ESTERIFICATION OF OCTANOIC ACID AND ETHANOL USING SULFATED ZIRCONIA IN THE PRESENCE OF TRIGLYCERIDES: KINETIC AND MODELLING STUDY

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Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in Partial Fulfillment of the required for the Degree of Bachelor Engineering in Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
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MAY 2009

I declare that this thesis entitled *"Esterification of Octanoic acid and ethanol using sulfated zirconia in the presence of triglycerides: Kietic and Modelling Study"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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To my beloved father and mother,
BINAR ANAK BARAYUN & EVELIN TEMAH ANAK BEGINDA

Sister and brother,
MARYLIN BINAR & BRILLIANT ELEXIUS BINAR

"Forgive us when we fall down and lift us back up and rebuild our walls, so that the enemy is defeated in our lives"

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ABSTRACT

The esterification of octanoic acid and ethanol using sulfated zirconia in the presence of triglycerides is one of the methods to produce biodiesel. As the fuel used today, petroleum is estimated depleted around 30-45 years in the future, Biodiesel is an alternative biofuel that can be produced using esterification method. The esterification of octanoic acid is done to determine the best operation condition to yield better conversion of octanoic acid. The operation conditions for the esterification of octanoic acid are temperature of reaction, amount of sulfated zirconia used, amount of triglycerides presence and molar ratio of octanoic acid to ethanol. The temperature of reaction ranged from 30ºC to 50ºC. The amount of sulfated zirconia used ranged from 0.5g to 1.5g. The amount of triglycerides presence ranged from 30ml to 70ml. The molar ratio of octanoic acid to ethanol ranged to 1:1 to 1:5. The best operating condition achieved for the esterification of octanoic acid and ethanol were 30ºC reaction temperature, 1.5g sulfated zirconia used, 1:1 molar ratio of octanoic acid to ethanol and 50ml of triglycerides presence in the esterification. The kinetic model been used is pseudo-homogeneous kinectic model based on the experimental data gained. The pseudo-homogeneous kinetic model gives a good agreement between the experimental data and the model used.

ABSTRAK

Esterifikasi oktanoik asid dan etanol dengan menggunakan zirkonia sulfat dalam kehadiran minyak masak merupakan satu kaedah untuk menghasilkan biodiesel. Bahan bakar yang digunakan pada maka kini, petroleum dijangka akan habis dalam masa 30-45 tahun di masa yang akan datang. Biodiesel merupakan alternatif bahan bakar bio yang boleh dihasilkan dengan menggunakan kaedah esterifikasi. Esterifikasi oktanoik asid dilakukan untuk menentukan keadaan kendalian yang terbaik untuk menghasilkan konversi oktanoik asid yang lebik baik. Keadaan kendalian untuk esterifikasi oktanoik asid adalah suhu tindak balas, jumlah zikornia sulfat yang digunakan, jumlah minyak masak yang hadir dalam esterifikasi dan nisbah molar oktanoik asid kepada etanol. Suhu tindak balas adalah dari 30ºChingga 50ºC. Jumlah zirkonia sulfat yang digunakan adalah dari 0.5g hingga 1.5g. Jumlah minyak masak yang hadir dalam esterifikasi adalah dari 30ml hingga 70ml. Nisbah molar oktanoik asid kepada etanol adalah dari 1:1 hingga &0ml. Keadan kendalian yang terbaik yang diperolehi dari esterifikasi oktanoik asik adalah pada suhu 30ºC, 1.5g zirkonia sulfat digunakan, 1:1 nisbah molar octanoik asid kepada etanol dan 50ml minyak masak digunakan untuk esterifikasi. Model kinetik yang digunakan adalah *pseudo-homogeneous* berdasarkan data experiment yang diperolehi. Model kinetik *pseudo-homogeneous* memberikan keputusan yang sejajar antara data experimen dan model itu sendiri.

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SYMBOLS	TITLE	PAGE
r	rate of reaction,	14
kc	kinetic constant,	14
ke	equilibrium constant,	14
K_M	adsorption parameter for methanol	14
K_W	adsorption parameter for water,	14
x_A	the molar fraction of the free oleic acid,	14
x_M	the molar fraction of the methanol,	14
A	preexponential factorof frequency factor	40
E	activation energy , J/mol	40
R	gas contant = 8.134 J/mol K	40
T	absolute temperature, K (Kelvin)	40

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Today's increasing price of petrol fuel make researcher to find the alternative fuel that non-petrol-based and reliable. This is because fuel used today relies in one source, petroleum. Petroleum reservoir in world is estimated depleted around 30-45 years in the future. To cope with this situation, alternative fuel that based on agricultural origin known as biodiesel are being increasingly considered as alternatives to gasoline and gas oil as sources of energy. Specifically, biodiesel has a substantial potential to reduce oil imports, dependent on petroleum and ensure continuity in the energy supply.

Biodiesel is the alternative fuel that consists of alkyl esters of long chain fatty acids. Biodiesel is made from oils or fats which are hydrocarbon. From the past, fresh soil beans oil is common used as biodiesel. Biodiesel also can be made from mustard seed oil or waste vegetables oil such as used oil from restaurant deep fryer. The advantages of using biodiesel are reducing emissions of gaseous pollutants such as carbon dioxide, can particulate matter and made from organic compounds. Biodiesel is commonly produced by transesterification of triglycerides and synthesized using alkaline catalysts. The alkaline catalysts show high performance, providing biodiesel fuel of high quality, but the oils often contain significant amounts of free fatty acids, which cannot be converted into biodiesel fuel and later then become soap.

Esterification of free fatty acids is other method in producing biodiesel that can be used as pretreatment before reaction of transesterification which convert the free fatty acids into methyl esters thus prevent saponification happens. The reaction is shown by following scheme,

R−COOH	R'−OH	R−COOR'	H_2O	
fatty acid	alcohol	biodiesel	water	(1)

Esterification of free fatty acids use catalysts to faster the reaction rate. Catalysts that commomly used in esterification is strong liquid mineral, acid catalysts. This homogenous catalyst has its side reaction that not only increasing the biodiesel production but also affect the properties of biodiesel produced.

Heterogeneous catalysts such as solid acid catalysts is the best solution due to its benefits not only on the purity of the secondary product, glycerin, but also because it will simplified downstreaming separation process, since it does not need any washing or neutralizing equipment .The heterogeneously catalyst available is resins, Cs-heteropoly acid, H zeolite and modified zirconia. The system chooses for in this esterification is octanoic acids as free fatty acids and ethanol as alcohol using sulfated zirconia as solid acids catalyst.

1.2 Problem Statement

The heterogeneously catalyzed esterification process to biodiesel production is lacking in the studies for its kinetic model and how to determine the optimum operating conditions. The importance of this data is to develop kinetic model that can represent the esterification process. Based on this problem, further research of heterogeneously catalyzed esterification based on kinetic study is done by esterification of octanioic acid and ethanol using sulfated zirconia in the presence of triglycerides.

1.3 Objective of Study

- To obtain optimum operation condition to the esterification of free fatty acid using solid acid catalyst.

- To develop a kinetic for the esterification of free fatty acid using solid acid catalyst based on the results obtains from the study.

1.4 Rational and Significance

Most of the literature review about esterification of free fatty acids is lacking about the information on its kinetic models. This model is useful reactor design. The optimum operation condition is essential in producing better quality of biodiesel.

1.5 Scope of Study

The study of esterificication of free fatty acids using solid acid catalyst will be carried out in the lab scaled batch reactor. The free fatty acids used is octanoic acid and alcohol is ethanol. Sulfated zirconia used as the solid acid catalyst. The range of study for operating; 30ºC-50ºC for temperature, 0.5g-1.5g for weight of catalyst, 30-50ml concentration of triglycerides and 1:1 -1:5 molar ratio of alcohol/free fatty acids. The kinetic model used is based on the pseudo-homogeneous kinetic model.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is non-petroleum-based diesel which consists of long-chain fatty acid methyl ethers (FAME) obtained from renewable lipids that are found in vegetable oils or animal fat. It can be used both as an alternative fuel and as an additive for commercial petroleum diesel. The advantages of using this alternative fuel other than petroleum based diesel because it is contains more than 10% oxygen, which would increase the rate of complete fuel combustion and reduce the production of pollutants. Biodiesel commonly produced by the process of transesterification of triglycerides and methanol to form methyl ester and using a homogeneous catalyst, such as sodium or potassium hydroxide dissolved in methanol. Before the transesterification took place, esterification of free fatty acids is essential to prevent free fatty acids in the base oil from coverting to soap (Saponification reaction) during the transesterification process.

2.2 Esterification

Esterification is a chemical reaction that involves two reactants, an alcohol and an acid which produce an ester as the reaction product. Esterification of free fatty acids is a fundamental step in producing biodiesel.

Caetano C.S et al., (2009) studied the esterification of fatty acids to biodiesel over polymers with sulfonic acid groups. The esterification is done using using poly(vinyl alcohol) cross-linked with sulfosuccinic acid (SSA) and polystyrene cross-linked with divinylbenzene with sulfonic acid groups, as catalysts, at 60ºC. In their findings, it was observed that the catalytic activity of poly(vinyl alcohol) (PVA) is higher than the obtained with the polystyrene (PS) ones. After about 2 h of reaction, an equilibrium conversion of 90% was achieved with PVA_SSA40 polymeric matrix. It was studied the influence of various reaction parameters, such as, molar ratio of palmitic acid to alcohol, catalyst loading and type of alcohol, on the activity of the most efficient catalyst, PVA_SSA40. In relation to the molar ratio of palmitic acid to alcohol, it was observed that when the molar ratio increases, the equilibrium conversion of palmitic acid increases from about 30% (1:3) to 90% (1:63). The esterification of palmitic acid with ethanol led to lower conversion, when compared with methanol. When the temperature was increased from 60ºC to 80ºC, an increase of the palmitic acid conversion was observed using ethanol.

Yu G.X et al., (2009) studied the esterification over rare earth oxide and alumina promoted sulfated zirconia (SZ). The esterification is done using ethanol and acetic acid. In their findings, both surface area and pore diameter of the SZ catalysts after promoted with rare earth oxide and alumina were significantly enhanced. Only tetragonal ZrO_2 (zirconia) crystal phase was formed for all the samples. In the synthesis of ethyl acetate by the esterification of ethanol and acetic acid, the catalytic activity of the SZ catalyst could not be promoted by only doping with rare earth oxides, including La_2O_3, Ce_2O_3 and Yb_2O_3. However, double promotion with Yb_2O_3 and Al_2O_3 could greatly enhance the catalytic activity and stability of the SZ catalysts. The SZAY (SO_4^{2-}/ZrO_2-Yb_2O_3-Al_2O_3) catalyst exhibited the optimal catalytic activity, reaching 86.60% at ethanol and

acetic acid molar ratio of 2:1 and 2.0 wt.%. of the catalyst, for a reaction time of 150 min under temperature of 87ºC. Their work shows that changes in catalyst activity were in close correlation with variations of the amount of moderately strong and super strong Lewis acidity. The loss of sulfur species by solvation and coking during the reaction led to the catalyst deactivation.

Ji-Yeon Park et al., (2009) studied the esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. In their findings, two heterogeneous acid catalysts Amberlyst 15 and Amberlyst BD20 were compared to determine the characteristics of a catalyst with good efficiency properties. Amberlyst BD20 showed good catalytic efficiency for high FFA oils. After reuse, the activity of Amberlyst BD20 did not decrease. An SEM micrograph revealed that the Amberlyst BD20 had no pores. Although the presence of pores in a catalyst increases the amount of active sites and thus enhances the reaction rate, a catalyst without pores is deemed to be desirable to reduce the inhibiting effect of water during the esterification of high FFA oils.

2.3 Catalyst

Catalyst is used in the estericifation process to enhance or accelerates chemical reaction process. Catalysts can be divided into two types, homogenous catalysts such as the strong liquid mineral acids, such as sulphuric acids and hydrochloric acids, heterogeneous catalyst such as solid acid catalysts with mainly Brønsted acid sites.

2.4 Homogeneous Catalyst

Aranda et al., (2007) studied acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. In their finding, small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst. The acid strength of the catalyst was responsible for the higher activity of sulfuric and methanesulfonic acids by releasing more H^+ species to protonate the carboxylic moiety of the fatty acid (rate determinant step). The higher polarity and shorter chain of methanol resulted higher activity compare to ethanol and this shows the presents steric hindrance in the reaction because higher water inhibition which attributed to phase miscibility and emulsion formation. The obtained kinetic parameters were similar to the ones reported for transesterification reaction which is indicated a similar rate determinant step because of the lower activation energy. Despite the similar protonation energy of fatty acid, Quantum chemistry studies have shown that the double bond of oleic acid increase the reactivity of carboxylic moiety of the fatty acid.

Sun R.C et al., (2000) studied fractional isolation, physico-chemical characterization and homogeneous esterification of hemicelluloses from fast-growing poplar wood. In their finding, during the alkaline treatment of the dewaxed and partially delignified fast-growing poplar wood, some alkali-labile linkages between lignin molecules, or between lignin and polysaccharides, might be broken by alkali. Acidic moieties such as carboxylic or phenolic groups, ionized in alkaline solution, might also promote the solubilization of the hemicelluloses and residual lignin, either by increasing the solubility of individual fragments or by inducing the swelling of the cell wall.

