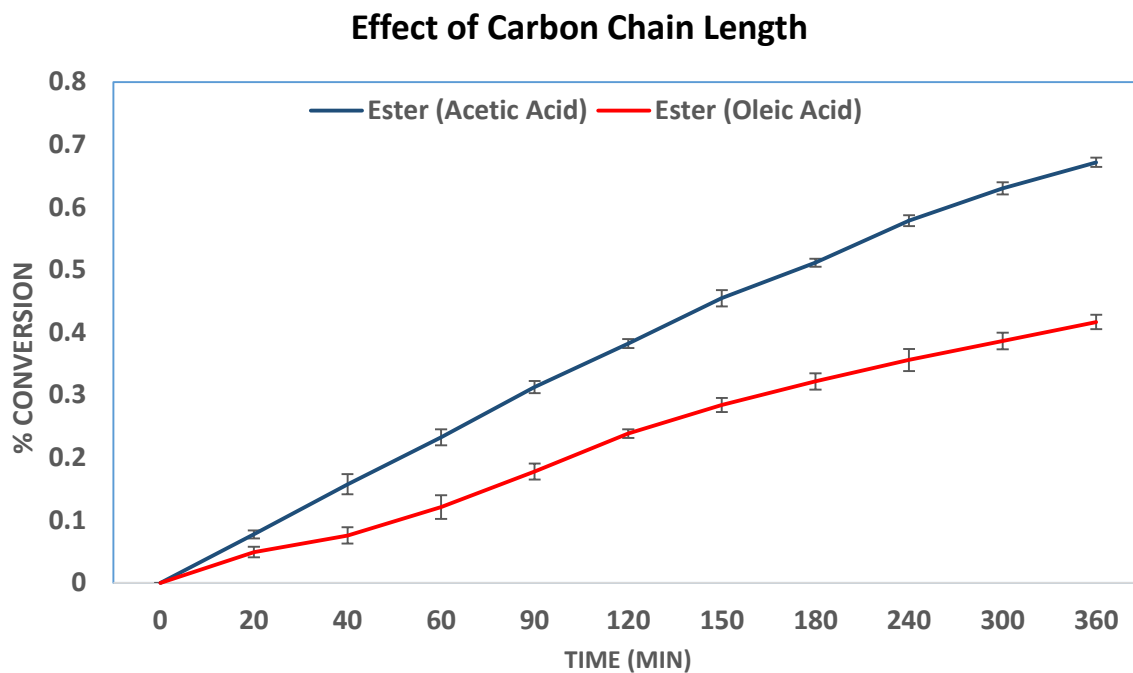


**Figure 4.3** Effect of molar ratio on the acetic acid esterification

#### 4.4 Effect of Fatty Acid Carbon Chain-Length

The effect of fatty acid carbon chain-length on percent conversion is shown in Figure 4.4. In comparison to 67.1% ester conversion with acetic acid a lower ester conversion of only 41.6% was noted with oleic acid: ethanol feedstock mixture at best esterification conditions of 1:5, molar ratio, 4% acidic resin catalyst concentration and 75 °C temperature. This difference in behavior of fatty acid conversion at same reaction conditions is due to the difference in chemistry of both the fatty acids molecules. Acetic acid consists of short carbon chain length molecules (C-2) while oleic acid comprise of long carbon chain molecules (C-18:1). Short chain fatty acids have easy accessibility in the porous structure of amberlyst 15 whereas long chain fatty acids are hindered by their large molecular sizes reducing surface contact area with the

catalyst for reaction at sulfonic sites. Molecular operating modeling software was used in the esterification group work studies to find the chain length of acetic and oleic acid as reported earlier (Khan et al., 2016).



**Figure 4.4** Carbon chain length effect on fatty acid esterification.

#### 4.5 Values of Surface Reaction Kinetic Rate Constants

Calculated values of surface reaction rate constants are shown in Table 4.1 and 4.2 respectively. Here small  $k$  represent the reaction rate constant for esterification reaction. Capital  $K$  is the equilibrium rate constant for adsorption, surface reaction and desorption steps. Last 3 columns in the tables show the values of root mean square error, normalized root mean square error, and linearity coefficient  $R^2$  respectively. Higher value of  $k$  means higher esterification rate constant for a model when all the reaction conditions were kept same.

**Table 4.1** Reaction rate constant values derived with Eley Rideal (ER) surface reaction kinetic model equations for acetic and oleic acid fatty acid molecules when adsorption of alcohol and surface reaction are the rate limiting steps.

Model	Rate Equation (r =)	Parameter Values	Units	RMSE	NRMSE	R <sup>2</sup>
ER Model for Acetic Acid (Alcohol Adsorption Rate limiting)	$k \frac{[A] - \frac{[E][W]}{K_1 K_2 K_3 [F]}}{\left[1 + \frac{[E][W]}{K_2 K_3 [F]} + \frac{[W]}{K_3}\right]}$	k=5.21E-04 K <sub>1</sub> =3.20E+01 K <sub>2</sub> =2.85E-04 K <sub>3</sub> =1.20E+03	1/min L/mol L/mol L/mol	4.41E-04	6.91E-02	<b>0.964</b>
ER Model for Acetic Acid (Surface Reaction Rate limiting)	$k \frac{K_1 [A][F] - \frac{[E][W]}{K_2 K_3}}{\left[1 + K_1 [A] + \frac{[W]}{K_3}\right]}$	k=4.31E+00 K <sub>1</sub> =4.30E-05 K <sub>2</sub> =4.00E+00 K <sub>3</sub> =4.68E+03	1/min L/mol L/mol L/mol	8.39E-04	1.31E-01	<b>0.947</b>
ER Model for Oleic Acid (Alcohol Adsorption Rate limiting)	$k \frac{[A] - \frac{[E][W]}{K_1 K_2 K_3 [F]}}{\left[1 + \frac{[E][W]}{K_2 K_3 [F]} + \frac{[W]}{K_3}\right]}$	k=4.45E-04 K <sub>1</sub> =3.07E+01 K <sub>2</sub> =1.50E-04 K <sub>3</sub> =1.20E+03	1/min L/mol L/mol L/mol	5.83E-04	1.99E-01	<b>0.770</b>
ER Model for Oleic Acid (Surface Reaction Rate limiting)	$k \frac{K_1 [A][F] - \frac{[E][W]}{K_2 K_3}}{\left[1 + K_1 [A] + \frac{[W]}{K_3}\right]}$	k=1.97E-01 K <sub>1</sub> =1.41E-03 K <sub>2</sub> =5.52E-03 K <sub>3</sub> =1.15E+04	1/min L/mol L/mol L/mol	5.42E-04	1.85E-01	<b>0.793</b>



