PRODUCTION OF BIODIESEL FROM PALM OIL THROUGH HETEROGENEOUS CATALYSIS USING CALCINED EGGSHELL

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SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in term of scope and quality for the award of the degree of Bachelor in Chemical Engineering.

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DECLARATION

I declare that this thesis entitled “Production of Biodiesel from Palm Oil through Heterogeneous Catalysis Using Calcined Eggshell” is the result of my own work except as cited in the references and summaries which have been duly acknowledge. The thesis has not been accepted for any degree.

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Finally, I feel pleasure to have good health, strength and perseverance to complete this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

B100	Pure biodiesel
B.E.T	Brunauer-Emmet-Teller
B.J.H.	Barrett, Joyner, Halenda
FAME	Free fatty acid methyl ester
FFA	Free fatty acid
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatography
Ppm	part per million
XRD	X-Rat diffraction

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ABSTRACT

In recent years, shortage of fossil fuel, increasing price of crude oil and environmental issues have led to the scientific and research study in alternative fuel. Biodiesel is one of the alternate biofuels, due to its comparable fuel properties and cleaner emission to environment. In this study, transesterification of refined palm oil with methanol catalyzed by heterogeneous catalyst, calcined eggshell was studied and the suitable kinetic model was identified. Calcined eggshell was prepared by washing the fresh eggshell with boiling water and followed by calcinations of fresh eggshell at 900 ^{0}C. The calcined eggshells were characterized by X-ray *Diffraction* (XRD),Physisorption analysis (B.E.T.) method, andFourier transforms infrared spectroscopy (FTIR). Through the analysis, the calcined eggshell was found that identical to the commercial Calcium Oxide. Transesterification was studied at different parameter such as temperature (45^{0}C-65^{0}C), agitation intensity (200 rpm-500 rpm), catalyst weight percent (1.5%-6%), and methanol to oil weight ratio (12:1-6:1). The highest yield is 72.03% of Fatty Acid Methyl Ester (FAME). The kinetic data was fit to the kinetic model developed using first order model. It is found that the calcined eggshell is a potential catalyst which is comparable to other commercial catalyst.

PENGHASILAN BIODIESEL DARI MINYAK SAWIT MELALUI PENGMANGKINAN HETEROGEN DENGAN MENGGUNAKAN KULIT TELUR TERBAKAR

ABSTRAK

Kebelakang ini, kekurangan minyak, kenaikan harga minyak mentah dan isu-isu terhadap alam sekitar mendorongkan pangajian saintifik dan penyelidikan untuk mendapat bahan bakar alternatif. Biodiesel sebagai salah satu biofuel yang standing dengan sifat-sifat bahan bakar yang sedia-ada serta pelepasan gas-gas yang lebih bersih. Dalam kajian ini, pengtransesteran minyak sawit tertapis dengan pemangkin yang berbentuk pepejal. Pemangkin yang digunakan adalah kulit telur terbakar telah dikaji dan model yang sesuai untuk system tindak bala selah dikajikan.Kulit telur terbakar telah disediakan dengan menggunakan telur kulit segar yang telah dibersihkan dengan air panas dan seterusnya pembakaran atau pengkalsinan kulit telur ke 900 darjah Celsius dalamudaraselama 3 jam. Pemangkin atau kulit telur terbakar yang telah disediakan kemudiannya dicirikan dengan menggunakan pembelauan sinar-X (*XRD*), spektrometer Fourier Transform infra merah (*FT-IR*) dan pengukuran luas permukaan Brunner-Emmett-Teller (*BET*).Dalam pengajian yang telah buat, kulit telur terbakar ini mempunyai ciri-ciri yang sama dengan Calcium Oksida. Selain itu, pengtransesteran minyak sawit kepada hasil dikaji pada pembolehuba htindak balas seperti nisbah molar metanol/minyak(12:1-6:1), jumlah berat pemangkin (1.5%-6%) yang digunakan, suhu tindak balas(45^{0}C- 65^{0}C), dan intensiti pergolakan(200 rpm -500 rpm). Hasil diperoleh adalah 72.03 % biodiesel di bawah keadaan tindak balas optimum. Tindak balas adalah sepadan kepada model yang dicipta, model tesebut adalah pseudo-homo first order. Sebagai kesimpulan, kulit telur terbakar adalah berpotensi dimana ianya adalah setanding dengan pemangkin yang sedia ada dalam pasaran.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Majority energy consumption worldwide came from fossil sources (petroleum, coal and natural gas) and shortage is predicted in coming 50 years. Therefore finding an alternative energy is crucial. Renewable energy such as biodiesel is important fuel in future. Biodiesel is a green fuel that can be used in standard diesel engine and also in pure form known as B100. (Benjamin, 2007)

Biodiesel refers as Fatty Acid Methy Ester (FAME) also known as mono alkyl ester. It is produced using 4 different methods using in the market. The methods are catalysis (transesterification), pyrolysis, direct bending and Micro-emulsion. Amongst the 4 methods, transesterification was chosen since it increases the cetane number and has higher combustion efficiency. The present research focuses on transesterification aid with catalyst. Transesterification process uses vegetable oil and animal fat as the raw materials by reacting with an alcohol (methanol).