Serio D.M et al., (2005) studied synthesis of biodiesel via homogeneous Lewis acid catalyst. The homogeneous catalysts used in their synthesis were carboxylic salts (Cd, Mn, Pb, Zn). In their finding, bivalent cations are catalysts for both transesterification and esterification reactions. Catalytic activities are related to the Lewis acid strength of the metals (which must have an optimal intermediate value) and to the molecular structure of the anion. The best catalytic performances were obtained

with cation metals having a complex stability constant with dibenzoilmetane in the range between 8.60 (corresponding to cadium) and 10.23 (corresponding to zinc). Then the stearates have better performances than acetates because their higher solubility in the oil phase where the reaction occurs.

The homogeneous catalysts suffer from several drawbacks, such as the existence of side reaction with reactant, corrosive nature and the separation of catalyst from products is difficult plus environmental threats. The alternative way to overcome these drawbacks is using heterogeneous catalyst. Solid acid catalysts properties are not corrosive, can be coated onto a support and easily reused. Ion –exchange resins, zeolites, sulfated zirconia and niobium acid are the examples of catalysts used in esterification reactions.

2.5 Heterogeneous catalyst

The heterogeneous catalyst is selected due to its activity and reusability compare to conventional homogeneous catalyst. Homogeneous catalysts have side reaction with reactant and corrosive nature that can harm the environment. This weakness of homogenous catalysts leads the heterogeneous catalyst to be selected for this experiment.

The heterogeneous catalyst use in the esterification of octanoic acids and ethanol is sulfated zirconia. Sulfated zirconia is choosen as the catalyst due to its importance of its catalytic activity, reusability and thermal resistant. This modified-zirconia catalyst is thermally stable than resin-type catalyst when used at higher temperature.

Peters et al., (2005) concluded that, solid acid catalysis is very effective from the aspect of activity and reusability compared with homogeneous catalysts. The activity per proton of solid acid catalysts is significantly different due to the specific reaction rate depends on the environment of the acid sites such as hydrophobicity. The diffusion of molecules to the active sites is important in the case of porous solid acids such as

zeolites. Peters (2005) studied comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol. The homogenous catalysts used are sulphuric acid, p-toluenesulphuric acid and a heteropolyacid. This homogenous catalysts is then compared with heterogeneous catalysts, Smopex-101, Amberlyst 15,sulphated zirconia. In his findings, among the solid acid catalysts, ion-exchange resins such as Smopex-101 and Amberlyst 15 were found to be the most effective.

Marchetti et al., (2006) studied heterogeneously catalyzed esterification of oil with high amount of free fatty acids using resins as a catalyst. In his finding, the esterification of free fatty acid using this heterogeneous catalyst appears to be a great alternative to purify frying oil; the final conversion achieved was around 80%". Dowex monosphere 550 A resin shows both better final conversion and a good reaction rate at the operation conditions compare to Dowex upcore Mono A-625 resin. This catalyst is applicable and suitable to carry on not only the esterification reaction but also the transesterification reaction. More study on the operational conditions should be done in order to have a good reaction time comparable with the one used for the conventional catalyst.

In Lopez et al., (2008) finding, the physical properties of the zirconia-supported catalysts at different calcination temperatures is differ from each calcination temperatures. For example in 400ºC, the pore volume is 0.24 cm^3/g and average pore diameter is 3.3 nm. The optimum calcination temperature for SZ for transesterification was 500ºC. For transesterification reactions, SZ catalysts have been typically calcined at temperatures ranging between 500ºC and 650ºC. The calcination duration affect the sulfur concentration and consequently the density of acid sites. Therefore, the SZ samples can also be calcined at temperatures lower than 500ºC showed lower catalytic activity. The loss of sulfur explains that the decrease in catalyst surface area with calcination temperature as it has been demonstrated that sulfate ions stabilize the zirconia structure and high surface area.

2.6 Kinetic Models

Most of the literature review about esterification of free fatty acids is lacking about the information on its kinetic models. This model is useful to develop a formula or equation to determine the optimum operation condition for esterification of free fatty acids with the selected parameters in order to gain the best final conversion of free fatty acids that later can produce the better quality of biodiesel.

Berrios et al., (2007) studied kinetics of the esterification of free fatty acids (FFA) in sunflower oil with methanol in the presence of sulphuric acid at concentrations of 5 and 10 wt% relative to free acids as catalyst and methanol/oleic acid mole ratios from 10:1 to 80:1. In their finding, the kinetic model used in his work relied according to following assumptions:

(a) The esterification reaction was a reversible heterogeneous process the rate of which under the operating conditions used was controlled by that of the chemical reaction.

(b) The rate of the non-catalysed reaction was negligible relative to the catalysed reaction.

(c) The chemical reaction occurred in the oil phase.

(d) The methanol/oleic acid mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

Berrios et al., (2007) concluded that 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 60ºC and agitation at a speed of 250 rpm or higher. Under these conditions, the acidity removed, E, expressed as the acid value (mg KOH/g oil), as a function of time (in min) conforms to the following equation:

$$E = \frac{A_0(e^{2K_2\alpha t} - 1)}{\beta(1 + e^{2K_2\alpha t}) + 0.5(e^{2K_2\alpha t} - 1)} \tag{2.1}$$

where α and β have the same meaning as in Equation (2.2) and (2.3), respectively, and K1 and K2 are calculated by using Equation (2.4) based on data in Table 2.1.

$$\alpha = \sqrt{\left(\frac{K^2}{4}\right) + K \cdot A_0} \tag{2.2}$$

$$\beta = \frac{\alpha}{K} \quad \text{and} \quad K = \frac{K_1}{K_2} \tag{2.3}$$

$$K = A \cdot \exp\left[\frac{-\Delta E}{R \cdot T}\right] \tag{2.4}$$

Table 2.1: Energy of activation and frequency factors

Energies of activation and frequency factors for the esterification of FFA in sunflower oil

	A	E (J/mol)	R^2
K_1 (5%)	$2.869 \times 10^{+6}$	50745.2	0.999
K_2 (5%)	37.068	31007.3	0.932
K_1 (10%)	$3.913 \times 10^{+5}$	44558.8	0.997
K_2 (10%)	707.166	42761.4	0.932

Steinigeweg et al., (2002) studied about esterification of a fatty acid by reactive distillation had derived a pragmatic kinetic model based on a Langmuir-Hinshelwood-Hougen-Watson and a pseudohomogeneous model. The esterification of a fatty acid by reactive distillation is carried out by esterification of the fatty acid decanoic acid with methanol and catalyzed heterogeneously by a strong acidic ion-exchange resin (Amberlyst 15). There are two different catalytic packings, Katapak-S and Katapak-SP, have been used for reactive distillation experiments. In Steinigeweg et al., (2002) kinetic study, they had developed a pseudohomogeneous kinetic model which is less complex and has a smaller number of parameters. The pseudohomogeneous kinetic model written as,

$$r = \frac{1}{m_{\text{cat}}} \frac{1}{\nu_i} \frac{\mathrm{d}n_i}{\mathrm{d}t} = k_1 a_{\text{DecH}} a_{\text{MeOH}} - k_{-1} a_{\text{MeDec}} a_{\text{H}_2\text{O}} \tag{2.5}$$

where r = of reaction,

m_{cat} = weight catalyst used

This kinetic model however had major drawback which is the neglect of sorption effects, for example the different affinities of the components toward the ion-exchange resin result in differences between the concentrations of the components in the polymeric resin and bulk liquid. The other model, based on a Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach is the simple method to account for the sorption of water. The LHHW equation for a reversible esterification using an ion-exchange resin as a catalyst written as,

$$r = \frac{1}{\nu_i} \frac{\mathrm{d}n_i}{\mathrm{d}t} = m_{\text{cat}} \times \left(\frac{k_1^* K_{\text{DecH}} a_{\text{DecH}} K_{\text{MeOH}} a_{\text{MeOH}} - k_{-1}^* K_{\text{MeDec}} a_{\text{MeDec}} K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}}}{1 + (K_{\text{DecH}} a_{\text{DecH}} + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{MeDec}} a_{\text{MeDec}} + K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}})^2} \right) \tag{2.6}$$

where r = of reaction,

m_{cat} = weight catalyst used

Steinigeweg et al., (2002) concluded that a method for the development of reactive distillation processes is applied for the esterification of decanoic acid with methanol. The thermodynamic aspects have been discussed and reaction kinetics has been investigated. A kinetic approach based upon the LHHW model has been shown that the water uptake by the polymeric catalyst has to be taken into account and that the model proposed is capable of describing the reaction rate as a function of the water content. The kinetic constants for the pseudohomogeneous model based on activities have been fitted.

Tesser R et al., (2005) studied kinetics of oleic acid esterification with methanol in the presence of triglycerides. The kinetics of oleic acid esterification with methanol is carried out by using an acid ion-exchange polymeric resin (Relite CFS) as the heterogeneous catalyst. The kinetics of the reaction has been studied by performing batch runs at different temperatures and in the presence of a certain amount of triglyceride for simulating an oil with a high content of free fatty acids, which is of great potential interest as a raw material in the biodiesel production process. In Tesser R et al., (2005) kinetic study, they had developed a the Langmuir-Hinshelwood type model written as,

$$r = \frac{k_c x_A x_M}{1 + K_M x_M + K_W x_W}\left(1 - \frac{1}{k_e}\frac{x_E x_W}{x_A x_M}\right)C_{cat} \tag{2.7}$$

where r = rate of reaction,

k_c = kinetic constant,

k_e = equilibrium constant,

K_M = adsorption parameter for methanol,

K_W = adsorption parameter for water,

x_A = the molar fraction of the free oleic acid,

x_M = the molar fraction of the methanol,

The k_c and k_e is calculated based on the data in Table 2.2

Table 2.2: Kinetic parameter and related uncertainties

Kinetic Parameters and Related Uncertainties		
parameter	ln(preexponential factor)	activation energy/ heat of reaction (kcal/mol)
k_c	12.93 ± 2.87	14.00 ± 0.99
k_e	4.17 ± 0.04	2.68 ± 0.05

Tesser R et al., (2005) concluded that kinetic parameters of a pseudohomogeneous second-order model have been determined by nonlinear regression on the experimental free-acidity data collected in different runs performed in a batch, well-stirred slurry reactor. A satisfactory agreement between the model and the experiments has been obtained, also considering that the model contains only two adjustable parameters at a given temperature. The kinetic parameters obtained are related to the intrinsic kinetics, with the limitation of internal and external mass transport separately investigated and excluded in the operating condition applied.

CHAPTER 3

METHODOLOGY

3.1 General Chemical and Properties

3.1.1 Octanoic acid

Octanoic acid or commonly known as Caprylic acid is the eight-carbon saturated fatty acid is choosen as the free fatty acid due to its properties in liquid form in room temperature. Molecular formula is $CH_3(CH_2)_6COOH$. The molar mass is 144.21144. The density of Octanoic acid is 0.910 g/cm^3. Melting point and boiling point is 16ºC-17ºC and 237ºC. Acidity of Octanoic acid is 4.89 pKa.

Figure 3.1 shown the chemical structure of octanoic acid.

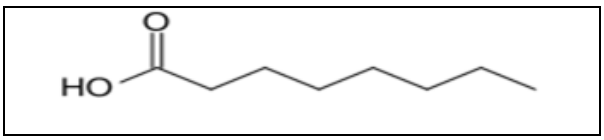

Figure 3.1

Octanoic acid is used commercially in perfumery and manufacture of dyes. This free fatty acid also use in treatment of bacterial infection such as Staphylococcus aureus due to its relatively short chain makes it can penetrate fatty cell wall membranes easily thus effective in combating certain lipid-coated bacteria. Octanoic acid also can be used

in dealing with candida in the intestines, which are frequently colonized by candida due to its anti-fungal properties.

3.1.2 Ethanol

Ethanol is used as alcohol in esterification instead of methanol due to it is safer to use and the final product can be considered 100% natural and renewable. Ethanol (C_2H_5OH) commercially called ethyl alcohol is a volatile, flammeable and colourless liquid. Ethanol is type of alcohol that used in thermometer and as the intoxicating ingredient of alcoholic beverages. Ethanol reacts with free fatty acids to produce ethyl ester and water:

$$RCOOH + HOCH_3CH_3 \rightarrow RCOOCH_2CH_3 + H_2O \qquad (3.1)$$

3.1.3 Sulfated zirconia

Sulfated zirconia is choosen as the catalyst due to its importance of its catalytic activity, reusability and thermal resistant. The triglyceride used in this experiment is domestic cooking oil.

3.1.4 Phenolphtalein

Phenolthalein used as the indicator in the titration process to indicate the presence of of an acid or base where in contact or presence of acid it will turn colorless and with base, it will turn into a pinkish violet color.

3.1.5 Sodium hydroxide (NaOH)

Sodium hydroxide used as an alkaline solution in the titration of ester which produced from the esterification of octanoic acid with ethanol. Sodium hydroxide is a

strong base because of it is a hydroxide anions and an ionic compound with containing sodium cations.

