

**ESTERIFICATION OF OLEIC ACID WITH ETHANOL BY USING
SULFATED ZIRCONIA CATALYST IN THE PRESENCE OF
TRIGLYCERIDES: KINETIC AND MODELING STUDY**

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UNIVERSITI MALAYSIA PAHANG

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BORANG PENGESAHAN STATUS TESIS♦

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SESI PENGAJIAN: 2008/2009

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ABDUL-RAFIQ BIN MOHAMAD YAZID

**A thesis submitted in fulfilment of the
requirement for the award of the degree of
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**Faculty of Chemical and Natural Resources Engineering
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Special Dedication of This Grateful Feeling to My...

Beloved parent;

Mr. Mohamad Yazid b. Abu Yamin & Mrs. Norhaini bt. Timin

For Their Love, Support and Best Wishes.

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ABSTRACT

This dissertation is about the esterification of oleic acid with ethanol by using sulfated zirconia as a catalyst in the presence of triglycerides. In this dissertation the kinetic and the modeling study about the reaction as well as the best operating parameter for the reaction will be studied and investigated. Biodiesel is the one the new possible substitute of regular fuel for engines and it can be produced from various animal fats and vegetable oils. The biodiesel has more advantages compared to the fossil based fuel because it has lower emission of carbon monoxide due to the better combustion, a better lubricating effect on engines, non sulfur emission and non particulate matter pollutant. In this study, there are four operating parameter were investigated and studied which are temperature, amount of catalyst, ratio of oleic acid to the ethanol and the addition of triglycerides. The best operating condition in this study has been produced 31.7% final conversion of oleic acid. The experimental data have been interpreted with pseudo-homogenous kinetic model and the rate constant has been determined from the calculation. It was found out that the sulfated zirconia catalyst was suitable to perform not only esterification reaction but also the tranesterification reaction in biodiesel production.

ABSTRAK

Disertasi ini adalah berkenaan pengesterifikasian asid oleik dengan etanol menggunakan “sulfated zirconia” sebagai pemangkin dengan kehadiran “triglycerides”. Di dalam disertasi ini, model kinetik dan juga pemodelan tindak balas disertai parameter operasi untuk tindak balas akan dipelajari dan disiasat. Biodiesel adalah satu sumber tenaga yang berpotensi untuk menjadi alternatif untuk digunakan di dalam enjin dan ia juga boleh dihasilkan dari pelbagai lemak haiwan dan minyak sayuran. Biodiesel mempunyai pelbagai kelebihan berbanding minyak bersumberkan fosil antaranya mengeluarkan karbon monoksida yang sedikit disebabkan pembakaran yang lebih sempurna, pelincir enjin yang efektif, tiada pelepasan sulfur dan tidak menghasilkan bahan yg mencemarkan alam. Di dalam kajian, terdapat parameter operasi yang diambil kira iaitu suhu, amaun pemangkin, nisbah asid oleic kepada alkohol dan juga penambahan “triglycerides”. Kombinasi operasi parameter yang terbaik telah dapat menghasilkan penukaran asid oleik kepada ester sebanyak 31.7%. Data eksperimen telah dianalisis kepada bentuk model “pseudo-homogenous” dan kadar tindakbalas telah diketahui melalui pengiraan yang dilakukan. Maka, telah diketahui bahawa pemangkin sulfated zirconia adalah sesuai digunakan dalam “esterification” dan juga “transesterification” di dalam penghasilan biodiesel.

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CHAPTER 1

INTRODUCTION

1.1 Background

In 1900, Rudolf Diesel demonstrated his compression ignition engine at the World's Exhibition in Paris. In that prototype engine, he used peanut oil which is the first biodiesel. Vegetable oils were used until the 1920's when an alteration was made to the engine for enabling it to use a residue of petroleum diesel. Although the diesel engine gained worldwide acceptance, biodiesel did not. With affordable price, availability, and government subsidies, petroleum diesel quickly became famous for the diesel engine.

In the mid 1970s, fuel shortages revived interest in developing biodiesel as an alternative to petroleum diesel. However, as the petroleum market was increasingly subsidized, biodiesel was again downgraded to a minority alternative status. This political and economic struggle continues to limit the impact of the biodiesel industry today.

Now, increasing concerns about the potential of global climate change, declining air and water quality, and serious human health concerns are inspiring the development of biodiesel. Biodiesel is made from recycled vegetable oil and various feedstock as for example soya beans. As part of an active carbon cycle biodiesel feedstock production reduces the buildup of greenhouse gases, and in turn, global warming.

Many fleet operators have made the switch to biodiesel, yet biodiesel consumption accounts for less than one percent of the total diesel fuel consumption in the United States. Additional industries finding cleaner alternatives to sulfur emitting diesel are transit bus fleets, heavy-duty truck fleets, airport shuttles, marine and national park boats and vehicles, mining, the military and many more.

Biodiesel as the one of the ester has been increasingly produced recently. The advantages of using this fuel are lower the emission of carbon monoxide (CO) due a better combustion, a better lubricating effect on engines, non sulfur emission and non particulate matter pollutant. Biodiesel can be produced by esterification of free fatty acid with alcohol to form an ester and water.

Usually, this biodiesel is synthesized using homogenous acid-catalyzed system like sulfuric acid and hydrochloric acid as catalyst. But this system has a drawback as the separation process is needed in order to separate homogenous catalyst from the ester. It is good way to use solid acid catalyst because it makes less harm to the environment compared to the homogenous system. Furthermore, the process complexity of the system can be reduced since there is no separation process involved in the system. By other means, less money spent will be required to setup this system.

The function of catalyst used in the reaction is mainly to reduce the activation energy of the reaction so less time is required to achieve high conversion. There are many type of catalysts that are suitable for the esterification reaction, these catalysts are ion exchange resin, zeolite, and superacid like sulfated zirconia and tungstated zirconia.

There is another method to produce biodiesel like transesterification. Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a similar to hydrolysis, except than alcohol is used instead of water (Song et al., 2007). But this kind of reaction has disadvantages as the reaction can be reversible and the reaction time take much longer compared to the esterification.

1.2 Identification of problem

The use of solid acid catalyst in biodiesel applications has gained attention in recent years. The problem we are facing right now, even though these acid solid catalysts are effective in esterification and transesterification but it required high temperature condition to achieved high conversion compared to base catalyst (Furuta et al., 2004). Some resins, such as Amberlyst-15, may be considered an exception as these catalysts catalyze appreciably both esterification and transesterification reactions under mild reaction conditions due to their high concentrations of acid sites (Lo'pez et al., 2005). However, thermal stability becomes an issue when resin-type catalysts are used at higher temperatures (for higher reaction rates, reactive distillation applications, or catalyst regeneration). In this study, the catalytic performance of thermally robust sulfated zirconia will be investigated. In order to produce a large scale of biodiesel production, an appropriate kinetic model must be chosen and developed first. The important of developing kinetic model before design a reactor is to ensure that the design of reactor satisfied with the optimum condition. There are many kinetic models that can be chosen such as pseudo-homogenous model, Langmuir-Hinshelwood model and Langmuir-Hinshelwood-Hougen-Watson model.

1.3 Statement of objectives

1. To study the effect of important operating parameters to the rate of reaction.
2. To develop a kinetic model for the fatty acid esterification reaction.

1.4 Scope of study

In this study, four parameters were investigated. These parameters are temperature, amount of catalyst, amount of triglycerides, and ratio of alcohol to acid. The selected temperature is 35°C, 45°C and 55°C. For the amount of catalyst, the amount used is 0.5gram, 1 gram and 1.5 gram. The ratio of acid to alcohol in this study is 1:1, 1:2 and 1:4. For the forth parameter which is amount of triglycerides, the amount used is 10 ml, 20 ml and 30 ml. Oleic acid and ethanol were used as the reactant and sulfated zirconia acted as a catalyst. The data obtained from the experiment was analyzed and fitted into an appropriate heterogenous kinetic model.

1.5 Rationale and significance

Due to the decreasing of the resource of fossil based fuel, the demand for the alternative fuel was increased. The objective for this research is to find the kinetic model for the esterification reaction which is useful for industries that want to construct a biodiesel reactor. Other than that, this renewable energy can reduce the pollution due to the lower emission of carbon dioxide. This advantage can attract many people to invest to commercialize this biodiesel. In addition, the source for biodiesel is easy to get since the source come from vegetable oil and animal fat that can be renewable. It also good opportunity for agriculture and rural economies since it can generate more profit and contribute more job opportunity to that sector.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is a fuel comprised of alkyl esters of long chain fatty acids (Van Gerpen et al., 2004). It is an alternative way to reduce emission of carbon monoxide (CO) and sulfur dioxide (SO₂). The composition of biodiesel is similar to petroleum based diesel so it can replace petroleum based diesel completely or can be blend with petroleum base diesel. Besides, the biodiesel production can give social impact to the country that their economy is base on agriculture. There are two ways to produce biodiesel which are esterification or transesterification reaction.

2.2 Esterification

Esterification is the general name for a chemical reaction in which two reactants typically an alcohol and an acid form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry.

Esterification is a reversible reaction. Hydrolysis involves adding water and a catalyst commonly NaOH to an ester to get the sodium salt of the carboxylic acid and alcohol. As a result of this reversibility, many esterification reactions are equilibrium reactions and therefore need to be driven to completion according to Le Chatelier's

principle. Esterifications are among the simplest and most often performed organic transformations.

A common type of esterification is a Fischer esterification. In the Fischer esterification, esters may be prepared by refluxing an acid (usually, but not always a carboxylic acid) and a primary or secondary alcohol in the presence of a catalyst (commonly concentrated sulfuric acid). Water is a byproduct, and it can be removed to force the equilibrium in the desired direction. Alternatively, where the ester has a suitable boiling point, it may be distilled off, once again causing the equilibrium to favor the product.

For example, esterification of acetic acid in excess ethanol possibly as the solvent in the presence of concentrated sulfuric acid as a catalyst results in an ester (ethyl acetate). Figure 2.1 shows the general esterification process.

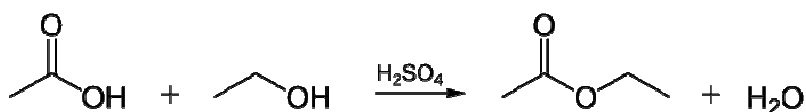


Figure 2.1 Esterification reaction

2.3 Transesterification

In organic chemistry, transesterification is the process of exchanging the alcohol group of an ester compound with another alcohol. These reactions are often catalyzed by the addition of an acid or base. Acids can catalyse the reaction by donating a proton to the carbonyl group, thus making it more reactive, while bases can catalyse the reaction by removing a proton from the alcohol, thus making it more reactive.

Transesterification is used in the synthesis of polyester, in which diesters undergo transesterification with diols to form macromolecules. For example,

dimethyl terephthalate and ethylene glycol react to form polyethylene terephthalate and methanol, which is evaporated to drive the reaction forward. The reverse reaction (methanolysis) is also an example of transesterification, and has been used to recycle polyesters into individual monomers. Figure 2.2 shows the general transesterification process.

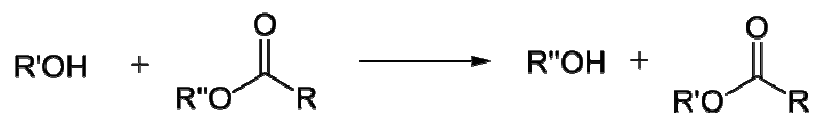


Figure 2.2 Transesterification reaction

Transesterification also has been used for producing biodiesel long time ago. There is method called supercritical process which is catalyst free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock and free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstock can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes. Vera et al. (2006) in their research of production of biodiesel by a two-step supercritical reaction process with adsorption refining, they were compared to the production of biodiesel by using one step supercritical reaction process. They were found out that the operating pressure for the production of biodiesel by the reaction of oils in supercritical methanol can be advantageously reduced if the reaction is allowed to proceed in two successive steps with intermediate removal of glycerol. The one-reactor setup works with molar methanol:oil=42 and a pressure of 14-43 MPa (270-350°C). In the two-reactor setup the decrease of methanol:oil to 10 results in a reduction of the working pressure to less than 4 MPa and of the pumping power to less than 25% the value for the one-reactor lay-out.

A low methanol:oil ratio also enables the use of adiabatic flash drums to vaporize the unreacted methanol at the outlet of the reactor, with a substantial decrease of the heat duty of the process. An additional heat exchanger contacting the streams entering and exiting the reactor enables an additional recovery of heat. The final heat duty can be reduced to almost half the value corresponding to the one-reactor lay-out with no heat recovery and no methanol removal.

