ESTERIFICATION OF OLEIC ACID WITH ETHANOL BY USING TUNGSTATED ZIRCONIA : KINETIC AND MODELING STUDY

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BORANG PENGESAHAN STATUS TESIS♦

JUDUL : ESTERIFICATION OF OLEIC ACID WITH ETHANOL BY USING TUNGSTATED ZIRCONIA : KINETIC AND MODELING STUDY

SESI PENGAJIAN: 2008/2009

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**A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering**

**Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang**

APRIL, 2009

To my beloved family

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ABSTRACT

The esterification of free fatty acids (FFA) mostly found in vegetable oils with ethanol using solid acid catalyst is one of promising method to convert FFA into Fatty Acid Ethyl Ester (FAEE) that is an alternative to replace fossil fuel as energy source mostly in transportation sector. The present study aimed to determine the optimum or best operating condition for the production of FAEE by esterification of oleic acid and ethanol with tungstated zirconia used as solid acid catalyst. Tungstated zirconia used must be activated at 800°C for it functions at the best state by providing most active site for the reaction occur besides providing alternative route that lower than activation energy for reaction to occur. Kinetic model has been developed after the optimum operating condition is determined. From the scope of study, the optimum operating condition of oleic acid esterification can be achieved at 50°C, 1.5 g tungstated zirconia solid catalyst and 5:1 ethanol to oleic acid molar ratio that brings 24.24% oleic acid conversion. Kinetic model used is pseudohomogeneous and from the model, activation energy for esterification which is 9.72 kJ/mol can be determined.

ABSTRAK

Proses pengesteran asid lemak bebas yang biasanya ditemui pada minyak sayuran dengan etanol menggunakan mangkin asid pepejal adalah satu cara yang meyakinkan untuk menukarkan asid lemak kepada Etil Ester Asid Lemak (EEAL) iaitu satu alternatif untuk menggantikan bahan api fosil sebagai sumber tenaga khususnya dalam sektor pengangkutan. Kajian terkini tertumpu kepada mencari keadaan optima atau terbaik untuk penghasilan EEAL melalui pengesteran asid oleik dan etanol dengan tungstated zirconia digunakan sebagai mangkin asid pepejal. Tungstated zirconia mesti diaktifkan pada suhu 800°C untuk berfungsi pada keadaan terbaik bagi menyediakan tapak aktif untuk tindakbalas berlaku di samping menyediakan laluan alternatif yang lebih rendah dari tenaga pengaktifan untuk tindakbalas berlaku. Model kinetik perlu diterbitkan selepas mencapai keadaan optima untuk digunakan dalam proses pengesteran. Daripada skop kajian, dapat dibuktikan keadaan optima pengesteran asid oleik dapat dicapai pada suhu 50°C, 1.5 g tungstated zirconia mangkin pepejal dan 5:1 nisbah molar etanol kepada asid oleik yang membawa kepada 24.24% perubahan asid oleik kepada ester. Model kinetic yang digunakan ialah model homogeneous palsu dan daripada model, tenaga pengaktifan proses pengesteran iaitu 9.72 kJ/mol dapat dikenal pasti.

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LIST OF ABBREVIATIONS/TERMINOLOGY/SYMBOLS

T - Temperature

°C - Degree Celcius

ml - Mililiter

kJ - KiloJoule

min - Minute

K - Kelvin

w/w - Weight per weight

kg - Kilogram

g - Gram

% - Percentage

rpm Revolutions per minute

M Molar (mol/dm^3)

FFA - Free Fatty Acid

LHHW- Langmuir-Hinshelwood-Hougen-Watson

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The modernization of today's life has changed the lifestyle of people. People need to move from one place to another to do their job in fast and effective ways. This kind of lifestyle has made a big impact especially in the expansion of transportation industry. Thus, the demands on fuel also increase every year. However, the quantity of fossil fuel is decreased and it is not a renewable source. Thus, we need to find the other sources other than fossil fuel as alternative to fulfill the demands of fuel.

Biodiesel fuel is the new possible alternative to replace the fossil fuel as the energy source especially in transportation sector. This fuel can be produced from esterification of free fatty acid (FFA) and alcohol. Free fatty acids are found easily in vegetable oils or animal fats. The possibility of using vegetable oil as energy source is proposed by Rudolph Diesel in 1892.

The substitution of biodiesel fuel to fossil fuel brings a lot of advantages for consumers. Compared to fossil fuel, the carbon dioxide (CO_2) which emitted from biodiesel would be recovered through the production of biomass (feedstock of biodiesel). It also does not contain sulfur to produce SO_2. The oxygen contained in biodiesel makes it fully combusted and thus the poisonous gas such as carbon monoxide (CO) can be reduced (Park et al., 2008).

The esterification process of free fatty acid with alcohol can be fasten with the presence of catalyst. The catalysts used can be homogeneous or heterogeneous. The homogeneous catalysts such as H_2SO_4 and NaOH are difficult to separate with ester (biodiesel fuel) (Furuta et al., 2006). Thus, these kinds of catalysts are not suitable for the present study. The heterogeneous catalysts that has been used by previous experiments such as Tungstated Zirconia(WO_3/ZrO_2), Amberlyst15, silica-alumina, SAC-13, Sulfated Zirconia, Titania Zirconia, Smopex-101, niobium acid and various zeolites. The solid acid catalyst chosen for the present study is tungstated zirconia.

1.2 Problem Statement

Biodiesel can be the most suitable replacement for the fossil fuel as energy source. Besides of it bring a lot of advantages compared to fossil fuel, the amount of fossil fuel is decreasing every year make it is important to produce biodiesel in a large amount. To produce it in large amount using a new solid acid catalyst, a reactor needs to be designed. Previous studies for biodiesel production do not mention much about the importance of kinetic modeling; therefore the present study will give attention about kinetic and modeling study and develop it.

1.3 Objectives

1) To determine the optimum operating conditions of the esterification of free fatty acid with alcohol selected.

2) To develop the kinetic modeling for the esterification process.

1.4 Scopes of Research

The present study, several important parameters will be investigated. These parameters are temperature, ratio of alcohol to free fatty acid, amount of catalyst used, and presence of triglycerides. The details of the scope are as below:

i) Temperature is between 30-50°C
ii) Amount of catalyst is between 0.5-1.5g
iii) Ratio of alcohol to free fatty acid- 1:1, 3:1, 5:1
iv) Volume of triglycerides is between 10ml, 30ml and 50ml

In this experiment, we will use oleic acid as free fatty acid, ethanol, and tungstated zirconia as the catalyst. Pseudohomogeneous model will be used since it is simple and easy to construct.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is the fuel alternative to petroleum based fuel which is manufactured from vegetable oils or animal fats by catalytically react it with short chain alcohol such as methanol or ethanol. Vegetable oils or animal fats contain many types of free fatty acids. These free fatty acids will react with short chain alcohol to produce biodiesel fuel. This reaction can be accelerated by adding acid or base catalyst. This catalyst however will not affect the yield gain but it just makes the reaction proceeds more quickly.

Biodiesel also can be blended with fossil fuel for use in the retail diesel fuel marketplace. European Union (EU) has started the usage fuel that has been blended with biodiesel since 2005. This blend fuel can be used to vehicle without modifying the engine. The blend fuel is usually labeled by ‘B’ factor. As example, B20 means there is 20% of biodiesel contain in that fuel and B100 means pure biodiesel. Biodiesel can be produced by esterification or transesterification process.

2.2 Transesterification

Transesterification is the process of exchanging the alkoxy group of an ester compound with another alcohol. These reactions are often catalyzed by the addition of an acid or base. The transesterification reaction will change the chain between alcohol and ester that react. Usually with the presence of triglycerides, transesterification will occur to produce ester and glycerol. Transesterification of triglycerides is shown in Figure 2.1:

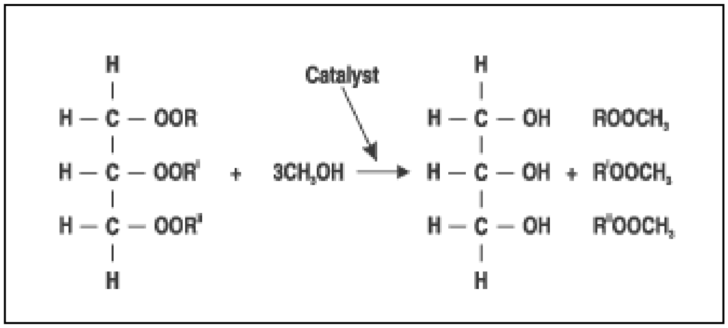

Figure 2.1: Transesterification of triglycerides with methanol to produce 3 molecules of methyl esters and 1 molecule of glycerol.

Transesterification process can be carried out using two methods which are supercritical reaction process and non-catalytic transesterification in bubble column reactor. Vera et al. (2005), has studied the supercritical reaction as shown in Figure 2.2. The term supercritical is used because this reaction has been constructed at temperatures higher than critical temperature of methanol. This reaction used methanol and triglycerides and did not use any of alkaline or acid catalysts. They studied about effect of number of reactor used in the reaction. The findings shows that one-reactor system works with molar ratio methanol: oil=42 and pressure needed is 14-43MPa but when two reactor system is applied, the molar ratio methanol: oil=10 and pressure needed is only 4MPa.

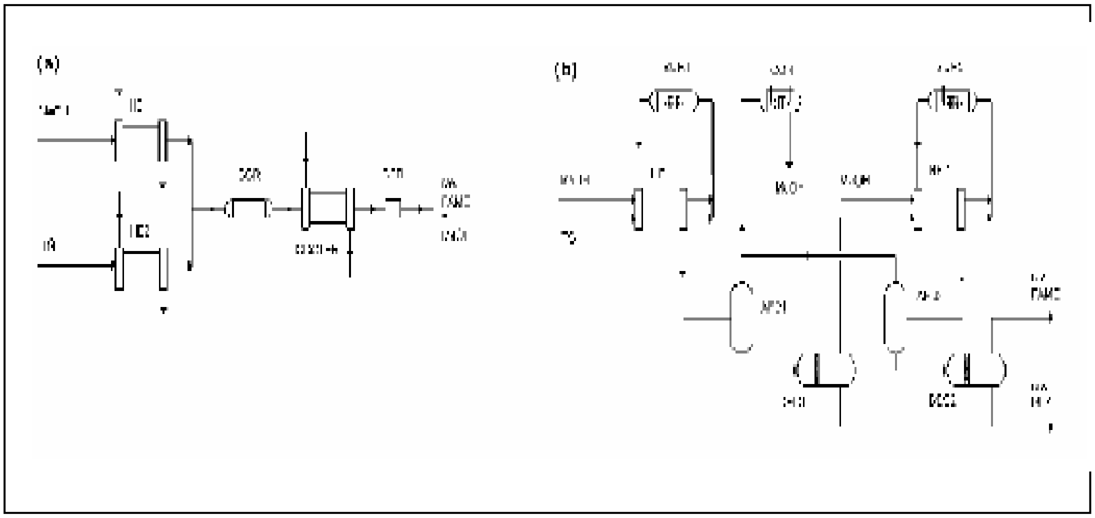

Figure 2.2: Experiment setup for supercritical reaction of transesterification.

Joelianingsih et al. (2007) has studied about non-catalytic transesterification in bubble column reactor. The reactants used are palm oil with superheated methanol. The study has been carried out at 523-563 K reactor temperature under atmospheric pressure. They found out that in the transesterification, the methyl ester content in the reaction product decreased as the reaction temperature was increased. At T=523 K, the methyl ester content is highest which is 95.17% w/w. Figure 2.3 shows the schematic flow diagram of reactor used in non-catalytic transesterification experiment.

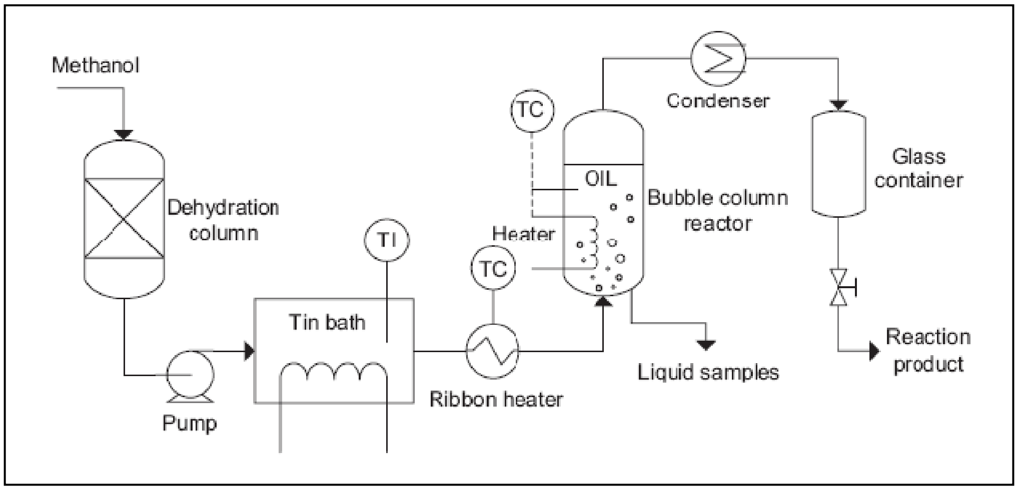

Figure 2.3: Experiment setup for non-catalytic transesterification through bubble column reactor

2.3 Esterification

Esterification process is reaction between acids such as carboxylic acid or free fatty acid with alcohol to produce ester and water. To produce biodiesel fuel, fatty acids will react with short chain alcohol to produce biodiesel fuel and water.

Lopez et al. (2008), has studied about the esterification of free fatty acid with ethanol. The free fatty acid used is caprylic acid and the study is about to determine the effect of three different solid acid catalysts in esterification process. Three different solid acid catalysts that has been used are sulfated zirconia, tungstated zirconia and titania zirconia. The study shows that sulfated zirconia catalyst was found to be the most active for this reaction. However, its activity was not easily regenerated. Compared to titania zirconia, tungstated zirconia has greater activity in esterification and it is easier to regenerate compare to sulfated zirconia by re-calcination in air. Thus, they conclude that tungstated zirconia catalyst is most suitable catalyst in esterification process of free fatty acid. The reaction of esterification is shown in Figure 2.4:

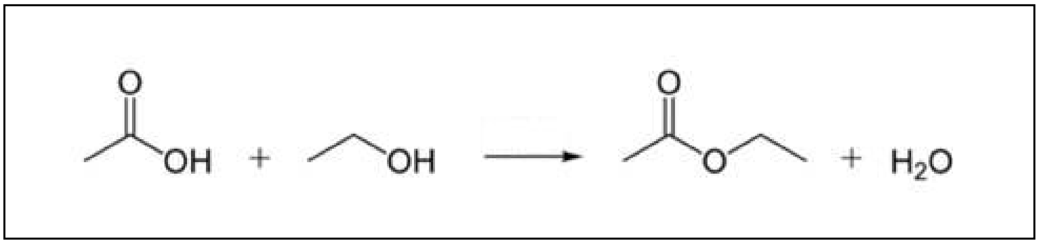

Figure 2.4: Esterification of free fatty acid with ethanol to produce ethyl ester and water.

Esterification can be carried by two methods, which is batch reaction and continuous reaction by using packed bed reactor. In batch reaction, powder-type catalyst is used since it has higher surface area compare to pellet-type catalyst. However, pellet-type is more suitable for packed bed reactor because of the possible loss of catalyst and pressure drop with the powder-type catalyst. The continuous reaction has advantage in mass production; however the conversion of FFA is might be lower than batch reaction.

Thus, the optimization of pellet-size catalyst is very important in order to maximize the activity of catalyst and make the conversion of FFA to be exact with batch reaction. (Park et al., 2008).