3.2 Research Equipment

Esterification of Octanoic acid and ethanol using sulfated zirconia with presence of triglycerides will be carried out in a batch reactor. The catalyst, sulfated zirconia (SZ) is calcinated between 300°C to 500°C in ambient air to activate the catalyst. In this experiment, the catalyst is calcinated at 400°C for 1 hour. Before the calcinations of sulfated zirconia, the catalyst is been heated at 100°C for 1 hour. The experimental design is shown in Figure 3.2.

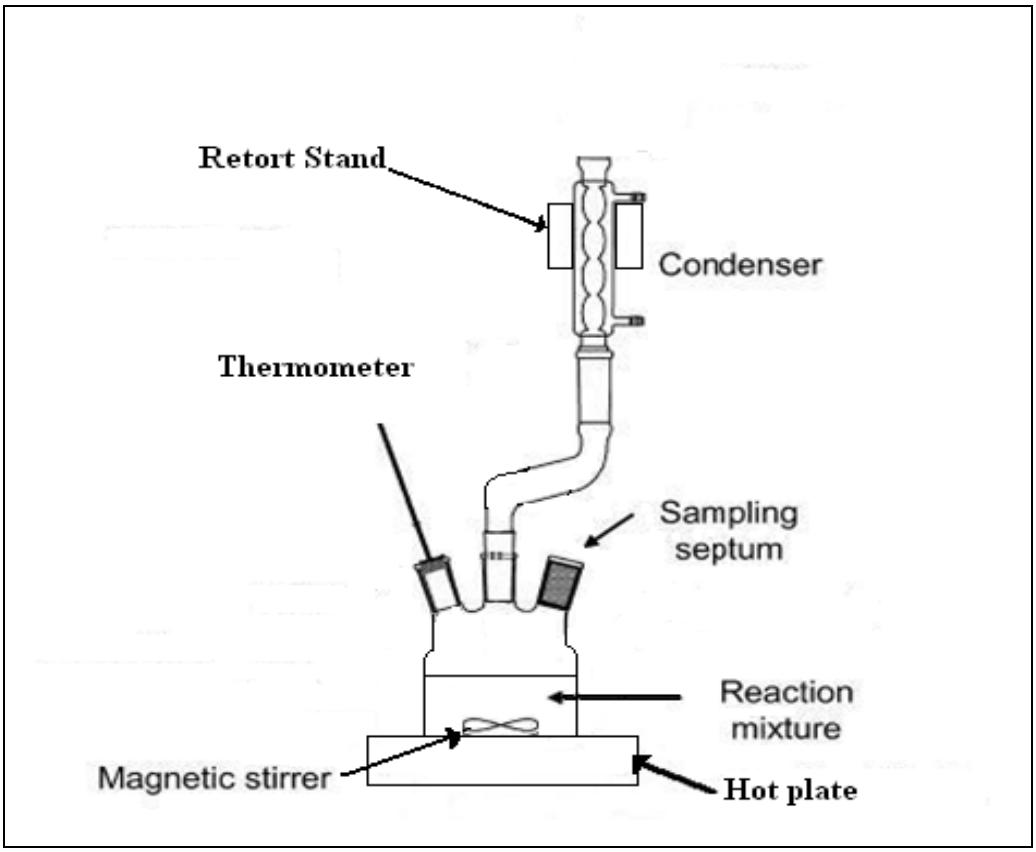

Figure 3.2: Experimental Design

Table 3.1: Research Equipment

No	Component	Function
1	Retort stand	To hold the condenser
2	Thermometer	To measure temperature of reaction mixture
3	Magnetic stirrer	To stir the reaction mixture so that it mixed well
4	Condenser	To condensate the vaporization of ethanol
5	Sampling septum	Part for taking sample of reaction mixture
6	Hot plate	To heat the reaction mixture into desired temperature

3.3 Experimental procedures without the presence of triglycerides

Figure 3.3 below shows the steps of experimental procedures for esterificifation of octanoic acid with etanol using sulfated zirconia without the presence of triglycerides.

The design of fix catalytic bed reactor is set according to figure 3.2.

↓

Mixture of ethanol and octanoic acid is placed inside the flask.

↓

The experiment starts when the reactor achieved the desired operating temperature.

↓

1 ml sample is taken from the batch reactor for every 10 minutes for the first hour and 30 minutes after. 10 samples is collected for 1 run of experiment

↓

Samples(1ml) taken from batch reactor immersed in the cold water to stop any reaction in the sample and centrifuged at 12000000 rpm for 20 minutes to separate the catalyst and the alcohol from the oil phase.

The samples then dissolved in 5ml of ethanol and 3 drops of phenolphthalein added to the sample.

The samples are titrated using 0.1 alkaline solutions NaOH. Phenolphthalein used as indicator. Titration method will determine the remaining free fatty acids.

Figure 3.3: Experimental procedures without the presence of triglycerides

3.4 Experimental procedures with the presence of triglycerides

Figure 3.4 below shows the steps of experimental procedures for esterificifation of octanoic acid with etanol using sulfated zirconia with the presence of triglycerides.

The design of fix catalytic bed reactor is set according to figure 3.2.

Mixture of ethanol and octanoic acid is placed inside the flask. The desired volume of triglycerides is added after.

The experiment starts when the reactor achieved the desired operating temperature.

1 ml sample is taken from the batch reactor for every 10 minutes for the first hour and 30 minutes after. 10 samples is collected for 1 run of experiment

Samples(1ml) taken from batch reactor immersed in the cold water to stop any reaction in the sample and centrifuged at 12000000 rpm for 20 minutes to separate the catalyst and the alcohol from the oil phase.

The samples then dissolved in 5ml of ethanol and 3 drops of phenolphthalein added to the sample.

The samples are titrated using 0.1 alkaline solutions NaOH. Phenolphthalein used as indicator. Titration method will determine the remaining free fatty acids.

Figure 3.4: Experimental procedures with the presence of triglycerides

3.5 Kinetic modeling procedures

1. The conversion of Octanoic acid calculated using Park Y.M et al., 2008

$$\text{Acid value} = \frac{M \times A \times F \times N}{S} \tag{3.2}$$

M= molecular weight of NaOH = 40g/mol

A= Amount of NaOH used

F= concentration coefficient of NaOH

N= Normal concentration of NaOH = 0.1 mol/l

S= sample weight = 0.867

$$\text{Conversion}\ (\%) = \frac{\text{Initial acid value} - \text{final acid value}}{\text{Initial acid value}} \times 100\% \tag{3.3}$$

2. From equation 3.3, the table conversion of octanoic acid constructed,

Time (minute)	NaOH (liter)	Acidity value	Conversion (%)
0	0.0436	0.201153403	0
10	0.0424	0.19561707	2.752293578
20	0.042	0.193771626	3.669724771
30	0.0409	0.188696655	6.19266055
40	0.0405	0.186851211	7.110091743
50	0.0404	0.18638985	7.339449541
60	0.0396	0.182698962	9.174311927
90	0.039	0.179930796	10.55045872
120	0.0387	0.178546713	11.23853211
150	0.0346	0.159630911	20.64220183

Table 3.2: Conversion of octanoic acid

3. Using the data gained for the conversion table 3.2, the kinetic study can be obtained with,

nRa=(kCaCb)-(krCcCd) (3.4)

where $A + B \underset{kr}{\overset{k}{\longleftrightarrow}} C + D$ (3.5)

A= Octanoic acid

B= Ethanol

C= Ethyl Octanoate

D= water

4. The data table for Ca, Cb, Cc and Cd constructed as shown in Table 3.3

Time (minute)	Conversion (%)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0275	4.45891	4.45891	0.12609	0.12609	0.01104
20	0.0375	4.41306	4.41306	0.17194	0.17194	0.00969
30	0.0619	4.30119	4.30119	0.28381	0.28381	0.00842
40	0.0711	4.25901	4.25901	0.32599	0.32599	0.00724
50	0.0734	4.24846	4.24846	0.33654	0.33654	0.00614
60	0.0917	4.16456	4.16456	0.42044	0.42044	0.00513
90	0.1055	4.10128	4.10128	0.48372	0.48372	0.0026
120	0.1124	4.06965	4.06965	0.51535	0.51535	0.00086
150	0.2064	3.63866	3.63866	0.94634	0.94634	0.00012

Table 3.3:Ca, Cb, Cc, Cd Data

5. The final model of the kinetic study is then gained from using POLYMATH 6.10 Educational Release 2006.

6. The final model of the kinetic study is,

Analytical polynomial derivative

Ca = 4.572654 -0.0141598 x time + 0.0001431 x time^2 -5.485E-07 x time^3

d(Ca)/d(time) = -0.0141598 + 0.0002862 x time -1.646E-06 x time^2

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of different reaction temperature

4.1.1 Conversion of Octanoic acid with reaction temperature of 30ºC

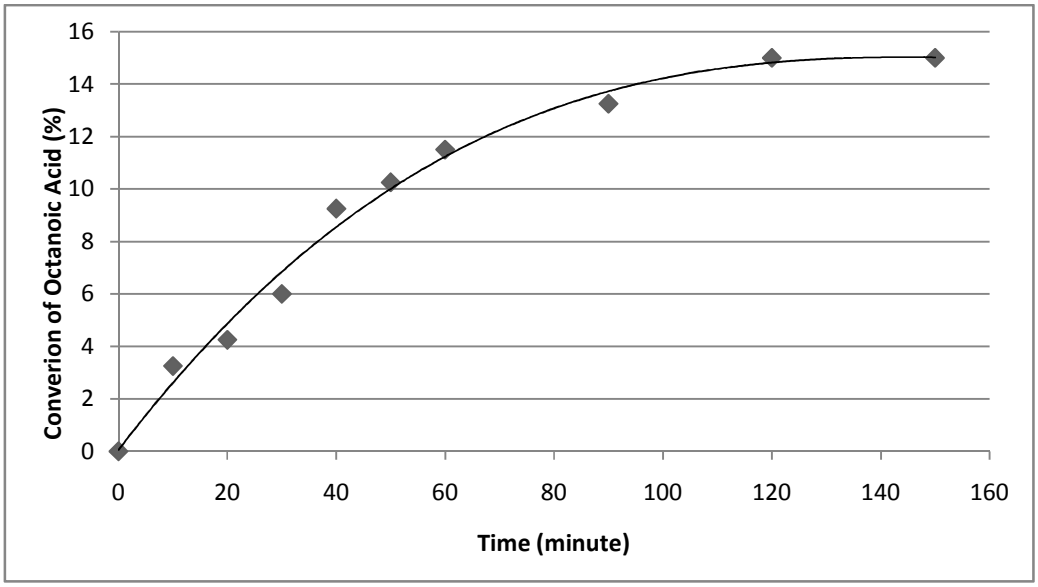

Figure 4.1: Conversion of Octanoic acid at reaction temperature of 30ºC

Figure 4.1 shows the conversion of Octanoic acid at 30ºC of reaction temperature with 0.5g sulfated zirconia, 1:1 molar ratio of Octanoic acid to ethanol without the presence of triglycerides. The final conversion of Otanoic acid using 30^0C of reaction

temperature is 15%. From figure 2, the reactions occur faster within the first 10 minutes and then react slowly after the first hour of time of reaction. The data table for Figure 4.1 is shown at Appendix A.