Vegetable oil and animal fat are organic triglyceride, which are the main source of producing biodiesel. Selection types of catalyst are depending on the content of FFA (free fatty acid) and water in the triglyceride. FFA will reduce the biodiesel yield during transesterification catalysed by using alkali catalyst due to soap formation (Endalew, 2011). In order to reduce the content of FFA, pre-treatment such as esterification with strong acid such as H_2SO_4 with alcohol is used to form ester(Sharma, 2008). In this study, refined palm oil will negligible amount of FFA will be used.

As mentioned, transesterification required catalyst to operate at ambient condition. 3 main categories of catalysts in the market are homogeneous, heterogeneous, and enzymatic. Homogeneous catalyst is in liquid form. Sodium Hydroxide and potassium hydroxide concentrated solution and the common catalyst used in producing biodiesel. Helwani, (2009) discussed that alkali catalyst is preferred since it is faster than acidic catalyst by 4000 times and stainless steel reactor couldn’t resist the corrosion action from strong and concentrated acid. Nevertheless, the use of homogeneous catalyst has caused great impact to environment and market value of glycerine. Separation of the homogeneous catalyst from glycerine is time. Studies on heterogeneous catalyst are important and it can overcome the drawback. Heterogeneous catalyst such as, Calcium Oxide, Iron Sulfate, Fe_2SO_4 can be separated by filtration from mixture of glycerine. Lipases also are used as enzyme in enzymatic transesterification. It shows good result in selectivity. However it required longer reaction time than base catalyzed system. (Sharma, 2008)

1.2 Problem statements

1. In market, the common catalyst such as NaOH, and KOH are expensive and high cost in recovery of glycerine. In order to recover the FAME, washing process is used. However, washing process will generate much waste water. It is another environmental problem. In addition, the catalyst such as sodium hydroxide is used in industries and not environmental friendly, the recovery of glycerol after the reaction is impossible.
2. In the view of waste to wealth, eggshell containing high percentages of Calcium carbonate and can be transformed into calcium oxide, a strong earth alkaline metal oxide, which can be used to catalysed the transesterification of vegetable oil for biodiesel production. This can be done via calcinations process. The treated eggshell catalyst is comparable with commercial catalyst and it wouldn’t cause any environment impact.

1.3 Research Objectives

1. To characterize calcined eggshell using X-ray Diffraction method (XRD), Fourier Transform Infrared (FTIR) and Physisorption analysis.
2. To study the effect of important parameters to the reaction.

3. To develop the suitable kinetic model.

1.4 Scope of the study

1. To characterize the calcined eggshell using FTIR, XRD and physisorption analysis.
2. To study the effect of important parameter such as temperature, agitation intensity, oil/methanol molar ratio and catalyst loading.
3. The fit the experimental data with the kinetic model such Pseudo-homo geneous model, Eley-Rideal model or Langmuir Hinshelwood model.

1.5 Significant of the study

Most of the vehicle still consuming petrol-diesel and it is one of the largest sources contributing to the greenhouse gases. The petro-diesel in future will be replaced by bio-fuel such as biodiesel. Biodiesel is environmental friendly by closed-carbon-cycle. This study is to generate more environment friendly catalysts to enhance the quantity and quality of the production of biodiesel.

Direct disposal of the crude glycerin prodeuced during the biodiesel production catalysed by homogeneous catalyst is not ethical due to its toxicity. Recovery of the glycerine after the transesterification can earn extra profit. Glycerine can be used as antifreeze agent and also as plasticiser. Therefore using solid catalyst, the recovery can be done by filter it using filtration method. The homogeneous catalyst otherwise are making the separation and liquid form of catalyst become difficult. The separation is costly and time consuming.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is an alternative choice of fuel for diesel engine. It is a renewable energy which is biodegradable, environment friendly and nontoxic. Using biodiesel can reduce the admission carbon dioxide from fossil fuel. The sources of biodiesel usually are vegetable oil and animal fat. The natural feedstock contains free fatty acid (FFA), phospholipids, water, odourants and other impurities (Meher, 2006).Major component in the feedstock are triglyceride which is a molecule of glycerol and 3 long chain carboxyl esters vary from C12 to C18. The different feedstock consist of different long chain carboxyl esters.