**Table 4.2** Reaction rate constant values derived with Langmuir Hinshelwood Hougen-Watson (LHHW) surface reaction kinetic model equations for acetic and oleic acid fatty acid molecules with adsorption of alcohol and surface reaction as the rate limiting step.

Model	Rate Equation (r =)	Parameter Values	Units	RMSE	NRMSE	R <sup>2</sup>
LHHW Model for Acetic Acid (Alcohol Adsorption Rate limiting)	$k \frac{[A] - \frac{[E][W]}{[F]K_1K_2K_3K_4K_5}}{\left[1 + \frac{[E][W]}{[F]K_2K_3K_4K_5} + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5}\right]}$	k=5.60E-04 K <sub>1</sub> =1.68E+01 K <sub>2</sub> =2.68E-02 K <sub>3</sub> =3.76E-02 K <sub>4</sub> =1.82E+01 K <sub>5</sub> =1.82E+01	1/min L/mol L/mol L/mol L/mol	4.57E-04	7.15E-02	<b>0.965</b>
LHHW Model for Acetic Acid (Surface Reaction Rate limiting)	$k \frac{K_1K_2[A][F] - \frac{[E][W]}{K_3K_4K_5}}{\left[1 + K_1[A] + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5}\right]^2}$	k=1.74E-01 K <sub>1</sub> =1.93E+01 K <sub>2</sub> =4.63E+00 K <sub>3</sub> =8.55E+00 K <sub>4</sub> =7.90E+02 K <sub>5</sub> =7.22E+02	1/min L/mol L/mol L/mol L/mol	1.55E-03	2.43E-01	<b>0.924</b>
LHHW Model for Oleic Acid (Alcohol Adsorption Rate limiting)	$k \frac{[A] - \frac{[E][W]}{[F]K_1K_2K_3K_4K_5}}{\left[1 + \frac{[E][W]}{[F]K_2K_3K_4K_5} + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5}\right]}$	k=4.48E-04 K <sub>1</sub> =7.30E-01 K <sub>2</sub> =1.24E-05 K <sub>3</sub> =1.48E-02 K <sub>4</sub> =7.01E+02 K <sub>5</sub> =4.36E+03	1/min L/mol L/mol L/mol L/mol	9.05E-04	3.09E-01	<b>0.794</b>
LHHW Model for Oleic Acid (Surface Reaction Rate limiting)	$k \frac{K_1K_2[A][F] - \frac{[E][W]}{K_3K_4K_5}}{\left[1 + K_1[A] + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5}\right]^2}$	k=2.63E-01 K <sub>1</sub> =3.00E+00 K <sub>2</sub> =2.35E-01 K <sub>3</sub> =8.05E-02 K <sub>4</sub> =1.65E+00 K <sub>5</sub> =8.61E-01	1/min L/mol L/mol L/mol L/mol	5.55E-04	1.89E-01	<b>0.793</b>

A higher value of k for the fatty acid (acetic and oleic) esterified, using two different rate limiting steps in a kinetic model shows that surface reaction is the rate limiting step to determine the reaction rate constant values. As considering surface reaction as rate limiting step value of

reaction rate  $k$  changes more abruptly. Furthermore validity of model for considering surface reaction as the rate limiting step is illustrated by the higher values of coefficient of linearity  $R^2$  for the model [Ahmedzeki et al., 2013; Ilgen et al., 2014; De Silva et al., 2015; Yaakob et al., 2004].

So In simple words we can say that long chain length oleic acid for ER model starts behaving like LHHW model as there is an increase in fatty acid carbon chain length that minimizes the concept of molecule approach from bulk of the reaction mixture. This is because bigger fatty acid molecule encapsulate the resin surface giving the response of fatty acid being present at or near the surface which is the main idea of LHHW model.

#### **4.6 Equivalent Comparison of Results**

Esterification reaction rate constant of  $k=1.46E-02$  /s for acetic acid using LHHW model considering surface reaction as rate limiting step in presence of ethanol at reaction conditions of  $70^{\circ}C$  temperature, stirring speed of 250rpm, 5% resin catalyst by weight of fatty acid in the reactor has been reported (Ahmedzaki et al., 2013). However current work reports in comparison a value of  $k=2.90E-03/s$  at  $75^{\circ}C$  reaction temperature, 900rpm batch stirring, 1:5 fatty acid to alcohol molar ratio and 4% acidic resin, Amberlyst 15, concentration by weight to the fatty acid. Difference in value of reaction rate is attributed to difference in reaction conditions and amount of catalyst used.