4.1.2 Conversion of Octanoic acid with reaction temperature of 40ºC

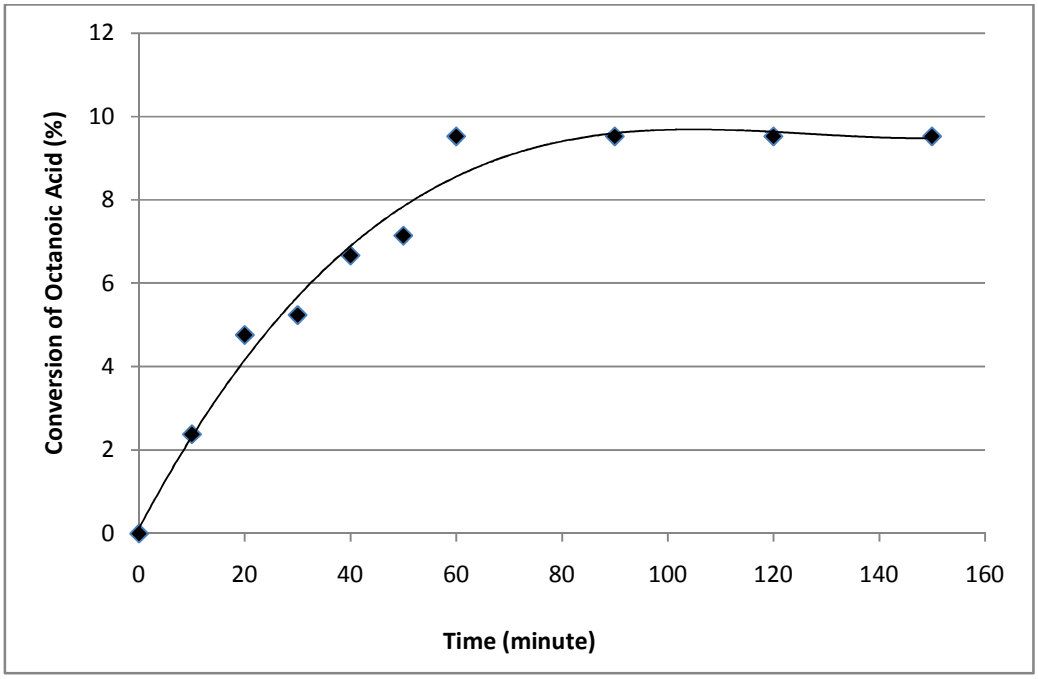

Figure 4.2: Conversion of Octanoic acid at reaction temperature of 40ºC

Figure 4.2 shows the conversion of Octanoic acid at 40^0C of reaction temperature with 0.5g sulfated zirconia, 1:1 molar ratio of Octanoic acid to ethanol without presence of triglycerides. From figure 4.2, the final conversion of Octanoic acid at 40^0C of reaction temperature is 9.5%. The reaction occurs faster for the first 10 minutes and then reacts slowly from 20 minutes to 50 minutes of reaction time. The reaction started to show the equilibrium condition after one hour of reaction time where the final conversion at constant value of 9.5%. The data table for Figure 4.2 is shown at Appendix A

4.1.3 Conversion of Octanoic acid with reaction temperature of 50ºC

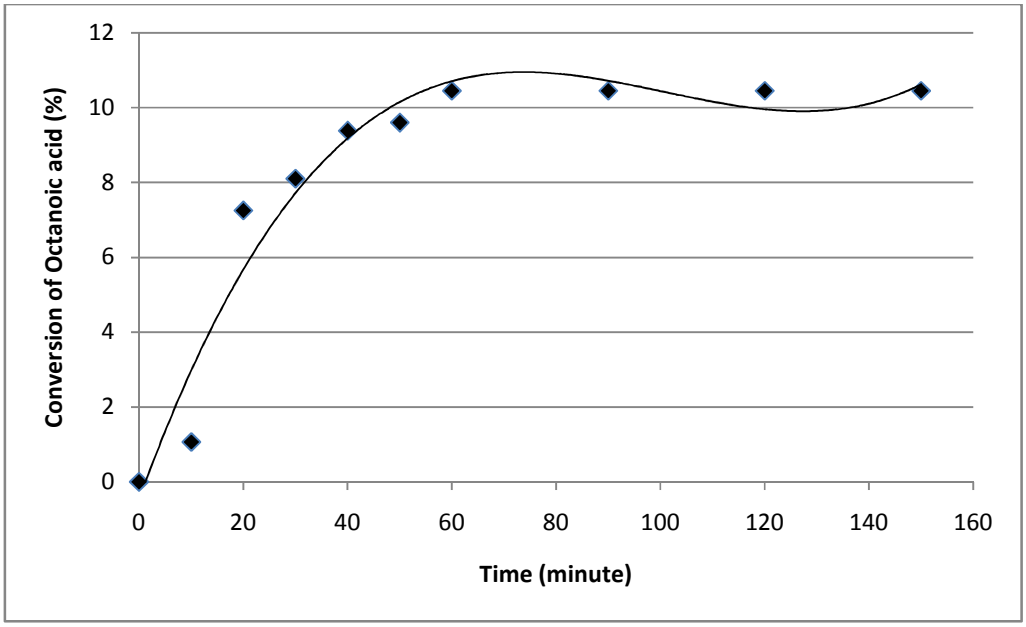

Figure 4.3: Conversion of Octanoic acid at reaction temperature of 50ºC

Figure 4.3 shows the Conversion of Octanoic acid at the reaction temperature of 50ºC with 0.5g sulfated zirconia, 1:1 molar ratio of Octanoic acid to ethanol without presence of triglycerides. The final conversion of Octanoic acid for 50^0C of reaction temperature is 10.4%. From figure 4.3, the reaction occur fastest within the first 20 minutes of reaction time and then react slowly when the reaction reached its equilibrium at the first hour after the reaction time with 10.4% conversion of Octanoic acid. The data table for Figure 4.3 is shown at Appendix A

4.1.4 Conversion of Octanoic acid with different reaction temperature

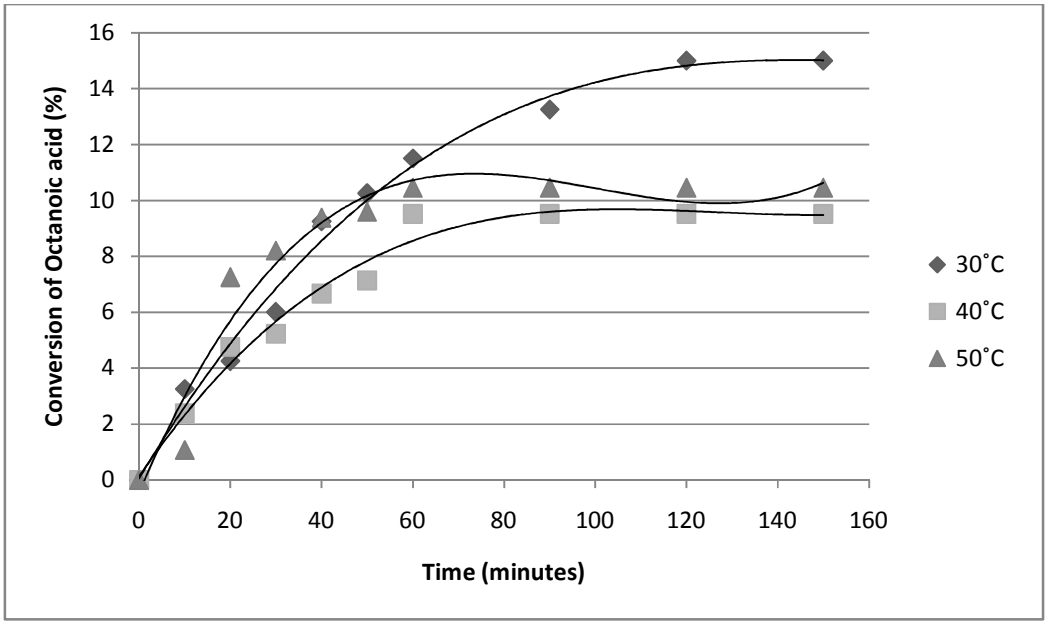

Figure 4.4: Conversion of Octanoic acid with different reaction temperature

Figure 4.4 shows the conversion of Octanoic acid with different reaction temperature with 0.5g sulfated zirconia, 1:1 molar ratio of Octanoic acid to ethanol with no presence of triglycerides. From figure 4.4, the highest conversion of Octanoic acid is 15% at 30^0C reaction temperature. The lowest conversion of Octanoic acid is 9.5% at 40^0C reaction temperature. While at 50^0C reaction temperature, the conversion of Octanoic acid is 10.4%. The reactions occur fastest at 50^0C reaction temperature for the first 20 minutes but react slower when the reaction reached its final conversion compare to the reaction at 30^0C reaction temperature where the final conversion of this reaction is higher. The results show the reaction exhibits an exothermic reaction. When the temperature increased, the final conversion of Octanoic acid is decreased. The data table for Figure 4.4 is shown at Appendix A

4.2 Effect of different amount of sulfated zirconia used

4.2.1 Conversion of Octanoic acid with 0.5g of sulfated zirconia

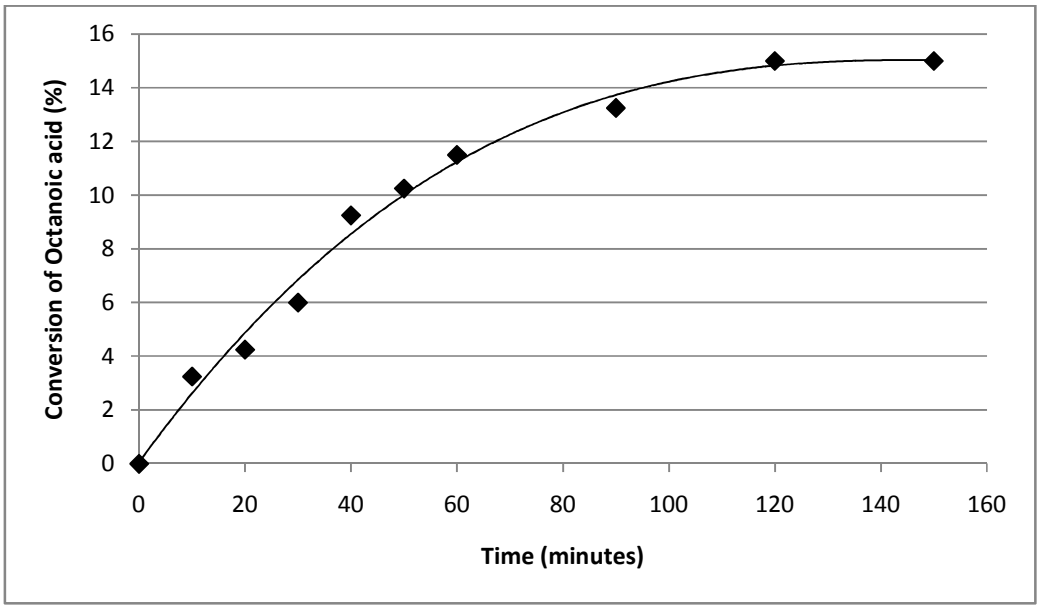

Figure 4.5: Conversion of Octanoic acid using 0.5g of sulfated zirconia

Figure 4.5 shows the conversion of Octanoic acid using 0.5g of sulfated zirconia with 30^0C of reaction temperature, 1:1 molar ratio of Octanoic acid to ethanol with no presence of triglycerides. From figure 4.5, the highest final conversion of Octanoic acid 0.5g of sulfated zirconia is 15%. The results shows the reaction occur faster after 20 minutes of reaction time and began to react slower after 120 minutes of reaction time where at this time the reaction almost achieves its equilibrium conversion. The data table for Figure 4.5 is shown at Appendix A

4.2.2 Conversion of Octanoic acid with 1.0g of sulfated zirconia

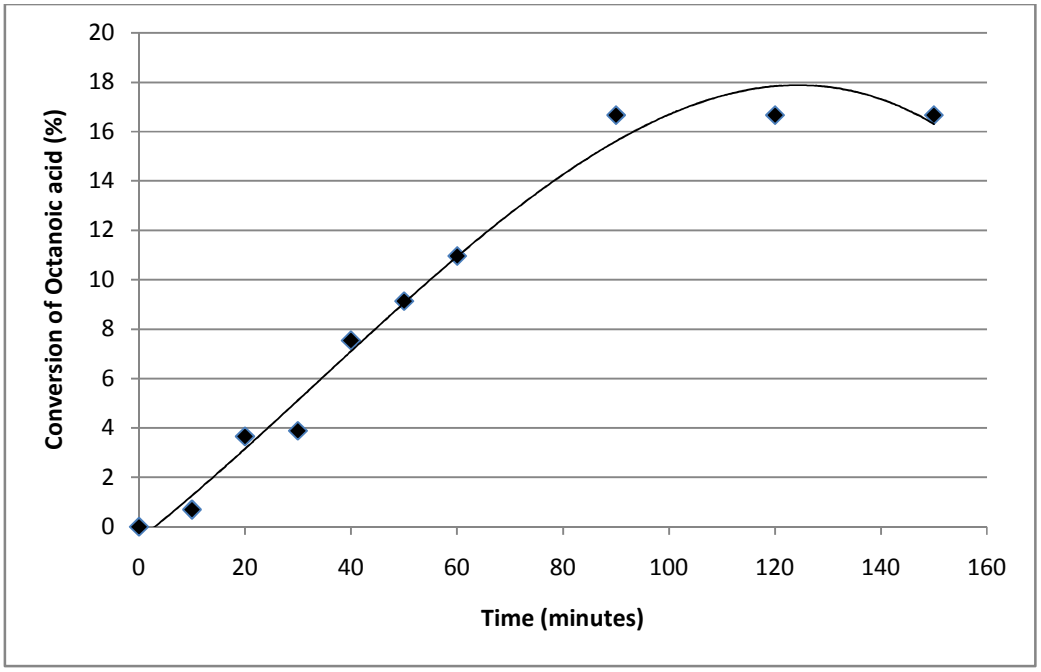

Figure 4.6: Conversion of Octanoic acid using 1.0g of sulfated zirconia

Figure 4.6 shows the conversion of Octanoic acid using 1.0g of sulfated zirconia with 30^0C of reaction temperature, 1:1 molar ratio of Octanoic acid to ethanol with no presence of triglycerides. The highest final conversion of Octanoic acid using 1.0g of sulfated zirconia is 16.6%. The results shows that the reaction occur slow after the first 20 minutes of reaction time and began to react slower after 90 minutes of reaction time. The data table for Figure 4.6 is shown at Appendix A