Recently government has the initiative to include the biodiesel in the fuel market. By blending the diesel fuel available with biodiesel to reduce the burden of consumption of diesel fuel alone. The future expected diesel fuel will be sold in the form of 5 percent biodiesel in mixture of diesel fuel in the market.As a result, biodiesel production is of interest of the world to reduce the consumption of diesel fuel in Malaysia that has created the global warming issues. (Siriwardhana, 2009)

2.2 Method of production of biodiesel

The few methods of biodiesel production are shown in Table 2.1 (Boro, 2012). After the comparison in the Table 2.1, Transesterification was chosen due to its flexibility and advantages.

Table 2.1 Methods of producing biodiesel, advantages and disadvantages.

Methods	Definition	Advantages	Disadvantages
Pyrolysis or thermal cracking	Method of conversion of one substance into desired products by application of heat with the aid of the catalyst in the absence of air or oxygen.	Low of processing costs, compatibility with infrastructure, engines and fuel standards, and flexible in choices of feed stock. The final products are identical to diesel fuel in composition.	High energy intensive.

Table 2.1 Continued

Methods	Definition	Advantages	Disadvantages
Micro-emulsions	Microemulsification uses vegetable oil mixed with alcohol and surfactant. The products can be blended with conventional diesel. The viscosity of the products was reduced to acceptable level.	Fuel viscosity is lower.Improve spray characteristics by explosive vaporization (flashing point）of the low boiling constituents in the micelles.	Lower cetane number and lower energy content.
Direct use and blending	Use vegetable oil directly orblend it with petrodiesel.	Liquid nature and portability Heat content (80% of diesel fuel) readily available; renewability	Higher viscosity, Lower volatility and occurring of reactivity of unsaturated hydrocarbon chains
Transesterification	Transesterifcation (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters(FAME) and glycerine.	Renewability, with higher cetane number, lower emissions and higher combustion efficiency	Glycerol disposal and waste water problem.

2.3 Source of natural oil

Vegetable oil separated into edible oil and inedible oil. Edible oils are palm oil, sunflower oil, soybean and rapeseed oil. Inedible oil is either contains poisons or spent oil. The inedible oil such as jatropha oil is potential to be produced as biofuel (Endalew, 2011). Table 2.2.shows some elements contain in the oil.

Table 2.2 Carboxyl compositions and level of unsaturation in different feedstock.

FAME name	Chemical formula*	Soybean	Jatropha	Sunflower	Rapeseed	Pongamia	Palm
Lauric	12:0	-		-	-	-	0.1
Myristic	14:0	-	0-0.1	-	-	-	1
Palmitic	14:0	11	14-15.3	6.08	3.49	11.65	42.8
Palmmitoleic	16:0	-	0-1.3	-	-	-	-
Stearic	18:0	4	3.7-9.8	3.26	0.85	7.5	4.5
Oleic	18:1	23	45.8	16.93	64.4	51.59	40.5
Linoleic	18:2	54	44.2	73.73	22.3	16.64	10.1
Linolenic	18:3	8	0-0.3	-	8.23	-	0.2
Arachidic	20:0	-	0-0.3	-	-	-	-
Behenic	20:1	-	0-0.2	-	-	-	-

Source: (Endalew, 2011)

However, selection of catalyst is depending on the concentration of FFA in the oil. Table 2.3 shows the acid value containing in the vegetable oil. Endalew (2011) told that high value of FFA contains will favor the formation of Ca soap via saponification reaction when CaO used as catalyst. High concentration of FFA can be treated via neutralization or esterification using sulfuric acid (Kouzu, 2008).

Table 2.3 Properties of different feedstock.

Type of oil	Density, (g/cm^3)	Flash point, ^{0}C	Acid value (mg KOH/g)
Soybean	0.91	254	0.2
Rapseed	0.91	246	2.92
Sunflower	0.92	274	0.15
Palm	0.92	267	0.1
Peanut	0.9	271	3
Corn	0.91	277	0.11
JatropaCurcas	0.92	225	28
Palanga	0.9	221	44
Sea Mango	0.92	-	20

Source: (Endalew, 2011)

2.3.1 Potential of palm oil as raw material for biodiesel production

In Malaysia, the palm oil is utilized in food industry. However, palm oil has a high potential to be produced as biodiesel and in future to replace the conventional diesel. As Malaysia is the world 2nd largest palm oil producer,(Sceptregrouplimited, 2010) and palm oil has the potential to replace the rapeseed oil in producing biodiesel in the Europe country. Table 2.4 shows the properties of palm oil.