The supercritical catalyst-free process can be run under fully dry conditions if glycerol removal is performed by adsorption in a packed bed. Common acid adsorbents (silica, acid resins) can retain glycerol and keep the biodiesel product inside the glycerol content specification of the quality norms. A convenient regeneration procedure seems to be the flushing of the adsorbed glycerol with a methanol stream and the recycling of this stream to the first supercritical reactor. Figure 2.3 shows the flowsheet of two step supercritical biodiesel production process.

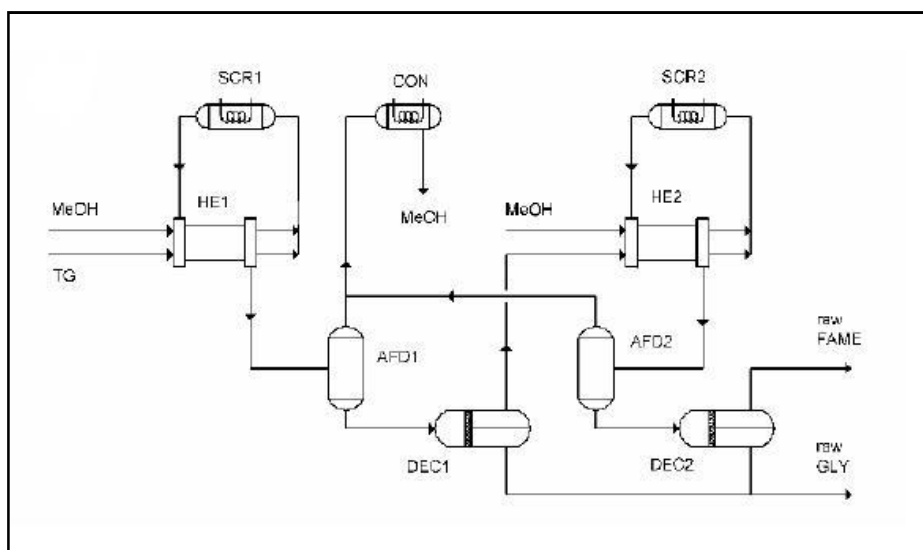


Figure 2.3 Flowsheet of two step supercritical biodiesel production process

2.4 Type of catalyst

The esterification process can be homogeneously or heterogeneously catalyzed. Homogeneous esterification can be defined as the esterification process occurring in the same phase which is liquid-liquid phase between catalyst and the reactant. Meanwhile, the heterogeneous esterification system occurs in liquid-solid phase.

Currently homogeneous catalyst is most used because it is cheaper as compared to the solid catalyst. Homogeneous catalysts can be categorized into two types which are acid-catalyst and base-catalyzed. Most people more prefer to use homogeneous acid catalyst since it is faster 4000 times than homogeneous base catalyst (Lotero et al., 2005).

2.5 Homogeneous catalyst

In the study of Donato et al. (2007), they tried to compare the performance of various homogeneous acid catalysts such as sulfuric acid, methanesulfonic acid, phosphoric acid and trichloroacetic acid.

Sulfuric acid and methanesulfonic acid showed very promising results. These two catalysts have the conversion rate over 80%. But when sulfuric acid compared to the methanesulfonic acid in terms of price and availability, sulfuric acid wins in this situation. However, people are concerned about these catalysts as they might be harmful to the environment if they are not treated carefully. Moreover, homogeneous catalysts are hard to separate since the product has to undergo a separation process because the product and the catalyst are mixed together.

They have made a conclusion that a small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst. Acid strength of the catalyst was responsible for the higher activity of sulfuric and methanesulfonic acids, releasing more H^+ species to protonate the

carboxylic moiety of the fatty acid (rate determinant step). Shorter chain and higher polarity of methanol has resulted in higher activity than ethanol, which presents steric hindrance in the reaction and shows higher water inhibition, attributed to phase miscibility and emulsion formation. Kinetic parameters obtained were similar to the ones reported for transesterification reaction, indicating a similar rate determinant step. Lower activation energy was the exception. Quantum chemistry studies have shown that despite the similar protonation energy of fatty acid, the double bond of oleic acid increase the reactivity of carboxylic moiety of the fatty acid.

The other study of homogenous catalyst such as esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides (Marchetti and Errazu, 2007) they want to find the most optimum operating condition for this reaction. The final purpose for their study is to find the kinetic model for this esterification reaction. They have studied four parameters for the reaction between well mixed sunflower oil and oleic acid with ethanol. For the first parameter, ratio of alcohol to acid oil, they find out that when the molar ratio of alcohol to acid oil was low, the reaction occurred faster but reached a lower final conversion compared with when a higher molar ratio was used. In the latter case, the final conversion reached was higher, but the initial reaction rate was slow.

For the second parameter which is amount of catalyst, the result shown that the reaction was highly depend on the amount of catalyst. The effect of the catalyst just did to the initial rate but nothing effected to the final conversion of free fatty acid.

For the third parameter, which is temperature, they were expected that the temperature affected to the final conversion of free fatty acid. Their assumption seems true since the final conversion increased when the temperature increased.

The last parameter that they have investigated is the initial amount of free fatty acid. The result showed when the free fatty acid (FFA) amount increased the rate of reaction increased as well as final conversion.

In other research of homogenous catalyst acid which is esterification of free fatty acids (FFA) in sunflower oil with methanol in the presence of sulphuric acid (Berrios et al., 2007), they carried out the experiment sunflower oil mix with oleic acid with the methanol in the presence of sulphuric acid. The experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order one for the reverse reaction. The influence of temperature on the kinetic constants was determined by fitting the results to the Arrhenius equation. The energy of activation for the forward reaction decreased with increasing catalyst concentration from 50745 to 44 559 J/mol. Based on the experimental results, a methanol/oleic acid mole ratio of 60:1, a catalyst (sulphuric acid) concentration of 5 wt% and a temperature of 60°C provided a final acid value for the oil lower than 1 mg KOH/g oil within 120 min. This is a widely endorsed limit for efficient separation of glycerin and biodiesel during production of the latter.

2.6 Heterogenous catalyst

Heterogenous catalysts now obtain many attentions from researchers around the world. They have performed many experiments to find most reliable and suitable catalyst to replace the homogenous catalyst which has some drawbacks. Many solid acid catalysts have been tested. These solid acid catalysts include ion-exchange resins (Altiokka et al., 2003), zeolites (Corma et al., 1989) and superacids like sulphated zirconia (Ardizzone et al., 1999) and niobium acid (Chen et al., 1984).

The esterification of free fatty acid and transesterification of vegetable oil with methanol has been carried out using Lewis solid acid but required high reaction temperature. Prior to that, the esterification of free fatty acid with methanol using solid acid catalyst in the reactor is a promising way to convert the reactant into valuable fatty acid methyl ester (FAME). Ni and Meunir (2007) in their experiment of esterification of free fatty acid in sunflower oil over solid acid catalyst using batch reactor have reported many aspects that affect the conversion rate of palmitic acid. They tested five catalysts which are sulfuric acid, silica alumina, tungstated zirconia, sulfated zirconia and SAC-13. The conversion of palmitic acid is measured at 60°C

over several of solid acid catalysts and acid sulfuric to investigate the optimum conversion of solid acid catalyst. The sulfated zirconia and SAC-13 give the best conversion rate over time but after consider the problem that sulfated zirconia had to activate above 400°C, the SAC-13 get advantage since it not required to be activated. One more problem that sulfated zirconia loss it weight due to the leaching of sulfate group. There is also probability the sulfated zirconia cannot be recovered to the initial activity condition because of the formation of carbon residue derived from the decomposition of the oil absorbed on the material (Ni and Meunir, 2007).

Lopez et al. (2007) in his finding showed that the fresh sulfated zirconia was found to be the most active for the reaction among three catalysts he was used (titania zirconia, tungstenated zirconia, sulfated zirconia) in the experiment of esterification and transesterification using modified zirconia catalyst. But sulfated zirconia has a limitation since it cannot easy to regenerate. Titania zirconia has greater activation energy for transesterification than tungstated zirconia. However they found that titania zirconia has weaker activation energy towards esterification. Thus, Lopez et al. (2007) suggested that tungstated zirconia is more suitable for the reaction since it is more active for the esterification than titania zirconia. This statement also has been strengthened by Park et al. (2008) in their study of heterogeneous catalyst using tungstated zirconia and sulfated zirconia. The sulfated zirconia and tungstated zirconia catalysts were found to be effective in the esterification of free fatty acid (FFA) to fatty acid methyl ester (FAME). However, sulfated zirconia was not selected because of the potential loss of sulfate ion (SO_4^{2-}) in its liquid-phase application. The pellet-type tungstated zirconia catalyst was used for the longer reaction test. The result showed that 65% conversion could be maintained for up to 140 hour. From the characterization results, the oxidation state of tungsten is mainly related to the catalytic activity of tungstenated zirconia. The activity could be regenerated through simple air re-calcination. The TPD results indicated that the surface acid strength was distributed widely. Moreover, there was a decrease in acidity with decreasing catalytic activity, which appears to be related to the oxidation state of the tungsten.

In the study of comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol (Peters et al., 2005), they have been tested

and compared several commercial solid acid catalyst which are Smopex-101, Amberlyst 15, sulfated ZrO₂, H-USY-20, H-BETA-12.5, H-MOR-45 and Nb₂O₅. In their research, they stated that the solid acid catalysis is very effective from the viewpoint of activity and reusability compared with homogeneous catalysts. The activity per proton of solid acid catalysts is significantly different because the specific reaction rate depends on the environment of the acid sites such as hydrophobicity. Furthermore, the diffusion of molecules to the active sites becomes important in the case of porous solid acids such as zeolites. Among the solid acid catalysts, ion-exchange resins such as Smopex-101 and Amberlyst 15 were observed to be the most effective. The weight-based activity of the heterogeneous catalysts tested decreases in the following order: Smopex- 101 > Amberlyst 15 > sulfated ZrO₂ > H-USY-20 > H-BETA-12.5 > H-MOR-45 > Nb₂O₅ > H-ZSM-5-12.5. Among the zeolites tested, H-USY zeolite with a Si/Al ratio of 20 gives the highest activity. No clear relationship has been observed between the total amount of acid sites, measured with the temperature-programmed decomposition of isopropylamine, and the catalytic activity. The activity of sulfated zirconia shows an optimum calcinations temperature, although both the amount and acidity of the acid sites increase monotonically with calcinations temperature. Most likely, at higher calcinations temperatures Lewis acid sites are formed and Brønsted acid sites are removed. As Brønsted acid sites are essential for catalysis of esterification reactions this explains the decrease in activity.

Omata et al. (2003) have made several conclusions in their research which entitled fatty acid esterification by reactive distillation. In their conclusion, they stated out that sulphated zirconia catalyst is suitable for the synthesis of 2-ethylhexyl dodecanoate by reactive distillation. As the local acid-to-alcohol molar ratio varies over three orders of magnitude, dehydration to ethers is a potential unwanted side reaction. Actually, however, no ether or alkene formation was observed, illustrating the selectivity of sulfated zirconia catalysts even for a high alcohol-to-acid molar ratio. Another conclusion is in free water the sulfated zirconia catalyst deactivates as a result of leaching. For this reason, L-L segregation into an organic and an aqueous phase must be prevented by proper design. In contrast, small amounts of water are allowable in the organic phase of the reaction mixture. The catalyst activity could be captured in a kinetic model based on liquid activities, in which the UNIQUAC model

was used to assess liquid activity coefficients. Kinetic data demonstrates that the sulfated zirconia catalyst is sufficiently active for industrial application. The RD system consists of the reactive distillation column (RDC) with 13 reactive stages, a decanter and a vacuum-evaporator. For operating temperatures of 400–440 K the space velocity is 0.022 kmol acid kg⁻¹ cat h⁻¹ and the product purity is 99.9%. The most significant design elements, such as the residence time, catalyst activity and catalyst loading, can be captured in a single dimensionless Damköhler numbers (Da), and used for design and scale-up purposes.

Teo and Saha (2004) in their research of heterogeneous catalysed esterification of acetic acid with isoamyl alcohol and kinetic studies, they have made a conclusion that the equilibrium conversion of acetic acid was found to increase slightly with an increase in temperature and also it increases appreciably with an excess of isoamyl alcohol in the reacting system. CT-175 catalyst can be repeatedly used without sacrificing its catalytic activity. Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley Rideal (ER) kinetic models were applied to correlate with the experimental kinetic data of the solid-liquid-liquid mode catalytic reaction. Langmuir-Hinshelwood-Hougen-Watson (LHHW) model gave a better representation of the kinetic behavior for all practical purposes on the reaction kinetics studied under the given conditions. According to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, acetic acid adsorbed on one catalytic centre reacts with isoamyl alcohol adsorbed on another catalytic centre to give isoamyl acetate and water each adsorbed on one centre. The surface reaction is the rate limiting step. The kinetic data for the esterification of acetic acid with isoamyl alcohol would be useful for the simulation and design of a reactive distillation column for removing acetic acid from aqueous streams.