4.2.3 Conversion of Octanoic acid with 1.5g of sulfated zirconia

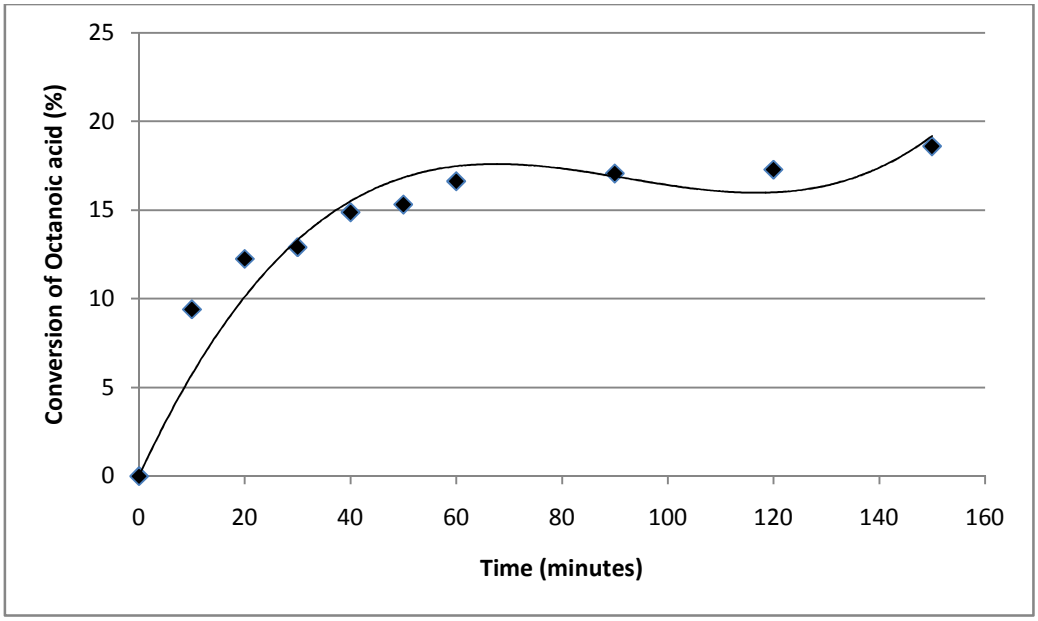

Figure 4.7: Conversion of Octanoic acid using 1.5g of sulfated zirconia

Figure 4.7 shows the conversion of Octanoic acid using 1.5g of sulfated zirconia with 30^0C of reaction temperature, 1:1 molar ratio of Octanoic acid to ethanol with no presence of triglycerides. From figure 4.7, the highest final conversion of Octanoic acid using 1.5g of sulfated zirconia is 18.6%. The final conversion is higher than final conversion of Octanoic acid using 1.0g of sulfated zirconia and 0.5g of sulfated zirconia. The results shows that the reaction react fastest for the first 20 minutes of reaction time and reached the highest final conversion at 150 minutes of reaction time. The data table for Figure 4.7 is shown at Appendix A

4.2.4 Conversion of Octanoic acid with different amount of sulfated zirconia

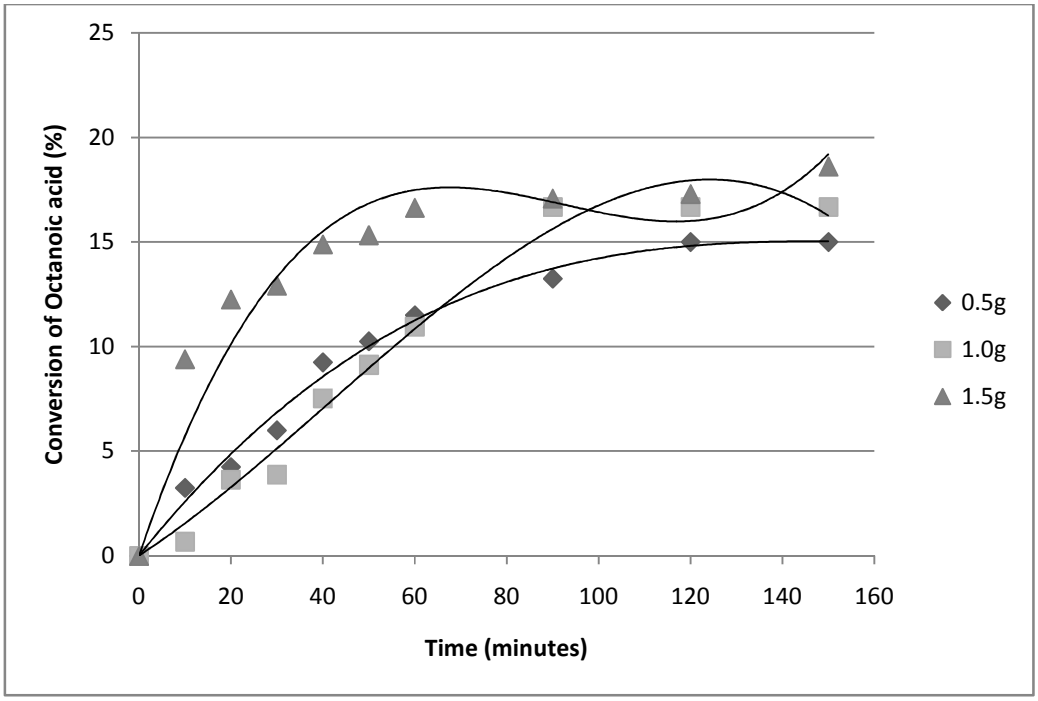

Figure 4.8: Conversion of Octanoic acid using different amount of sulfated zirconia

Figure 4.8 shows the conversion of Octanoic acid using different amount of sulfated zirconia with 30^0C of reaction temperature, 1:1 molar ratio of Octanoic acid to ethanol with no presence of triglycerides. From figure 9, the highest final conversion of Octanoic acid is 18.6% using 1.5g of sulfated zirconia. The lowest final conversion of Octanoic acid is 15% using 0.5g of sulfated zirconia. While using 1.0g of sulfated zirconia the final conversion of Octanoic acid is 16.6%. The reaction occurs fastest when the higher amount of sulfated zirconia used. This can be shown in the figure 4.8 where for the first 20 minutes of reaction time, the reaction rate of 1.5g sulfated zirconia used is much faster than the reaction rate of 1.0g and 0.5g sulfated zirconia used. The higher amount of sulfated zirconia used, the higher final conversion of Octanoic acid yielded. The data table for Figure 4.8 is shown at Appendix A

4.3 Effect of different molar ratio of Octanoic acid and ethanol

4.3.1 Conversion of Octanoic acid with molar ratio 1:1, Octanoic acid to ethanol

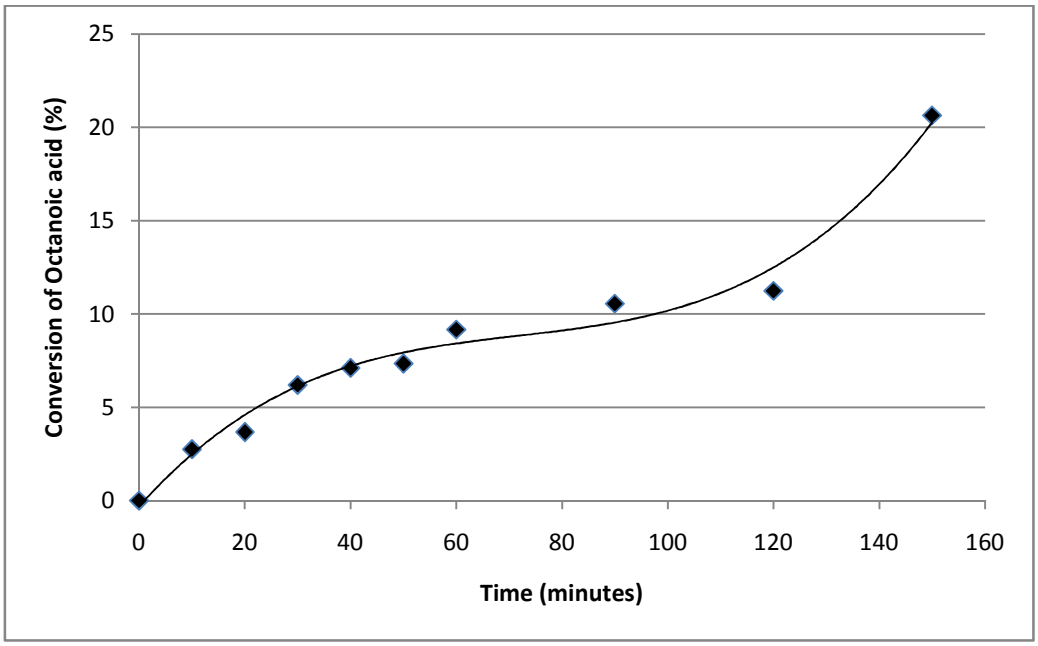

Figure 4.9: Conversion of Octanoic acid with molar ratio 1:1, Octanoic acid to ethanol

Figure 4.9: shows the conversion of Octanoic acid with molar ratio 1:1, Octanoic acid to ethanol with 30^0C of reaction temperature, 1.5g sulfated zirconia used and no presence of triglycerides. From figure 4.9, the highest final conversion of Octanoic acid for molar ratio 1:1, Octanoic acid to ethanol is 20.6%. The reaction occurs slow for the first hour and slowly increased to the highest final conversion at 150 minutes of reaction time. The data table for Figure 4.9 is shown at Appendix A

4.3.2 Conversion of Octanoic acid with molar ratio 1:3, Octanoic acid to ethanol

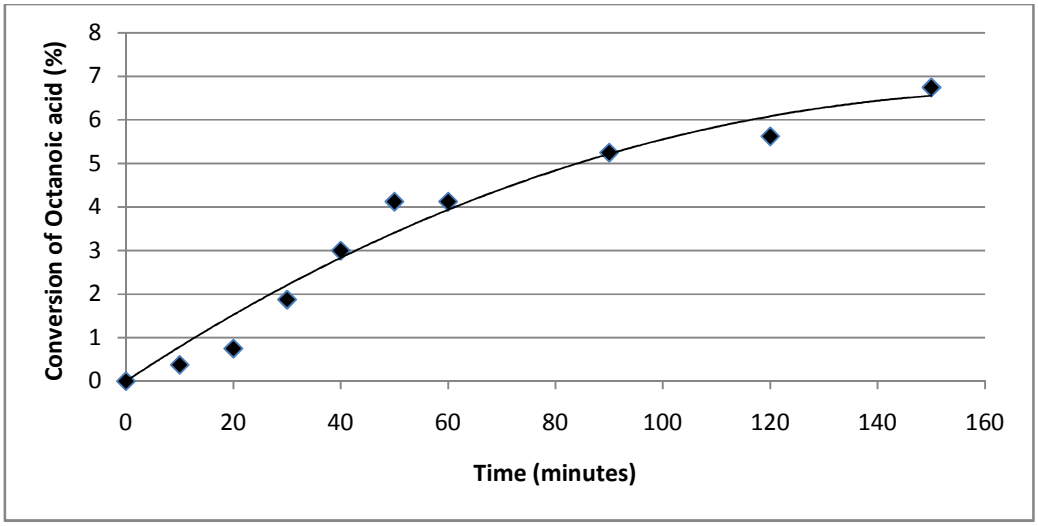

Figure 4.10: Conversion of Octanoic acid with molar ratio 1:3, Octanoic acid to ethanol

Figure 4.10 shows the conversion of Octanoic acid with molar ratio 1:3, Octanoic acid to ethanol with 30^0C of reaction temperature, 1.5g sulfated zirconia used and no presence of triglycerides. From figure 4.10, the final conversion of Octanoic acid with molar ratio 1:3, Octanoic acid to ethanol is 6.7%. The final conversion of Octanoic acid with molar ratio 1:3 is lower than the final conversion of Octanoic acid with molar ratio 1:1. The reaction occurs faster for the first hour of reaction time and then reached its final equilibrium at 6.7% of final conversion of Octanoic acid. The data table for Figure 4.10 is shown at Appendix A

4.3.3 Conversion of Octanoic acid with molar ratio 1:5, Octanoic acid to ethanol

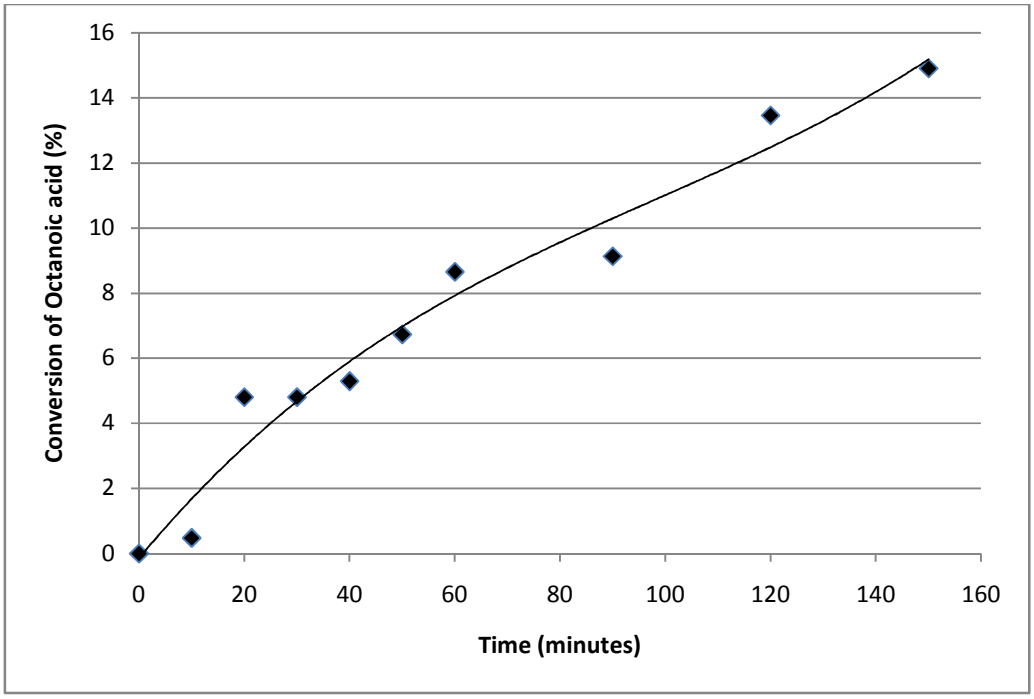

Figure 4.11: Conversion of Octanoic acid with molar ratio 1:5, Octanoic acid to ethanol