Figure 2.5 shows the experimental setup for batch reactor made by Ni and Meunier (2007). Batch reactor needs to be fixed in operation time to analyze the sample and to observe the difference in conversion when the operation conditions are vary. However, in order to produce biodiesel fuel in a large amount, batch reaction is not very suitable because it takes longer time period and space area used is relatively high compared to continuous reaction process.

Figure 2.6 shows the packed bed reactor for continuous production of biodiesel made by Park et. al (2008). Packed bed reactor is suitable for the industrial production of biodiesel to produce a very large amount to fulfill consumer demand.

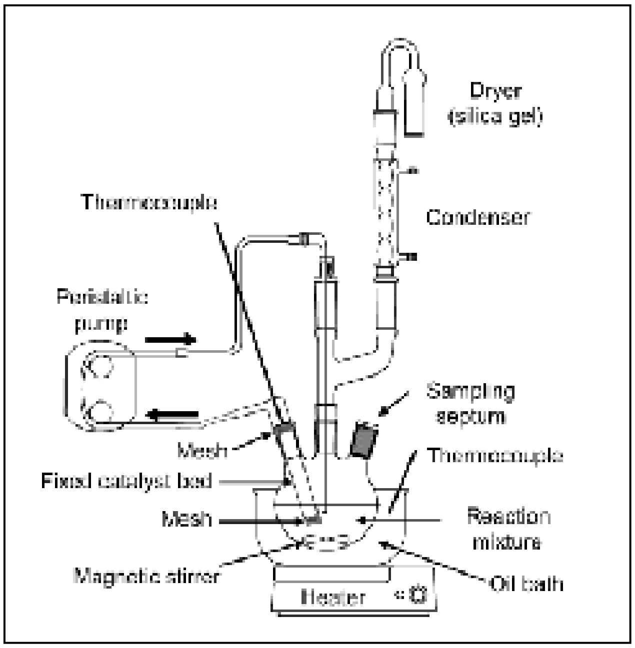

Figure 2.5: Schematic layout of the reactor system used for the experiments involving the recirculation of the reaction mixture through a fixed catalytic bed.

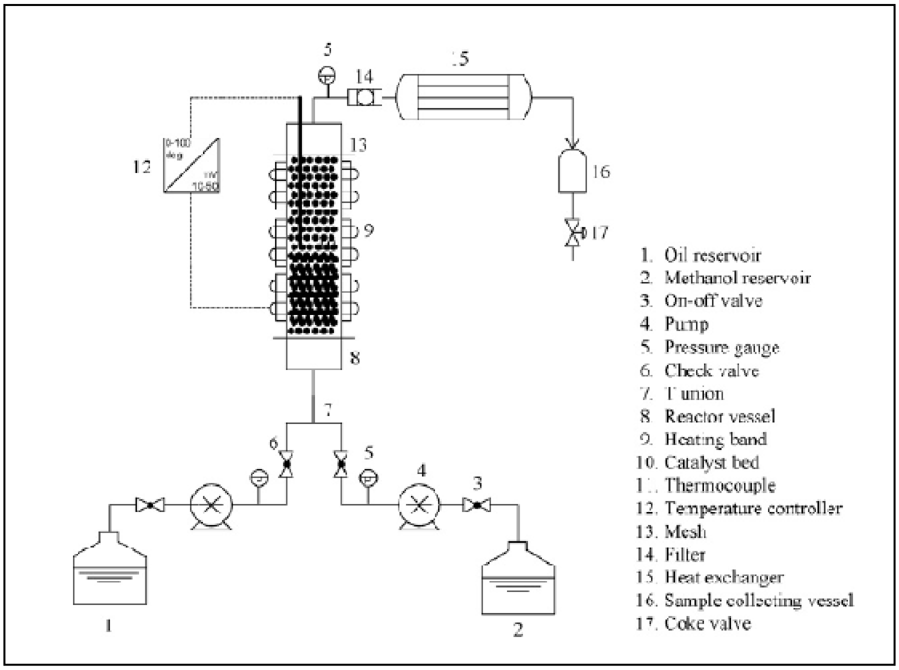

Figure 2.6: Schematic layout of the packed bed reactor for the continuous production of biodiesel.

2.4 Homogeneous Catalytic Esterification

Esterification of free fatty acid can be homogeneously or heterogeneously catalyzed. Marchetti and Errazu (2008) used homogeneous catalyst for the reaction of oleic acid with methanol. This study was carried out in the presence of triglycerides which is sunflower oil. The catalyst used is sulfuric acid (H_2SO_4). This study is about to determine the conversion of FFA when temperature, amount of alcohol, amount of catalyst and amount of initial FFA used are vary. The amount of catalyst used only affect the time of conversion. However, the final conversion is still the same between different amounts of catalyst used. When molar ratio was varied, the amount of alcohol affects the reaction. When the amount of alcohol is higher, the rate of reaction became slower but it reaches higher conversion of FFA. This reaction however, is hard to separate the catalyst from the product since it is miscible in the product. It has affected the yield gain and the purity of the product will become lower.

2.5 Heterogeneous Catalytic Esterification

Heterogeneous catalytic esterification is esterification which is using solid catalyst and the catalyst is not miscible in the reaction mixture. Park et al. (2008) studied the effect of various types of solid acid catalysts on the biodiesel production by varying the heterogeneous catalyst in the reaction. The solid catalysts used in the experiment are sulfated zirconia (SO_4^{2-}/ZrO_2), SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2, H-zeolite, Cs-heteropoly acid and tungstated zirconia(WO_3/ZrO_2). The finding shows that in biodiesel production, sulfated zirconia and tungstated zirconia are the suitable solid acid catalysts. However, sulfated zirconia is not selected because of the potential loss of SO_4^{2-} in its liquid phase application. Tungstated zirconia is the most suitable solid acid catalyst because it can be used for the long reaction. The result showed that 65% conversion could be maintained for up to 140 hours. Besides, the activity of this catalyst is easily regenerated through a simple air-calcination. The calcinations of tungstated zirconia is carried out by heat it in oven at 130°C for one hour, cooled to room temperature then the heating process continue at 800°C for one hour in furnace (Furuta et al. 2006)

Table 2.1 shows the past studies of biodiesel production via esterification and transesterification process using homogeneous and heterogeneous catalyst.

Table 2.1: Summary of esterification and transesterification process from previous studies.

Reaction	Catalyst	Findings	Author
Transesterification of soybean oil with methanol and esterification of n-octanoic acid with methanol	Titanium-, aluminium-, and potassium-doped zirconia	Titanium- and aluminium-doped zirconias are promising solid acid catalysts for both reaction	Furuta et. al. (2005)
Transesterification of used vegetable oils with methanol	H-zeolite, SO_4^{2-}/ZrO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2 and WO_3/ZrO_2	Tungstated zirconia, WO_3/ZrO_2 is the most suitable due to its high activity and stability	Y.-M. Park et al. (2008)
Esterification of oleic acid with refined sunflower oil with ethanol when operating condition varies	Sulfuric acid (H_2SO_4)	Rate of reaction increases when amount of catalyst and temperature increase. Conversion increases when amount of FFA and alcohol increase	Marchetti and Errazu (2008)
Esterification of oleic acid with methanol in the presence of triglycerides, kinetic studies	Ion-exchange sulfonic resin	Pseudohomogeneous second-order model have been determined by nonlinear regression	Tesser et al. (2005)
Esterification of a decanoic acid with methanol by reactive distillation	Amberlyst 15	Pseudohomogeneous kinetic model is not able to describe the experimental results and Langmuir – Hinshelwood – Hougen – Watson (LHHW) is derived.	Steinigeweg and Gmehling (2003)
Esterification of palmitic acid with methanol in sunflower oil using batch and fixed bed reactor	SAC-13 (Nafion/SiO_2), SAC-13 and sulfated zirconia	SAC-13 appeared as most promising catalyst	Ni and Meunier (2007)
Esterification of dodecanoic acid with 2-ethylhexanol by reactive distillation	Sulfated zirconia	Sulfated zirconia is suitable for the synthesis of 2-ethylhexyl dodecanoate by reactive distillation	Omota et al (2003)

Esterification and transesterification using modified-zirconia catalysts	Titania zirconia, sulfated zirconia and tungstated zirconia	Tungstated zirconia was found to be the most suitable for carrying as it is more active than TiZ and can be more easily regenerated than SZ	Lopez et al. (2008)
Esterification of acetic acid with butanol	Sulfuric acid, p-toluenesulfuric acid and a heteropolyacid (homogeneous) Smopex-101, Amberlyst 15, sulfated zirconia (heterogeneous)	Solid acid catalysis is very effective from the viewpoint of activity and reusability compared with homogeneous catalysts	Peters et al. (2006)
Heterogeneous catalysed esterification of acetic acid with isoamyl alcohol: kinetic studies	Purolite CT-175	Equilibrium conversion increase slightly with an increase temperature and isoamyl alcohol amount. LHHW model gave a better representation of the kinetic behavior for all practical purposes on the reaction kinetics study.	Teo and Saha (2004)
Esterification of FFA in sunflower oil with methanol	Sulfuric acid	Free fatty acids (FFA) in sunflower oil can be effectively removed by esterification with methanol, using a 5% sulphuric acid concentration relative to FFA, a methanol/oleic acid mole ratio of 60:1, a temperature of 60 _C and agitation at a speed of 250 rpm or higher.	Berrios et al. (2007)
Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids	Methanesulfonic and sulfuric acid	Small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst.	Aranda et al. (2007)

2.6 Kinetic Modeling

Kinetic modeling also plays an important part in esterification of free fatty acid to produce biodiesel. Biodiesel fuels need to produce it in large scale, in a short time, and lower in cost. To achieve this objective, the reactor is very important to be made. This reactor with high efficiency can be made if the kinetic modeling is developed. Steinigeweg and Gmehling (2003) have developed the pseudohomogeneous and Langmuir-Hinshelwood-Hougen-Watson (LHHW) model for the esterification of decanoic acid with methanol by reactive distillation by using Amberlyst 15. The models that have been studied are pseudohomogeneous and Langmuir-Hinshelwood-Hougen-Watson (LHHW) as shown in equation 2.1 and 2.2, respectively:

$$r = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = k_1 a_{DecH} a_{MeOH} - k_{-1} a_{MeDec} a_{H_2O} \tag{2.1}$$

$$r = \frac{1}{v_i} \frac{dn_i}{dt} = m_{cat}\, x\, (\frac{k_1 K_{DecH} a_{DecH} K_{MeOH} a_{MeOH} - k_{-1} K_{MeDec} a_{MeDec} K_{H2O} a_{H2O}}{1 + (K_{DecH} a_{DecH} + K_{MeOH} a_{MeOH} + K_{MeDec} a_{MeDec} + K_{H2O} a_{H2O})^2}) \tag{2.2}$$

Where:

m_{cat}=mass of catalyst

a_{DecH}=mole fraction of decanoic acid

a_{MeOH}=mole fraction of methanol

a_{MeDec}=mole fraction of methyl decanoate

a_{H2O}=mole fraction of water

Steinigeweg and Gmehling have found out that LHHW model is suitable for the study because pseudohomogeneous kinetic model is not able to describe the experimental results.

Tesser et al. (2005) then have carried the kinetic study of oleic acid esterification with methanol in the presence of triglycerides. The catalyst used is acid sulfonic resin.

They have found out that pseudohomogeneous second-order equilibrium model is suitable for the study.

$$r = k_c x_A x_M \left(1 - \frac{1}{k_e} \frac{x_E x_W}{x_A x_M}\right) C_{cat} \qquad (2.3)$$

Where:

x_m = molar fraction of methanol

x_a = molar fraction of oleic acid

CHAPTER 3

METHODOLOGY

3.1 Introduction

The method used to perform the esterification process is in batch mode. This method is used since it is the most easy method to prepare and to analyze. Materials used are non-toxic and not very dangerous except ethanol which is highly flammable. Several precaution steps are taken such as do the research away from ignition source, do not start the flame and used the condenser to prevent ethanol vaporise freely to the surrounding.

Catalyst used, tungstated zirconia need to prepare by preheating it at 130°C in an oven for 1 hour and then put into the furnace to be calcined at 800°C. Tungstated zirconia exhibited an optimum calcination temperature of 800°C based on research by Lopez et al. (2008).

The experimental studies are divided into 2 sections which are reaction studies and sample analysis. Reaction studies include the mixing of reactants in the batch reactor until samples at desired time are collected. Sample analysis is the step when the sample is analyzed by titration and results are taken.

3.2 Experimental Setup

Figure 3.1 and Figure 3.2 shows the experimental setup for esterification batch process and sample analysis, respectively and Table 3.1 listed the experimental apparatus and their functions. The illustrations of experimental setup can be referred to Appendix A.

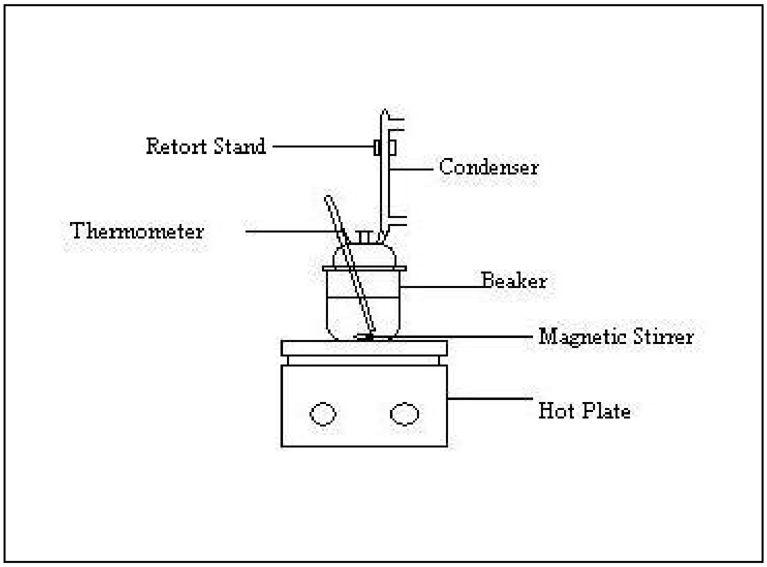

Figure 3.1: Experimental setup for reaction studies

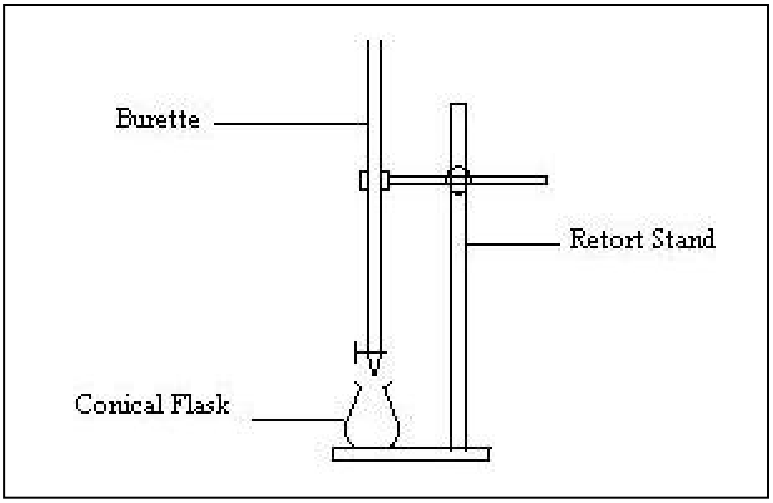

Figure 3.2: Setup for sample analysis

Table 3.1: Research apparatus and their functions

Apparatus	Function
Reactor	Place where the reaction taking place
Hot Plate	Supply heat to desired temperature for the reactor
Thermometer	Read the temperature inside the reactor
Condenser	Condense the distillate
Magnetic stirrer	Stir the reaction mixture
Retort Stand	Hold condenser and burette
Burette	Measure NaOH used in titration process
Conical Flask	Place for sample in titration process

3.3 Experimental Procedures

Esterification process needs to be done by following the right steps in order to optimize the efficiency and to avoid error that may occur. Figure 3.3 shows the summary of experimental methodology for the process.