Similarly for esterification of acetic acid using LHHW model with surface reaction as rate limiting step Toor noted (Toor et al., 2011) reaction rate of  $k = 0.7E-02/min$  and  $1.5E-02/min$  for use of n-butanol and  $k=1.2E-02/min$  and  $3.3E-02/min$  for use of iso-butanol alcohol at catalyst loading of 22.43 to 67.30  $kg/m^3$  respectively. Esterification was studied at  $78-93^{\circ}C$  reaction temperature, reactions were run at 1:5 fatty acid to alcohol molar ratio in the batch

reactor. However in equivalent units this work reports reaction rate constant  $k=1.74E-01/\text{min}$  at catalyst loading  $41.96 \text{ kg/m}^3$  at  $75^\circ\text{C}$ .

In the same way for acetic acid esterification using ER model with surface reaction as rate limiting step, a reaction rate constant  $k=8.7E-01 \text{ L}^2/\text{gm/mol}$  has been reported (Silva et al., 2014), at acidic catalyst loading of  $50\text{gm/L}$ , reaction temperature  $62^\circ\text{C}$  and 1:1 acetic acid to ethanol molar ratio. In comparison current work reports reaction rate constant value in equivalent units  $k=4.437E-04 \text{ L}^2/\text{gm/mol}$  at catalyst loading of  $23.82 \text{ gm/L}$  at  $75^\circ\text{C}$  reaction temperature, 1:5 molar ratio of acetic acid to ethanol at 900 rpm.

For esterification of oleic acid considering ER model with surface reaction as rate limiting step. A reaction rate constant  $k=2.68E-04 \text{ mol/gmcat-min}$ , at molar ratio 1:3, oleic acid to methanol at  $65^\circ\text{C}$  and 3% weight amberlyst 46 acidic resin by weight of fatty acid in the reactor has been reported (Ilgen et al., 2014) From this current research work we report in equivalent units reaction rate constant value  $k=1.58E-02 \text{ mol/gmcat-min}$ , while performing oleic acid esterification at 1:5 oleic acid to ethanol molar ratio at  $75^\circ\text{C}$  and 4% by weight amberlyst 15 resin catalyst by weight of fatty acid in the reactor. This difference in value can be attributed to different acidic resin surface and reaction conditions used.

Finally in absence of publications on surface reaction kinetic rate constants for oleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ) esterification with ethanol using LHHW model while considering surface reaction as rate limiting step. A work on Palmitic acid ( $\text{C}_{16}\text{H}_{32}\text{O}_2$ ) esterification with methanol using LHHW model was considered (Yaakob et al., 2004). Current research work reports a reaction rate constant equivalent of  $k=0.48 \text{ gm-cat/L-mol/s}$  at molar ratio of 1:5 oleic acid to ethanol, at 900rpm and  $75^\circ\text{C}$  with Amberlyst 15 acidic resin catalyst loading of  $36 \text{ gm-cat/L}$  in comparison to reported value for palmitic acid of  $k=0.576 \text{ gm-cat/L-mol/s}$  at molar ratio of 1:4 palmitic acid

to methanol, at 200-800rpm and 75°C reaction temperature when amberlyst 15 catalyst loading was 0-10 gm-cat/L.

These comparison show that reported data from this research work can be transformed to units as reported by other researchers.

## **Conclusion and Recommendations.**

### **5.1 Conclusion**

Esterification conversion efficiency increases with increase in reaction temperature, catalyst concentration, fatty acid to alcohol molar ratio in the batch of reaction mixture. Dry Amberlyst 15 is an effective acidic resin catalyst for esterification of acetic acid and oleic acid. Molecular structure and carbon chain length in the fatty acid plays a vital role in the esterification. Higher carbon chain length and bigger fatty acid molecule adversely affect the esterification efficiency. In the studied esterification at fixed 900rpm, the effective reaction conditions for acetic acid were 75 °C temperatures, 4% catalyst concentration by weight of fatty acid and 1:5 acetic acid to ethanol molar ratio. At the best reaction condition of acetic acid, the esterification reaction of oleic acid was only 41.6%, while for acetic acid it was 67.1%. Experimental esterification data fitted to two surface reaction kinetic models, i.e., ER and LHHW, showed short carbon chain length acetic acid best fitted the ER model and long carbon chain length oleic acid best followed the LHHW model. The reaction rate constants for acetic acid from the ER and LHHW models were 4.31/min ( $R^2 > 0.94$ ) and 0.174/min ( $R^2 > 0.92$ ), respectively. However, the reaction rate constants for oleic acid were 0.263/min ( $R^2 > 0.79$ ) for LHHW model and 0.197/min ( $R^2 > 0.79$ ) for ER model. Determination of reaction rate constants from these heterogeneous surface reaction kinetic models can be used for designing scaled up esterification reactors.

## 5.2 Recommendations and scope

Considering the achievements and scope of the current research, following recommendations are made for future research at NUST, PAKISTAN.

- Development of high temperature and pressure reaction systems that can utilize exhaust heat energy from industrial flue gases for efficient conversion of oils into esters (biodiesel).
- A study to compare Impact of saturation and unsaturation like C18, C18:1, C18:2) in fatty acid molecules along with chain length on catalytic surfaces for esterification.
- Presence of moisture in the fatty acid feed stock for maximum heterogeneous esterification reaction need to be studied to further explore the reaction rate constants from surface reaction kinetic models.
- There is a need to study coupling of lipid accumulation in selected consortium of microbes by feeding kitchen waste with the extraction of short chain fatty acids from microbes by environment friendly CO<sub>2</sub> absorption solvent systems for in-situ extraction and their conversion into esters on the surfaces of catalytic structures like water treatment resins.