2.7 Kinetic modeling

For kinetic modeling part, recently, pseudo-homogeneous model and an adsorption-based model have been investigated. The pseudo-homogeneous model has a smaller number of parameters and is less complex. The pseudo-homogeneous model can be written as:

$$r = k_1 a_{\text{AcOH}} a_{\text{MeOH}} - k_{-1} a_{\text{MeOAc}} a_{\text{H}_2\text{O}} \quad (2.1)$$

Whereas adsorption based model can be written as:

$$r = \frac{k_1 a_{\text{AcOH}}^1 a_{\text{MeOH}}^1 - k_{-1} a_{\text{MeOAc}}^1 a_{\text{H}_2\text{O}}^1}{(a_{\text{AcOH}}^1 + a_{\text{MeOH}}^1 + a_{\text{MeOAc}}^1 a_{\text{H}_2\text{O}}^1)^2} \quad (2.2)$$

Even though pseudo-homogeneous is less complex but it has major drawbacks since the model neglects the sorption effect of water. To overcome this problem, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was introduced. This model is the simplest method to account for the sorption of water. The Langmuir-Hinshelwood-Hougen-Watson model can be written as:

$$r = m \times \left(\frac{k_1^* K_{\text{DecH}} a_{\text{DecH}} K_{\text{MeOH}} a_{\text{MeOH}} - k_{-1}^* K_{\text{MeDec}} a_{\text{MeDec}} K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}}}{1 + (K_{\text{DecH}} a_{\text{DecH}} + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{MeDec}} a_{\text{MeDec}} + K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}})^2} \right) \quad (2.3)$$

Steinigeweg and Gmehling (2002) have investigated the reaction kinetics on the esterification of decanoic acid with methanol. The catalyst used in this experiment was ion-exchange resin (Amberlyst 15). A kinetic approach based upon the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was derived. It has been shown that the water uptake by the polymeric catalyst has to be taken into account and that the model proposed was capable of describing the reaction rate as a function of the water content.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The experiment were carried out in University Malaysia Pahang (UMP) where there are all equipped to make required measurement. In this chapter, the methodologies of the experiment are discussed.

3.2 Materials and equipments

Table 3.1 : List of chemicals and equipments used in the experiment

Chemicals/Equipment	Functions
Oleic acid	Free fatty acid
Ethanol	Alcohol
Sulfated zirconia	Catalyst used in the experiment
Phenolphthalein	Acted as indicator in sample analysis
Sodium Hydroxide	Solution used for titration
Heating plate	Heating plate
Retort stand	Used to support the condenser from falling
Beaker 500ml	Used as a reactor for esterification reactions
Magnetic stirrer	To stir the mixture
Thermometer	Used to read the temperature
Condenser	Used for
Pipette	Used to take a sample from the beaker

3.3 Experimental procedure

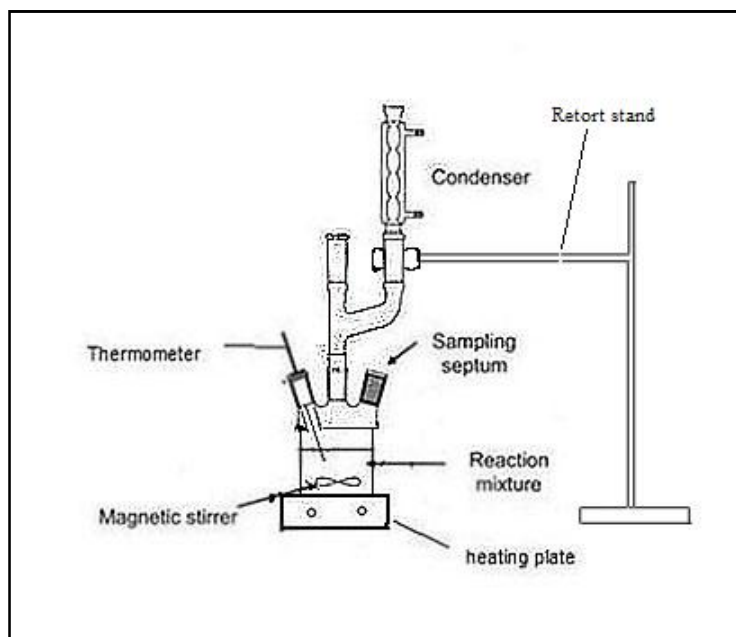


Figure 3.1 Schematic layout of the reactor system used for the experiments.

Figure 3.1 shows the layout of the apparatus based on batch catalytic reactor. The experiment was conducted for four parameters. These parameters are the weights of catalyst, amount of triglycerides, temperature and ratio of alcohol. For all parameter, the experiment repeated just once only.

For the first parameter, temperature, the sulfated zirconia catalyst was poured into the reactor. After that, the ethanol was poured into the reactor and followed by oleic acid. The heating plate than was turned on. The temperature controlled by knob at the heating plate. The temperature was set at 35°C, 45°C and 55°C.

After that, the experiment proceeds for the weight of catalyst parameter, the volume of the reactant remained same but the weight of the sulfated zirconia varied at 0.5gram, 1gram and 1.5gram. The temperature was set at 35°C.

For the third parameter, the ratio of alcohol to the acid, the ratio used is 1:1, 1:2 and 1:4. The temperature and weight of catalyst is 35°C and 0.5gram respectively. For the fourth parameter which is amount of triglycerides, normal

cooking oil was added into the reactor and was varied at 10ml, 20ml and 30ml. The temperature, weight of catalyst and ratio of alcohol to the acid is 35°C, 0.5gram and 1:4 respectively.

For the sampling method, 2 ml from the reactor was collected by using pipette every 10 minute for the first hour and every 30 minute for the next hour. To settle down all the catalyst in the sample, the sample was centrifuged for about 20 minute at 12000 rpm. In order to determine the acid concentration, the titration method was conducted using sodium hydroxide and phenolphthalein. The result was recorded in the table.

3.4 Composition analysis

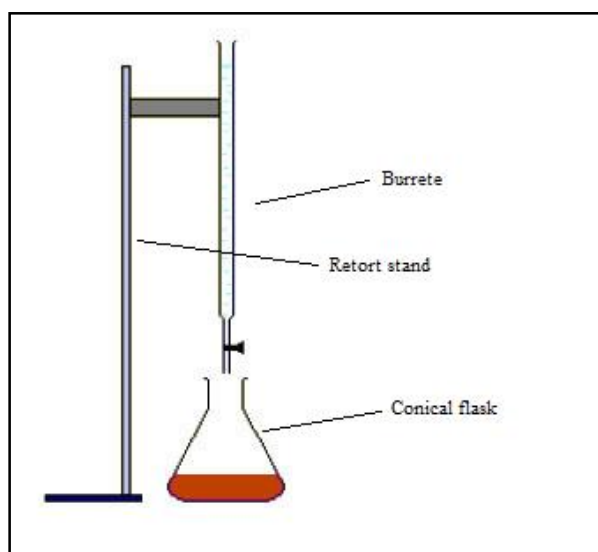
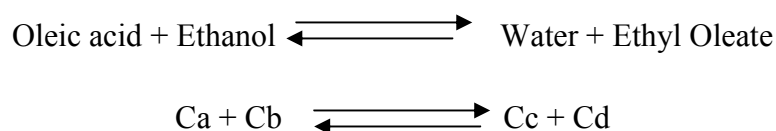


Figure 3.2 Schematic layout of the titration setup used for the experiments.

Figure 3.2 shows the titration setup used for the sample analysis. 1.5ml of sample was added to the conical flask. A few drops of phenolphthalein were added to the conical flask as indicator. The titration begins by adding with the 0.1M NaOH from the burette slowly. The titration stopped when the mixture becomes pink colored. The esterification of the oleic acid with the ethanol can be represented by using this expression:



The data obtained from the experiment were used to determine the acid value of the samples. The conversion of oleic acid to the ethyl ester was calculated by titration with a 0.1 M NaOH standard solution, according to Eq.

$$\text{Conversion \%} = \frac{\text{Initial acid value} - \text{Final acid value}}{\text{Initial acid value}} \quad (3.1)$$

$$\text{acid value} = \frac{M \times A \times F \times N}{S} \quad (3.2)$$

Where M is the molecular weight of NaOH; A the amount of NaOH standard solution used in the titration; F the concentration coefficient of the NaOH standard solution; N the normal concentration of the NaOH standard solution; S is the sample weight.

3.5 Kinetic modeling

From the percentage of conversion, the molarity of the reactants and products can be determined. In order to develop pseudo-homogenous model, the reaction rate, r_a must be found first. The reaction rate can be found from the value of slope in the graph of oleic acid concentration versus time. An example plot of CA versus time and the corresponding third degree polynomial fit are shown in Figure 3.3

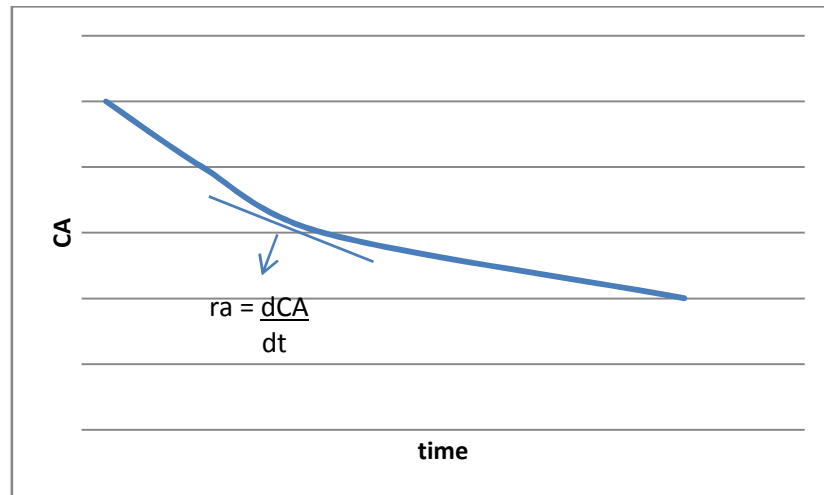


Figure 3.3 Example of slope determination

The graph was constructed by using the well known Polymath™ v6.1 software and the r_a was calculated by using linear and polynomial method under regress and analyze menu in Polymath V6.1.

By using pseudo-homogenous model, the reaction constant for the forward reaction and reverse reaction, k and k'' was determined using Polymath™ v6.1 software. This calculation has been done by using non-linear regression method that found in the Polymath™ v6.1. The initial guess of 0.01 and 0.001 for k and k'' respectively has been made. The pseudo-homogenous model can be written as:

$$-r_a = kC_aC_b - k''C_cC_d \quad (3.3)$$

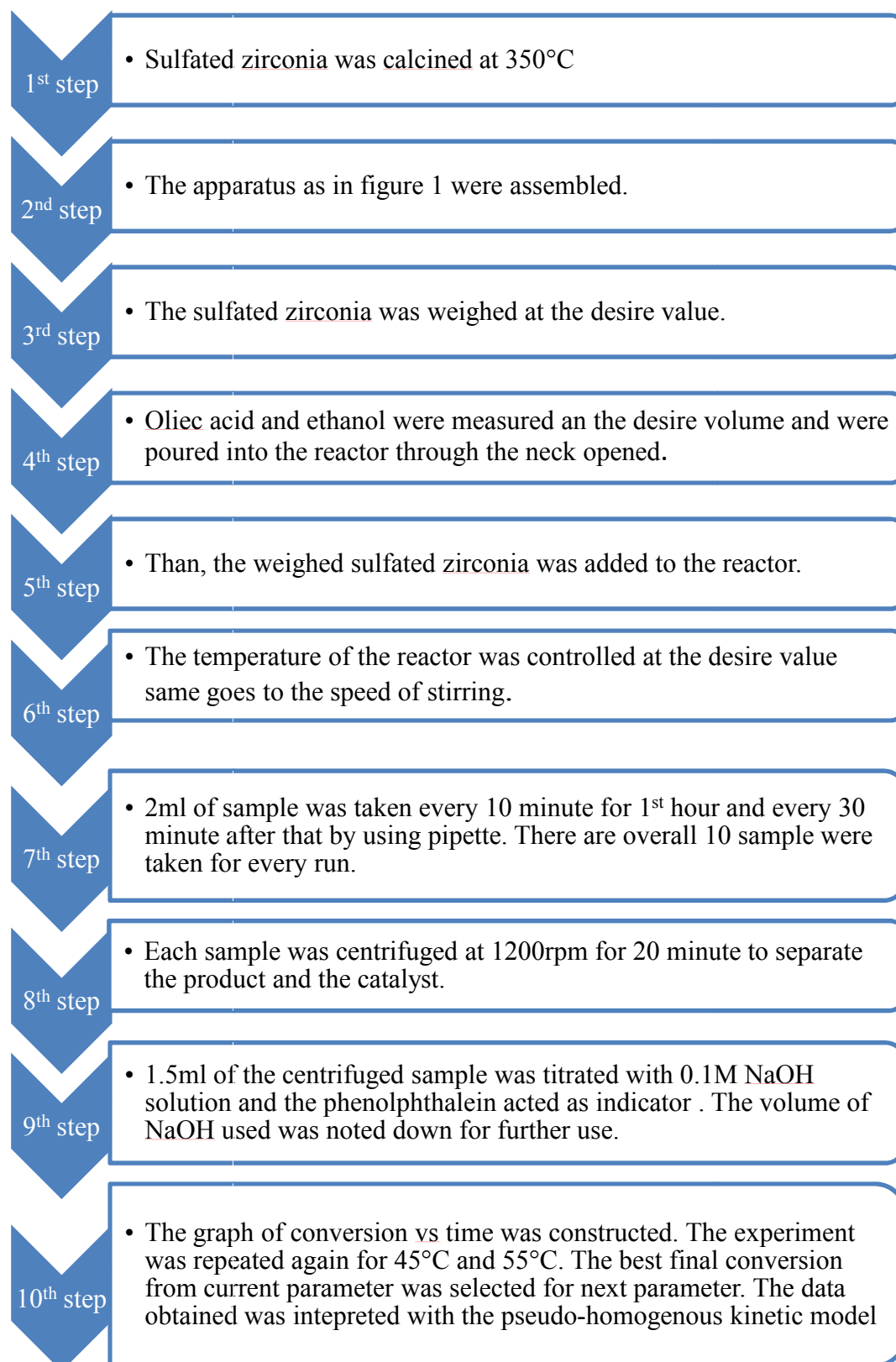


Figure 3.4 Flow Chart for the research methodology

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of temperature

Figure 4.1 show that the final conversion of free fatty acid is 22.92%. The reaction conditions for the reaction are 35°C, 0.5 gram of catalyst, 1:1 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.1.

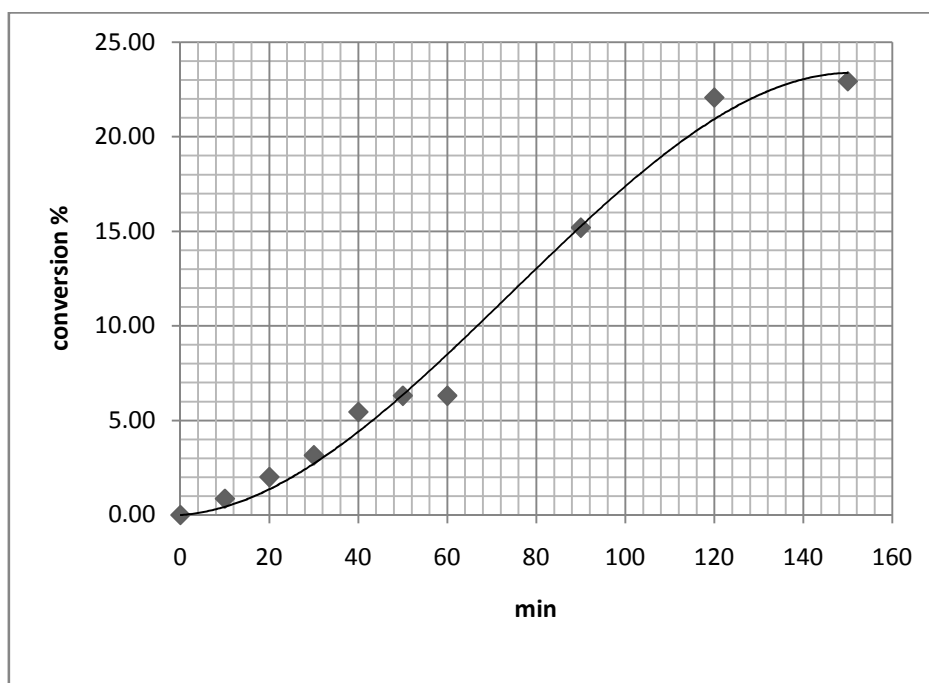


Figure 4.1 The reaction conversion versus time for the temperature of 35°C

Figure 4.2 show that the final conversion of free fatty acid is 17.31%. The reaction conditions for the reaction are 45°C, 0.5 gram of catalyst, 1:1 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.2.

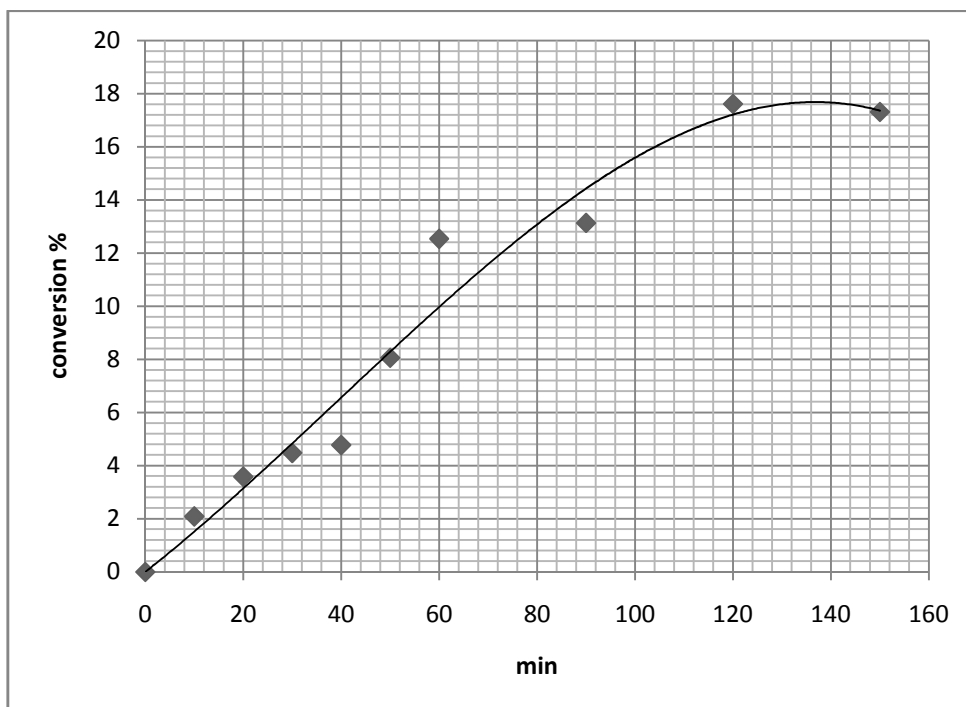


Figure 4.2 The reaction conversion versus time for the temperature of 45°C

Figure 4.3 show that the final conversion of free fatty acid is 10.76%. The reaction conditions for the reaction are 55°C, 0.5 gram of catalyst, 1:1 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.3.

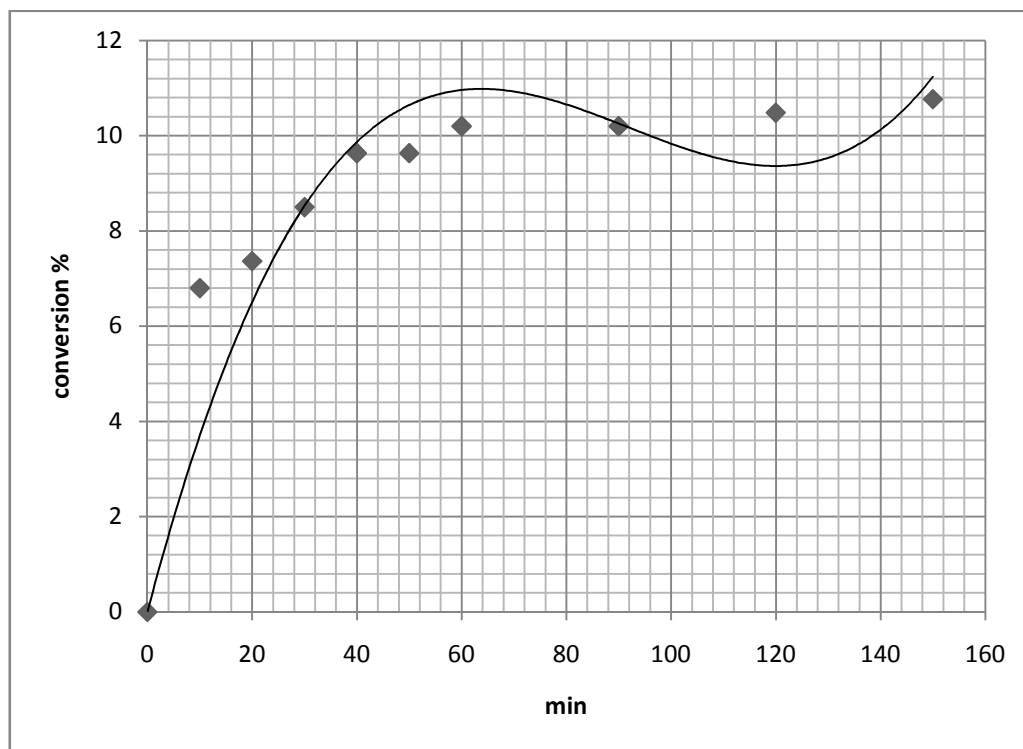


Figure 4.3 The reaction conversion versus time for the temperature of 55°C

4.1.1 Comparison graph between different temperature

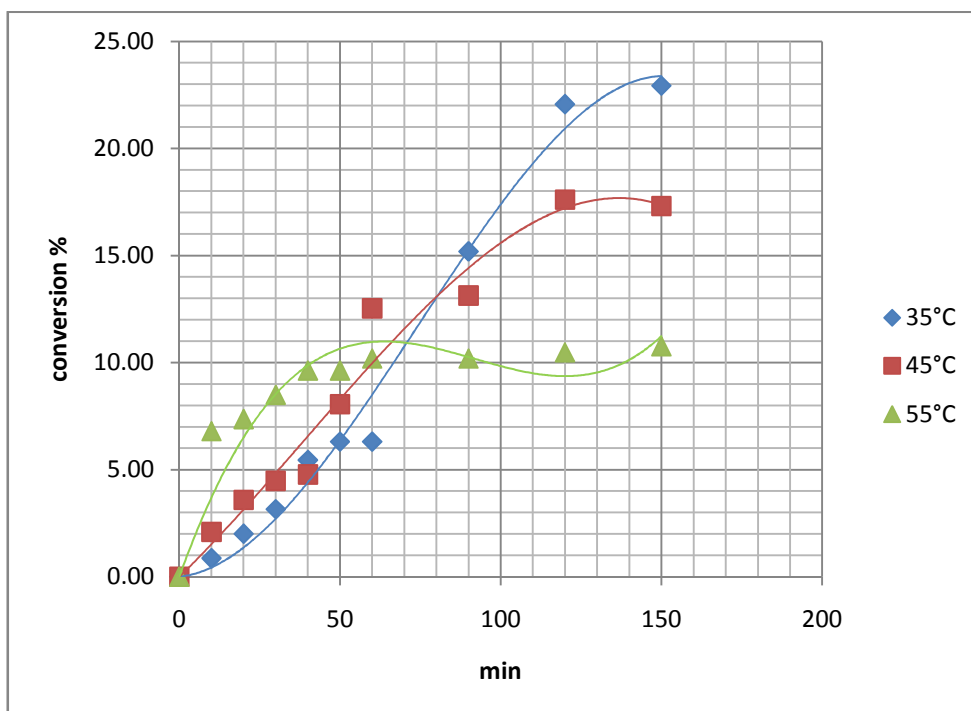


Figure 4.4 Effect of different reaction temperatures.

Figure 4.4 shows the effects on temperatures were studied at 35°C, 45°C and 55°C. The remaining reaction condition parameters were kept constant. The result shows that increase the temperature does not increase to the conversion. In the equilibrium reaction, the standard heat of reaction is negative for the exothermic reaction. As a result, increasing the temperature will decrease the rate constant (k) value and subsequently decrease the final conversion. In other reason, note that the reaction is reversible. The reaction of reverse reaction will increase if the temperature is increase since that forward reaction is exothermic reaction. So as a result, the conversion will low as the reaction tend to move backward.