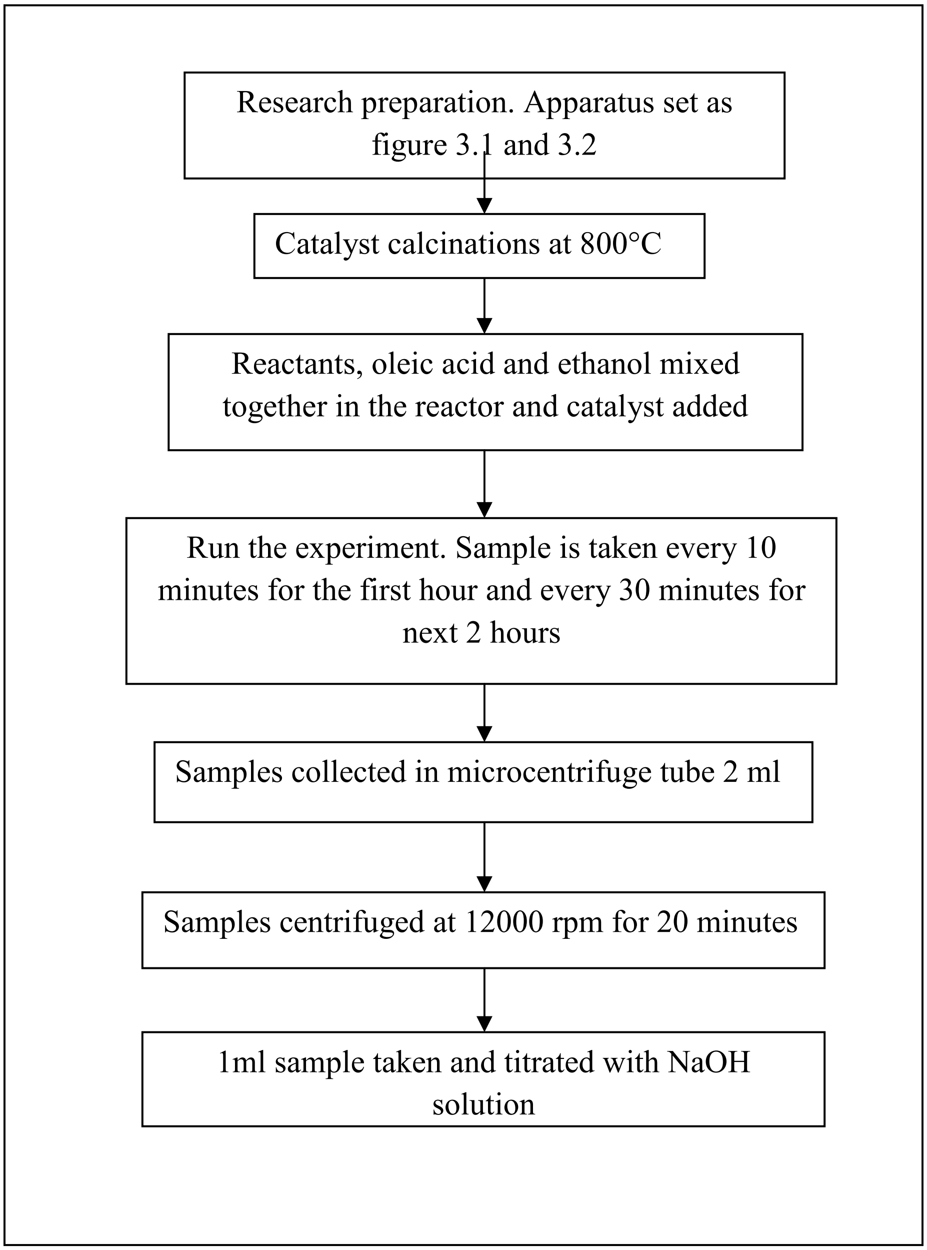

Figure 3.3: Summary of experimental methodology

3.3.1 Esterification of Oleic Acid

Material and chemical used is shown in Table 3.2:

Table 3.2: List of equipments and chemicals for reaction.

Equipment/Chemical	Functions
Beaker 500 ml	Base of reactor. Place where reaction takes place
Head of reaction flask	Top of the reactor. Necks used to put condenser and thermometer
Parafilm	Use to attach top and bottom parts of the reactor
Aluminium foil	
Hot plate	Supply heat to the reactor
Condenser	Condense the sample from being released to atmosphere
Stopper	Shut the neck of reaction flask head
Thermometer	Read the temperature inside the reactor
Oleic acid	Reactants of the process
Ethanol	
Tungstated Zirconia	Catalyst

PROCEDURE:

Beaker 500 ml is connected with head of reaction flask by using parafilm and then sealed with aluminium foil tightly in order to prevent leaking of reactant. Oleic acid and ethanol as the reactants are mixed together in the beaker. Tungstated zirconia catalyst added and magnetic stirrer also put in the reactor. 3 necks of reaction flask head then shut by using stopper and the other 2 are connected to thermometer and condenser.

Reactants heated to desired temperature and stirred slowly. When the temperature achieved, reaction time is started. For the first hour, 2 ml of samples are taken and filled into microcentrifuge tubes by using pipette every 10 minutes and for the next 2 hours samples taken every 30 minutes. Samples then placed into beaker filled with ice in order to reduce the temperature to stop the reaction. This step also can avoid error that may occur by leaving the samples at room temperature as it may react and the conversion will be increased.

After 3 hours of reaction, 11 samples are collected and centrifuged by using microcentrifuge to separate solid catalyst and the sample. Sample is centrifuged for 20 minutes at 12000 rpm. After centrifuge process, sample is crystal clear and the solid catalyst is at the bottom of the tube as shown in Figure 3.4.

The reaction is divided into 2 phase which is without triglycerides and by adding triglycerides. Purpose of adding triglycerides is to study about effect when transesterification and esterification happen at the same time in the reactor. Cooking oil acts as triglycerides is simply added into the reaction when the operating condition that reaches maximum value of conversion in esterification reaction obtained. Triglycerides added at 10 ml, 30 ml and 50 ml.

Figure 3.4: Sample after the centrifugal process

3.3.2 Analysis of Sample

Material and chemical used is shown in Table 3.3:

Table 3.3: List of equipments and chemicals for analysis.

Equipment/Chemical	Functions
Retort stand	Hold a vertical burette for titration
Burette	Place for NaOH solution and to control the NaOH drops
Conical flask	Sample placed in it and color change observed
NaOH	Used to neutralize the sample
Ethanol	To dilute the sample
Phenolphtalein solution	As indicator for color change occur

PROCEDURE:

1 ml of sample from the esterification reaction is taken and filled into a conical flask. The sample is taken carefully to avoid from catalyst that may affect the titration because of the acidity of catalyst.

Sample in the conical flask mixed with 10 ml of ethanol in order to dilute the sample. Sample is shaken firmly until sample and ethanol are homogeneous. 3 drops of phenolphthalein indicator added into the mixture.

Sodium hydroxide solution 0.05M filled into the burette and holds it by using retort stand. Titration begins by letting the NaOH solution drops into the conical flask filled with sample. Along the titration process conical flask is shake slowly.

Titration stops when the color of sample changed to light pink and the volume of NaOH used recorded into log book.

3.3.3 Development of Kinetic Modeling

Software used shown in Table 3.4

Table 3.4: List of software used in kinetic modeling development

Software	**Function**
Microsoft Excel	Made all the table
Polymath	Solve the regression for kinetic model development

PROCEDURE:

Data collected in a table of two column which have time and volume of Sodium Hydroxide (NaOH) used until the color of solution changed from clear to light pink. From volume of NaOH used, acid value can be determined by using equation from Park et. al. (2008) as shown below:

$$\text{Acid Value} = (M \times A \times F \times N)/S \qquad (3.1)$$

Where:

M = Molecular weight of NaOH
A = amount of NaOH standard solution used in titration
F = concentration coefficient of NaOH standard solution
N = normal concentration of NaOH standard solution
S = sample weight
From value of acid value, conversion can be determined by:

$$\text{Conversion (\%)} = [(\text{initial acid value} - \text{final acid value})/(\text{initial acid value})] \times 100\% \qquad (3.2)$$

The details of conversion obtained can be seen in Appendix C. From value of conversions obtained, the concentration at certain period can be determined by equation:

$$C_A = C_{Ao}(1 - X) \qquad (3.3)$$

Where:

C_{Ao} = initial concentration of oleic acid
C_A = concentration of oleic acid at certain period
X = conversion

Graph of concentration of oleic acid need to be constructed to determine rate law, r_A. For batch reactor, rate law is:

$$r_A = \frac{dCa}{dt}$$

From the equation, r_A is the gradient of slope in C_A versus time (t) graph.

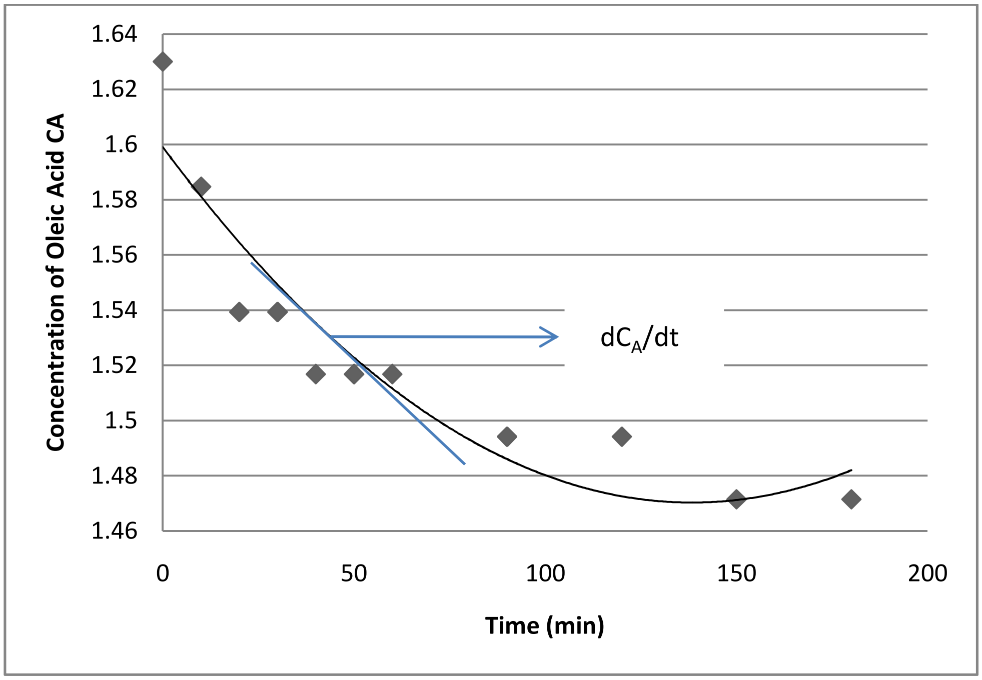

Figure 3.5: Determination of reaction rate value, r_A at desired time

After all r_A are known, all data are put into Polymath software to do mathematical regression.

Reaction of Oleic Acid + Ethanol $\rightleftarrows$ Ethyl Ester + Water can be simplified as:

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

Rate law can be solved by using pseudohomogeneous model:

$$-r_A = k' C_A C_B - k'' C_C C_D \qquad (3.4)$$

From Arrhenius equation in Fogler (2006),

Rate constant, $k = A \exp(-E/RT)$

Where:

A = pre-exponential factor
E = activation energy, J/mol or cal/mol
R = gas constant = 8.314 J/mol·K = 1.987 cal/mol·K
T = absolute temperature, K

Deriving the equation, $\ln k = \ln A - (E/RT)$ (3.5)

By plotting the graph of ln k versus 1/T, pre-exponential factor, A is the y-interception and activation energy is the gradient of the slope multiply by gas constant.

CHAPTER 4

RESULT AND DISCUSSION

From previous study carried by Marchetti and Errazu, (2008), four types of parameter are studied to determine the effect to esterification reaction which is amount of catalyst, temperature, amount of alcohol and amount of free fatty acid. In this research, these parameters are applied to obtain the maximum conversion of oleic acid.

4.1 Effect of Catalyst Amount

First parameter studied is amount of catalyst. Three experiments ran by using three amount of catalyst and the conversions have been determined. The other three parameters fixed as shown in Table 4.1:

Table 4.1: Operating condition for catalyst effect

Parameter	Condition
Temperature	40°C
Reactants molar ratio	5:1
Presence of triglycerides	No

Figure 4.1 shows the effect of amount catalyst of 0.5 g to the esterification process while Figure 4.2 and 4.3 shows effect of 1 g and 1.5 g of catalyst, respectively. The highest conversion is at 150th and 180th minutes where the conversion recorded is 9.72% for the amount of catalyst of 0.5 g, 15.28% for the amount of catalyst of 1 g and 20.99% for the amount of catalyst of 1.5 g.

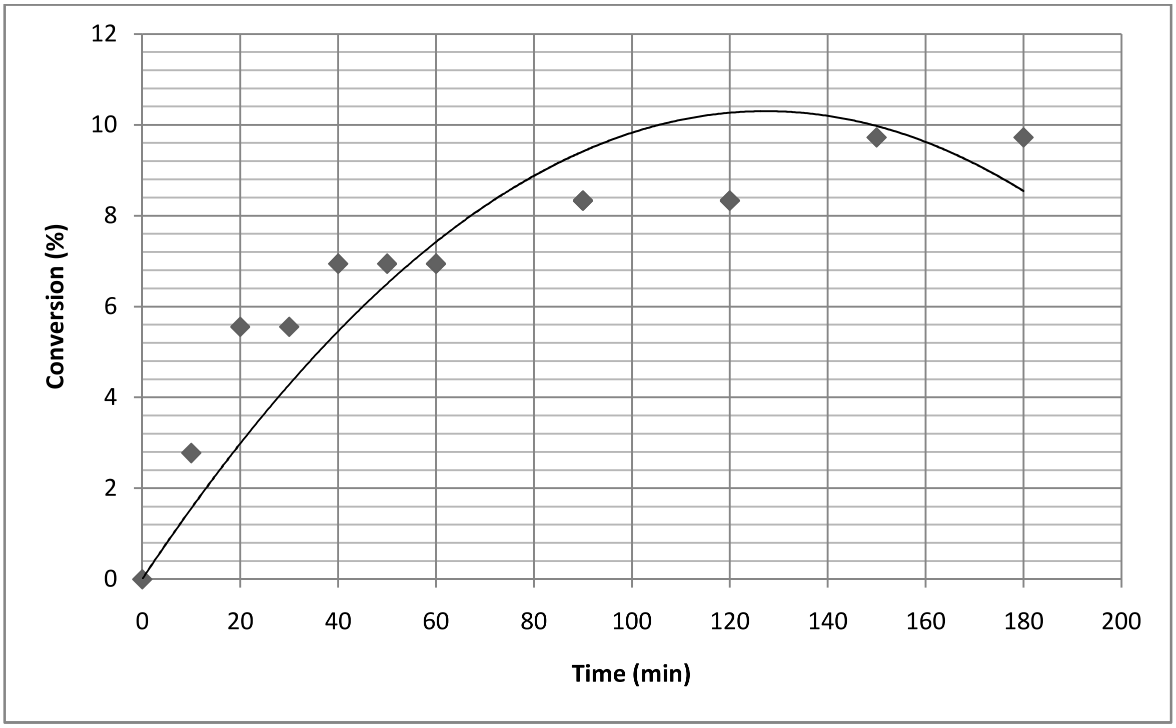

Figure 4.1: Effect of amount catalyst = 0.5 g to conversion of oleic acid.