## References

- Ahmedzeki NS, Alhassani MH, Al-jandeel HA. (2013). Heterogeneously catalyzed esterification reaction: experimental and modeling using Langmuir- Hinshelwood approach. *Iraqi Journal of Chemical and Petroleum Engineering*, 14(4):45–52.
- Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. (2012). Production of biodiesel using high free fatty acid feedstocks. *Renewable Sustainable Energy Reviews*, 16(5):3275–3285.
- Boey P-L, Ganesan S, Maniam GP, Khairuddean M, Efendi J. (2013). A new heterogeneous acid catalyst for esterification: Optimization using response surface methodology. *Energy Conversion and Management*, 65:392–396.
- Borges ME, Diaz L. (2012). Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renewable Sustainable Energy Reviews*, 16(5):2839–2849.
- Boro J, Thakur AJ, Deka D. (2011). Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. *Fuel Processing Technology*, 92(10):2061–2067.
- Brahmkhatri V, Patel A. (2010). Supported heteropolyacids: Synthesis, characterization and effect of supports on esterification reactions. *Kinetics and Catalysis*, 51(3)380–384.
- Caetano CS, Guerreiro L, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. (2009). Esterification of fatty acids to biodiesel over polymers with sulfonic acid groups. *Applied Catalysis A: General*, 359(1-2): 41-46.
- Feng Y, Zhang A, Li J, He B. (2010). A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. *Bioresource Technology*, 102(3):3607-36099

- Food Chemicals Codex. (2003). Institute of Medicine (U.S.). Committee on Food Chemicals Codex, National Academies Press.
- Giri BY, Rao KN, Devi BLAP, Lingaiah N, Suryanarayana I, Prasad RBN, Prasad PSS. (2005). Esterification of palmitic acid on the ammonium salt of 12-tungstophosphoric acid: The influence of partial proton exchange on the activity of the catalyst. *Catalysis Communication*, 6(12):788–792.
- Hayyan A, Alam MZ, Mirghani MES, Kabbashi NA, Hakimi NINM, Siran YM, Tahiruddin S. (2010). Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. *Bioresource Technology*, 101(20):7804–7811.
- Huang GH, Chen F, Wei D, Zhang XW, Chen G. (2010). Biodiesel production by microalgal biotechnology. *Applied Energy*, 87(1):38–46.
- Huang YS, Sundmacher K. (2006). Kinetics Study of propyl acetate synthesis reaction catalyzed by Amberlyst 15. *International Journal of Chemical Kinetics*, 39(5):245-253.
- Ilgen O. (2014). Investigation of reaction parameters, kinetics and mechanism of oleic acid esterification with methanol by using Amberlyst 46 as a catalyst. *Fuel Processing Technology*, 124:134–139
- Jamal Y, Rabie A, Boulanger BO. (2015) Determination of methanolysis rate constants for low and high fatty acid oils using heterogeneous surface reaction kinetic models. *Reaction Kinetics, Mechanisms and Catalysis* 114(1):63–74.
- Jamal Y, Luo G, Kuo CH, Rabie A, Boulanger BO. (2014). Sorption kinetics, thermodynamics and regeneration for lipid feedstock deacidification using a mixed-bed Ion-exchange resin. *Journal of Food Process Engineering*, 37(1):27–36.
- Jiang Y, Lu J, Sun K, Ma L, Ding J. Esterification of oleic acid with ethanol catalyzed by sulfonated cation exchange resin: experimental and kinetic studies. *Energy Conversion and Management*. 76: 980-985.



- Khan JA, Jamal Y, Shahid A, Boulanger BO. (2016) Esterification of acetic and oleic acids within an Amberlyst 15 packed catalytic column. *Korean Journal of Chemical Engineering*. 33(2):582-586.
- Lam MK, Lee KT, Mohamed AR. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances*, 28(4):500–518.
- Lee MJ, Wu HT, Lin HM. (2000). Kinetics of Catalytic Esterification of Acetic Acid and Amyl Alcohol over Dowex. *Industrial and Engineering Chemistry Research*, 39 (11), 4094–4099.
- Liu W, Yin P, Zhang J, Tang Q, Qu R. (2014) Biodiesel production from esterification of free fatty acid over PA/NaY solid catalyst. *Energy Conversion Management*, 82:83–91.
- Lucena IL, Saboya RMA, Oliveira JFG, Rodrigues ML, Torres AEB, Cavalcante CL. (2011). Oleic acid esterification with ethanol under continuous water removal conditions. *Fuel*, 90(2)902-904.
- Mandake MB, Anekar S V, Mumbai N. (2013). Kinetic study of catalyzed and uncatalyzed esterification reaction of acetic acid with methanol. *American International Journal of Research in Formal, Applied & Natural Sciences*, 3(1):114–21.
- Marchetti JM, Miguel VU, Errazu a. F. (2007). Heterogeneous esterification of oil with high amount of free fatty acids. *Fuel*, 86(5-6):906–910.
- Math MC, Kumar SP, Chetty SV. (2009). Technologies for biodiesel production from used cooking oil – a review. *Energy for Sustainable Development*, 14(4):339–345.
- Mathiyazhagan M, Ganapathi A. (2011). Factors affecting biodiesel production. *Research Plant Biology*, 1(2):1–5.
- Park J-Y, Kim D-K, Lee J-S. (2010). Esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. *Bioresource Technology*, 101(1):S62– S65.