4.2 Effect of weight of catalyst

Figure 4.5 show that the final conversion of free fatty acid is 12.50%. The reaction conditions for the reaction are 35°C, 1 gram of catalyst, 1:1 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.4.

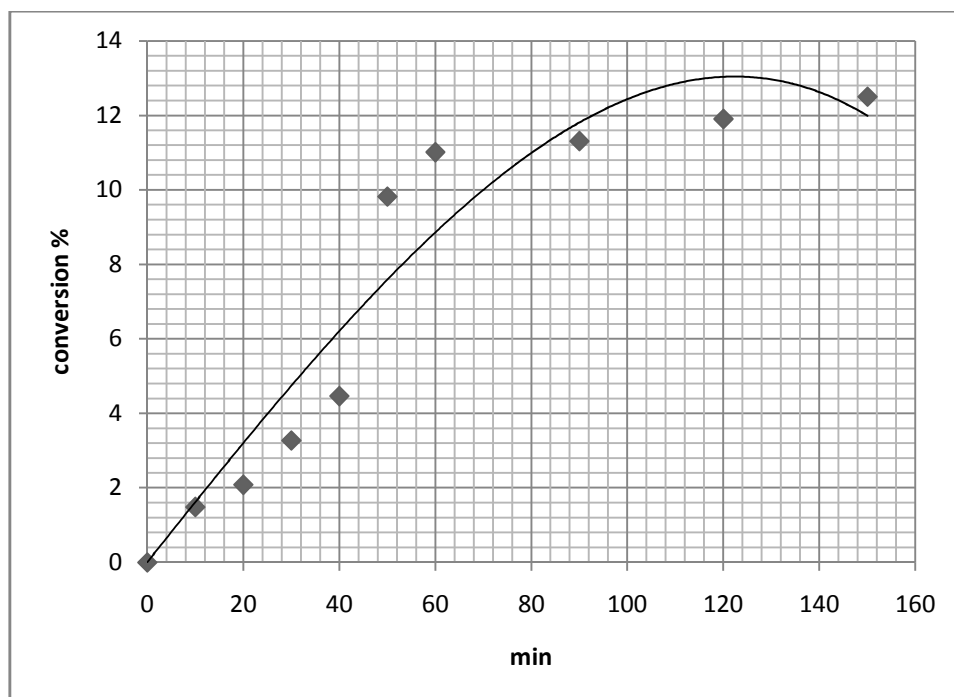


Figure 4.5 The reaction conversion versus time for the amount of catalyst of 1 gram

Figure 4.6 show that the final conversion of free fatty acid is 17.8%. The reaction conditions for the reaction are 35°C, 1.5 gram of catalyst, 1:1 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.5.

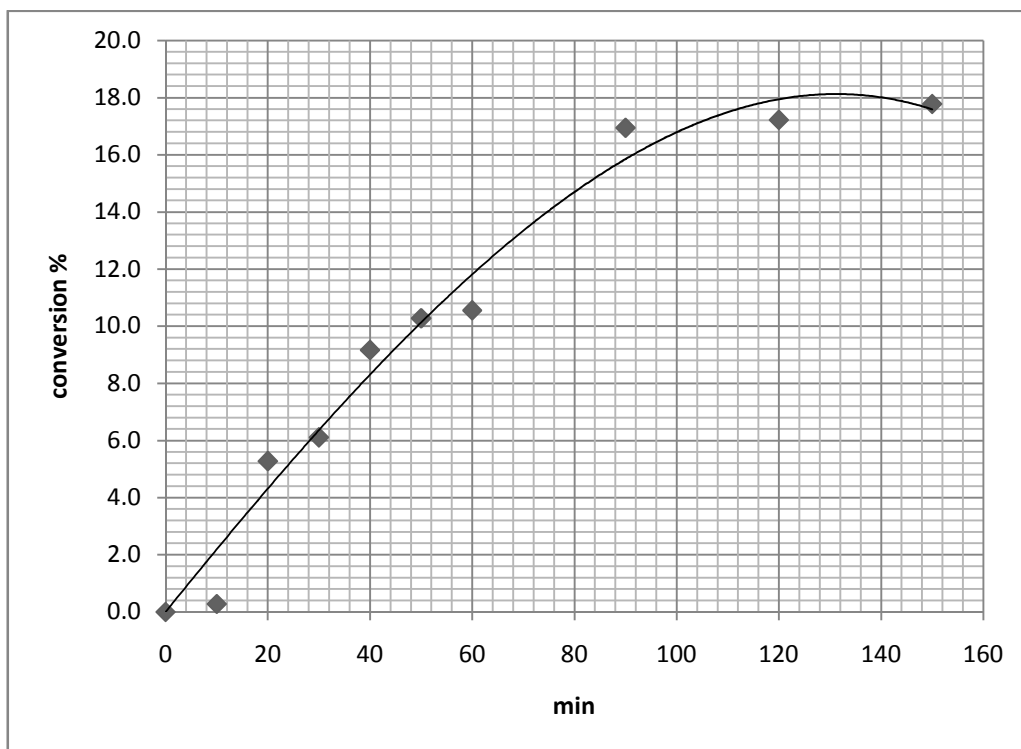


Figure 4.6 The reaction conversion versus time for the amount of catalyst of 1.5gram

4.2.1 Comparison graph between different weight of catalyst

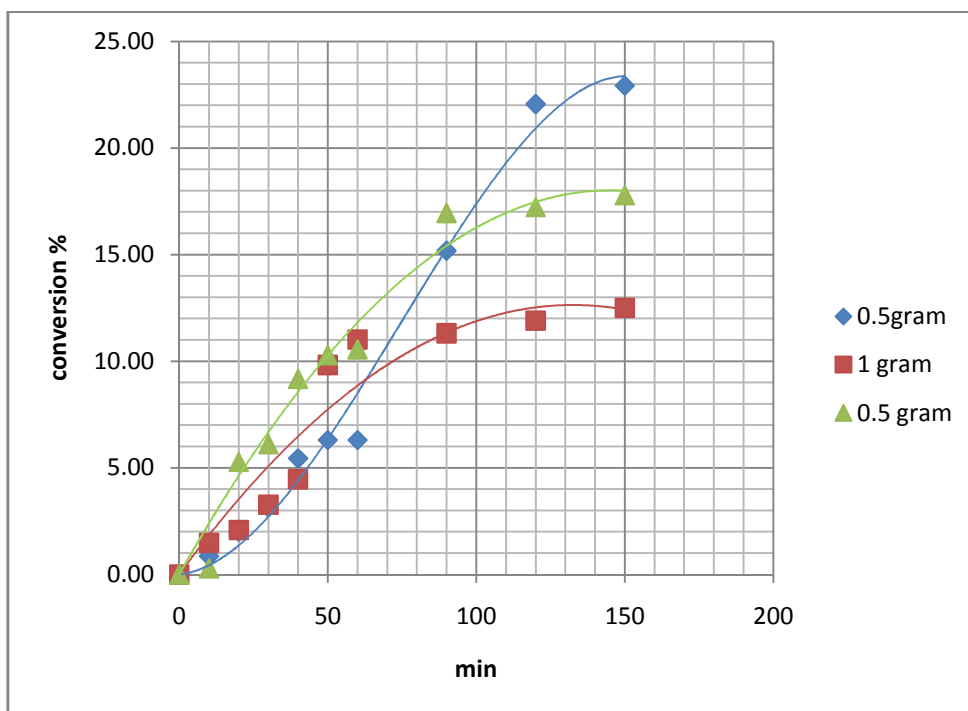


Figure 4.7 Effect of different amounts of catalyst.

Figure 4.7 show the effect of different amount of catalyst of 0.5gram, 1gram and 1.5gram. The results show that with the amount of catalyst of 0.5gram, the conversion is higher as compared to the catalyst of 1 gram and 1.5gram. As we know, the catalyst will speed up the reaction by providing alternative pathway that reduces the activation energy of the reaction. Increasing the weight of catalyst will increase the active site of the catalyst so more reactant molecule can be absorbed by the catalyst and subsequently increasing the reaction rate. But in this experiment, somehow the 0.5 gram of catalyst not follows the actual fact. This may happen due to the error when conducting the experiment. As a conclusion, 1.5 gram of catalyst will be taken as the reaction conditions for the subsequent experimental studies.

4.3 Effect of ratio of oleic acid to alcohol

Figure 4.8 show that final conversion of free fatty acid is 23.6%. The reaction conditions for the reaction are 35°C, 1.5 gram of catalyst, 1:2 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.6.

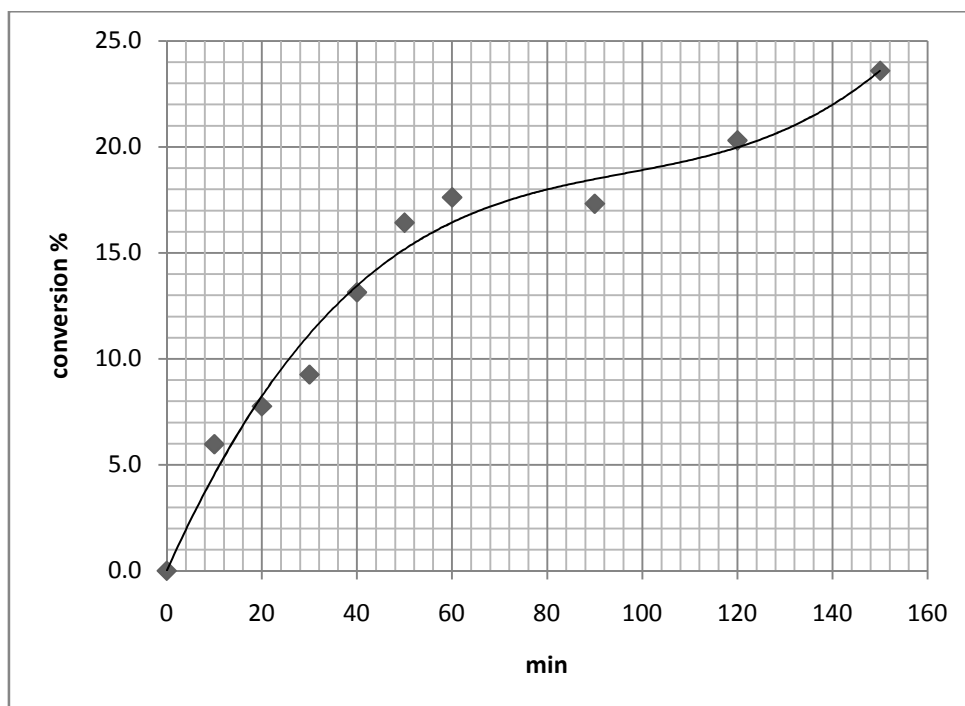


Figure 4.8 The reaction conversion versus time for the ratio of oleic acid to the alcohol of 1:2

Figure 4.9 show that final conversion of free fatty acid is 24.2%. The reaction conditions for the reaction are 35°C, 1.5 gram of catalyst, 1:4 ratio of oleic acid to alcohol and no addition of cooking oil. The detail calculated value shown in Appendix A.7.