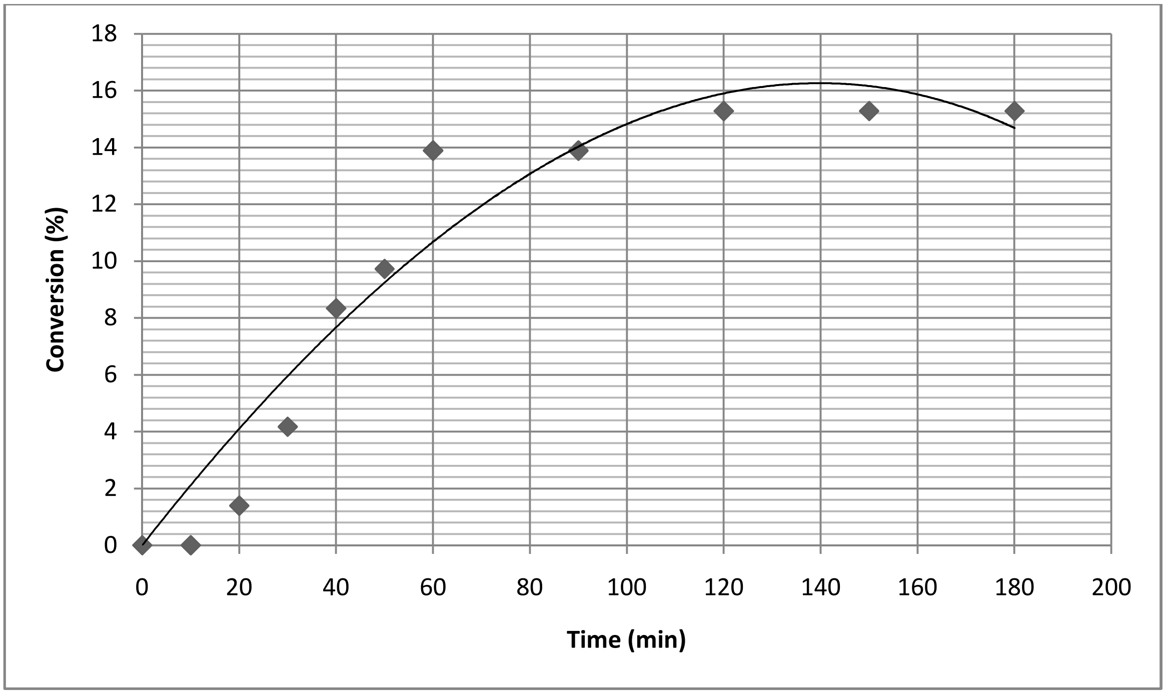

Figure 4.2: Effect of amount catalyst = 1.0 g to conversion of oleic acid

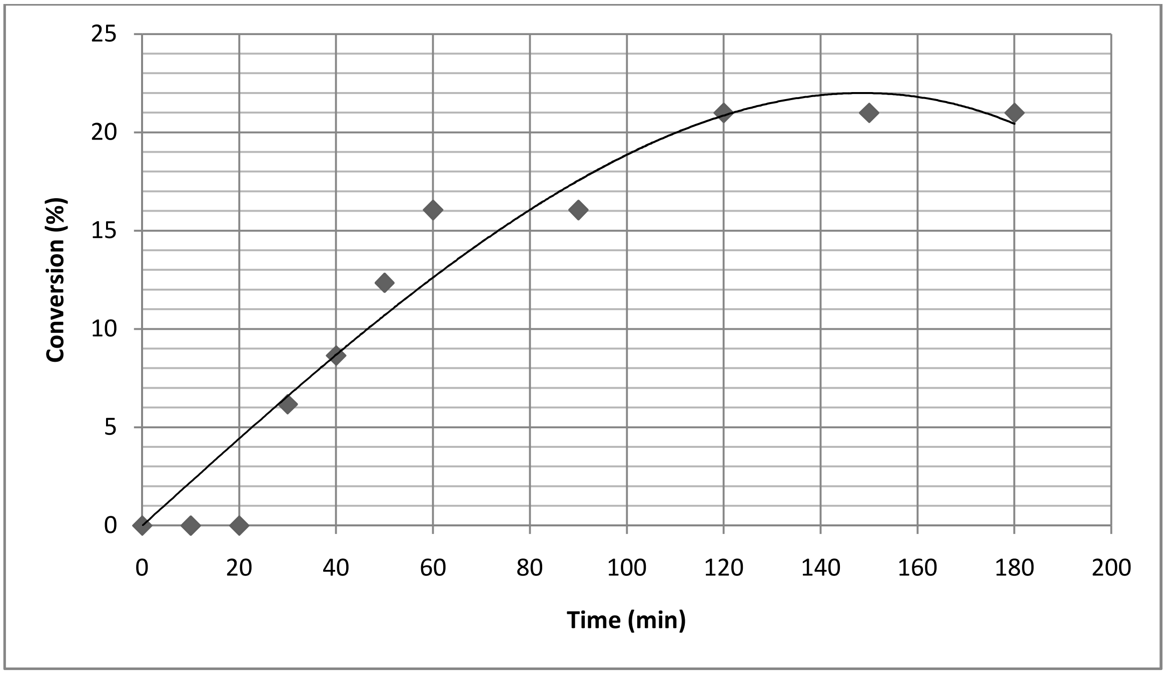

Figure 4.3: Effect of amount catalyst = 1.5 g to conversion of oleic acid

Figure 4.4 shows the effect of different amount of catalyst to the reaction conversion. As the amount of catalyst increases, the rate of reaction increases. In order to make reaction occurs, activation energy need to achieve. Activation energy, E_a is the energy difference between the reactants and the transition state. It is the energy barrier that must be exceeded for reactants to be converted to products.

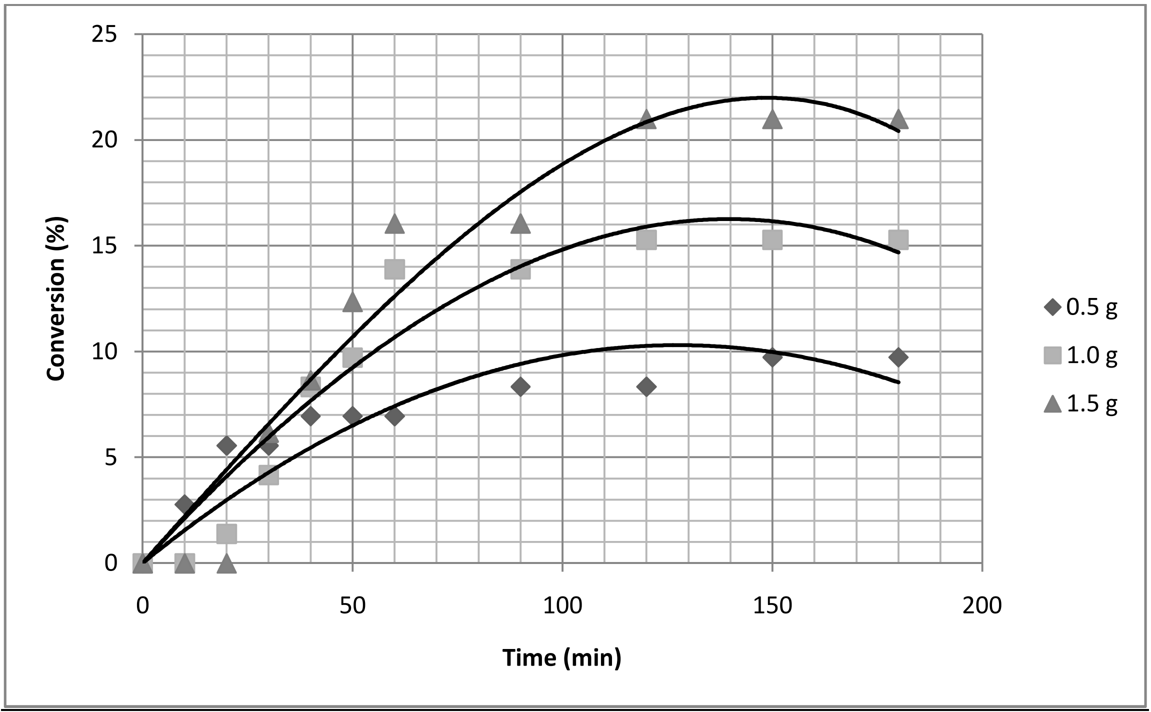

Figure 4.4: Effect of different amounts of tungstated zirconia as catalyst.

Figure 4.5 shows the energy of reaction need to exceed the activation energy in order to have product from the reaction. The catalyst provides an alternative route for the reaction with lower activation energy, so the rate of reaction will be increased. However, when the reaction is over, mass of catalyst is still the same with the mass before reaction starts and amount of product produced from reaction is same with or without catalyst presence. From here it is proven that catalyst not disturbing the stoichiometry for both reactant and product.

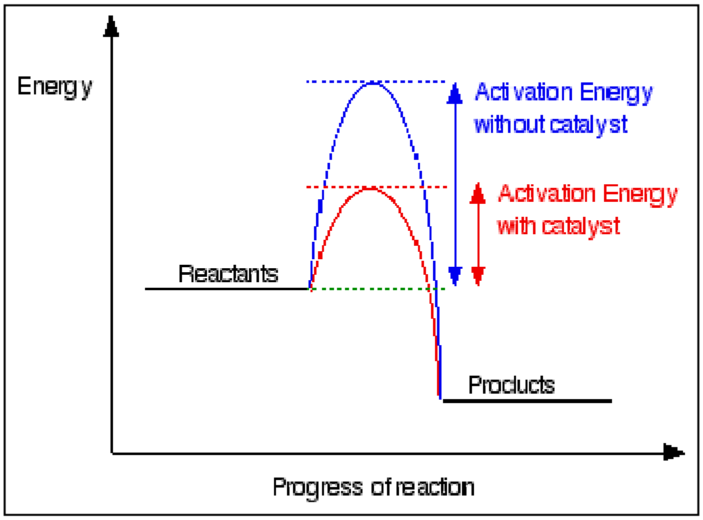

Figure 4.5: The relation of activation energy and progress of reaction

The catalyst function is to increase the rate of reaction by providing active site for reaction to occur. When the amount of catalyst increases, number of active site also increases and the rate of reaction also will be increase. Marchetti and Errazu, (2008) and Omota et. al. (2003) showed the identical results in their study.

Thus, mass of catalyst of 1.5g is fixed for the studies of the effect of temperature, reactant ratio and presence of triglycerides.

4.2 Effect of Temperature

From previous run, amount of catalyst at 1.5 g is selected to be fixed during the studies for the next parameter. The experiments are performed at 30°C, 40°C and 50°C and the conversions are determined. For this parameter, at temperature 40°C has been studied from previous run and need only to run for 30°C and 50°C.

Three other parameters fixed as shown in Table 4.2:

Table 4.2: Operating condition for temperature effect

Parameter	Condition
Mass of catalyst	1.5 g
Reactants molar ratio	5:1
Presence of triglycerides	No

Figure 4.6 shows the effect of temperature of 30°C while Figure 4.7 shows the effect of temperature 50°C to the esterification process. The oleic acid conversion under 1.5 g of catalyst and 40°C shows identical results as in Figure 4.3. Figure 4.6 showed activities giving 12.72% yield while in Figure 4.7 maximum yield recorded is 24.24%.

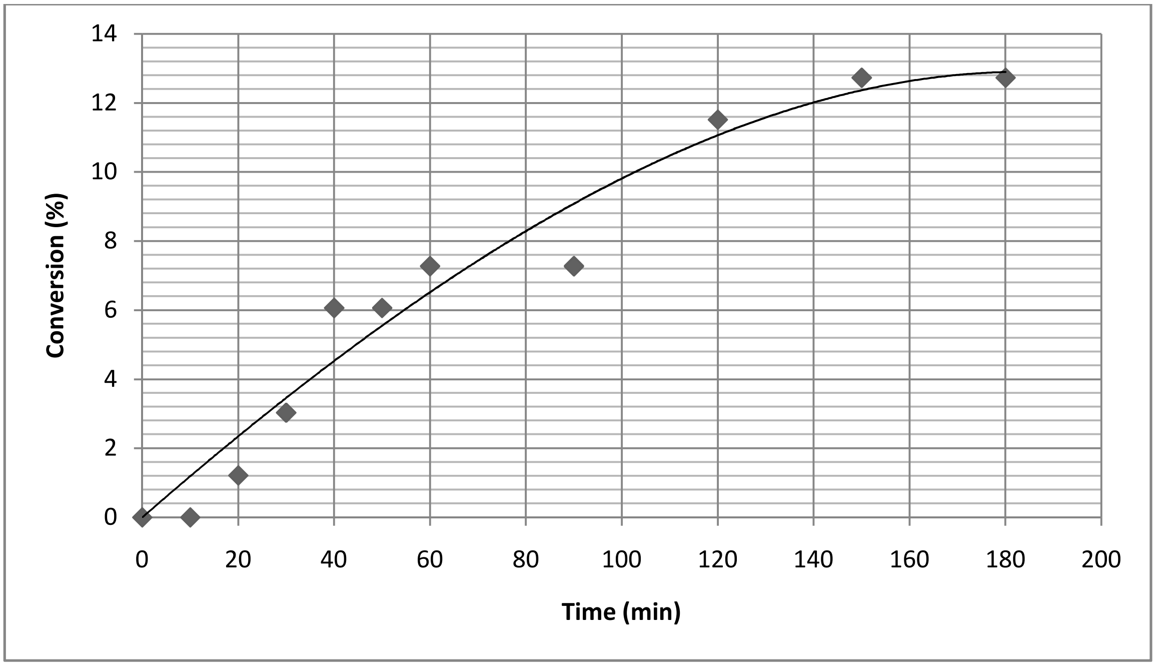

Figure 4.6: Effect of temperature = 30°C to conversion of oleic acid.

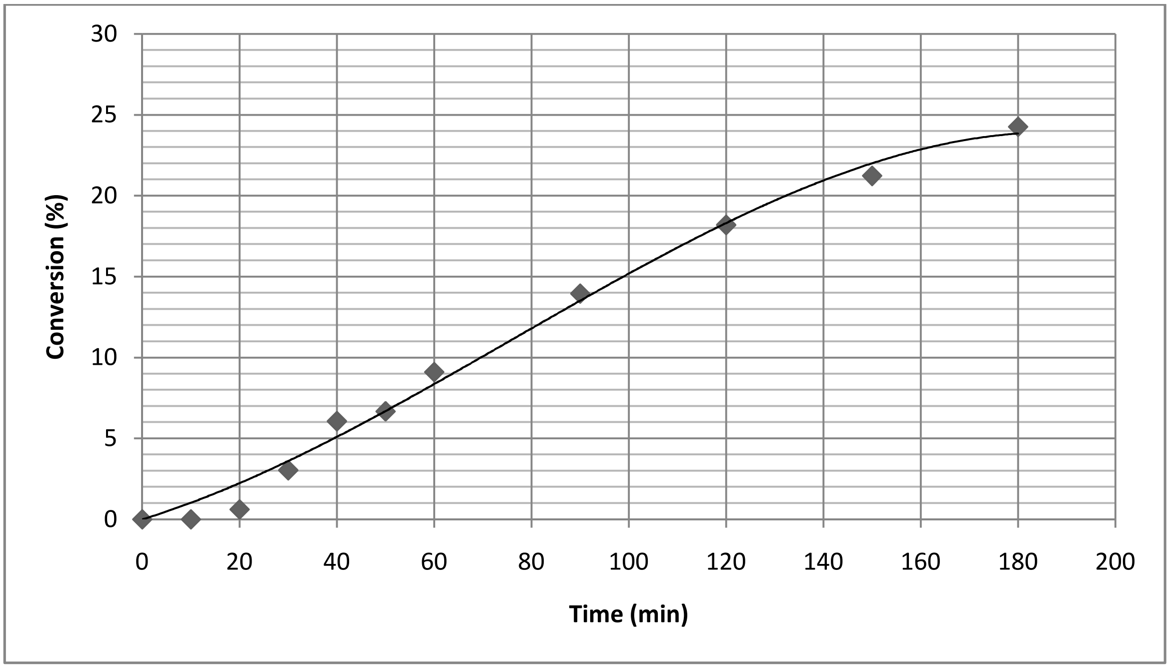

Figure 4.7: Effect of temperature = 50°C to conversion of oleic acid

Figure 4.8 shows the difference of rate of reaction for three different operating temperatures. The reaction operates at 30°C gives the lowest conversion, while 50°C gives the highest conversion.