Figure 4.11 shows the conversion of Octanoic acid with molar ratio 1:5, Octanoic acid to ethanol with 30^0C of reaction temperature, 1.5g sulfated zirconia used and no presence of triglycerides. The highest final conversion of Octanoic acid with molar ratio 1:5 Octanoic acid to ethanol is 14.9%. The final conversion of Octanoic acid with molar ratio of 1:5 Octanoic acid to ethanol is higher than final conversion of Octanoic acid with molar ratio of 1:3 but lower than final conversion of Octanoic acid with molar ratio 1:1 Octanoic acid to ethanol. The reaction occurs faster within the first hour of reaction time and reacts slowly when the conversion of Octanoic reached its final value. The data table for Figure 4.11 is shown at Appendix A

4.3.4 Conversion of Octanoic acid with different molar ratio of Octanoic acid to ethanol

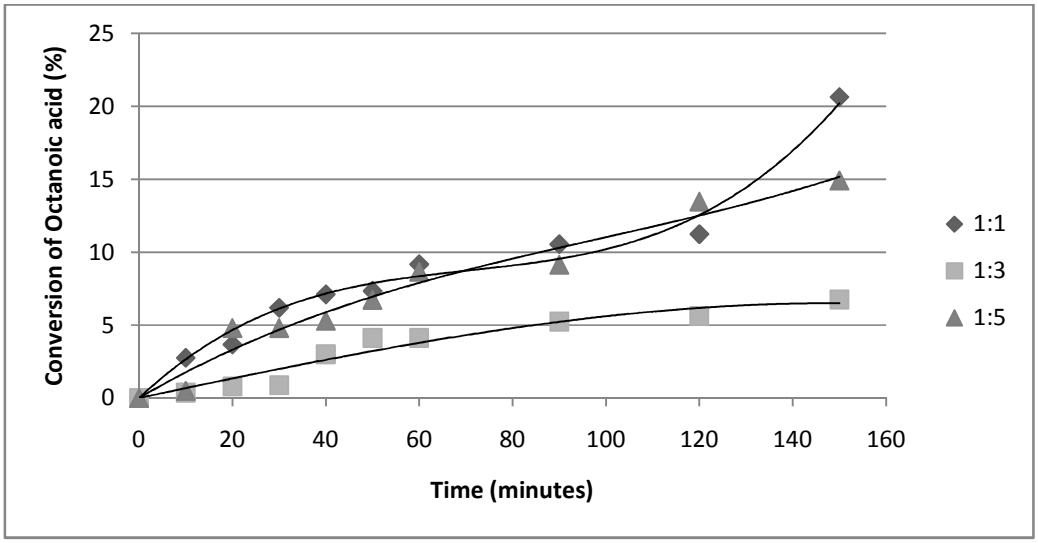

Figure 4.12: Conversion of Octanoic acid with different molar ratio of Octanoic acid to ethanol

Figure 4.12 shows conversion of Octanoic acid with different molar ratio of Octanoic acid to ethanol with 30^0C of reaction temperature, 1.5g sulfated zirconia used and no presence of triglycerides. From figure 4.12, the highest final conversion of Octanoic acid is 20.6% with molar ratio 1:1, Octanoic acid to ethanol. The lowest final conversion of Octanoic acid is 6.7% with molar ratio 1:3, Octanoic acid to ethanol. The reaction rates of 1:1 molar ratio Octanoic acid to ethanol react faster at the first hour of reaction time and reached a higher final conversion of Octanoic acid. The non-common behavior for reaction in molar ratio 1:1, Octanoic acid to ethanol is due to dissolution versus kinetics effect. (Marchetti et al., 2008). The dissolution effect of ethanol over the reaction takes place for the first minutes of reaction time than the kinetics effect producing a smaller reaction rate. The data table for Figure 4.12 is shown at Appendix A

4.4 Effect of the presence of triglycerides

4.4.1 Conversion of Octanoic acid with presence of 30ml triglycerides

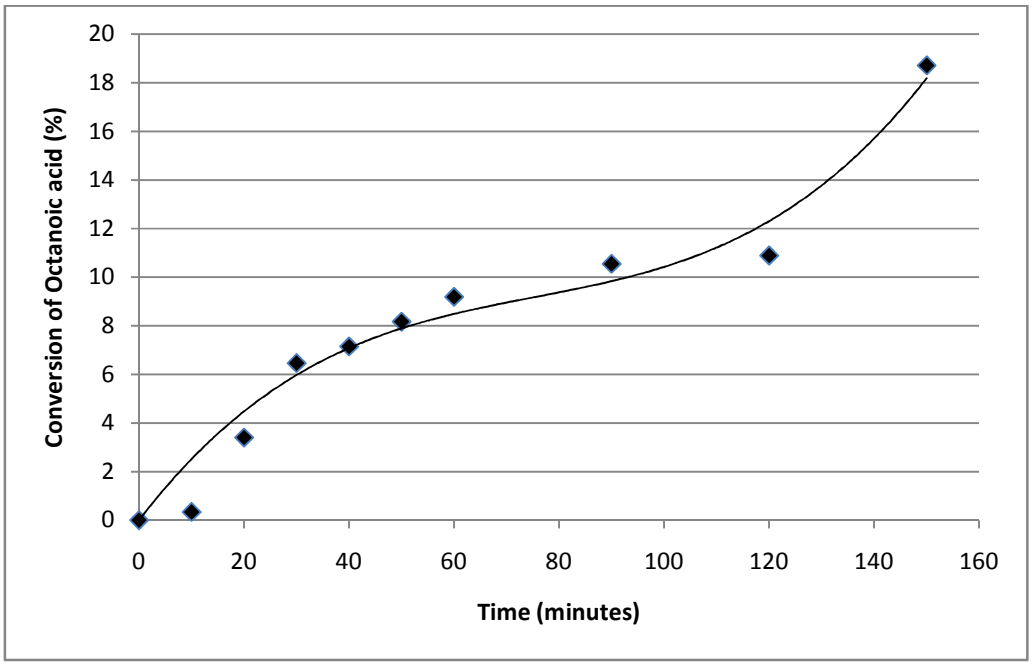

Figure 4.13: Conversion of Octanoic acid with presence of 30ml triglycerides

Figure 4.13 shows the conversion of Octanoic acid with presence of 30ml triglycerides at 30^0C reaction temperature, 1.5g sulfated zirconia used and 1:1 molar ratio of Octanoic acid to ethanol. From figure 4.13, the final conversion of Octanoic acid with presence of 30ml triglycerides is 18.7%. The reaction rate occurs slow for the first 20 minutes of reaction time and the reaction reacts slowly until the final conversion of Octanoic acid reached. The data table for Figure 4.13 is shown at Appendix A

4.4.2 Conversion of Octanoic acid with presence of 50ml triglycerides

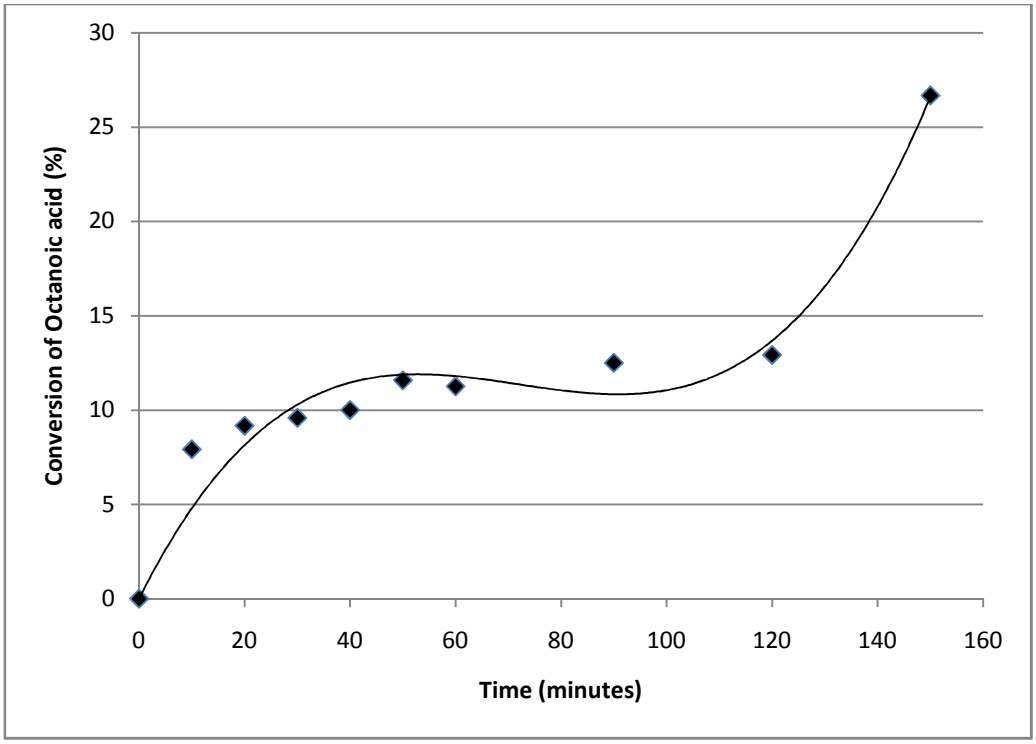

Figure 4.14: Conversion of Octanoic acid with presence of 50ml triglycerides

Figure 4.14 shows conversion of Octanoic acid with presence of 50ml triglycerides at 30^0C reaction temperature, 1.5g sulfated zirconia used and 1:1 molar ratio of Octanoic acid to ethanol. The final conversion of Octanoic acid with presence of 50ml triglycerides is 26.6%. From figure 4.14, the reaction reacts faster for the first 20 minutes of reaction time compare to the reaction at the conversion of Octanoic acid with presence of 30ml. The data table for Figure 4.14 is shown at Appendix A

4.4.3 Conversion of Octanoic acid with presence of 70ml triglycerides

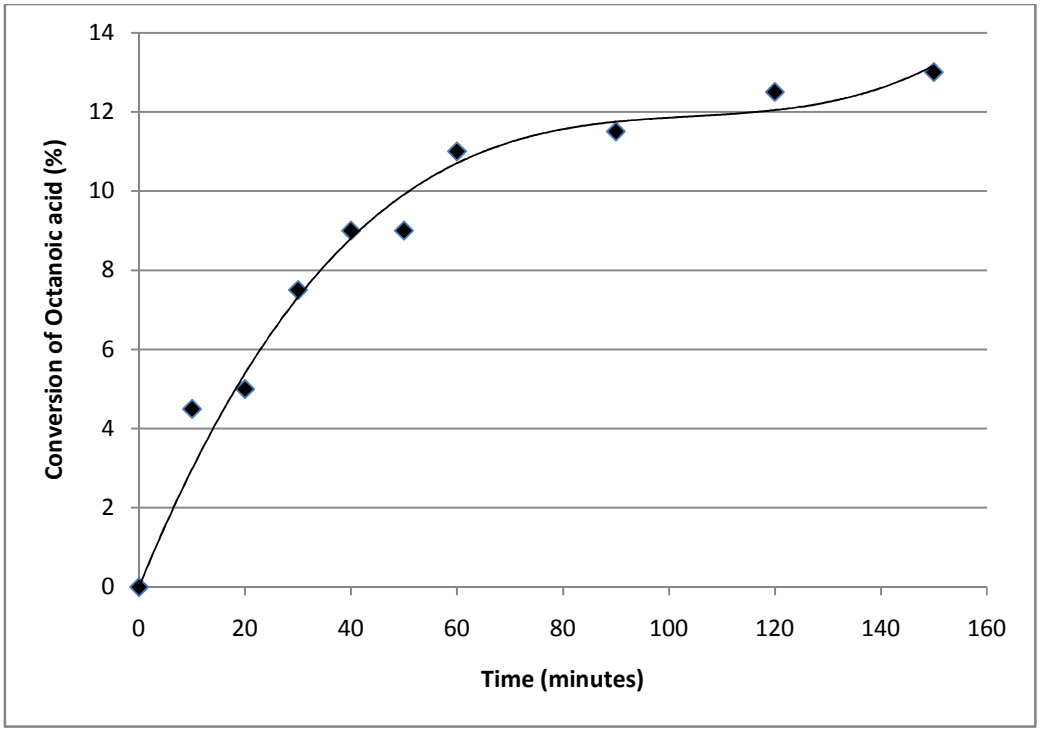

Figure 4.15: Conversion of Octanoic acid with presence of 70ml triglycerides

Figure 4.15 shows conversion of Octanoic acid with presence of 70ml triglycerides at 30^0C reaction temperature, 1.5g sulfated zirconia used and 1:1 molar ratio of Octanoic acid to ethanol. From figure 4.15, the final conversion of Octanoic acid with presence of 70ml triglycerides is 13%. The reaction occurs faster for the first 20 minutes of reaction time compare to reaction at the conversion of Octanoic acid with presence of 30ml triglyceride but reached the lowest value conversion of Octanoic acid at final conversion. The data table for Figure 4.15 is shown at Appendix A