- Pirola C, Manenti F, Galli F, Bianchi CL. (2014). Heterogeneously catalyzed free fatty acids esterification in (Monophasic Liquid)/Solid Packed Bed Reactors (PBR). *Chemical Engineering Transactions*, 37:553–558.
- Sharma M, Toor AP, Wanchoo RK. (2014). Kinetics of the esterification reaction between pentanoic acid and methanol catalyzed by noncorrosive cation exchange resin. *Chemical and Biochemical Engineering Quarterly*, 28(1):79–85.
- Silva ECL De, Bamunusingha BANN, Gunasekera MY. (2014). Heterogeneous Kinetic Study for Esterification of Acetic Acid with Ethanol. *Engineer*, XLVII(01):9–16.
- Singh N, Raj K, Sachan PK. (2013). Kinetic study of catalytic esterification of butyric acid and ethanol over Amberlyst 15. *ISRN Chemical Engineering*, 1–6, doi:10.1155/2013/520293
- Son SM, Kimura H, Kusakabe K. (2011). Esterification of oleic acid in a three-phase, fixed-bed reactor packed with a cation exchange resin catalyst. *Bioresource Technology*, 102(2):2130–2132.
- Teo HTR, Saha B. (2004) Heterogeneous catalysed esterification of acetic acid with isoamyl alcohol: Kinetic studies. *Journal of Catalysis*, 228(1):174–182.
- Toor AP, Sharma M, Kumar G, Wanchoo RK. (2011). Kinetic study of Esterification of acetic acid with n-butanol and isobutanol catalyzed by ion exchange resin. *Bulletin of Chemical Reaction Engineering and Catalysis*, 6(1):23–30.
- Veljkovic VB, Lakicevic SH, Stamenkovic OS, Todorovic ZB, Lazic ML. (2006). Biodiesel production from tobacco (*Nicotiana tabacum* L.) Seed Oil with a high content of free fatty acids. *Fuel*. 85(17-18):2671–2675.
- Yaakob AQ, Bhatia S. (2004). Esterification of Palmitic Acid with Methanol in the Presence of Macroporous Ion Exchange Resin as Catalyst. *International Islamic University Malaysia Engineering Journal*. 5(2):35–51.

- Yu W, Hidajat K, Ray AK. (2004). Determination of adsorption and kinetic parameters for methyl acetate esterification and hydrolysis reaction catalyzed by Amberlyst 15. Applied Catalysis A: General. 260(2)191-205.

## APPENDIX-1

### Langmuir-Hinshelwood- Hougen-Watson (LHHW) Model

**Esterification Reaction:**



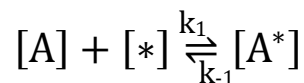
Where A = Alcohol, F = Fatty Acid, E= Ester, W = Water

#### **Case 1: Alcohol adsorption on resin catalyst is the rate limiting step (R.L.S)**

The LHHW model derivation considering alcohol adsorption as rate limiting step is derived as following.

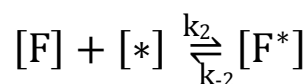
Here [\*] = concentration of available surface site on catalyst (acidic resin), [A\*], [F\*], [E\*] and [W\*] are concentration of molecules bounded at surface site. [A], [F], [E] and [W] are the concentration in the bulk of the solution.

Step 1. Alcohol Adsorption

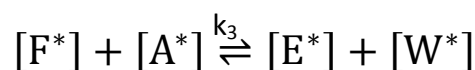


Here the above reaction is the **rate limiting step**.

Step 2. Fatty Acid Adsorption

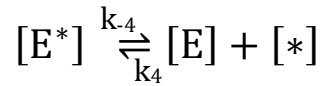


Step 3. Surface Reaction

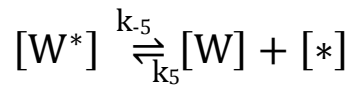


$k_{-3}$

Step 4. Ester desorption



Step 5. Water desorption



Equilibrium constant K for each step is defined as

$$K_1 = \frac{k_1}{k_{-1}} = K_{Ad(Alcohol)}$$

$$K_2 = \frac{k_2}{k_{-2}} = K_{Ad(Fatty\ Acid)}$$

$$K_3 = \frac{k_3}{k_{-3}} = K_{Reaction} = K_R$$

$$K_4 = \frac{k_{-4}}{k_4} = K_{Dep(Ester)}$$

$$K_5 = \frac{k_{-5}}{k_5} = K_{Dep(Water)}$$

Ad = Adsorption, Dep = Desorption

Equation 1:

$$r_1 = k_1[A][*] - k_{-1}[A^*]$$

$$r_1 = k_1 \left[ [A][*] - \frac{1}{K_1} [A^*] \right] \text{----- (R.L.S)}$$

Equation 2:

$$r_2 = k_2[F][*] - k_{-2}[F^*]$$

$$r_2 = k_2 \left[ [F][*] - \frac{1}{\frac{k_2}{K_2}} [F^*] \right]$$

$$\frac{r_2}{k_2} = 0 = [F][*] - \frac{1}{K_2} [F^*]$$

$$[F^*] = K_2 [F][*]$$

Equation 3:

$$r_3 = k_3 [A^*][F^*] - k_{-3} [E^*][W^*]$$

$$r_3 = k_3 \left[ [A^*][F^*] - \frac{1}{\frac{k_3}{k_{-3}}} [E^*][W^*] \right]$$

$$\frac{r_3}{k_3} = 0 = [A^*][F^*] - \frac{1}{K_3} [E^*][W^*]$$

$$[A^*] = \frac{[E^*][W^*]}{[F^*]K_3}$$

Equation 4:

$$r_4 = k_{-4} [E^*] - k_4 [E][*]$$

$$r_4 = k_4 \left[ \frac{k_{-4}}{k_4} [E^*] - [E][*] \right]$$

$$r_4 = K_4 [K_4 [E^*] - [E][*]]$$

$$\frac{r_4}{k_4} = 0 = K_4 [E^*] - [E][*]$$

$$[E^*] = \frac{[E][*]}{K_4}$$

Equation 5:

$$r_5 = k_{-5}[W^*] - k_5[W][*]$$

$$r_5 = k_5 \left[ \frac{k_{-5}}{k_5} [W^*] - [W][*] \right]$$

$$\frac{r_5}{k_5} = 0 = K_5[W^*] - [W][*]$$

$$[W^*] = \frac{[W][*]}{K_5}$$

ST = Total number of sites available on catalyst (acidic resin) surface. It is defined by balance equation as following

$$ST = [*] + [A^*] + [F^*] + [E^*] + [W^*]$$

Putting values of  $[A^*]$ ,  $[F^*]$ ,  $[E^*]$ ,  $[W^*]$  in the above equation

$$ST = [*] + \frac{[E^*][W^*]}{[F^*]K_3} + K_2[F][*] + \frac{[E][*]}{K_4} + \frac{[W][*]}{K_5}$$

$$ST = [*] + \frac{[E][*][W][*]}{[F][*]K_3K_4K_2K_5} + K_2[F][*] + \frac{[E][*]}{K_4} + \frac{[W][*]}{K_5}$$

$$ST = [*] \left[ 1 + \frac{[E][W]}{[F]K_3K_4K_2K_5} + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5} \right]$$

$$[*] = \frac{ST}{\left[1 + \frac{[E][W]}{[F]K_3K_4K_2K_5} + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5}\right]}$$

Substituting the values  $[A^*]$ ,  $[F^*]$   $[E^*]$  and  $[W^*]$  in equation 1, R.L.S

$$r_1 = k_1 \left[ [A][*] - \frac{1}{K_1} [A^*] \right]$$

$$r_1 = k_1 \left[ [A][*] - \frac{1}{K_1} \frac{[E^*][W^*]}{[F^*]K_3} \right]$$

$$r_1 = k_1 \left[ [A][*] - \frac{[E][*][W][*]}{[F][*]K_1K_2K_3K_4K_5} \right]$$

$$r_1 = k_1 \left[ [A][*] - \frac{[E][*][W]}{[F]K_1K_2K_3K_4K_5} \right]$$

$$r_1 = k_1[*] \left[ [A] - \frac{[E][W]}{[F]K_1K_2K_3K_4K_5} \right]$$

Substituting value of  $[*]$  in above equation

$$r_1 = k_1 ST \frac{[A] - \frac{[E][W]}{[F]K_1K_2K_3K_4K_5}}{\left[1 + \frac{[E][W]}{[F]K_2K_3K_4K_5} + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5}\right]}$$

As pure catalyst (acidic resin) was used therefore  $ST = 1$

Hence  $k_1 ST = k$  i.e rate constant for rate limiting step.

Therefore reaction rate for limiting step can be defined as following.

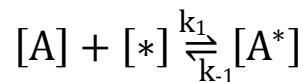
$$r_1 = \frac{k \left[ [A] - \frac{[E][W]}{[F]K_1K_2K_3K_4K_5} \right]}{\left[ 1 + \frac{[E][W]}{[F]K_2K_3K_4K_5} + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5} \right]}$$

### Case 2: Surface reaction on catalyst is rate limiting step (R.L.S)

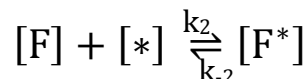
LHHW model derivation considering surface reaction as rate limiting step is derived as following.

Here  $[*]$  = concentration of available surface site on catalyst (acidic resin),  $[A^*]$ ,  $[F^*]$ ,  $[E^*]$  and  $[W^*]$  are concentration of molecules bounded at surface site.  $[A]$ ,  $[F]$ ,  $[E]$  and  $[W]$  are the concentration in the bulk of the solution.

Step 1. Alcohol Adsorption

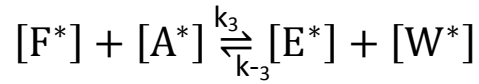


Step 2. Fatty Acid Adsorption



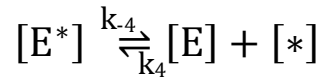


Step 3. Surface Reaction

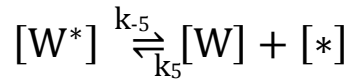


Here the above reaction is the **rate limiting step**.

Step 4. Ester desorption



Step 5. Water desorption



Equilibrium constant K for each step is defined as

$$K_1 = \frac{k_1}{k_{-1}} = K_{Ad(Alcohol)}$$

$$K_2 = \frac{k_2}{k_{-2}} = K_{Ad(Fatty\ Acid)}$$

$$K_3 = \frac{k_3}{k_{-3}} = K_{Reaction} = K_R$$

$$K_4 = \frac{k_{-4}}{k_4} = K_{Dep(Ester)}$$

$$K_5 = \frac{k_{-5}}{k_5} = K_{Dep(Water)}$$

Ad = Adsorption, Dep = Desorption

Also

$$\frac{r_1}{k_1}, \frac{r_2}{k_2}, \frac{r_4}{k_4}, \frac{r_5}{k_5} = 0$$

Equation 1:

$$r_1 = k_1 \left[ [A][*] - \frac{1}{K_1} [A^*] \right]$$
$$[A^*] = K_1 [A][*]$$

Equation 2:

$$r_2 = k_2 \left[ [F][*] - \frac{1}{K_2} [F^*] \right]$$
$$[F^*] = K_2 [F][*]$$

Equation 3:

$$r_3 = k_3 \left[ [A^*][F^*] - \frac{1}{K_3} [E^*][W^*] \right] \text{----- (R.L.S)}$$