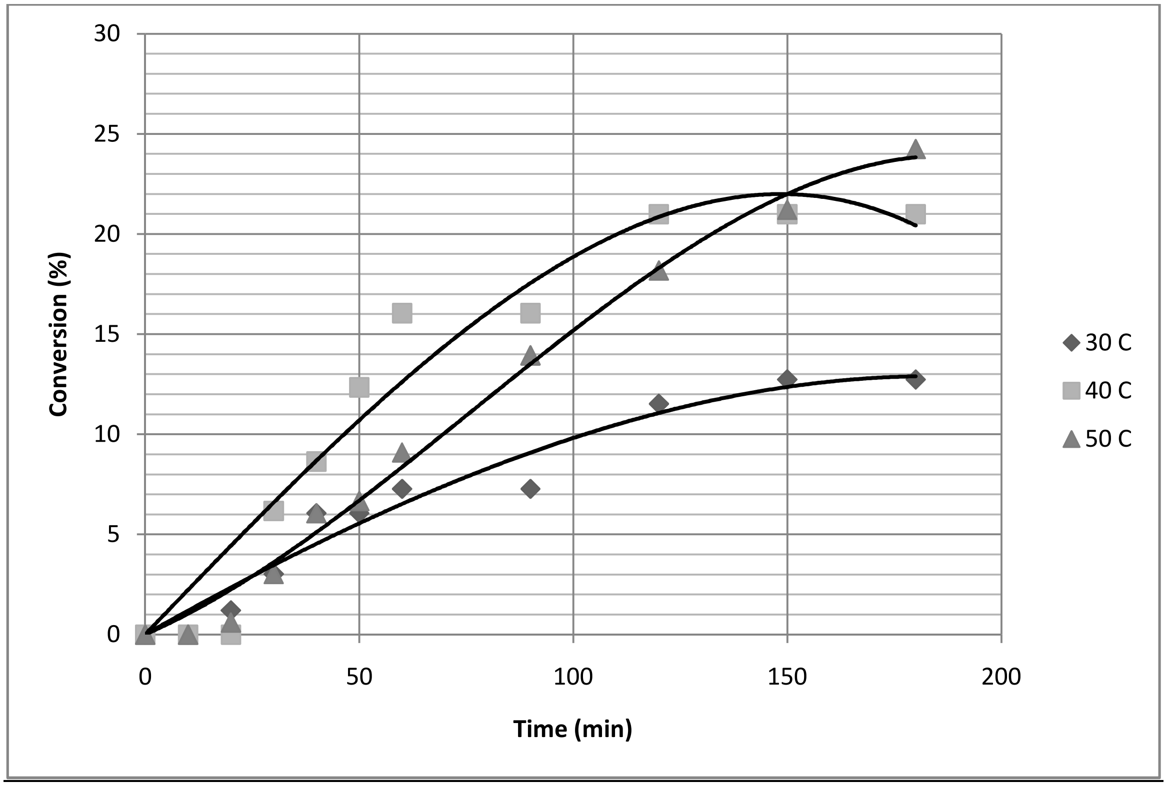

Figure 4.8: Effect of different reaction temperatures

The variations in temperature showed that the reaction displayed typical endothermic behavior since the activities need heat in order to increase rate of reaction and conversion of oleic acid.

Rate constant, k plays major part in determining the rate of reaction since k is proportional to rate of reaction as shown in equation below:

$$r = k(C_A C_B - (C_C C_D/K)) \quad (4.1)$$

where A and B are the reactants and K is equilibrium constant.

From Arrhenius equation:

$$k=A*\exp^{(-E/R*T)}$$

where:

k = rate constant
A = pre-exponential factor or frequency factor
E = activation energy
R = gas constant
T = absolute temperature

k is proportional to temperature. It is proven that when temperature of reactor is increases, k value increases and rate of reaction, r is also increases.

Thus, temperature of 50°C is fixed for the next experimental run.

4.3 Effect of Molar Ratio

From previous runs, amount of catalyst at 1.5 g and 50°C are selected. The molar ratio of ethanol to oleic acid is studied and experiments run at 1:1, 3:1 and 5:1 and the conversions are determined subsequently. The calculations for the volume of reactants used are stated in Appendix B.

Three other parameters fixed as shown Table 4.3:

Table 4.3: Operating condition for molar ratio effect

Parameter	**Condition**
Mass of catalyst	1.5 g
Temperature	50°C
Presence of triglycerides	No

Figure 4.9 shows effect of reactants molar ratio of 1:1. The activity giving 5.578% yield after 3 hours runs at 180th minutes. Figure 4.10 shows maximum conversion is 9.64% at 150th minutes. For molar ratio of 5:1, Figure 4.7 shows the identical results.

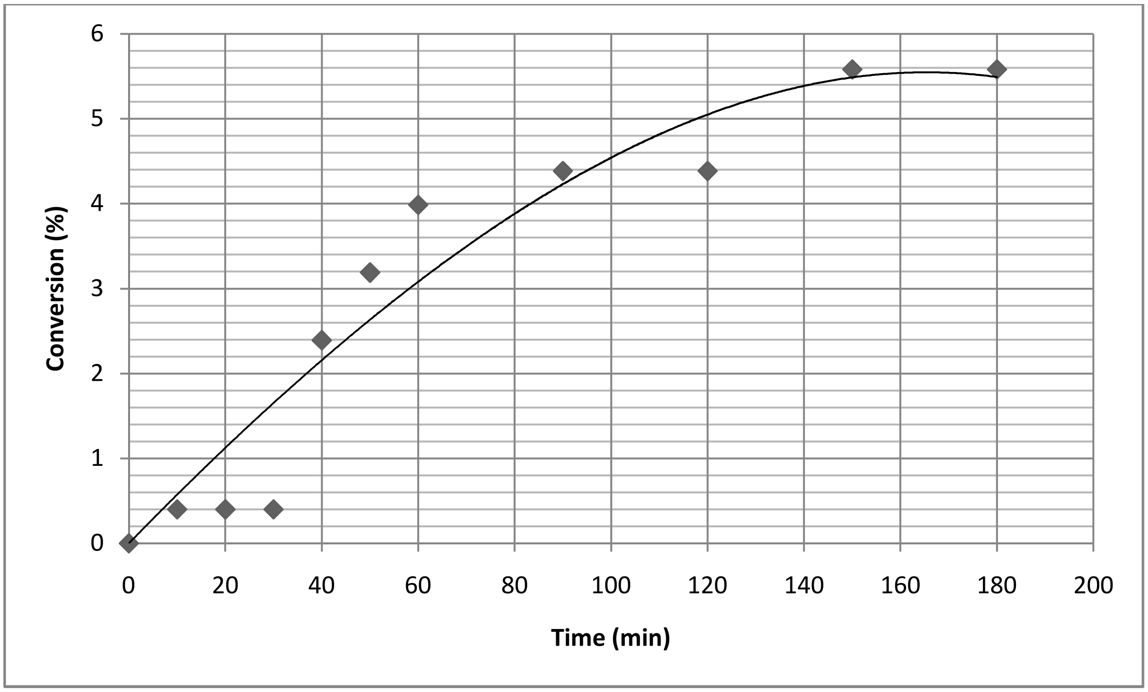

Figure 4.9: Effect of molar ratio 1:1 to conversion of oleic acid

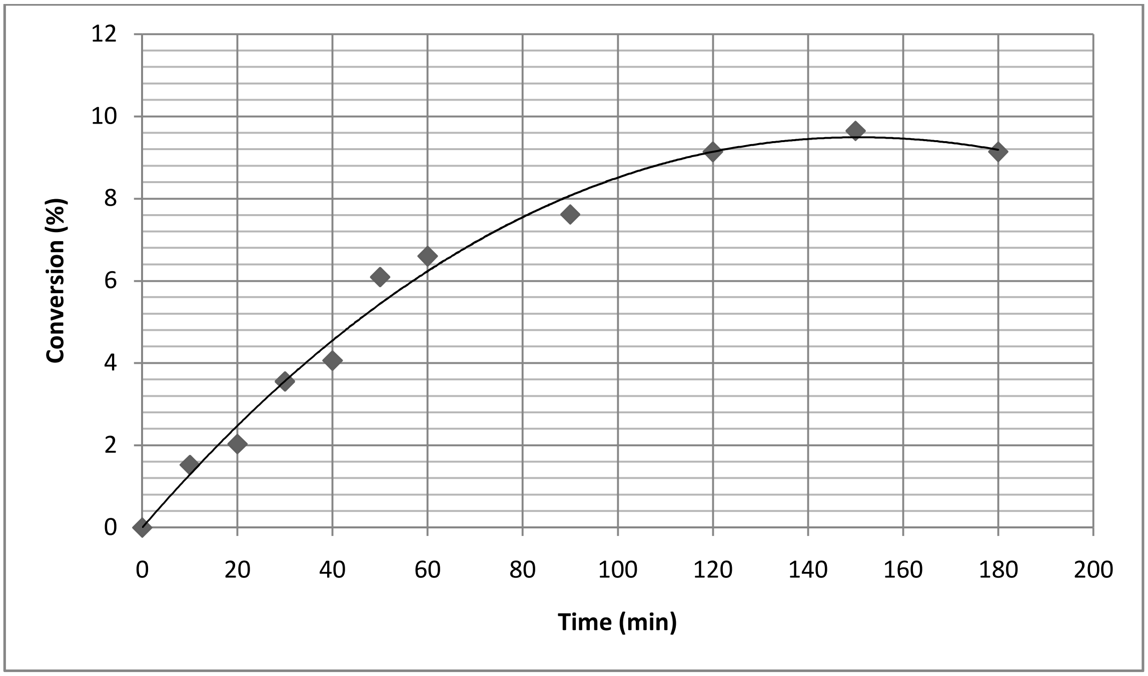

Figure 4.10: Effect of molar ratio 3:1 to conversion of oleic acid

Figure 4-11 shows the curves for molar ratio ethanol to oleic acid of 1:1, 3:1 and 5:1. Molar ratio 5:1 shows the highest value of conversion which is 24.24%.

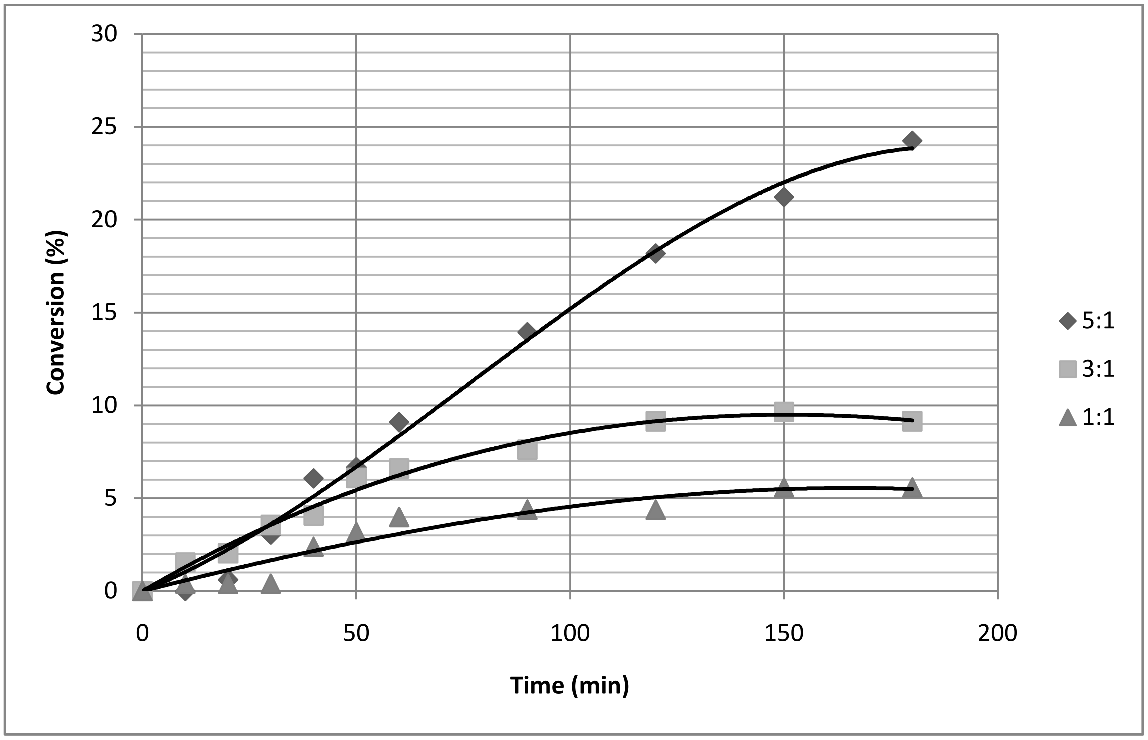

Figure 4.11: Effect of different molar ratio ethanol to oleic acid

From the stoichiometry equation, 1 mol ethanol reacts with 1 mol of oleic. However there is much difference in both volumes. 1 mol ethanol is equal to 60 mL while 1 mol of oleic acid is equal to 315 mL. Thus, by adding the ethanol in excess, the conversion and rate of reaction can be increased due to higher surface area contact and bigger momentum of atom reacted.

Thus, molar ratio ethanol to oleic acid that has to be fixed is 5:1 for the next run.

4.4 Effect by Additional of Triglycerides.

Three conditions that show the highest value in conversion have been determined. The next parameter is to study about the effect in conversion when triglycerides are added into the reactor.

Cooking oil acts as triglycerides source since the presence of triglycerides in composition of cooking oil. Cooking oil used is palm cooking oil. Amounts of triglycerides in the range of 10-50 ml are studied and the conversion versus time is recorded.

Three other parameters fixed are shown in Table 4.4:

Table 4.4: Operating condition for additional triglycerides

Parameter	**Condition**
Mass of catalyst	1.5 g
Temperature	50°C
Reactants molar ratio	5:1

Cooking oil is simply added and mixed together in the reactor. Figure 4.12 shows effect in conversion when 10 ml of triglycerides added into the reaction. It shows the highest conversion achieved is 4.26%. Figure 4.13 shows the effect of addition of 30 ml and the final conversion is 10.24% while effect of addition of 50 ml triglycerides is shown in Figure 4.14 with final conversion of 11.61%.