4.4.4 Conversion of Octanoic acid with different amount of triglycerides

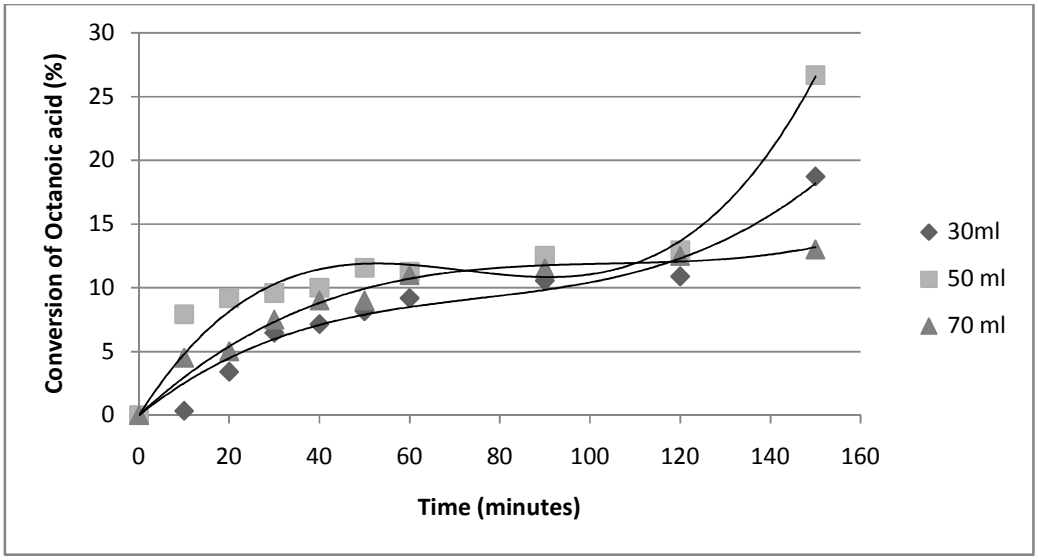

Figure 4.16: Conversion of Octanoic acid with different amount of triglycerides

Figure 4.16 shows conversion of Octanoic acid with different amount of triglycerides at 30^0C reaction temperature, 1.5g sulfated zirconia used and 1:1 molar ratio of Octanoic acid to ethanol. From figure 17, the highest final conversion of Octanoic acid is 26.6% with presence of 50ml triglycerides. The lowest final conversion of Octanoic acid is 13% with presence of 70ml of triglycerides. The reaction of conversion of Octanoic acid with presence of 50ml triglycerides occur fastest for the first 20 minutes of reaction time compare to the reaction at conversion of Octanoic acid with presence of 30ml triglycerides and 70ml triglycerides. The higher amount of triglycerides used shows the higher final conversion of Octanoic acid but when high amount of triglycerides used, the final conversion lower. The final conversion continued increased from 30ml triglycerides used to 50ml triglycerides used. The final conversion decreased when 70ml triglycerides used. This shows that when 70ml triglycerides used, two reaction occurs, esterification of Octanoic acid and transesterification of Octanoic acid. This selectivity of the esterification affected the final conversion of Octanoic acid. The data table for Figure 4.16 is shown at Appendix A

4.5 Kinetic modeling study

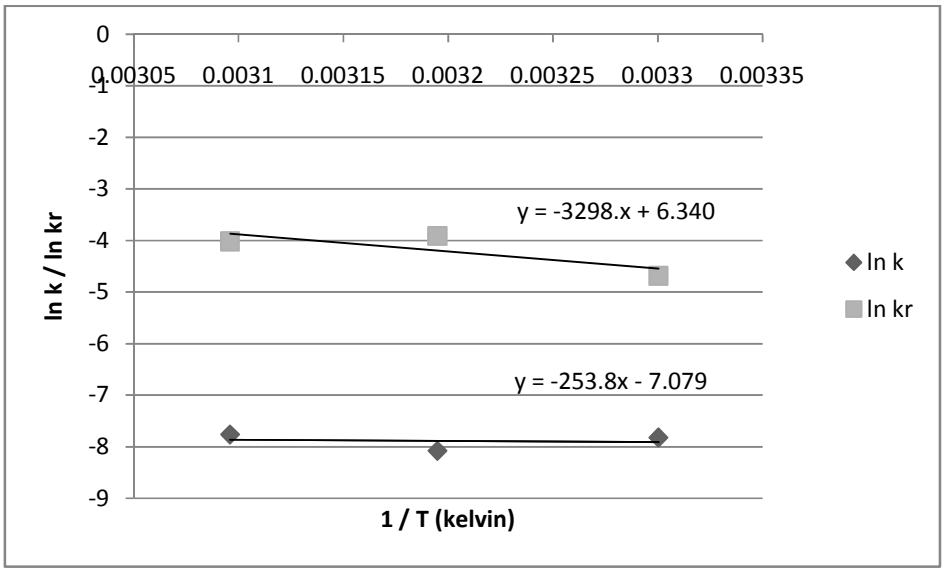

Figure 4.17: Arrhenius-type plot for the reaction rate constant k and kr

Figure 4.17 shows the Arrhenius plot for the esterification of octanoic acid and ethanol using sulfated zirconia for reaction temperature of 30ºC, 40ºC and 50ºC. The activation energy, E for reaction rate constant k is 27 kJ mol^{-1}. The activation energy, E for reaction rate constant kr is 2 kJ mol^{-1}. The activation energy, E is calculated using the Arrhenius equation,

$$K = Ae^{-E/RT} \quad (4.1)$$

where A = preexponential factorof frequency factor

E = activation energy , J/mol

R = gas contant = 8.134 J/mol K

T = absolute temperature, K (Kelvin)

After taking the natural logarithm of Equation (4.1), the equation becomes

$$\ln K = \ln A - \frac{E}{\ } \qquad (4.2)$$

Equation (4.2) same as the linear equation y = mx+ c (4.3)

where $m = \frac{E}{\ }$ is slope of the plotted graph (4.4)

$$c = \ln A \qquad (4.5)$$

The results show the direct reaction of estericification of octanoic acid with ethanol using sulfated ziconia used more activation energy than the reversible reaction of estericification of octanoic acid with ethanol using sulfated ziconia.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Esterification of Octanoic acid and ethanol using sulfated zirconia in the presence of triglycerides achieved in the best operation condition with 30°C reaction temperature, 1.5g of sulfated zirconia used, 1:1 molar ratio of Octanoic acid to ethanol and 50ml of triglycerides used. The final conversion of Octanoic acid is higher when the temperature of reaction decreased. The reaction exhibit an exothermic reaction. The Octanoic acid conversion increased with the increasing of the amount of catalyst, sulfated zirconia used. The conversion of Octanoic acids is higher when low molar ratio of octanoic acid to ethanol used. The conversion of Octanoic acid is higher when higher amount of triglycerides used but limited to 50ml triglycerides only. The kinetic model that been developed is based on rate of reaction of the esterification that is ;

$$nRa=(kCaCb)-(krCcCd) \quad (3.4)$$

5.2 Recommendation

The esterification of Octanoic acid and ethanol using sulfated zirconia with the presence of triglycerides can be done more with a broader range of the parameter in temperature, molar ratio of octanoic acid to ethanol, amount of sulfated zirconia used and the amount of triglycerides presence in the esterification. The reaction time can be lengthen more to 5 or 6 hours aparts from using 3 hours of reaction time. The conversion of octanoic acid will increase with the increasing of reaction time.

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APPENDICES

Appendix A

30^0C reaction temperature

time	NaOH (l)	Acidity value	Conversion
0	0.04	0.184544406	0
10	0.0387	0.178546713	3.25
20	0.0383	0.176701269	4.25
30	0.0376	0.173471742	6
40	0.0363	0.167474048	9.25
50	0.0359	0.165628604	10.25
60	0.0354	0.163321799	11.5
90	0.0347	0.160092272	13.25
120	0.034	0.156862745	15
150	0.034	0.156862745	15

40^0C reaction temperature

time	NaOH (l)	Acidity value	Conversion
0	0.042	0.193771626	0
10	0.041	0.189158016	2.38095238
20	0.04	0.184544406	4.76190476
30	0.0398	0.183621684	5.23809524
40	0.0392	0.180853518	6.66666667
50	0.039	0.179930796	7.14285714
60	0.038	0.175317186	9.52380952
90	0.038	0.175317186	9.52380952
120	0.038	0.175317186	9.52380952
150	0.038	0.175317186	9.52380952

50^0C reaction temperature

time	NaOH(l)	Acidity value	Conversion
0	0.0469	0.216378316	0
10	0.0464	0.214071511	1.06609808
20	0.0435	0.200692042	7.24946695
30	0.0431	0.198846597	8.10234542
40	0.0425	0.196078431	9.38166311
50	0.0424	0.19561707	9.59488273
60	0.042	0.193771626	10.4477612
90	0.042	0.193771626	10.4477612
120	0.042	0.193771626	10.4477612
150	0.042	0.193771626	10.4477612

0.5g sulfated zirconia

time	NaOH (l)	Acidity value	Conversion
0	0.04	0.184544406	0
10	0.0387	0.178546713	3.25
20	0.0383	0.176701269	4.25
30	0.0376	0.173471742	6
40	0.0363	0.167474048	9.25
50	0.0359	0.165628604	10.25
60	0.0354	0.163321799	11.5
90	0.0347	0.160092272	13.25
120	0.034	0.156862745	15
150	0.034	0.156862745	15

1.0g sulfated zirconia

time	NaOH (l)	Acidity value	Conversion
0	0.0438	0.202076125	0
10	0.0435	0.200692042	0.68493151
20	0.0422	0.194694348	3.65296804
30	0.0421	0.194232987	3.88127854
40	0.0405	0.186851211	7.53424658
50	0.0398	0.183621684	9.13242009
60	0.039	0.179930796	10.9589041
90	0.0365	0.16839677	16.6666667
120	0.0365	0.16839677	16.6666667
150	0.0365	0.16839677	16.6666667

1.5 sulfated zirconia

time	NaOH (l)	Acidity value	Conversion
0	0.0457	0.210841984	0
10	0.0414	0.19100346	9.409190372
20	0.0401	0.185005767	12.25382932
30	0.0398	0.183621684	12.91028446
40	0.0389	0.179469435	14.87964989
50	0.0387	0.178546713	15.31728665
60	0.0381	0.175778547	16.63019694
90	0.0379	0.174855825	17.0678337
120	0.0378	0.174394464	17.28665208
150	0.0372	0.171626298	18.59956236

1:1 molar ratio octanoic acid:ethanol

time	NaOH (l)	Acidity value	Conversion
0	0.0436	0.201153403	0
10	0.0424	0.19561707	2.752293578
20	0.042	0.193771626	3.669724771
30	0.0409	0.188696655	6.19266055
40	0.0405	0.186851211	7.110091743
50	0.0404	0.18638985	7.339449541
60	0.0396	0.182698962	9.174311927
90	0.039	0.179930796	10.55045872
120	0.0387	0.178546713	11.23853211
150	0.0346	0.159630911	20.64220183

1:3 molar ratio octanoic acid:ethanol

time	NaOH (l)	Acidity value	Conversion
0	0.0267	0.123183391	0
10	0.0266	0.12272203	0.37453184
20	0.0265	0.122260669	0.74906367
30	0.0262	0.120876586	1.87265918
40	0.0259	0.119492503	2.99625468
50	0.0256	0.11810842	4.11985019
60	0.0256	0.11810842	4.11985019
90	0.0253	0.116724337	5.24344569
120	0.0252	0.116262976	5.61797753
150	0.0249	0.114878893	6.74157303

1:5 molar ratio octanoic acid:ethanol

time	NaOH (l)	Acidity value	Conversion
0	0.0208	0.095963091	0
10	0.0207	0.09550173	0.480769231
20	0.0198	0.091349481	4.807692308
30	0.0198	0.091349481	4.807692308
40	0.0197	0.09088812	5.288461538
50	0.0194	0.089504037	6.730769231
60	0.019	0.087658593	8.653846154
90	0.0189	0.087197232	9.134615385
120	0.018	0.083044983	13.46153846
150	0.0177	0.0816609	14.90384615