Table 2.4 Properties of Palm Oil

Properties	Value
Kinetic viscosity (38^{0}C)	39.6
Cetane number	42.0
Cloud point(^{0}C)	31
Flash point(^{0}C)	267
Density(kg/m^3)	918

2.4 Catalysts

2.4.1 Homogeneous catalysts

In the homogeneous base-catalyzed transesterification (Helwani, 2009) reported that alkaline metal alkoxides (combination of alkaline with alcohol), hydroxide, carbonates shown high performance in production of biodiesel. The by product can be recovered but formation of acetaldehyde and formaldehyde is occur because of overheated in recovery process. The most common basic catalyst NaOH (Zhang, 2010) residue in glycerine need large amount of water to wash the mixture of biodiosel. This process is not environmental friendly and glyceride discarded as waste causes environmental issues. In the acid-catalyzed reaction is much slower than alkaline reaction by 4000 times. Unlike base catalyst the triglycerides is protonated by acid catalyst to create tetrahedral intermediate. Therefore the two different homogeneous catalysts to be discernible and to proceed through different reaction rates (Endalew, 2011). However acidic catalysts are better in taking place of esterification of FFA. An example of acidic homogeneous catalyst is H_2SO_4.

Condition of acidic transesterification of acidic catalyst required high temperature as to speed up the reaction.

2.4.2 Heterogeneous catalysts

Heterogeneous system is different from homogeneous catalyst system. Endelew (2011) and Fogler (2006) stated that heterogeneous system consists catalysis, adsorption and desorption of reactant and product on the surface. Besides that, mass transfer phenomenon occurs during the catalytic reaction. These are the important parameter that used to calculate the rate of reaction. Findings are vital to study the important parameter to optimize the production.

In solid acid catalyst system, the absorbing element is the triglyceride on the surface of the catalyst but alcohol will react with the triglyceride absorbed on the surface of catalyst. The mechanism is based on the lewis /bronsted solid acid. The situation is same as solid base catalyst but alcohol will be absorbed on the surface and triglyceride will react with the absorbed alcohol. Few mechanism were studied such as, Langmuir-Hinshelwood (LH) and Eley- Rideal(ER) kinetic model.

Heteropoly acid as one of the solid acidic catalyst reviewed by Helwani (2011) perfectly synthesized biodiesel in short time. One of the examples is $Cs_{2.5}PW$. This catalyst can function under presence of water. It is so efficient that can produce 99% of biodiesel and not much affected by the appearance of FFA. Another type of solid acidic catalyst is the commercial type acidic resin catalyst, named Amberlyst15. Amberlyst may consider as efficient in both transesterification and esterification.

However, thermal-stability has to be overcome during operation under high temperature. (Lopez, 2008) & (Tesser, 2010)

Basic-porous supported catalyst such as alkaline metal oxide/zeolite having large surface area that provides high active site for the reaction to occur. This type catalyst can be prepared via impregnation method. Example ETS-10 containing lithium ions that is new generation in transesterification. Recently few solid form catalysts such as $CaTiO_3$, $CaMnO_3$, and alumina/silica supported K_2CO_3 is reported by Boro, (2012). Although the catalyst can be reused but the preparation method of these catalysts is not environmental friendly. Some abandoned waste like eggshell and oysters shell contains 95 percent of calcium carbonates and can be generated it into calcium oxide as catalyst. This catalyst can be generated again by calcinations. Yoosuk, (2010) revealed advance methods, such as hydration method. This method is to increase the surface area per gram of catalyst. CaO will react with water in the reflux system in 60 degree Celsius. Calcium oxide then transform to calcium hydroxide. Second step is to calcine the sample from first step in 600 degree celcius and calcium form again but with more porous than the untreated calcium oxide. The comparison and summary of homogeneous and heterogeneous catalyst is shown in Table 2.5.

Table 2.5 Comparison of the advantages and disadvantages for the different type of catalysts.

Type	Advantages	Disadvantages
Homogeneous	*Operate at ambient conditions. *Base catalysts give favorable kinetic. Since it’s high activity and give high yield in short time *Basic catalysts are 4000 times faster reaction than acid catalyzed transesterification *Basic methoxides are more effective than hydroxides *Acid catalysts can be used for both esterification and transesterification simultaneously *Acid catalysts are suitable for low grade of feedstock and high contains of FFA	*Separation and waste problems after reaction *Catalyst impossible to be reused *Limited to batch type of reactors *Basic catalysts are sensitive to the presence ofFFA and water *Higher production cost compared with heterogeneous catalyst *Acid catalysts are corrosive, give very slow reaction rate and operate under high temperature. *Acid catalysts require higher molar ratio of methanol to oil, higher temperature, concentrated acid and more waste from neutralization reaction