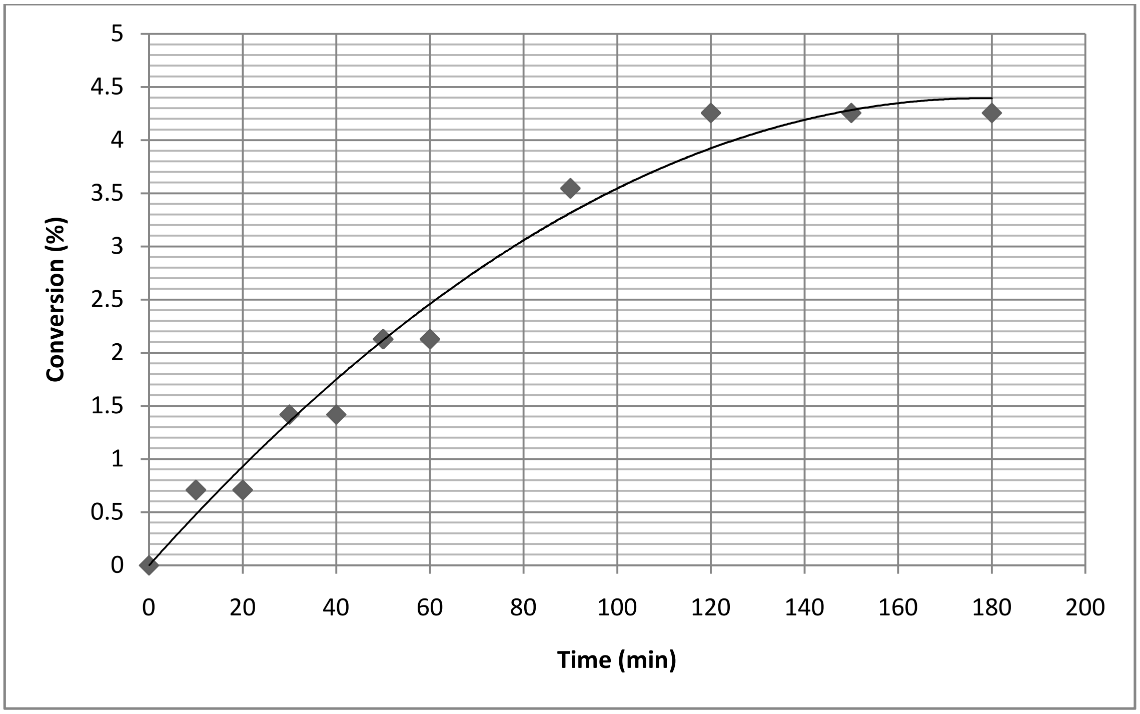

Figure 4.12: Effect of additional of 10 ml of triglycerides to conversion of oleic acid

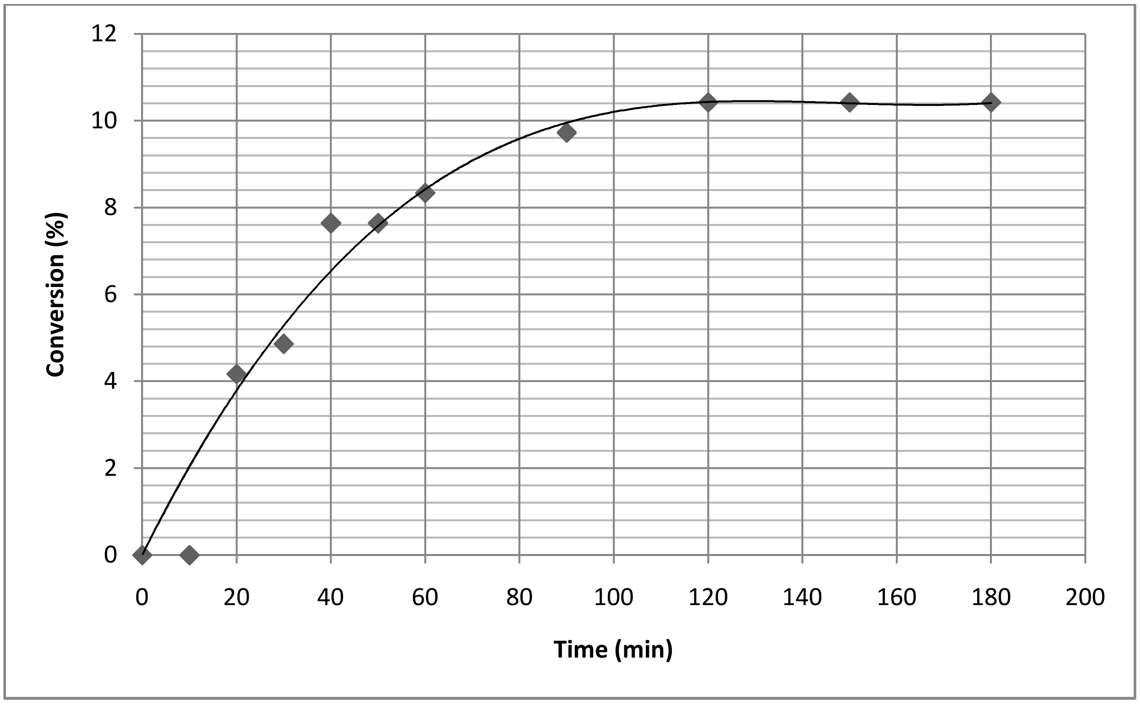

Figure 4.13: Effect of additional of 30 ml of triglycerides to conversion of oleic acid

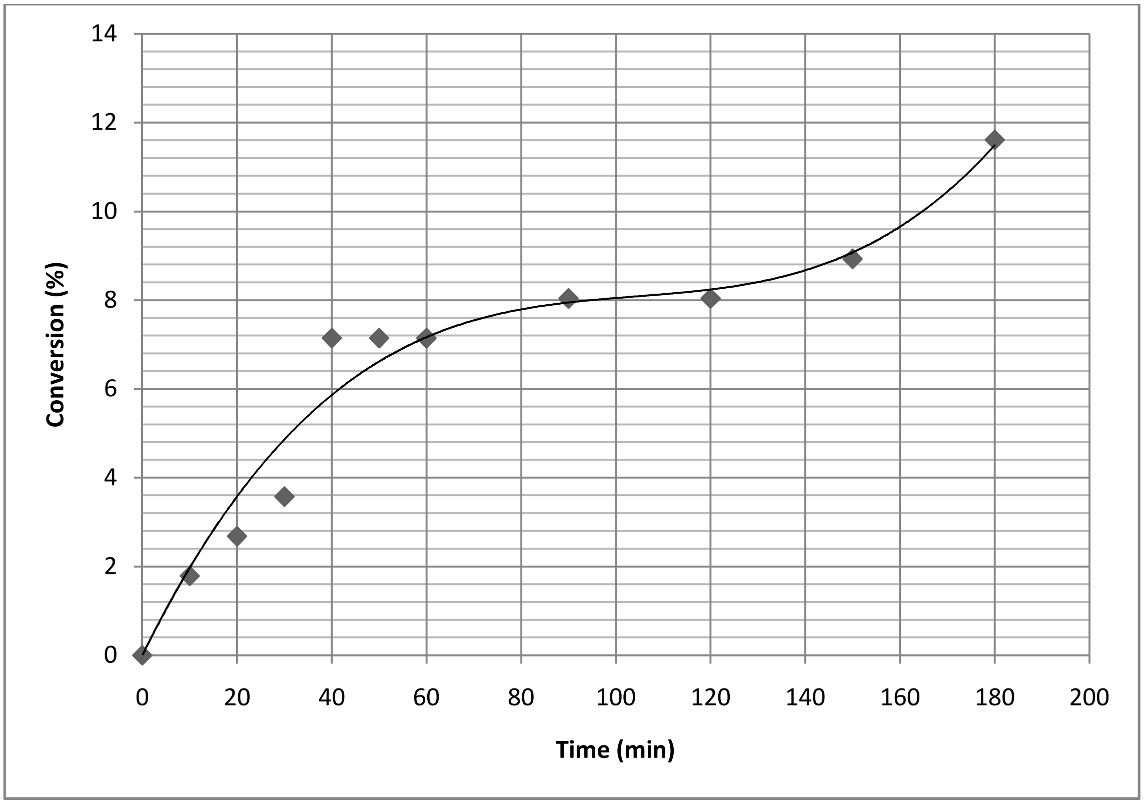

Figure 4.14: Effect of additional of 50 ml of triglycerides to conversion of oleic acid

Figure 4-15 shows the curves for different amounts of triglycerides which is 10 ml, 30 ml and 50 ml. From this figure, the effect by adding different amount of triglycerides can be analyzed clearly.

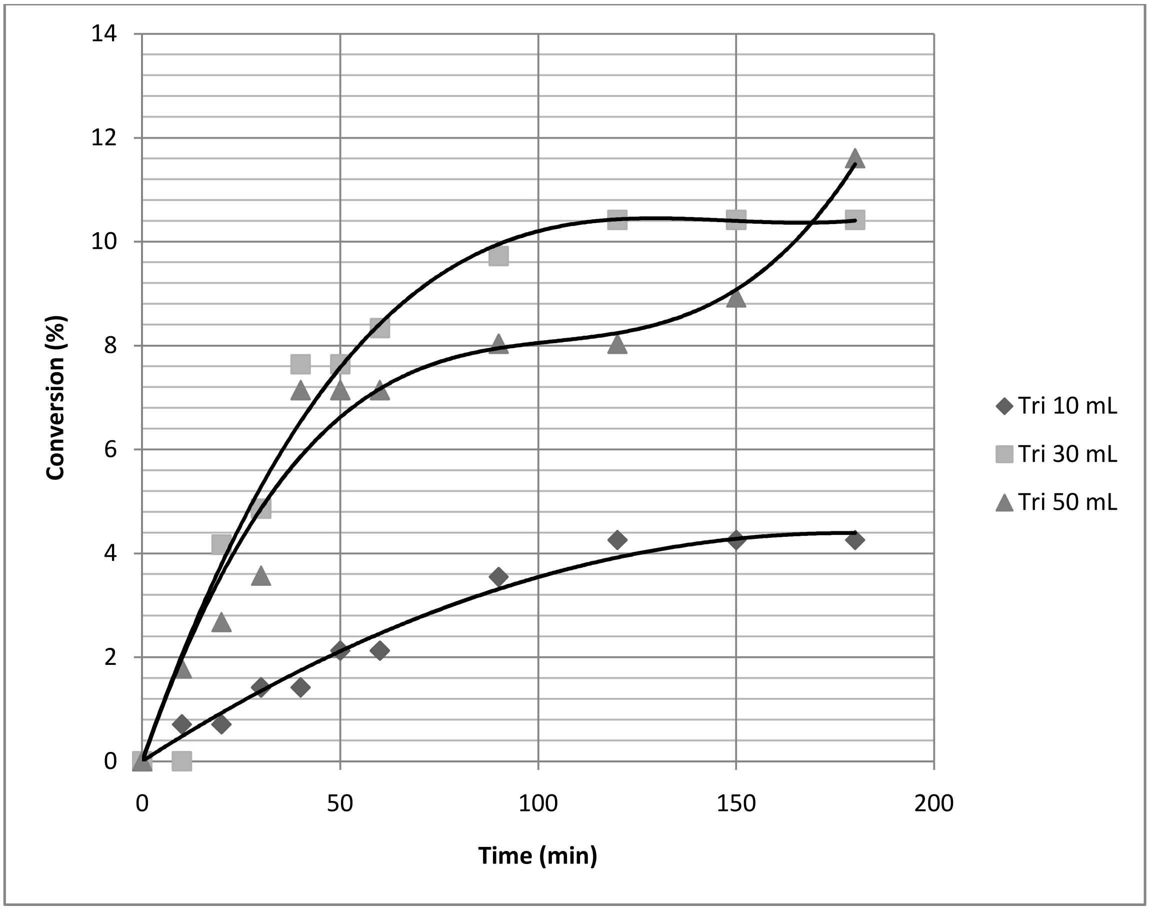

Figure 4.15: Effect of different amount of triglycerides to conversion of oleic acid

The presence of triglycerides will carry out transesterification reaction which is triglycerides will react with ethanol to produce ethyl esters. When the amount of triglycerides is increased, the amount of ethyl ester produced also will be increased. Appendix F shows the free fatty acid composition in some common edible oils and fats. In palm oil that been used in the experimental research, it contains high amount of oleic acid by 40 percent by mass of oil. When oil is added into reaction, the amount of oleic acid reacts in the reaction increases and the production of ethyl ester also increases. It is proved in Figure 4.15 where the amount of 50 ml brought highest conversion compare to 30 ml and 10 ml.

Figure 4-16 shows the reaction without triglycerides has higher value of conversion compared to reaction with triglycerides.

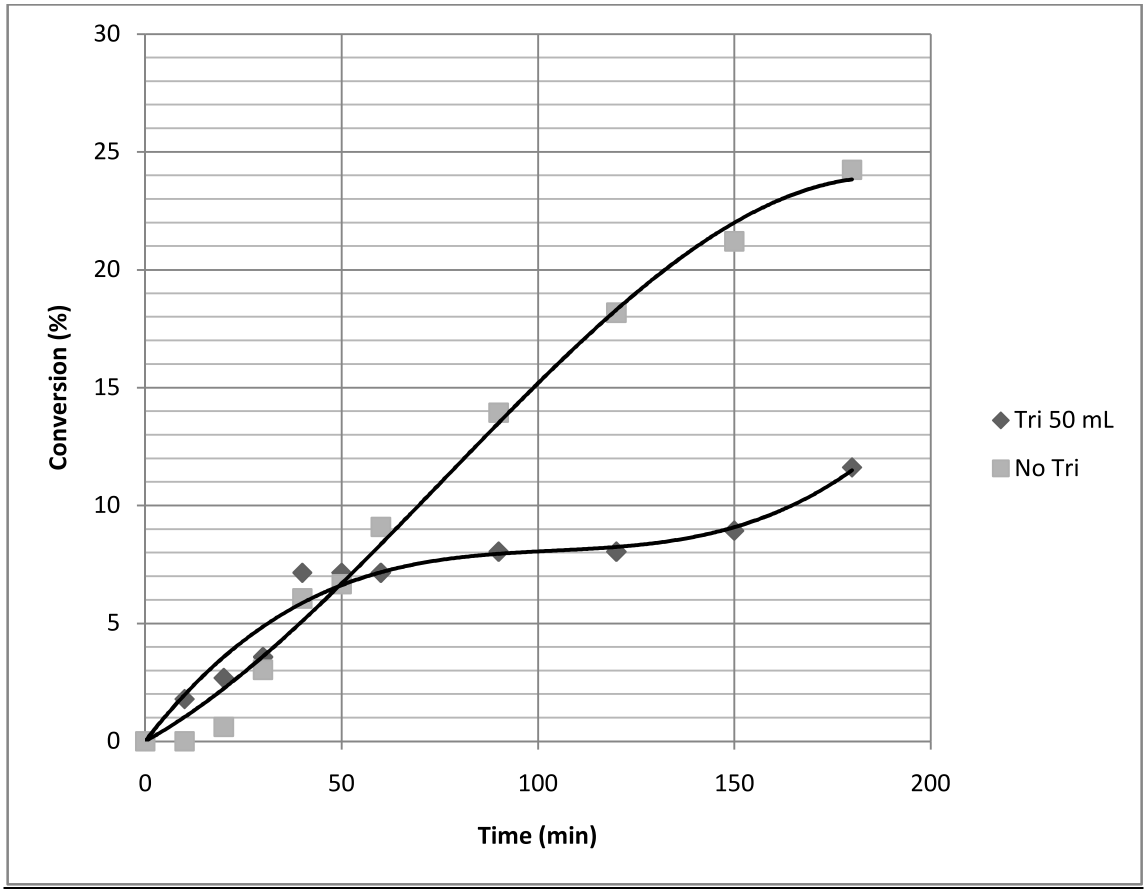

Figure 4.16: Effect of reaction with and without triglycerides.

Esterification reaction of oleic acid needs tungstated zirconia as catalyst to react with ethanol while triglycerides also need tungstated zirconia to perform transesterification reaction. Thus, presence of triglycerides will reduce selectivity of esterification since transesterification produced undesired product which is glycerol that disturb esterification of oleic acid process.

However, the conversion with presence of triglycerides can be increased by adding more catalyst to increase number of active site for reaction of occur besides can provides alternative path which is low than activation energy of reaction.