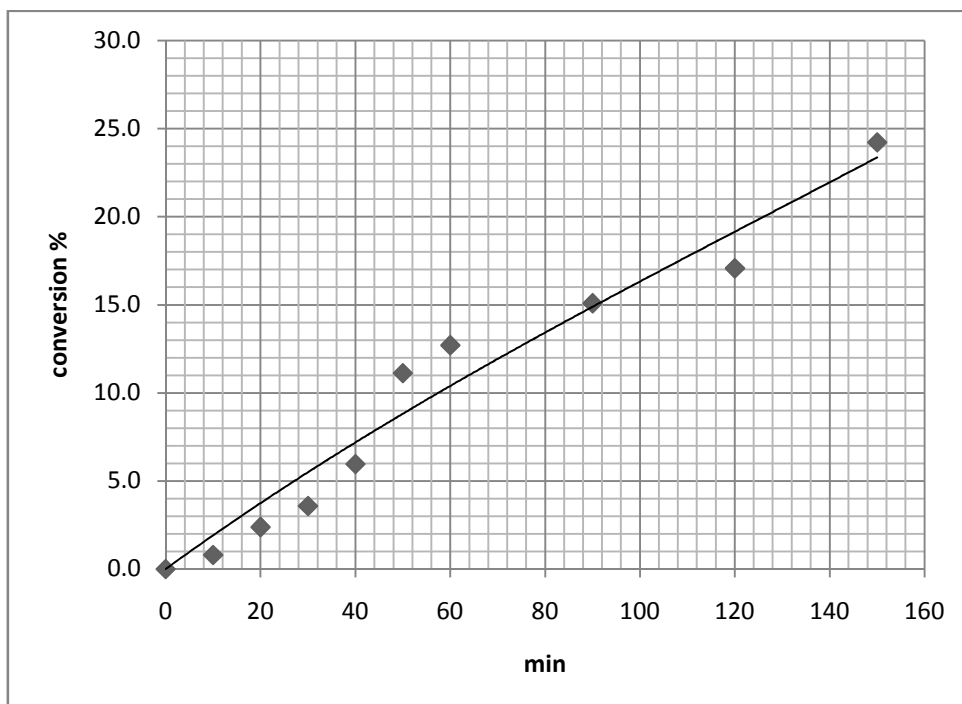


Figure 4.9 The reaction conversion versus time for the ratio of oleic acid to the alcohol of 1:4

4.3.1 Comparison graph between different ratio of oleic acid to the alcohol

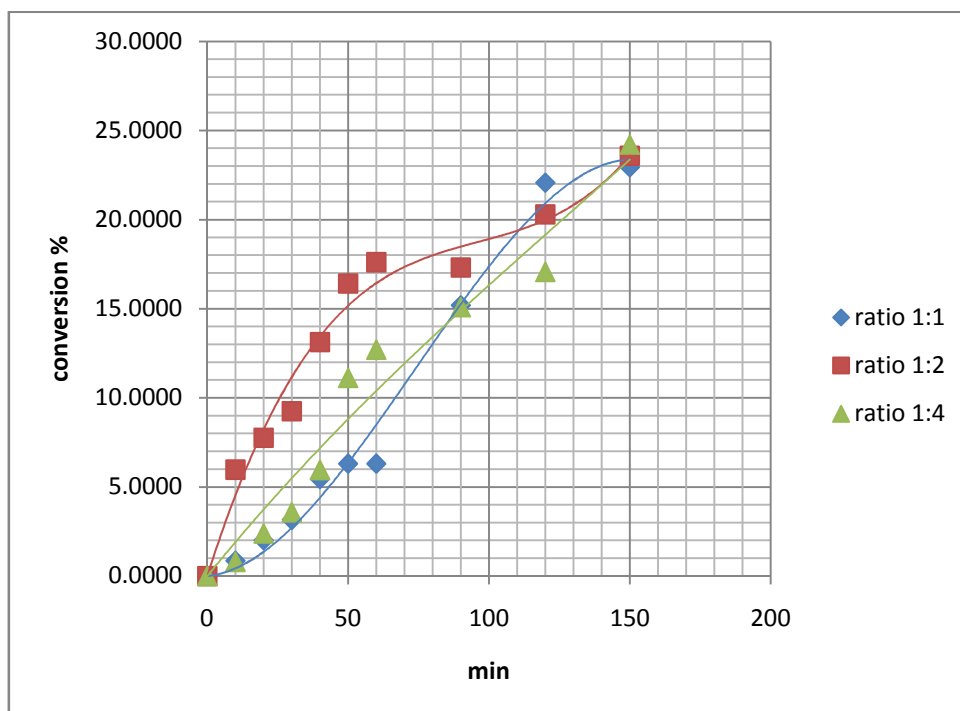


Figure 4.10 Effect of different reactant ratio.

Figure 4.10 shows the effect of different ratio of oleic acid to the ethanol. For the studies ratio of oleic acid to the ethanol, the other parameters are kept constant as above. As shown at the graph, the ratio of 1:4 has the higher final conversion compared to ratio of 1:2 and 1:1. At the end of the experiment, the conversion at ratio 1:4 still increases. But for the case of reaction rate, it seem that ratio of 1:2 have higher reaction rate compared to 1:4 and 1:2 ratio. The odd case here is the ratio of 1:4 has lower reaction rate compared to the 1:2 ratio. This non-common behavior is due to dissolution versus kinetics effect. For short times, when the amount of alcohol is high, a dissolution effect of the alcohol over the reaction mixture takes places with a stronger influence than that provided by the kinetics, producing a smaller reaction rate. However, as time continues, the reaction also continues to take place and the high concentration of alcohol produces that the final conversion achieved is higher but required a longer reaction time. Contrarily, when small amounts of alcohol are used, the dissolution effect is less intense, but also, because the concentration is lower, the final conversion achieved is smaller (Marchetti et al., 2008).

4.4 Effect of amount of triglycerides

Figure 4.11 show that final conversion of free fatty acid is 18.5%. The reaction conditions for the reaction are 35°C, 1.5 gram of catalyst, 1:4 ratio of oleic acid to alcohol and 20ml of cooking oil. The detail calculated value shown in Appendix A.8.

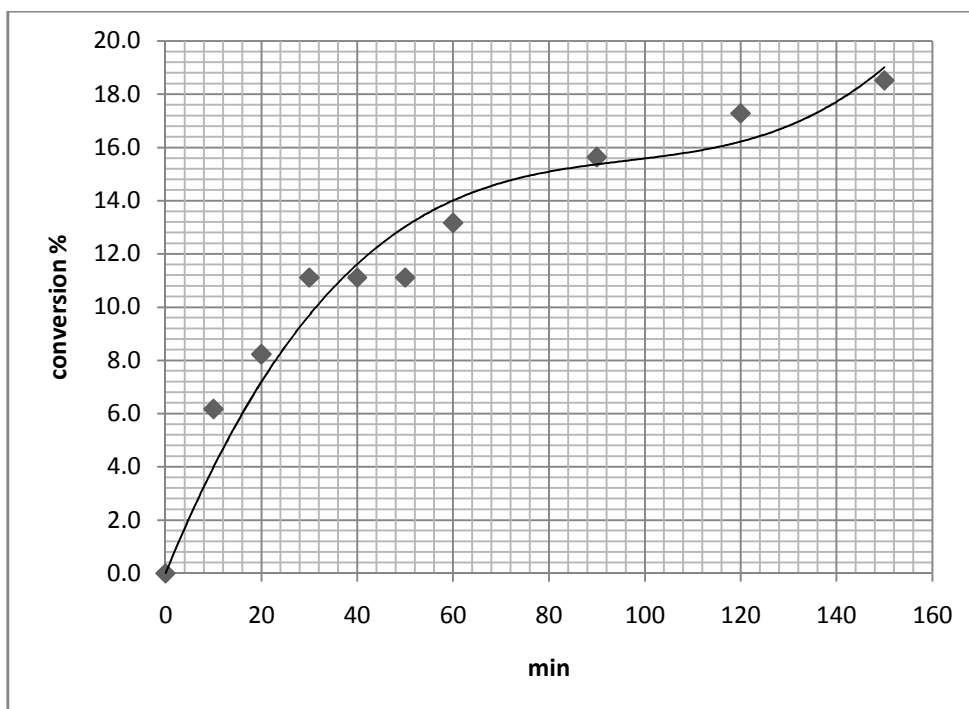


Figure 4.11 The reaction conversion versus time for the amount of cooking oil of 20ml

Figure 4.12 show that final conversion of free fatty acid is 26.6%. The reaction conditions for the reaction are 35°C, 1.5 gram of catalyst, 1:4 ratio of oleic acid to alcohol and 30ml of cooking oil. The detail calculated value shown in Appendix A.9.

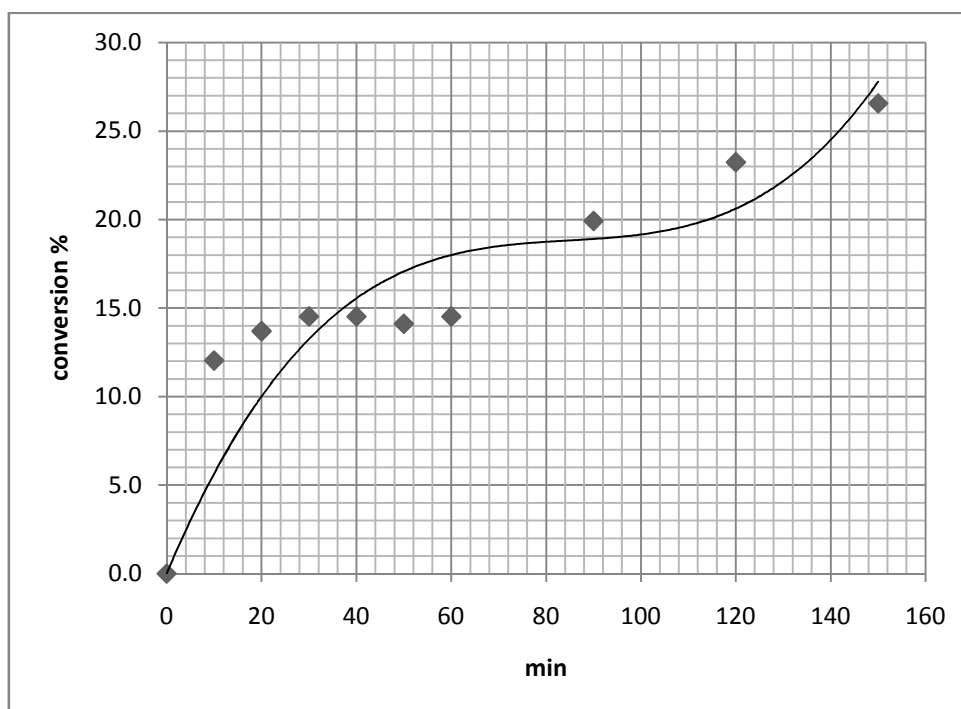


Figure 4.12 The reaction conversion versus time for the amount of cooking oil of 30ml

Figure 4.13 show that final conversion of free fatty acid is 31.7%. The reaction conditions for the reaction are 35°C, 1.5 gram of catalyst, 1:4 ratio of oleic acid to alcohol and 40ml of cooking oil. The detail calculated value shown in Appendix A.10.

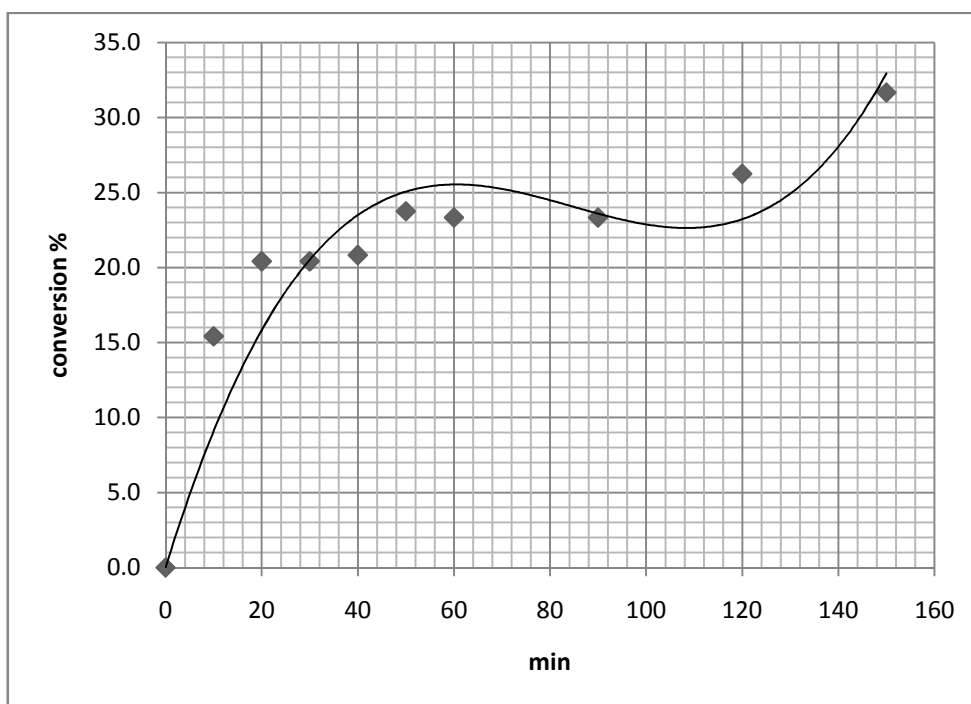


Figure 4.13 The reaction conversion versus time for the amount of cooking oil of 40ml