Equation 4:

$$r_4 = k_4 \left[ \frac{k_{-4}}{k_4} [E^*] - [E][*] \right]$$
$$\frac{r_4}{k_4} = 0 = K_4 [E^*] - [E][*]$$
$$[E^*] = \frac{[E][*]}{K_4}$$

Equation 5:

$$r_5 = k_5 \left[ \frac{k_{-5}}{k_5} [W^*] - [W][*] \right]$$
$$\frac{r_5}{k_5} = 0 [K_5 [W^*] - [W][*]$$

$$[W^*] = \frac{[W][*]}{K_5}$$

ST = Total number of sites available on catalyst (acidic resin) surface. It is defined by balance equation as following

$$ST = [*] + [A^*] + [F^*] + [E^*] + [W^*]$$

Putting values of  $[A^*]$ ,  $[F^*]$ ,  $[E^*]$ ,  $[W^*]$  in the above equation

$$ST = [*] + K_1[A][*] + K_2[F][*] + \frac{[E][*]}{K_4} + \frac{[W][*]}{K_5}$$

Taking  $[*]$  common

$$ST = [*] \left[ 1 + K_1[A] + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5} \right]$$

$$[*] = \frac{ST}{\left[ 1 + K_1[A] + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5} \right]}$$

Substituting this value for  $*$ ,  $[A^*]$ ,  $[F^*]$ ,  $[E^*]$  and  $[W^*]$  in equation 3, (R.L.S)

$$r_3 = k_3 \left[ K_1[A][*]K_2[F][*] - \frac{[E][*][W][*]}{K_3K_4K_5} \right]$$

$$r_3 = k_3[*]^2 \left[ K_1[A]K_2[F] - \frac{[E][W]}{K_3K_4K_5} \right]$$

Substituting value of  $[*]$  in above equation

$$r_3 = \frac{k_3(ST)^2 \left[ K_1K_2[A][F] - \frac{[E][W]}{K_3K_4K_5} \right]}{\left[ 1 + K_1[A] + K_2[F] + \frac{[E]}{K_4} + \frac{[W]}{K_5} \right]^2}$$

As pure catalyst (acidic resin) was used therefore  $ST = 1$  or  $(ST)^2 = (1)^2 = 1$

Hence  $k_3(ST)^2 = k$  i.e. rate constant for rate limiting step.

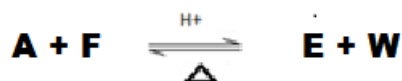
Therefore reaction rate for surface reaction as rate limiting step can be defined as following.

$$r_3 = \frac{k \left[ K_1 K_2 [A][F] - \frac{[E][W]}{K_3 K_4 K_5} \right]}{\left[ 1 + K_1 [A] + K_2 [F] + \frac{[E]}{K_4} + \frac{[W]}{K_5} \right]^2}$$

## APPENDIX-2

### Eley Rideal (ER) Model

**Esterification Reaction:**



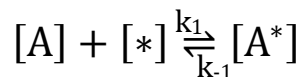
Where A = Alcohol, F = Fatty Acid, E= Ester, W = Water

#### **Case 1: Alcohol adsorption on resin catalyst is the rate limiting step (R.L.S)**

The ER model derivation considering alcohol adsorption as rate limiting step derived is as following.

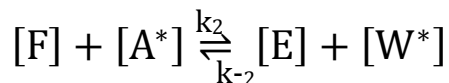
Here [\*] = concentration of available surface site on catalyst (acidic resin), [A\*] and [W\*] are concentration of molecules bounded at surface site. [A], [F], [E] and [W] are the concentration in the bulk of the solution.

Step 1. Alcohol Adsorption

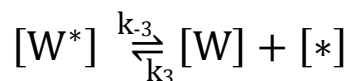


Here the above reaction is the **rate limiting step**.

Step 2. Surface Reaction



Step 3. Water desorption



Equilibrium constant K for each step is defined as

$$K_1 = \frac{k_1}{k_{-1}} = K_{Ad}$$

$$K_2 = \frac{k_2}{k_{-2}} = K_{\text{Reaction}} = K_R$$

$$K_3 = \frac{k_{-3}}{k_3} = K_{\text{Dep}}$$

Ad = Adsorption, Dep = Desorption

Equation 1:

$$r_1 = k_1[A][*] - k_{-1}[A^*]$$

$$r_1 = k_1 \left[ [A][*] - \frac{k_{-1}}{k_1} [A^*] \right]$$

$$r_1 = k_1 \left[ [A][*] - \frac{1}{K_1} [A^*] \right] \text{----- (R.L.S)}$$

Equation 2:

$$r_2 = k_2[A^*][F] - k_{-2}[E][W^*]$$

$$r_2 = k_2 \left[ [A^*][F] - \frac{1}{\frac{k_2}{k_{-2}}} [E][W^*] \right]$$

$$\frac{r_2}{k_2} = 0 = [A^*][F] - \frac{1}{K_2} [E][W^*]$$

$$[A^*] = \frac{[E][W^*]}{K_2[F]}$$

Equation 3:

$$r_3 = k_{-3}[W^*] - k_3[W][*]$$

$$r_3 = k_3 \left[ \frac{k_{-3}}{k_3} [W^*] - [W][*] \right]$$

$$r_3 = k_3 [K_3 [W^*] - [W][*]]$$

$$\frac{r_3}{k_3} = 0 = K_3 [W^*] - [W][*]$$

$$[W^*] = \frac{[W][*]}{K_3}$$

ST = Total number of sites available on catalyst (acidic resin) surface. It is defined by balance equation as following

$$ST = [*] + [A^*] + [W^*]$$

Putting values of  $[A^*]$  and  $[W^*]$  in the above equation

$$ST = [*] + \frac{[E][W^*]}{K_2[F]} + \frac{[W][*]}{K_3}$$

$$ST = [*] + \frac{[E][W][*]}{K_2 K_3 [F]} + \frac{[W][*]}{K_3}$$

Taking  $[*]$  common

$$ST = [*] \left[ 1 + \frac{[E][W]}{K_2 K_3 [F]} + \frac{[W]}{K_3} \right]$$

$$[*] = \frac{ST}{\left[1 + \frac{[E][W]}{K_2 K_3 [F]} + \frac{[W]}{K_3}\right]}$$