Table 2.5 Continued

Type	Advantages	Disadvantages
Enzymatic	*High in term selective *FFA are converted to biodiesel *Operate at low reaction temperature, can operate with the presence of water *Easy for separation products *Environmentally friendly *Higher purity than base catalysts *Can be implemented as homogeneous or heterogeneous catalysts	* Expensive *Enzyme is inhibited in the presence of methanol *Enzyme are sensitive to temperature, denaturization happened during high temperature
Heterogeneous	*Environmentally friendly, recyclable, less disposal problems. *Easy separation of products, higher selectivity, catalyst with higher life span. *Acid heterogeneous catalyze both esterification and transesterification simultaneously and insensitive to FFA and water. *Comparatively cheap. *Can be used in continuous fixed bed reactors. *Generable from organic waste.	*Currently moderate conversion compared to high active basic homogeneous. *Mass transfer limitation due to the presence of three phase and need good mixing. *Basic catalyst only operates at low FFA and anhydrous condition and pretreatment is required for high FFA feedstock. *High alcohol to oil ratio required, high temperature. *Acidic catalysts are low acid site concentration, low micro porosity, and high cost compared with basic catalyst.

2.5 Important operating parameter of the reaction

Temperature is an important element in transesterification. However, temperature range is depending on the oil and alcohol used. It greatly influences the reaction rate and conversion (Poljanšek, 2012). Lower temperature will prolonging the reaction time. Besides time of reaction, the conversion will change since rate of both forward and backward reaction will increases or decreases when changing the temperature as according the La Chatelier’s principle.(Vicente, 2005)

Ratio of methanol to oil also will affect the reaction rate and conversion of oil. According La Chatelier’s principle, the higher the concentration of reactant will favour more FAME production. However, too much of alcohol used will causes the mass transport limitation and make recovery process complicated (Zhu, 2006).

Since the alcohol and oil are immiscible. Therefore, stirring plays important role in the yield of biodiesel. Stirring speed also affects the reaction where higher the speed mixing, the oil will transport into the mixture quickly and eliminate the rate of mass transfer (Cintas et al, 2010).

Amount catalyst used will affecting the rate. (Poljanšek, 2012) More catalyst will provide higher surface area for reactant to react(Veljkovic et al., 2009). However, catalysts such as Sodium Methoxide will absorb some of the glycerol and methanol. This causes the recovery much difficult (Cintas et al, 2010)

2.5.1 Other influences

As Meher,(2006) relate that concentration of the (Free Fatty Acid) FFA will affect the choice of the type of catalyst. FFA reduces the activity of the base catalyst and to form soap. While using acidic catalyst could convert the FFA to ester. FFA in feedstock is favor for base catalyzed reaction with less than 3%. Also, the moisture content told by Yan (2008) will lead the formation of soap via saponification process. However, water could increase conversion of FAME in the process of transesterification using base catalyst.

2.5.2Operating condition

Transesterification process can be done in the presence of catalyst around 35-65^{0}C and atmospheric pressure but still it need the assist of agitation to mix the two immiscible liquid. Time taken is depending on the selection of catalyst. Boey, (2009) justified the CaO catalyst modified for waste mud crab (*Scylla serrata*) takes 2.5 hrs to reach equilibrium and one hours for NaOH to obtain the equlibrium. In addition, the reaction would perform in the range as stated below:

i. Agitation intensity :300 rpm- 1000 rpm (depending to the size of reactor)
ii. MR(molar ratio alcohol: oil): 3:1 to 15:1
iii. Catalyst weight % of oil :0.5%-10% (depending on catalyst used)

2.6 Kinetic study

In research of the biodiesel production found that the transesterification involving a number of consecutive reversible reaction (Hoque, 2011). Early of the kinetic model of transesterification of palm oil with methanol using KOH done by Darnoko, (2000) was pseudo-second order respective to triglyceride, diglyceride and monoglyceride but forward reactions are only considered. Until Vicente, (2005) found that the transesterification of sunflower and methanol using KOH is 2nd order as well for 3 consecutive forward and reversible reactions. In Poljanšek, (2012) proposed the three reversible reaction of formation FAME. The triglyceride is transform into diglyceride and monoglyceride before forming glycerin. However, in some of the research is still focusing in the pseudo homogeneous model as developed by Jain (2010). Where the model developed is first order with respected to the formation of Fatty acid methyl ester (FAME) and 0.93 accurate value, R^2 fitted to the experimental data.