4.5 Kinetic Modeling

Pseudohomogeneous model as stated in equation 3.4 is used in kinetic modeling studies. The model used because it is less complex and has a smaller number of parameters stated by Steinigeweg and Gmehling (2003). Since esterification of oleic acid is reversible reaction, 2 rate constants studied which is forward and backward reaction. Rate constants determined by using Polymath™ software by solving it via nonlinear regression as shown in Appendix E. The k' and k" values obtained from kinetic modeling studies are recorded in Table 4.5 and Figure 4.17 is constructed.

Table 4.5: Value of k' and k" obtained from Polymath™

T (K)	1/T	k'	ln k'	k"	ln k"
303	0.0033	0.0001684	-8.69	0.035	-3.35
313	0.003195	0.0003802	-7.87	0.030	-3.49
323	0.003096	0.0002107	-8.47	0.0048	-5.33

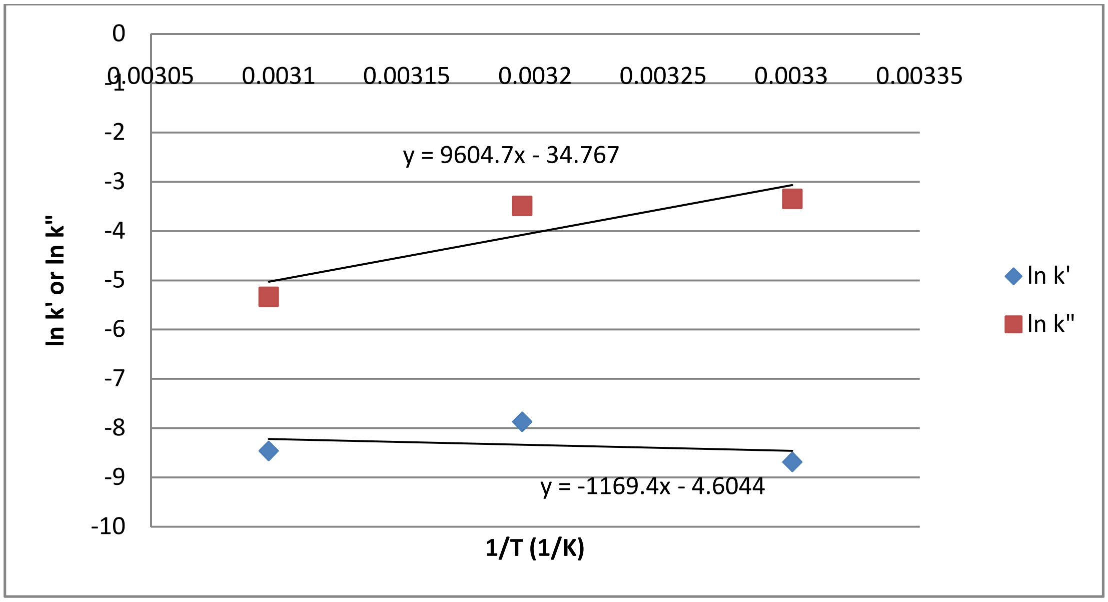

Figure 4.17: Arrhenius diagram of the rate constants for the esterification reaction. The lines represent the results of the overall fit (eq 3.5)

By deriving the Arrhenius equation as shown in equation 3.5, the equation can be correlated to the linear equation shown in Figure 4.17. The activation energy, E obtained by multiplying the gradient of the slope with gas constant while pre-exponential factor, A is the exponential of interception at y-axis. The values obtained are recorded in Table 4.6:

Table 4.6: Kinetic parameters and related uncertainties

Reaction Direction	Pre-exponential factor, A	Activation energy, E (kJ/mol)
Forward	0.01	9.72
Backward	8.02×10^{-16}	-79.85

Activation energy for esterification forward reaction shows in Table 4.6 is 9.72 kJ/mol. The kinetic and modeling study of esterification reaction using tungstated zirconia is never being discussed in previous studies but the activation energy is significantly lower compared to study by Steinigeweg and Gmehling (2003) which used Amberlyst 15. The activation energy obtained is 68.71 kJ/mol.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

By performing the research studies based on the scope of study that has been proposed, the best operating condition for biodiesel fuel production via esterification of oleic acid with ethanol has been determined

The amount of catalyst that resulting in highest value of oleic acid conversion is 1.5 g. This amount of catalyst is bringing forward to the study of varying the temperature of the reaction. The studies of three variables of temperature which is 30°C, 40°C and 50°C resulting in 50°C is the most suitable temperature for esterification reaction since the reaction is an endothermic reaction which is absorbing heat during the reaction. The best amount of catalyst and temperature then brought forward to the studies of varying the molar ratio of ethanol to oleic acid. The result is molar ratio ethanol to oleic acid 5:1 is the best molar ratio since it shows the highest conversion after 3-hour of reaction.

Additional of cooking oil as triglycerides is to study the effect when transesterification and esterification occur simultaneously. The result is when triglycerides is added, the conversion became low. This is because the selectivity of catalyst to catalyze either esterification or transesterification reaction.

Data recorded used in development of kinetic modeling by using Polymath™. The constant value, k’ and k” obtained for every reaction temperature studies and used to construct a linear equation. By simply multiplying ln for both side of Arrhenius equation, the activation energy and pre-exponential factor of esterification reaction can be determined.

5.2 Recommendation

Due to short period of the research, the range of study for each parameter is too small. This research can be expanded by adding more variable but it must be carried out a longer period.

Since the batch process is the easiest process compared to semi-batch or continuous, it is selected in doing this research. However, the maximum conversion for 3 hours is just 24.24% which is a very low conversion. This can be improved by doing it using continuous reaction as shown by Furuta et. al. (2006) and Park et. al. (2008).

The time of reaction must be longer than 3 hours in order to achieve the equilibrium constant.

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APPENDIX A

Experimental Diagram

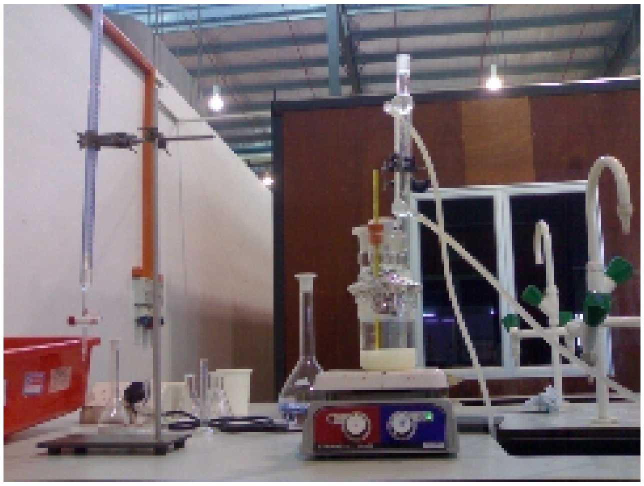


Figure A.1: Analytical and reaction studies.

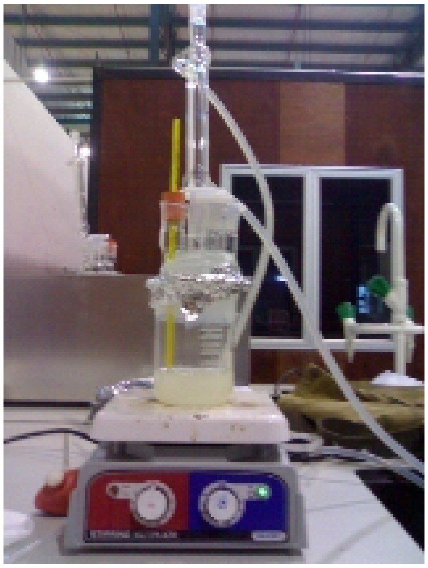


Figure A.2: Experimental setup for reaction study

Figure A.3: Sample in microcentrifuge tube after being centrifuged

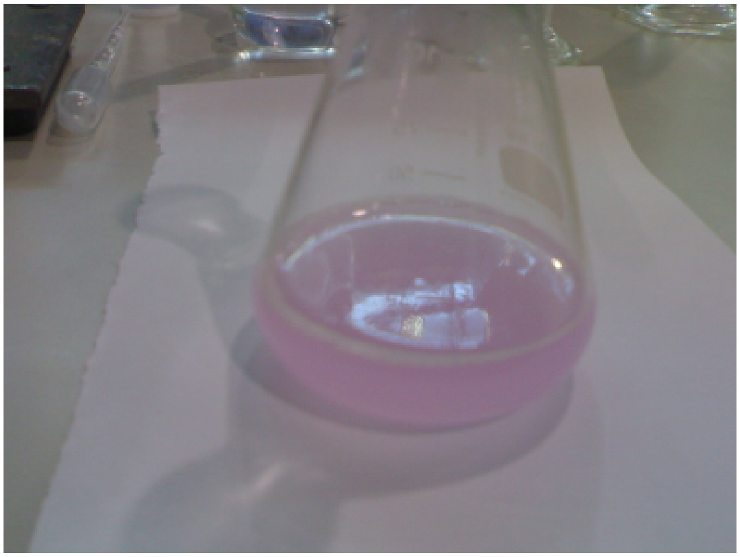


Figure A.4: Color of sample changed to light pink after titration process

APPENDIX B

Calculation of Molar Ratio Ethanol and Oleic Acid

Chemical Substance Data:

Table B.1: Data of the reactants

Oleic Acid	Details	Ethanol
282.46	**Molar Mass (g/mol)**	46.069
0.895	**Density (g/ml)**	0.7898
3.17	**Molarity (mol/L)**	17
315	**Volume of 1 mole (ml)**	60

Volumes of reactants are fixed to 150ml.

<u>Molar ratio ethanol to oleic acid=1:1</u>

$$\frac{60}{(60+315)} = \frac{x}{150}$$

x = 24 ml of ethanol
Volume of oleic acid = 150 – 24 = 126 ml

<u>Molar ratio ethanol to oleic acid=3:1</u>

$$\frac{180}{180+315} = \frac{x}{150}$$

x = 54.55 ml of ethanol
Volume of oleic acid = 150 – 54.55 = 95.45 ml

Molar ratio ethanol to oleic acid=5:1

$$\frac{300}{300+315}=\frac{x}{150}$$

x = 73 ml of ethanol
Volume of oleic acid = 150 – 73=77 ml

APPENDIX C

Data of Oleic Acid Conversion

C.1 Calculation of Oleic Acid Conversion

From Y. M. Park et. al.(2008)

Conversion(%) = [(initial acid value - final acid value)/(initial acid value)] x 100%

Acid Value = (M x A x F x N)/S
where:
M = molecular weight of NaOH = 40 g/mol
A = amount of NaOH standard solution used in titration = as shown in table
F = concentration coefficient of NaOH standard solution = 1
N = normal concentration of NaOH standard solution = 0.05 mol/L
S = sample weight = 0.87 g

C.2 Effect of Catalyst Amount

Table C.1: Effect of tungstated zirconia 0.5 g

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0144	0.03310345	0
10	0.014	0.03218391	2.78
20	0.0136	0.03126437	5.56
30	0.0136	0.03126437	5.56
40	0.0134	0.0308046	6.94
50	0.0134	0.0308046	6.94
60	0.0134	0.0308046	6.94
90	0.0132	0.03034483	8.33
120	0.0132	0.03034483	8.33
150	0.013	0.02988506	9.72
180	0.013	0.02988506	9.72

Table C.2: Effect of Tungstated zirconia 1.0 g

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0144	0.03310345	0
10	0.0144	0.03310345	0
20	0.0142	0.03264368	1.39
30	0.0138	0.03172414	4.17
40	0.0132	0.03034483	8.33
50	0.013	0.02988506	9.72
60	0.0124	0.02850575	13.89
90	0.0124	0.02850575	13.89
120	0.0122	0.02804598	15.28
150	0.0122	0.02804598	15.28

180	0.0122	0.02804598	15.28

Table C.3: Effect of tungstated zirconia 1.5 g

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0162	0.03724138	0
10	0.0162	0.03724138	0
20	0.0162	0.03724138	0
30	0.0152	0.03494253	6.173
40	0.0148	0.03402299	8.64
50	0.0142	0.03264368	12.345
60	0.0136	0.03126437	16.049
90	0.0136	0.03126437	16.049
120	0.0128	0.02942529	20.988
150	0.0128	0.02942529	20.988
180	0.0128	0.02942529	20.988

C.3 Effect of Temperature

Table C.4: Effect of temperature 30°C

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.033	0.07586207	0
10	0.033	0.07586207	0
20	0.0326	0.07494253	1.21
30	0.032	0.07356322	3.03
40	0.031	0.07126437	6.06

50	0.031	0.07126437	6.06
60	0.0306	0.07034483	7.27
90	0.0306	0.07034483	7.27
120	0.0292	0.06712644	11.52
150	0.0288	0.0662069	12.73
180	0.0288	0.0662069	12.73

Table C.5: Effect of temperature 50°C

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.033	0.07586207	0
10	0.033	0.07586207	0
20	0.0328	0.0754023	0.606
30	0.032	0.07356322	3.03
40	0.031	0.07126437	6.06
50	0.0308	0.0708046	6.67
60	0.03	0.06896552	9.09
90	0.0284	0.06528736	13.939
120	0.027	0.06206897	18.182
150	0.026	0.05977011	21.212
180	0.025	0.05747126	24.242

C.4 Effect of Reactants Molar Ratio

Table C.6: Effect of molar ratio 1:1

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0502	0.1154023	0
10	0.05	0.11494253	0.398
20	0.05	0.11494253	0.398

30	0.05	0.11494253	0.398
40	0.049	0.11264368	2.39
50	0.0486	0.11172414	3.187
60	0.0482	0.1108046	3.984
90	0.048	0.11034483	4.382
120	0.048	0.11034483	4.382
150	0.0474	0.10896552	5.578
180	0.0474	0.10896552	5.578

Table C.7: Effect of molar ratio 3:1

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0394	0.09057471	0
10	0.0388	0.0891954	1.523
20	0.0386	0.08873563	2.03
30	0.038	0.08735632	3.55
40	0.0378	0.08689655	4.061
50	0.037	0.08505747	6.091
60	0.0368	0.0845977	6.599
90	0.0364	0.08367816	7.61
120	0.0358	0.08229885	9.137
150	0.0356	0.08183908	9.65
180	0.0358	0.08229885	9.137

C.5 Effect of Amount Triglycerides

Table C.8: Effect of 10 ml triglycerides

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0282	0.06482759	0
10	0.028	0.06436782	0.709
20	0.028	0.06436782	0.709
30	0.0278	0.06390805	1.418
40	0.0278	0.06390805	1.418
50	0.0276	0.06344828	2.128
60	0.0276	0.06344828	2.128
90	0.0272	0.06252874	3.546
120	0.027	0.06206897	4.255
150	0.027	0.06206897	4.255
180	0.027	0.06206897	4.255

Table C.9: Effect of 30 ml triglycerides

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0288	0.0662069	0
10	0.0288	0.0662069	0
20	0.0276	0.06344828	4.17
30	0.0274	0.06298851	4.86
40	0.0266	0.06114943	7.64
50	0.0266	0.06114943	7.64
60	0.0264	0.06068966	8.33
90	0.026	0.05977011	9.72
120	0.0258	0.05931034	10.42
150	0.0258	0.05931034	10.42
180	0.0258	0.05931034	10.42

Table C.10: Effect of 50 ml triglycerides

Time (min)	Volume of NaOH (L)	Acid Value	Conversion (%)
0	0.0224	0.05149425	0
10	0.022	0.05057471	1.79
20	0.0218	0.05011494	2.68
30	0.0216	0.04965517	3.57
40	0.0208	0.04781609	7.14
50	0.0208	0.04781609	7.14
60	0.0208	0.04781609	7.14
90	0.0206	0.04735632	8.036
120	0.0206	0.04735632	8.036
150	0.0204	0.04689655	8.929
180	0.0198	0.04551724	11.607