30ml triglycerides

time	NaOH (l)	Acidity value	Conversion
0	0.0294	0.135640138	0
10	0.0293	0.135178777	0.34013605
20	0.0284	0.131026528	3.40136054
30	0.0275	0.126874279	6.46258503
40	0.0273	0.125951557	7.14285714
50	0.027	0.124567474	8.16326531
60	0.0267	0.123183391	9.18367347
90	0.0263	0.121337947	10.5442177
120	0.0262	0.120876586	10.8843537
150	0.0239	0.110265283	18.707483

50ml triglycerides

time	NaOH (l)	Acidity value	Conversion
0	0.024	0.110726644	0
10	0.0221	0.101960784	7.916666667
20	0.0218	0.100576701	9.166666667
30	0.0217	0.10011534	9.583333333
40	0.0216	0.099653979	10
50	0.0215	0.099192618	11.57407407
60	0.0213	0.098269896	11.25
90	0.021	0.096885813	12.5
120	0.0209	0.096424452	12.91666667
150	0.0176	0.081199539	26.66666667

70ml triglycerides

time	NaOH (l)	Acidity value	Conversion
0	0.02	0.092272203	0
10	0.0191	0.088119954	4.5
20	0.019	0.087658593	5
30	0.0185	0.085351788	7.5
40	0.0182	0.083967705	9
50	0.0182	0.083967705	9
60	0.0178	0.082122261	11
90	0.0177	0.0816609	11.5
120	0.0175	0.080738178	12.5
150	0.0174	0.080276817	13

Appendix B

0.5 sulfated zirconia

time	conversion (X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0325	4.435988	4.435988	0.149013	0.149013	0.011039
20	0.0425	4.390138	4.390138	0.194863	0.194863	0.009686
30	0.06	4.3099	4.3099	0.2751	0.2751	0.008418
40	0.0925	4.160888	4.160888	0.424113	0.424113	0.007237
50	0.1025	4.115038	4.115038	0.469963	0.469963	0.00614
60	0.115	4.057725	4.057725	0.527275	0.527275	0.005129
90	0.1325	3.977488	3.977488	0.607513	0.607513	0.00261
120	0.15	3.89725	3.89725	0.68775	0.68775	0.000861
150	0.15	3.89725	3.89725	0.68775	0.68775	0.000119

1.0 sulfated zirconia

time	conversion(X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0068	4.553822	4.553822	0.031178	0.031178	0.009235
20	0.0365	4.417648	4.417648	0.167353	0.167353	0.007664
30	0.0388	4.407102	4.407102	0.177898	0.177898	0.006233
40	0.0753	4.23975	4.23975	0.345251	0.345251	0.004943
50	0.0913	4.16639	4.16639	0.418611	0.418611	0.003794
60	0.1096	4.082484	4.082484	0.502516	0.502516	0.002787
90	0.1667	3.820681	3.820681	0.76432	0.76432	0.000608
120	0.1667	3.820681	3.820681	0.76432	0.76432	0.000302
150	0.1667	3.820681	3.820681	0.76432	0.76432	0.000568

1.5 sulfated zirconia

time	conversion (X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.094	4.15401	4.15401	0.43099	0.43099	0.003496
20	0.1225	4.023338	4.023338	0.561663	0.561663	0.002333
30	0.1291	3.993077	3.993077	0.591924	0.591924	0.00138
40	0.1488	3.902752	3.902752	0.682248	0.682248	0.000637
50	0.1532	3.882578	3.882578	0.702422	0.702422	0.000105
60	0.1663	3.822515	3.822515	0.762486	0.762486	0.000217
90	0.1707	3.802341	3.802341	0.78266	0.78266	7.87E-05
120	0.1729	3.792254	3.792254	0.792747	0.792747	0.002268
150	0.186	3.73219	3.73219	0.85281	0.85281	0.00635

1:1 molar ratio octanoic acid to ethanol

time	conversion (X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0275	4.458913	4.458913	0.126088	0.126088	0.011039
20	0.0375	4.413063	4.413063	0.171938	0.171938	0.009686
30	0.0619	4.301189	4.301189	0.283812	0.283812	0.008418
40	0.0711	4.259007	4.259007	0.325994	0.325994	0.007237
50	0.0734	4.248461	4.248461	0.336539	0.336539	0.00614
60	0.0917	4.164556	4.164556	0.420445	0.420445	0.005129
90	0.1055	4.101283	4.101283	0.483718	0.483718	0.002601
120	0.1124	4.069646	4.069646	0.515354	0.515354	0.000861
150	0.2064	3.638656	3.638656	0.946344	0.946344	0.000119

1:3 molar ratio octanoic acid to ethanol

time	conversion(X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	13.755	0	0	0
10	0.0037	4.568036	13.73804	0.016965	0.016965	0.008458
20	0.0079	4.548779	13.71878	0.036222	0.036222	0.008883
30	0.0087	4.545111	13.71511	0.03989	0.03989	0.009085
40	0.02996	4.447633	13.61763	0.137367	0.137367	0.009064
50	0.0412	4.396098	13.5661	0.188902	0.188902	0.00882
60	0.0412	4.396098	13.5661	0.188902	0.188902	0.008353
90	0.0524	4.344746	13.51475	0.240254	0.240254	0.005613
120	0.0561	4.327782	13.49778	0.257219	0.257219	0.000867
150	0.0674	4.275971	13.44597	0.309029	0.309029	0.005887

1:5molar ratio octanoic acid to ethanol

time	conversion (X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	22.925	0	0	0
10	0.0048	4.562992	22.90299	0.022008	0.022008	0.019142
20	0.048	4.36492	22.70492	0.22008	0.22008	0.014507
30	0.048	4.36492	22.70492	0.22008	0.22008	0.010463
40	0.0529	4.342454	22.68245	0.242547	0.242547	0.00701
50	0.0673	4.27643	22.61643	0.308571	0.308571	0.004148
60	0.0865	4.188398	22.5284	0.396603	0.396603	0.001877
90	0.0913	4.16639	22.50639	0.418611	0.418611	0.001391
120	0.1346	3.967859	22.30786	0.617141	0.617141	0.000661

150	0.149	3.901835	22.24184	0.683165	0.683165	0.008031

30^0C reaction temperature

time	conversion(X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0325	4.435988	4.435988	0.149013	0.149013	0.01117
20	0.0425	4.390138	4.390138	0.194863	0.194863	0.008284
30	0.06	4.3099	4.3099	0.2751	0.2751	0.005908
40	0.0925	4.160888	4.160888	0.424113	0.424113	0.004041
50	0.1025	4.115038	4.115038	0.469963	0.469963	0.002682
60	0.115	4.057725	4.057725	0.527275	0.527275	0.001833
90	0.1325	3.977488	3.977488	0.607513	0.607513	0.002338
120	0.15	3.89725	3.89725	0.68775	0.68775	0.007424
150	0.15	3.89725	3.89725	0.68775	0.68775	0.01709

40^0C reaction temperature

time	conversion (X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0238	4.475877	4.475877	0.109123	0.109123	0.003916
20	0.0476	4.366754	4.366754	0.218246	0.218246	0.003607
30	0.0523	4.345205	4.345205	0.239796	0.239796	0.003306
40	0.0667	4.279181	4.279181	0.30582	0.30582	0.003014
50	0.0714	4.257631	4.257631	0.327369	0.327369	0.002731
60	0.0952	4.148508	4.148508	0.436492	0.436492	0.002456
90	0.0952	4.148508	4.148508	0.436492	0.436492	0.001687
120	0.0952	4.148508	4.148508	0.436492	0.436492	0.000996
150	0.0952	4.148508	4.148508	0.436492	0.436492	0.000386

50^0C reaction temperature

time	conversion (X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0107	4.535941	4.535941	0.04906	0.04906	0.007819
20	0.0725	4.252588	4.252588	0.332413	0.332413	0.006844
30	0.082	4.20903	4.20903	0.37597	0.37597	0.005987
40	0.0938	4.154927	4.154927	0.430073	0.430073	0.005246
50	0.0959	4.145299	4.145299	0.439702	0.439702	0.004624

60	0.1045	4.105868	4.105868	0.479133	0.479133	0.004119
90	0.1045	4.105868	4.105868	0.479133	0.479133	0.003308
120	0.1045	4.105868	4.105868	0.479133	0.479133	0.003556
150	0.1045	4.105868	4.105868	0.479133	0.479133	0.004861

30ml triglycerides

time	conversion(X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0034	4.569411	4.569411	0.015589	0.015589	0.012471
20	0.034	4.42911	4.42911	0.15589	0.15589	0.009458
30	0.0646	4.288809	4.288809	0.296191	0.296191	0.006927
40	0.0714	4.257631	4.257631	0.327369	0.327369	0.004876
50	0.0816	4.210864	4.210864	0.374136	0.374136	0.003306
60	0.0918	4.164097	4.164097	0.420903	0.420903	0.002217
90	0.1054	4.101741	4.101741	0.483259	0.483259	0.001835
120	0.1088	4.086152	4.086152	0.498848	0.498848	0.00578
150	0.1871	3.727147	3.727147	0.857854	0.857854	0.014053

50ml triglycerides

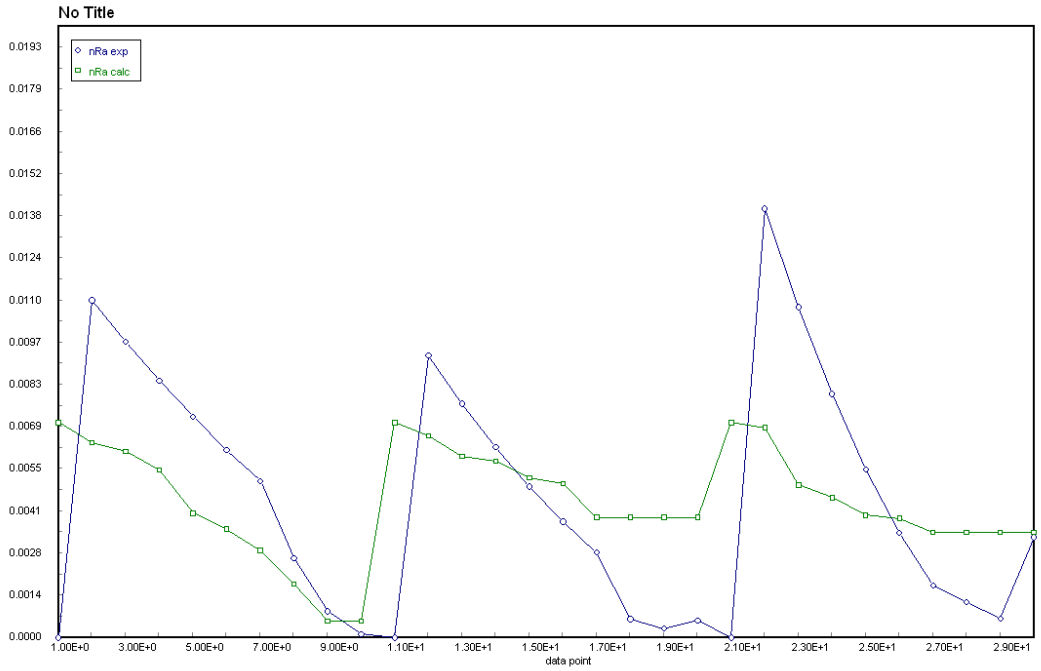
time	conversion(X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.0792	4.221868	4.221868	0.363132	0.363132	0.003496
20	0.0917	4.164556	4.164556	0.420445	0.420445	0.002333
30	0.0958	4.145757	4.145757	0.439243	0.439243	0.00138
40	0.1	4.1265	4.1265	0.4585	0.4585	0.000637
50	0.1157	4.054516	4.054516	0.530485	0.530485	0.000105
60	0.1152	4.056808	4.056808	0.528192	0.528192	0.000217
90	0.125	4.011875	4.011875	0.573125	0.573125	7.87E-05
120	0.1292	3.992618	3.992618	0.592382	0.592382	0.002268
150	0.2667	3.362181	3.362181	1.22282	1.22282	0.00635

70ml triglycerides

time	conversion(X)	Ca	Cb	Cc	Cd	nRa
0	0	4.585	4.585	0	0	0
10	0.045	4.378675	4.378675	0.206325	0.206325	0.011207
20	0.05	4.35575	4.35575	0.22925	0.22925	0.009128
30	0.075	4.241125	4.241125	0.343875	0.343875	0.007274
40	0.09	4.17235	4.17235	0.41265	0.41265	0.005644

50	0.09	4.17235	4.17235	0.41265	0.41265	0.004239
60	0.11	4.08065	4.08065	0.50435	0.50435	0.003058
90	0.115	4.057725	4.057725	0.527275	0.527275	0.000865
120	0.125	4.011875	4.011875	0.573125	0.573125	0.000693
150	0.13	3.98895	3.98895	0.59605	0.59605	0.002543

Appendix C



Non linear graph for temperature parameter.

POLYMATH Report No Title
Nonlinear Regression (L-M) 27-Apr-2009

Model: nRa = (k*Ca*Cb)-(kr*Cc*Cd)

Variable	Initial guess	Value	95% confidence
k	1.	0.0003351	2.412E-08

kr	1.	0.0095943	2.144E-06

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.176074
R^2adj	0.1466481
Rmsd	0.0006491
Variance	1.354E-05

General

Sample size	30
Model vars	2
Indep vars	4
Iterations	5