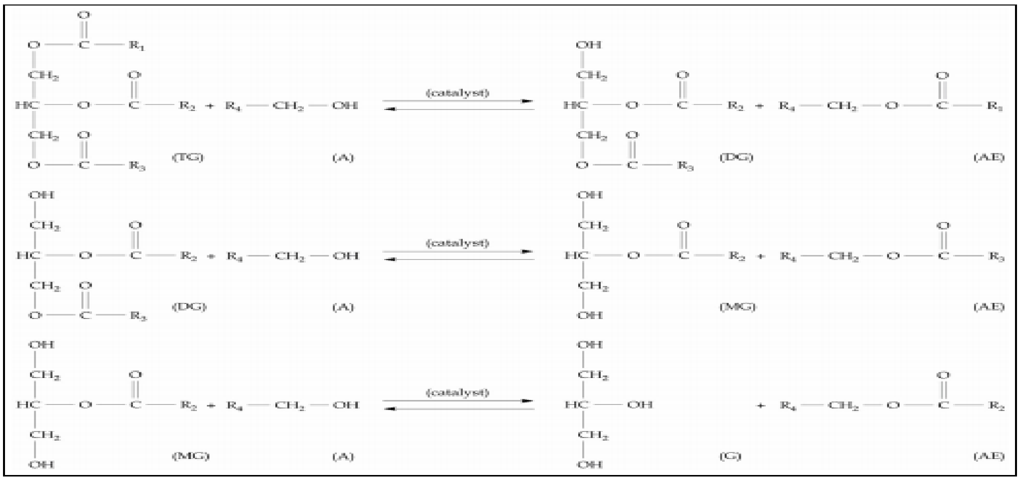
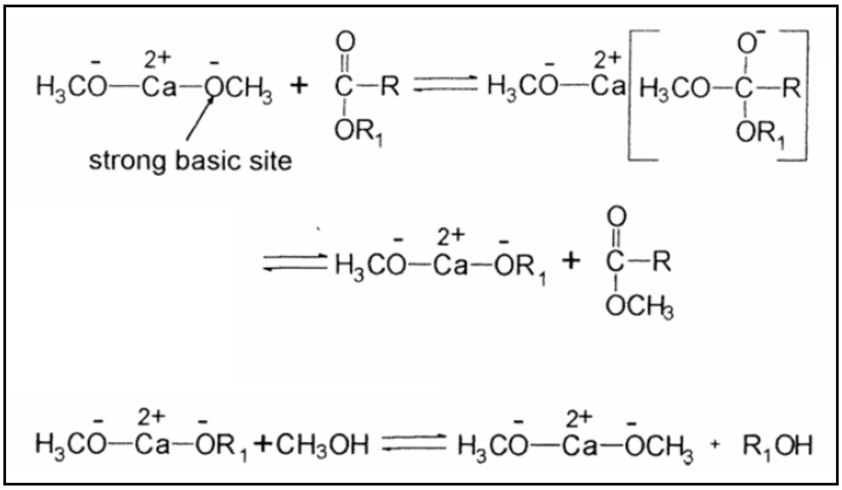


Figure 2.1 Three consecutive formation of FAME

Source: (Poljanšek, 2012)

In the study of heterogeneous catalysis, some of the researches are investigate the kinetic on the surface of the catalyst in example using Calcium Methoxide. The strong basic sites of Calcium oxide with methanol can catalyze thereaction with high methyl ester yield of 91 % (Sirikulbodee, 2007). The mechanism of Calcium Methoxide formed after combination of calcium oxide with methanol was shown as below in Figure 2.2.This study can be used to combine with suitable model such as Langmuir Hinshelwood model and E-R (EleyRideal model) that approach the study of surface kinetic. Until now, the model based on heterogeneous catalytic is still very rare.

Figure 2.2 Transesterification mechanism of Calcium Methoxide with oil.



CHAPTER 3

METHODOLOGY

3.1 Material/Apparatus/Equipment

Table 3.1 and 3.2 show the amount of reactant needed for the present study. The detail calculation was shown in Appendix A.

Table 3.1 Chemicals

Chemical	Function
Refined Palm Oil (Carrefour)	Reactant
Methanol (99.8% purity from R&M Chemicals)	Reactant
Calcium Oxide(Powder) (R&M Chemicals)	Pure substance used to compare with calcined eggshell
Calcium Carbonate(Powder) (R&M Chemicals)	Pure substance used to compare with fresh eggshell
Methyl Palmitate (Purchased from sigma Aldrich)	GC Standard substance
Methyl Linoleate (Purchased from sigma Aldrich)	Standard substance
Methyl Streate (Purchased from sigma Aldrich)	Standard substance
Methyl Oleate (Purchased from sigma Aldrich)	Standard substance
n-hexane	Solvent for sample dilution

Table 3.2 Material/Apparatus

Apparatus	No.	Function
Vials	50	For preparing the GC sample and standard
Syringe Filters	25	Filtration of catalyst
3 Necked Round Bottom Batch Reactor (500 ml) With Condenser	1	Reaction take place and condenser for condensation of methanol vapor
Pasteur Pipette	5	Withdraw the sample from reactor
Heating plate with magnetic stirrer	1	Supply heat to the reactor uniformly
Thermometer	2	To indicate the temperature.
Syringe	5	Used with the filter.
Micropipet*	1	Used to measure the small portion of sample
Micropipet Tips*	5	Used to measure the small portion of sample
Pipette (10ml)	1	Measure the volume of hexane used for dilution
Vaccum Assisted(Pipette)	1	Used with pipette
Volumetric Flask 10 Ml	10	Dilution for sample
Mortar And Pestle	1	To crash the eggshell to powder form
Retort-stand	2	Clamp the condenser and reactor
Filter Paper	1 pack	Filter out the catalyst from product