4.4.1 Comparison graph between different amount of triglycerides

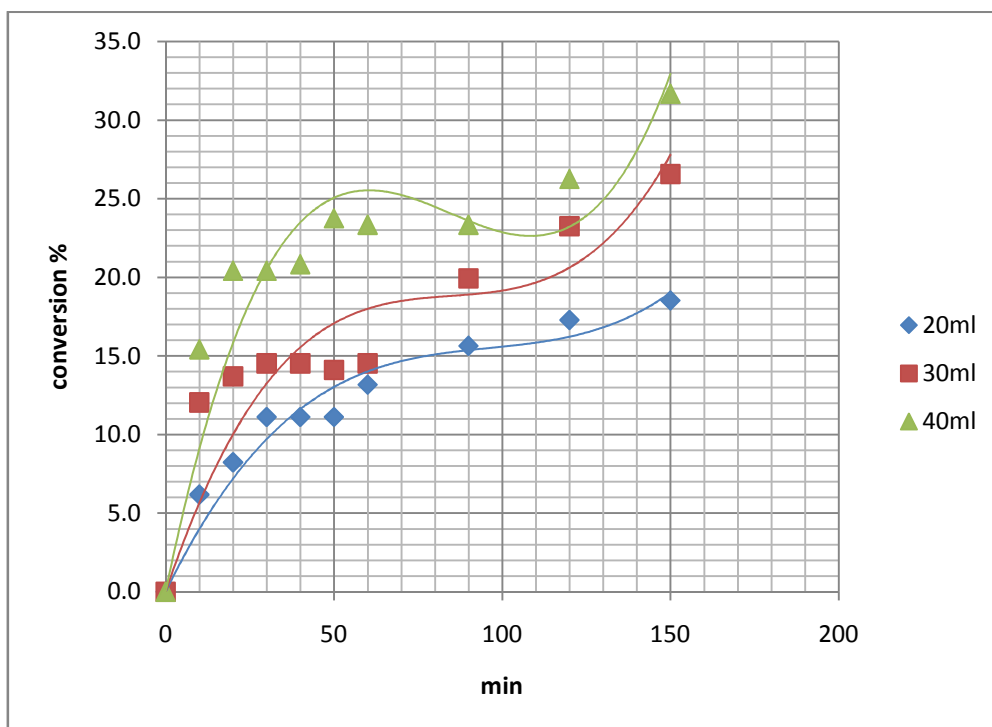


Figure 4.14 Effect of different amounts of cooking oil.

Figure 4.14 shows the effect of different amount of cooking oil of 20ml, 30ml and 40ml. For the studies of effect of the amount of the triglycerides, other parameters were selected by choosing the best parameters earlier which are 35°C, 1:4 ratio of oleic acid to alcohol and 0.5 gram of catalyst. When the amount of triglycerides is increased, the reaction reached a higher final conversion. The reaction rate also increases with increasing the amount of triglycerides. The transesterification of triglycerides contribute to the increasing of final conversion. In this experiment we use normal cooking oil from oil palm as a source of triglycerides that also contains free fatty acid. This lead to the conclusion that free fatty acid contain in cooking oil also increase the final conversion. Higher amount of free fatty acid has led to higher final conversion.

4.5 Kinetic modeling

The kinetic modeling for the esterification can be express by using simple pseudo-homogenous model. There are two unknown constant that must to be find in the model which are forward rate constant (k) and backward rate constant (k''). In order to determine the value of k and k'', the calculated concentration of the reactants and products along with the reaction rate ($-r_a$) was entered to the Polymath™ software package. In the current study, the pseudo-homogenous was developed by using the data from 35°C, 45°C and 55°C experiment. The model used for the modeling is pseudo-homogenous and can be written as:

$$-r_a = kC_aC_b - k''C_cC_d \quad (4.1)$$

Table 4.1 : Value of calculated k and k''

T(°C)	k	k''	1/T(K)	ln k	ln k''
35	0.0007567	0.0014799	0.003245	-7.18654	-6.51578
45	0.000694	0.0112479	0.003144	-7.27304	-5.76226
55	0.0013467	0.0885401	0.003049	-6.61010	-2.42430

Table 4.1 shows the calculated value from the Polymath software for each reaction temperature. Appendix B.1, B.2 and B.3 shown the detail calculated value and Polymath results for reaction rate. For further analysis about kinetic model, the relationship of the rate constant and Arrhenius equation was investigated. The Arrhenius equation is a simple equation for the temperature dependence of the rate constant. The Arrhenius can be shown as:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4.2)$$

Where E_a is activation energy, A is pre-exponential factor and R is the gas constant. Figure 4.17 and 4.18 shows the Arrhenius diagram of the rate constant for forward and backward esterification reaction. The values of parameters obtained at each temperature have then been correlated by means of Arrhenius equation, allowing an evaluation of activation energy of the esterification reaction. The ln version of Arrhenius equation can be expressed as below:

$$\ln k = \ln A - \frac{E}{RT} \quad (4.3)$$

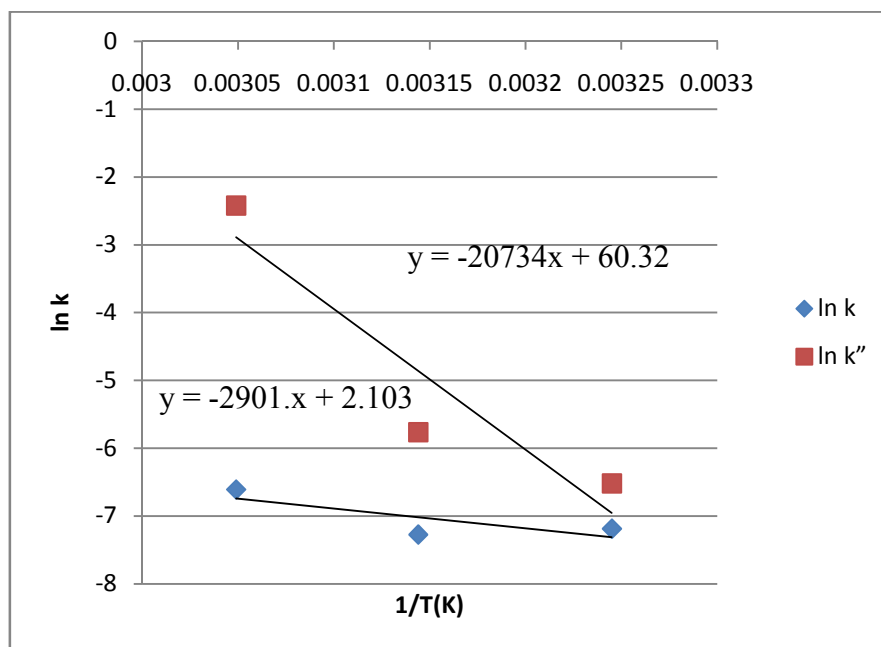


Figure 4.15 Arrhenius-type plot for forward rate constant and backward rate constant

By correlating the linear equation from the graph to the ln version of Arrhenius equation, the value of pre-exponential factor (A) and activation energy (Ea) are obtained and shown as in Table 4.1.

Table 4.2 : Kinetic parameters and related uncertainties

Reaction direction	A	Ea
Forward	8.191	24.12kJ/mol
Backward	1.573×10^{26}	172.39kJ/mol

The obtained value of apparent activation energy for forward reaction, 24.12 kJ/mol is lower as compared to the value of activation energy obtained by Omota et al. (2002) which is 55.5 kJ/mol by using the same catalyst. The Polymath results of k and k'' shown in Appendix C.1, C.2 and C.3. The different of the activation energy

between this study and Omota finding may happened as the reactants they used for that research purpose is 2-ethyl-hexanol and dodecanoic acid.

CHAPTER 5

CONCLUSION

5.1 Conclusion

In this study, it has been proven that sulfated zirconia is an attractive alternative to produce biodiesel by direct esterification of an oleic acid compared to the conventional ways to produce biodiesel by using homogenous catalyst. The investigation was carried out by using batch reactor with stirrer.

The variation in temperature showed that the reaction displayed exothermic behavior. As the reaction is exothermic, any temperature increase will decrease equilibrium conversion but not to the reaction rate.

When the amount of catalyst was increased, both reaction rate and the equilibrium conversion are affected. However, the experiment with the 0.5 gram of catalyst gives an error result. Supposingly, it will give lower reaction rate and equilibrium conversion as compared with 1.5 gram and 1 gram.

When the ratio of oleic acid to the alcohol was increased, the final conversions of oleic acid slightly increased. But in the other hand, it showed the reaction rate is affected to the ratio. The lower ratio will give fast initial reaction rate but the higher ratio give slow initial reaction rate.

The addition of triglycerides to the reaction has improved both the reaction rate and the final conversion. The source of triglycerides which come from the

cooking oil contains free fatty acids. This free fatty acid has increased the final conversion.

It can be concluded that the best operational conditions based on the present study, which will give the best final conversion of 31.7% with a good reaction rate, are $T = 35^{\circ}\text{C}$, $W_{\text{cat}} = 1.5$, ratio = 1:4 and addition 40ml of cooking oil.

5.2 Recommendations

It is recommended to extend the experiment time for future study to improve the result as the reaction behavior may differ if the reaction time is lengthen. In addition, other parameters can be added to the current parameters such as catalyst calcined temperature and the effect of various pre-treatment of catalyst which can improve the final result as well as to improve our knowledge about the esterification reaction and the catalyst used.

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APPENDIX A

A.1 Details of calculated value of conversion for 35°C

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	34.9	0.1070	0.00
10	34.6	0.1061	0.86
20	34.2	0.1048	2.01
30	33.8	0.1036	3.15
40	33	0.1011	5.44
50	32.7	0.1002	6.30
60	32.7	0.1002	6.30
90	29.6	0.0907	15.19
120	27.2	0.0834	22.06
150	26.9	0.0825	22.92

A.2 Details of calculated value of conversion for 45°C

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	33.5	0.102682	0
10	32.8	0.1005364	2.089552239
20	32.3	0.0990038	3.582089552
30	32	0.0980843	4.47761194
40	31.9	0.0977778	4.776119403
50	30.8	0.0944061	8.059701493
60	29.3	0.0898084	12.53731343
90	29.1	0.0891954	13.13432836
120	27.6	0.0845977	17.6119403
150	27.7	0.0849042	17.31343284

A.3 Details of calculated value of conversion for 55°C

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	35.3	0.108199	0
10	32.9	0.100843	6.79886686
20	32.7	0.10023	7.36543909
30	32.3	0.099004	8.49858357
40	31.9	0.097778	9.63172805
50	31.9	0.097778	9.63172805
60	31.7	0.097165	10.1983003
90	31.7	0.097165	10.1983003
120	31.6	0.096858	10.4815864
150	31.5	0.096552	10.7648725

A.4 Details of calculated value of conversion for 1 gram weight of catalyst

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	33.6	0.102989	0
10	33.1	0.101456	1.488095238
20	32.9	0.100843	2.083333333
30	32.5	0.099617	3.273809524
40	32.1	0.098391	4.464285714
50	30.3	0.092874	9.821428571
60	29.9	0.091648	11.01190476
90	29.8	0.091341	11.30952381
120	29.6	0.090728	11.9047619
150	29.4	0.090115	12.5

A.5 Details of calculated value of conversion for 1.5 gram weight of catalyst

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	36	0.1103	0.0
10	35.9	0.1100	0.3
20	34.1	0.1045	5.3
30	33.8	0.1036	6.1
40	32.7	0.1002	9.2
50	32.3	0.0990	10.3
60	32.2	0.0987	10.6
90	29.9	0.0916	16.9
120	29.8	0.0913	17.2
150	29.6	0.0907	17.8

A.6 Details of calculated value of conversion for 1:2 ratio of oleic acid to the ethanol

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	33.5	0.102682	0
10	31.5	0.096552	5.97014925
20	30.9	0.094713	7.76119403
30	30.4	0.09318	9.25373134
40	29.1	0.089195	13.1343284
50	28	0.085824	16.4179104
60	27.6	0.084598	17.6119403
90	27.7	0.084904	17.3134328
120	26.7	0.081839	20.2985075
150	25.6	0.078467	23.5820896

A.7 Details of calculated value of conversion for 1:4 ratio of oleic acid to the ethanol

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	25.2	0.077241	0
10	25	0.076628	0.79365079
20	24.6	0.075402	2.38095238
30	24.3	0.074483	3.57142857
40	23.7	0.072644	5.95238095
50	22.4	0.068659	11.11111111
60	22	0.067433	12.6984127
90	21.4	0.065594	15.0793651
120	20.9	0.064061	17.0634921
150	19.1	0.058544	24.2063492

A.8 Details of calculated value of conversion for an addition of 20ml of cooking oil

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	24.3	0.0745	0.0
10	22.8	0.0699	6.2
20	22.3	0.0684	8.2
30	21.6	0.0662	11.1
40	21.6	0.0662	11.1
50	21.6	0.0662	11.1
60	21.1	0.0647	13.2
90	20.5	0.0628	15.6
120	20.1	0.0616	17.3
150	19.8	0.0607	18.5