APPENDIX D

Data of Reaction Rate Obtained from Polymath™

Table D.1: Reaction rate at temperature 30°C

C_A	C_B	C_C	C_D	$-r_A$
1.63	8.15	0	0	0.002461
1.63	8.15	0	0	0.002299
1.610277	8.130277	0.019723	0.019723	0.002142
1.580611	8.100611	0.049389	0.049389	0.001989
1.531222	8.051222	0.098778	0.098778	0.001841
1.531222	8.051222	0.098778	0.098778	0.001698
1.511499	8.031499	0.118501	0.118501	0.00156
1.511499	8.031499	0.118501	0.118501	0.001173
1.442224	7.962224	0.187776	0.187776	8.29E-04
1.422501	7.942501	0.207499	0.207499	5.28E-04
1.422501	7.942501	0.207499	0.207499	2.70E-04

Table D.2: Reaction rate at temperature 40°C

C_A	C_B	C_C	C_D	$-r_A$
1.63	8.15	0	0	0.005292
1.63	8.15	0	0	0.004921
1.63	8.15	0	0	0.004552

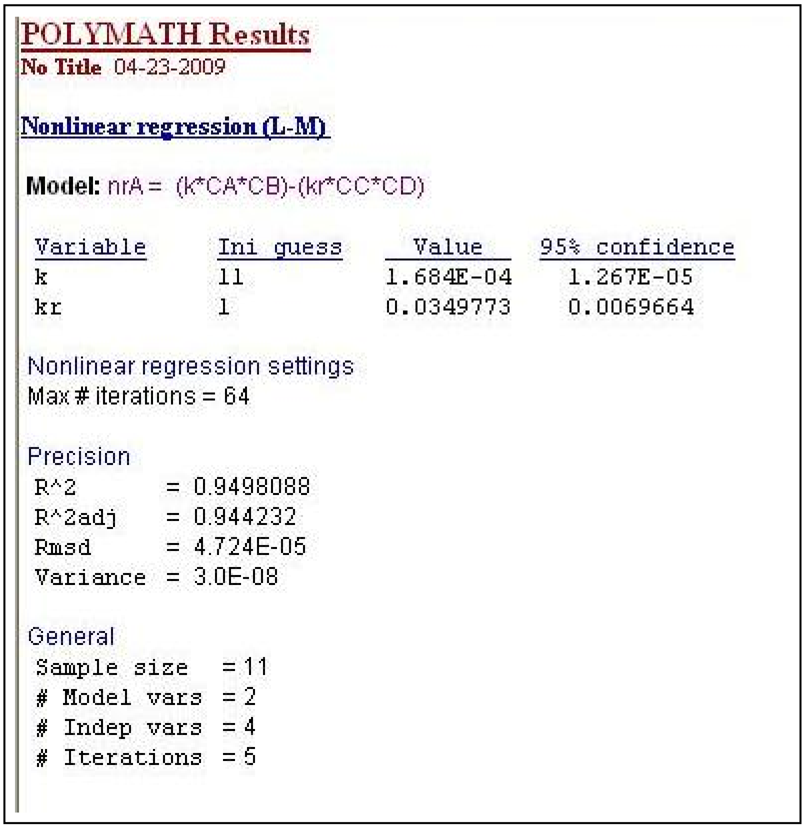
1.529429	8.049429	0.100571	0.100571	0.004186
1.489168	8.009168	0.140832	0.140832	0.003822
1.428858	7.948858	0.201142	0.201142	0.003462
1.368385	7.888385	0.261615	0.261615	0.003104
1.368385	7.888385	0.261615	0.261615	0.002046
1.287863	7.807863	0.342137	0.342137	0.001014
1.287863	7.807863	0.342137	0.342137	6.00E-06
1.287863	7.807863	0.342137	0.342137	-9.77E-04

Table D.3: Temperature 50°C

C_A	C_B	C_C	C_D	$-r_A$
1.63	8.15	0	0	0.002235
1.63	8.15	0	0	0.002403
1.620057	8.140057	0.009943	0.009943	0.00254
1.580611	8.100611	0.049389	0.049389	0.002648
1.531222	8.051222	0.098778	0.098778	0.002726
1.521279	8.041279	0.108721	0.108721	0.002774
1.481833	8.001833	0.148167	0.148167	0.002791
1.402778	7.922778	0.227222	0.227222	0.002665
1.333666	7.853666	0.296334	0.296334	0.002268
1.284277	7.804277	0.345723	0.345723	0.001602
1.234888	7.754888	0.395112	0.395112	6.66E-04

APPENDIX E

Kinetic Modeling by Polymath™



```
POLYMATH Results
No Title  04-23-2009

Nonlinear regression (L-M)

Model: nrA =  (k*CA*CB)-(kr*CC*CD)

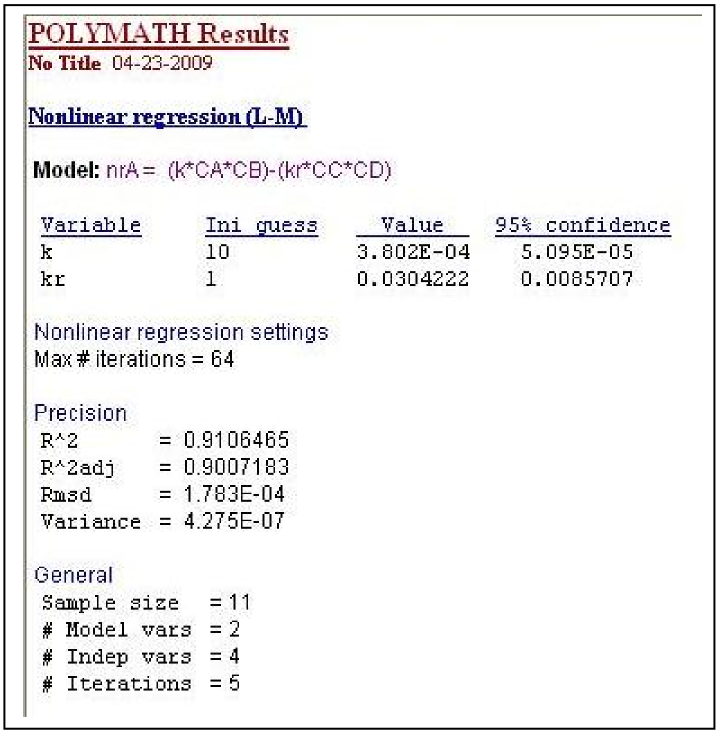
 Variable      Ini guess      Value      95% confidence
 k             11           1.684E-04      1.267E-05
 kr            1            0.0349773      0.0069664

Nonlinear regression settings
Max # iterations = 64

Precision
 R^2       = 0.9498088
 R^2adj    = 0.944232
 Rmsd      = 4.724E-05
 Variance  = 3.0E-08

General
 Sample size   = 11
 # Model vars  = 2
 # Indep vars  = 4
 # Iterations  = 5
```

Figure E.1: Polymath™ results for 30°C reaction temperature



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POLYMATH Results
No Title  04-23-2009

Nonlinear regression (L-M)

Model: nrA =  (k*CA*CB)-(kr*CC*CD)

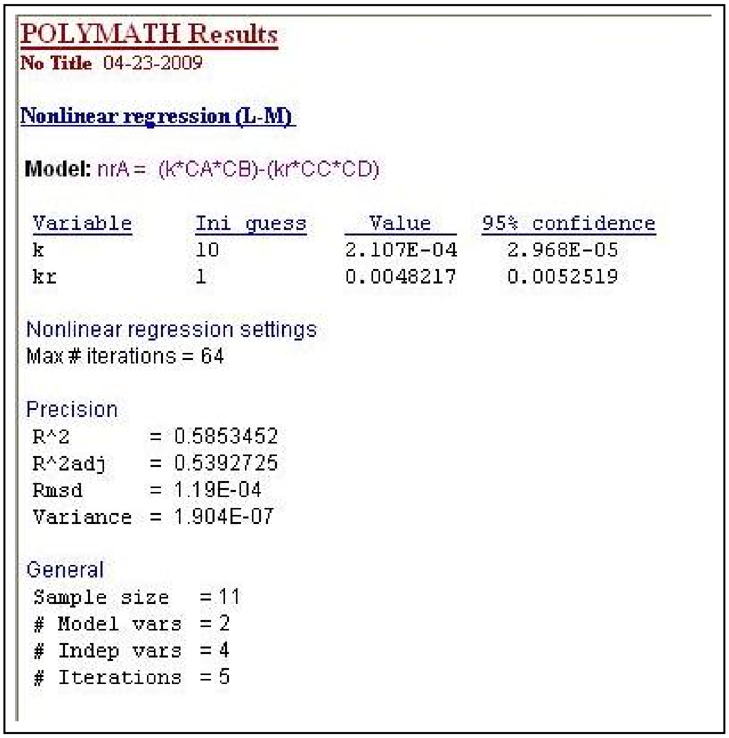
Variable       Ini guess     Value      95% confidence
k              10            3.802E-04    5.095E-05
kr             1             0.0304222    0.0085707

Nonlinear regression settings
Max # iterations = 64

Precision
R^2        = 0.9106465
R^2adj     = 0.9007183
Rmsd       = 1.783E-04
Variance   = 4.275E-07

General
Sample size   = 11
# Model vars  = 2
# Indep vars  = 4
# Iterations  = 5
```

Figure E.2: Polymath™ results for 40°C reaction temperature



```
POLYMATH Results
No Title  04-23-2009

Nonlinear regression (L-M)

Model: nrA =  (k*CA*CB)-(kr*CC*CD)

Variable       Ini guess     Value      95% confidence
k              10            2.107E-04    2.968E-05
kr             1             0.0048217    0.0052519

Nonlinear regression settings
Max # iterations = 64

Precision
R^2        = 0.5853452
R^2adj     = 0.5392725
Rmsd       = 1.19E-04
Variance   = 1.904E-07

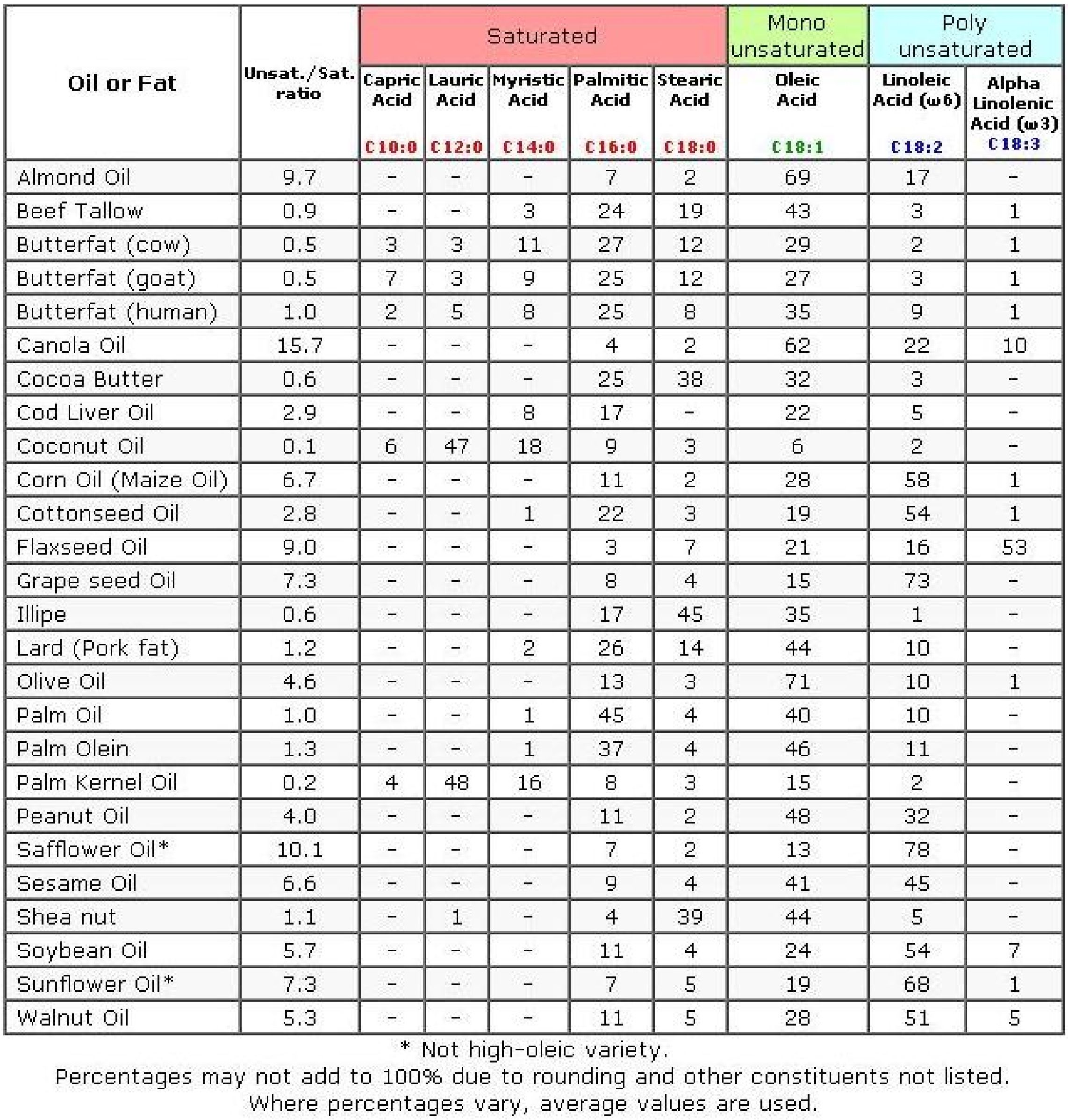
General
Sample size   = 11
# Model vars  = 2
# Indep vars  = 4
# Iterations  = 5
```

Figure E.3: Polymath™ results for 50°C reaction temperature

APPENDIX F

Fatty Acid Composition of Some Common Edible Fats and Oils.

Table F.1: Fatty acid composition.



Oil or Fat	Unsat./Sat. ratio	Saturated					Mono unsaturated	Poly unsaturated	
		Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid (ω6) C18:2	Alpha Linolenic Acid (ω3) C18:3
Almond Oil	9.7	-	-	-	7	2	69	17	-
Beef Tallow	0.9	-	-	3	24	19	43	3	1
Butterfat (cow)	0.5	3	3	11	27	12	29	2	1
Butterfat (goat)	0.5	7	3	9	25	12	27	3	1
Butterfat (human)	1.0	2	5	8	25	8	35	9	1
Canola Oil	15.7	-	-	-	4	2	62	22	10
Cocoa Butter	0.6	-	-	-	25	38	32	3	-
Cod Liver Oil	2.9	-	-	8	17	-	22	5	-
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil (Maize Oil)	6.7	-	-	-	11	2	28	58	1
Cottonseed Oil	2.8	-	-	1	22	3	19	54	1
Flaxseed Oil	9.0	-	-	-	3	7	21	16	53
Grape seed Oil	7.3	-	-	-	8	4	15	73	-
Illipe	0.6	-	-	-	17	45	35	1	-
Lard (Pork fat)	1.2	-	-	2	26	14	44	10	-
Olive Oil	4.6	-	-	-	13	3	71	10	1
Palm Oil	1.0	-	-	1	45	4	40	10	-
Palm Olein	1.3	-	-	1	37	4	46	11	-
Palm Kernel Oil	0.2	4	48	16	8	3	15	2	-
Peanut Oil	4.0	-	-	-	11	2	48	32	-
Safflower Oil*	10.1	-	-	-	7	2	13	78	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Shea nut	1.1	-	1	-	4	39	44	5	-
Soybean Oil	5.7	-	-	-	11	4	24	54	7
Sunflower Oil*	7.3	-	-	-	7	5	19	68	1
Walnut Oil	5.3	-	-	-	11	5	28	51	5

* Not high-oleic variety.
Percentages may not add to 100% due to rounding and other constituents not listed.
Where percentages vary, average values are used.