3.1.1 Equipment setup

A 500 ml three-necked glass flask equipped with a condenser was used as a reactor and a thermometer. Hot plate magnetic stirrer with water bath was used to provide heat control the reaction temperature, and mix the reactants and catalyst using the magnetic stirrer. It can be heated from 30-200^{0}C and the stirring speed can be varied from 0-1100 rpm.

Figure 3.1 Experimental setup: 3 necked-flask equipped with condenser

3.2 Catalyst preparation

Eggshell is the most abandoned waste that containing high percentage of Calcium carbonate and it's up to 95% (Boro, 2012). Decompose of the Calcium Carbonate to calcium oxide will occur at around 810 till 830 ^{0}C(Engin, 2006). The protein complex in eggshell decomposed at 800 degree Celsius.

In order to get effective result, eggshell was calcined at 900 degree Celsius for 3 hours (Engin, 2006). Also, if overheated, the calcium oxide will crystallize to form a closer pack crystal and thus reduce the inhabitated surface area for the reaction. This has been proven by Viriya (2012) in the physisorption testing (Brunaurer-Emmett-Teller method).

The eggshell was collected from the café of UMP. Approximate 500 grams. Eggshell was been cleaned by boiling water as to remove the odor and crushed into small pieces with mortar. The membrane layers were removed from the eggshell as well. Further step was rinsing with deionized water. The fresh eggshell was then placed in the furnace and annealed it up to 900 degree Celsius for calcinations process. The calcinations shall be 3 hours. The Calcined sample was powdered in the agate mortar and stored in the desiccators for dewatering. After a day of drying and cooling, the calcined eggshell was placed into a container.

Figure 3.2: Cleaning fresh eggshell

Figure 3.3: Crushed fresh eggshell

Figure 3.4: Calcined eggshell

3.3 Catalyst characterization

3.3.1 X-Ray Diffraction (XRD)

XRD analysis is used to reveal the information about the crystal structure. X-ray beam from source was diffracted by a specific set of crystallographic planes in the sample. Therefore the analysis can identify the different structure of crystal in the sample. Each crystal has its own identical diffraction degree due to different crystal arrangement. XRD analysis was done by preparing powder form of Calcium Oxide, pure Calcium Carbonate, calcined eggshell and fresh eggshell in 5 g each. The XRD working in Cu/30 kV/15 mA, speed 1 degree per minute and samples were scanned in 2θ (20 to 60 degree).

Figure 3.5 XRD instrument

3.3.2 Fourier Transform Infrared(FTIR)

FTIR (model Thermo Nicolet) was used to analyse the functional group exist in each samples by obtain an infrared spectrum of absorption, emission, photoconductivity. The samples were powderedand tested by FTIR spectra in the range4000–400 cm^{-1}. The spectrum was taken at room temperature.

Figure 3.6 FTIR spectrometer

3.3.3 Physisorption Analysis

The physical adsorption test was conducted using the Physisorption analyser (Model Thermo Surfer) to check the porosity and surface area of the samples. The samples in the powder form and was degassed overnight at 150 degree Celsius. Then, the samples underwent nitrogen adsorption process on surface of the catalyst at 77 Kelvin. The samples were re-run again to get blank result by using gas Helium in order to obtain accurate result.

Figure 3.7 Physisorption analyser

3.3.4 Particle size distribution

The size distributions of the catalyst were analyzed using Mastersizer. The data needed are reflex index and absorption index of samples. As the Calcined Eggshell was in the powder form is an important date for the suitable filter selection.

Figure 3.8 Particle size analyser

3.4 Transesterification reaction

Refined palm oil (RPO) usually has low free fatty acid, in around 0.2% (max) of FFA (PORAM handbook, 2012). Therefore, further treatment on the palm oil used is unnecessary. The methanol-to-oil molarratio of 12:1 was added into heated RPO following by 1.5 wt% of Calcined Eggshell. Thereaction was run at this temperature for 3 hours and 30 minutes. Detailed calculation and formulas are presented in Appendix A.