A.9 Details of calculated value of conversion for an addition of 30ml of cooking oil

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	24.1	0.0739	0.0
10	21.2	0.0650	12.0
20	20.8	0.0638	13.7
30	20.6	0.0631	14.5
40	20.6	0.0631	14.5
50	20.7	0.0634	14.1
60	20.6	0.0631	14.5
90	19.3	0.0592	19.9
120	18.5	0.0567	23.2
150	17.7	0.0543	26.6

A.10 Details of calculated value of conversion for an addition of 40ml of cooking oil

Time(min)	NaOH (ml)	Acidity	Conversion (%)
0	24	0.0736	0.0
10	20.3	0.0622	15.4
20	19.1	0.0585	20.4
30	19.1	0.0585	20.4
40	19	0.0582	20.8
50	18.3	0.0561	23.8
60	18.4	0.0564	23.3
90	18.4	0.0564	23.3
120	17.7	0.0543	26.3
150	16.4	0.0503	31.7

APPENDIX B

B.1 Polymath result of reaction rate (r_a) for 35°C

t (min)	CA (mol/L)	CB (mol/L)	CC (mol/L)	CD (mol/L)	r_a
0	2.67	2.67	0	0	0.000414
10	2.647049	2.64704871	0.022951289	0.022951	-0.00123
20	2.616447	2.61644699	0.053553009	0.053553	-0.00263
30	2.585845	2.58584527	0.084154728	0.084155	-0.00381
40	2.524642	2.52464183	0.145358166	0.145358	-0.00475
50	2.501691	2.50169054	0.168309456	0.168309	-0.00546
60	2.501691	2.50169054	0.168309456	0.168309	-0.00594
90	2.264527	2.26452722	0.405472779	0.405473	-0.00598
120	2.080917	2.08091691	0.589083095	0.589083	-0.00392
150	2.057966	2.05796562	0.612034384	0.612034	0.000221

POLYMATH Report
Polynomial Regression

No Title
19-Apr-2009

Model: $CA = a_0 + a_1*t + a_2*t^2 + a_3*t^3$

Variable	Value	95% confidence
a0	2.653502	0.060524
a1	0.0004141	0.0038547
a2	-8.781E-05	6.481E-05
a3	3.874E-07	2.92E-07

Analytical polynomial derivative

$$CA = 2.653502 + 0.0004141*t - 8.781E-05*t^2 + 3.874E-07*t^3$$

$$d(CA)/d(t) = 0.0004141 - 0.0001756*t + 1.162E-06*t^2$$

t	d(CA)/d(t)
0	0.0004141
10	-0.0012258
20	-0.0026333
30	-0.0038084
40	-0.004751

50	-0.0054612
60	-0.005939
90	-0.0059776
120	-0.0039243
150	0.0002209

General

Degree of polynomial = 3

Regression including a free parameter

Number of observations = 10

Statistics

R ²	0.9883753
R ² adj	0.982563
Rmsd	0.0073788
Variance	0.0009074

B.2 Polymath result of reaction rate (r_a) for 45°C

t (min)	CA (mol/L)	CB (mol/L)	CC (mol/L)	CD (mol/L)	r_a
0	2.67	2.67	0	0	0.0036374
10	2.614209	2.614209	0.055791045	0.055791	0.0040288
20	2.574358	2.574358	0.095641791	0.095642	0.0043159
30	2.550448	2.550448	0.119552239	0.119552	0.0044988
40	2.542478	2.542478	0.127522388	0.127522	0.0045776
50	2.454806	2.454806	0.21519403	0.215194	0.004552
60	2.335254	2.335254	0.334746269	0.334746	0.0044223
90	2.319313	2.319313	0.350686567	0.350687	0.0034078
120	2.199761	2.199761	0.470238806	0.470239	0.0014553
150	2.207731	2.207731	0.462268657	0.462269	-0.001435

POLYMATH Report

Polynomial Regression

No Title

19-Apr-2009

Model: CA = a0 + a1*t + a2*t² + a3*t³

Variable	Value	95% confidence
a0	2.665167	0.0766621
a1	-0.0036374	0.0048825
a2	-2.217E-05	8.208E-05
a3	1.737E-07	3.699E-07

Analytical polynomial derivative

$$CA = 2.665167 - 0.0036374*t - 2.217E-05*t^2 + 1.737E-07*t^3$$

$$d(CA)/d(t) = -0.0036374 - 4.435E-05*t + 5.211E-07*t^2$$

t	d(CA)/d(t)
0	-0.0036374
10	-0.0040288
20	-0.0043159
30	-0.0044988
40	-0.0045776
50	-0.004552
60	-0.0044223
90	-0.0034078
120	-0.0014553
150	0.0014351

General

Degree of polynomial = 3

Regression including a free parameter

Number of observations = 10

Statistics

R ²	0.9665253
R ² adj	0.949788
Rmsd	0.0093463
Variance	0.0014559

B.3 Polymath result of reaction rate (r_a) for 55°C

t (min)	CA (mol/L)	CB (mol/L)	CC (mol/L)	CD (mol/L)	r _a
0	2.67	2.67	0	0	0.0088755
10	2.48847	2.48847	0.18152975	0.18153	0.0069149
20	2.473343	2.473343	0.19665722	0.196657	0.0051765
30	2.443088	2.443088	0.22691218	0.226912	0.0036604
40	2.412833	2.412833	0.25716714	0.257167	0.0023666
50	2.412833	2.412833	0.25716714	0.257167	0.001295
60	2.397705	2.397705	0.27229462	0.272295	0.0004457
90	2.397705	2.397705	0.27229462	0.272295	-0.000769
120	2.390142	2.390142	0.27985836	0.279858	1.78E-05
150	2.382578	2.382578	0.2874221	0.287422	0.0028046

POLYMATH Report

Polynomial Regression

No Title

19-Apr-2009

Model: $CA = a_0 + a_1*t + a_2*t^2 + a_3*t^3$

Variable	Value	95% confidence
a0	2.624744	0.0664623
a1	-0.0088755	0.0042329
a2	0.0001036	7.116E-05
a3	-3.705E-07	3.207E-07

Analytical polynomial derivative

$$CA = 2.624744 - 0.0088755*t + 0.0001036*t^2 - 3.705E-07*t^3$$

$$d(CA)/d(t) = -0.0088755 + 0.0002072*t - 1.111E-06*t^2$$

t	d(CA)/d(t)
0	-0.0088755
10	-0.0069149
20	-0.0051765
30	-0.0036604
40	-0.0023666
50	-0.001295
60	-0.0004457
90	0.0007685
120	-1.784E-05
150	-0.0028046

General

Degree of polynomial = 3

Regression including a free parameter

Number of observations = 10

Statistics

R ²	0.9016189
R ² adj	0.8524284
Rmsd	0.0081028
Variance	0.0010943

APPENDIX C

C.1 Polymath result of forward rate constant (k1) and backward rate constant (k2) for 35°C

POLYMATH Report
Nonlinear Regression (L-M)

No Title
19-Apr-2009

Model: $nra = k1*CA*CB - k2*CC*CD$

Variable	Initial guess	Value	95% confidence
k1	0.01	0.0007567	0.0001036
k2	0.001	0.0014799	0.0037192

Nonlinear regression settings

Max # iterations = 64

Precision

R ²	0.6357614
R ² adj	0.5902316
Rmsd	0.0002215
Variance	6.135E-07

General

Sample size	10
Model vars	2
Indep vars	4
Iterations	4

Source data points and calculated data points

	CA	CB	CC	CD	nra	nra calc	Delta nra
1	2.67	2.67	0	0	0.005414 1	0.005394 7	1.942E-05
2	2.64704871 1	2.64704871 1	0.02295128 9	0.02295128 9	0.005225 8	0.005301 6	-7.575E-05
3	2.61644699 1	2.61644699 1	0.05355300 9	0.05355300 9	0.004833 3	0.005176 2	-0.000342 9
4	2.58584527 2	2.58584527 2	0.08415472 8	0.08415472 8	0.004608 4	0.005049 5	-0.000441

							1
5	2.52464183 4	2.52464183 4	0.14535816 6	0.14535816 6	0.004551	0.004792	-0.000241
6	2.50169054 4	2.50169054 4	0.16830945 6	0.16830945 6	0.005461 2	0.004694 1	0.000767 1
7	2.50169054 4	2.50169054 4	0.16830945 6	0.16830945 6	0.004639	0.004694 1	-5.506E- 05
8	2.26452722 1	2.26452722 1	0.40547277 9	0.40547277 9	0.004377 6	0.003637 3	0.000740 3
9	2.08091690 5	2.08091690 5	0.58908309 5	0.58908309 5	0.003924 3	0.002763 3	0.001161
10	2.05796561 6	2.05796561 6	0.61203438 4	0.61203438 4	0.001220 9	0.002650 6	- 0.001429 7

C.2 Polymath result of forward rate constant (k1) and backward rate constant (k2) for 45°C

POLYMATH Report

Nonlinear Regression (L-M)

No Title
19-Apr-2009

Model: $nra = k1*CA*CB - k2*CC*CD$

Variable	Initial guess	Value	95% confidence
k1	0.01	0.000694	0.0001955
k2	0.001	0.0112479	0.0106068

Nonlinear regression settings

Max # iterations = 64

Precision

R ²	0.5809634
R ² adj	0.5285838
Rmsd	0.000374
Variance	1.749E-06

General

Sample size	10
Model vars	2
Indep vars	4
Iterations	4

Source data points and calculated data points

CA	CB	CC	CD	nra	nra calc	Delta nra
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1	2.67	2.67	0	0	0.0036374	0.0049477	-0.0013103
2	2.614208955	2.614208955	0.055791045	0.055791045	0.0040288	0.0047081	-0.0006793
3	2.574358209	2.574358209	0.095641791	0.095641791	0.0043159	0.0044967	-0.0001808
4	2.550447761	2.550447761	0.119552239	0.119552239	0.0044988	0.0043538	0.000145
5	2.542477612	2.542477612	0.127522388	0.127522388	0.0045776	0.0043034	0.0002742
6	2.45480597	2.45480597	0.21519403	0.21519403	0.004552	0.0036614	0.0008906
7	2.335253731	2.335253731	0.334746269	0.334746269	0.0044223	0.0025245	0.0018978
8	2.319313433	2.319313433	0.350686567	0.350686567	0.0034078	0.0023501	0.0010577
9	2.199761194	2.199761194	0.470238806	0.470238806	0.0014553	0.0008712	0.0005841
10	2.207731343	2.207731343	0.462268657	0.462268657	-0.0014351	0.0009792	-0.0024143

C.3 Polymath result of forward rate constant (k1) and backward rate constant (k2) for 55°C

POLYMATH Report

Nonlinear Regression (L-M)

No Title

19-Apr-2009

Model: nra = k1 *CA*CB-k2*CC*CD

Variable	Initial guess	Value	95% confidence
k1	0.01	0.0013467	0.0003562
k2	0.001	0.0885401	0.0347424

Nonlinear regression settings

Max # iterations = 64

Precision

R ²	0.8347023
R ² adj	0.8140401
Rmsd	0.0003812
Variance	1.817E-06

General

Sample size	10
Model vars	2
Indep vars	4
Iterations	4

Source data points and calculated data points

	CA	CB	CC	CD	nra	nra calc	Delta nra
1	2.67	2.67	0	0	0.008875 5	0.009600 6	- 0.000725 1
2	2.48847025 5	2.48847025 5	0.18152974 5	0.18152974 5	0.006914 9	0.005421 8	0.001493 1
3	2.47334277 6	2.47334277 6	0.19665722 4	0.19665722 4	0.005176 5	0.004814 2	0.000362 3
4	2.44308781 9	2.44308781 9	0.22691218 1	0.22691218 1	0.003660 4	0.003479 2	0.000181 2
5	2.41283286 1	2.41283286 1	0.25716713 9	0.25716713 9	0.002366 6	0.001984 6	0.000382
6	2.41283286 1	2.41283286 1	0.25716713 9	0.25716713 9	0.001295	0.001984 6	- 0.000689 6
7	2.39770538 2	2.39770538 2	0.27229461 8	0.27229461 8	0.000445 7	0.001177 5	- 0.000731 8
8	2.39770538 2	2.39770538 2	0.27229461 8	0.27229461 8	- 0.000768 5	0.001177 5	-0.001946
9	2.39014164 3	2.39014164 3	0.27985835 7	0.27985835 7	0.000017 8	0.000758 9	- 0.000741 1
10	2.38257790 4	2.38257790 4	0.28742209 6	0.28742209 6	0.002804 6	0.000330 4	0.002474 2