Substituting the value of  $[A^*]$  in equation 1, R.L.S

$$r_1 = k_1 \left[ [A][*] - \frac{[E][W^*]}{K_1 K_2 [F]} \right]$$

$$r_1 = k_1 \left[ [A][*] - \frac{[E][*][W]}{K_1 K_2 K_3 [F]} \right]$$

$$r_1 = k_1 [*] \left[ [A] - \frac{[E][W]}{K_1 K_2 K_3 [F]} \right]$$

Substituting value of  $[*]$  in above equation

$$r_1 = k_1 (ST) \frac{\left[ [A] - \frac{[E][W]}{K_1 K_2 K_3 [F]} \right]}{\left[ 1 + \frac{[E][W]}{K_2 K_3 [F]} + \frac{[W]}{K_3} \right]}$$

As pure catalyst (acidic resin) was used therefore  $ST = 1$

Hence  $k_1 ST = k$  i.e rate constant for the rate limiting step.

Therefore reaction rate for the limiting step can be defined as following.

$$r_1 = \frac{k \left[ [A] - \frac{[E][W]}{K_1 K_2 K_3 [F]} \right]}{\left[ 1 + \frac{[E][W]}{K_2 K_3 [F]} + \frac{[W]}{K_3} \right]}$$

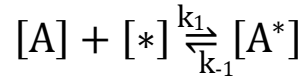
**Case 2: Surface reaction on catalyst is the rate limiting step (R.L.S)**



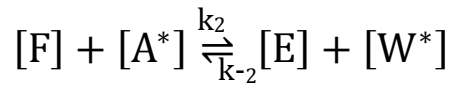
ER model derivation considering surface reaction as rate limiting step is derived as following.

Here [\*] = concentration of available surface site on catalyst (acidic resin), [A\*] and [W\*] are concentration of molecules bounded at surface site. [A], [F], [E] and [W] are the concentration in the bulk of the solution.

Step 1. Alcohol Adsorption

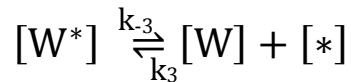


Step 2. Surface Reaction



Here the above reaction is the **rate limiting step**.

Step 3. Water desorption



Equilibrium constant K for each step is defined as

$$K_1 = \frac{k_1}{k_{-1}} = K_{Ad}$$

$$K_2 = \frac{k_2}{k_{-2}} = K_{Reaction} = K_R$$

$$K_3 = \frac{k_{-3}}{k_3} = K_{Dep}$$

Ad = Adsorption, Dep = Desorption

Equation 1:

$$r_1 = k_1 \left[ [A][*] - \frac{1}{K_1} [A^*] \right]$$

$$[A^*] = K_1[A][*]$$

Equation 2:

$$r_2 = k_2 \left[ [A^*][F] - \frac{1}{K_2} [E][W^*] \right] \text{----- (R.L.S)}$$

Equation 3:

$$r_3 = k_3 \left[ \frac{k_{-3}}{k_3} [W^*] - [W][*] \right]$$

$$\frac{r_3}{k_3} = 0 = [K_3[W^*] - [W][*]$$

$$[W^*] = \frac{[W][*]}{K_3}$$

ST = Total number of sites available on catalyst (acidic resin) surface. It is defined by balance equation as following

$$ST = [*] + [A^*] + [W^*]$$

Putting values of  $[A^*]$  and  $[W^*]$  in the above equation

$$ST = [*] + K_1[A][*] + \frac{[W][*]}{K_3}$$

Taking  $[*]$  common

$$ST = [*] \left[ 1 + K_1[A] + \frac{[W]}{K_3} \right]$$

$$[*] = \frac{ST}{\left[ 1 + K_1[A] + \frac{[W]}{K_3} \right]}$$

Substituting this value for  $[A^*]$ , and  $[W^*]$  in equation 2, (R.L.S)

$$r_2 = k_2 \left[ K_1[A][*][F] - \frac{[E][W][*]}{K_2K_3} \right]$$

$$r_2 = k_2[*] \left[ K_1[A][F] - \frac{[E][W]}{K_2K_3} \right]$$

Substituting value of  $[*]$  in above equation

$$r_2 = k_2(ST) \frac{\left[ K_1[A][F] - \frac{[E][W]}{K_2K_3} \right]}{\left[ 1 + K_1[A] + \frac{[W]}{K_3} \right]}$$

As pure catalyst (acidic resin) was used therefore  $ST = 1$

Hence  $k_2(ST) = k$  i.e. rate constant for the rate limiting step.

Therefore reaction rate for surface reaction as rate limiting step can be defined as following.

$$r_2 = \frac{k \left[ K_1[A][F] - \frac{[E][W]}{K_2K_3} \right]}{\left[ 1 + K_1[A] + \frac{[W]}{K_3} \right]}$$