Factors affecting the methyl ester content andyield were studied including methanol-to-oil molar ratio, temperature, catalyst loading, and yield variation with time. After completion ofeach batch, the catalyst particles were physically separated from the mixture by filtration. (Poljansek, 2011)

3.4.1 Study on effect of temperature

The study was carried at different temperature, from 45 to 65 degree Celsius. The transesterification reaction was fixed at 1 to 12 molar ratio of oil to methanol, agitation intensity of 500 rpm, 1.5 weight percent. In this study samples were taken every 15 minutes. The samples were withdrawn quickly in around 3ml-5ml using dropper and samples were further placed in a syringe and filters using a syringe equipped with filter. In this method, the Calcined Eggshell was removed and reaction stopped. The samples were kept in -20 degree Celsius for further analysis.

3.4.2 Effect of agitation intensity

The study was carried at different agitation speed, varied from 200 to 500 rpm (revolution per minute). Experiment was fixed at 12:1 ratio, 5 wt % of oil catalyst and 65 degree Celsius. Result will be taken after 3 and a half hour. The samples were stored at -20 degree Celsius.

3.4.3 Methanol to oil ratio

In this study methanol to oil ratio was varied from 12:1 to 6:1. Experiment was fixed at 65 degree Celsius, 5 wt % of oil catalyst and 500 rpm. The sampleswere cooled down to -20 degree Celsius.

3.4.4 Study on Weight Percentage of Catalyst

Experiment was fixed at 65 degree Celsius, 12:1 methanol to oil ratio and 500 rpm. The catalyst loading weight was varied 1.5 wt% to 6 wt%. The sampleswere cooled down to -20 degree Celsius.

3.5 Sample Analysis using Gas Chromatography

The transesterification reaction process will be producing 4 majors FAMEs. Each type of Fatty Acid Methyl Ester (FAME) has its own retention time. Therefore, in order to identify the amount of FAME in the sample, pure standard was prepared in various concentrationand used to generate a calibration curve. The calibration curve is then used to identify the concentration of sample. Pure standards were Methyl palmitate, Methyl Oleate, Methyl Sterate and Methyl Linoleate. GC-FID (Model HP6890) equipped with HP-INNOWAX, (30m, 0.25 mm, 0.25 micrometer)used as analytical equipment. In the equipment, gas Helium in 75 cm/s was used as carrier gas in split ratio 20:1. Oven was operated under 150^0C (1min), to 230 (2.9 ^{0}C/min) and 230^0C (1min). Example of GC analysis result is in Appendix B. Detailed calculations and formulas are presented in Appendix C.

In this study the FAME was calculated using yield %. As in Equation 3.1

$$\text{Yield \%} = \frac{mass\ of\ FAME\ obtained\ \ from\ GC\ with\ help\ of\ standard\ \ curve}{Theoretical\ \ mass\ of\ FAME} \times 100\% \quad \text{(Eq. 3.1)}$$

Figure 3.9 Gas Chromatography instrument

3.5.1 Standard preparation

The stock standard in each 25 mg was weighed out the appropriate amount of standard required and diluted into 10 ml into a volumetric flask and mix-up with n-hexane for dilution into desired concentration 2500 ppm. Further the stock solution will be used to prepare the standard into 2500, 2000, 1500, 1000 and 500ppm. Accompany with the GC analysis result of different concentration, the calibration curve was generated as Concentration versus area. Where area in GC analysis is represent the concentration of FAMEs injected. The sample purity are more than 99 percents, further purification is not needed. The standard curve were plotted and shown in section of results and discussion.

3.5.2 Sample preparation

Samples taken from each experimentwere diluted and sent to GC for analysis. The samples were diluted into 2500 ppm and mixed well with the n-Hexane.

3.6 Kinetic modeling

The reaction kinetics model is an important in designing the reactor .Below is the pathway of three consecutive formations FAME. These 3 consecutive reaction is simplified into Equation 3.2,, the overall transesterification.

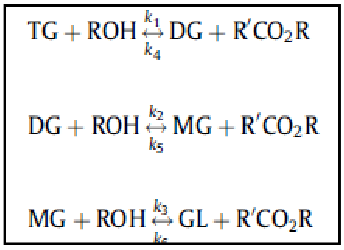


Figure 3.10 Three consecutive reactions of transesterification

$$TG + 3ROH \overset{\text{catalyst}}{\leftrightarrow} 3R'CO_2R + Gl \qquad \text{(Eq. 3.2)}$$

Where, [TG]= Triglyceride, [DG]=Diglyceride, [MG]=Monoglyceride, [GI]=Glycerol, [A]=Alcohol, [R'CO$_2$R]=FAME, k$_n$=reaction constant.

From the previous study from Jain (2010). Proposed that the equation, 3.3 or kinetic model was fitted to the experimental data. The equation was originally modified from pseudo-homogeneous first order. Later, the model was modified by adding the Arrhenius equation instead of kinetic constant, k_1. Using the model or Equation 3.4 shown as below, the k_1 and C was calculated using POLYMATH as shown in section of results and discussion.

$$\ln(\text{rate}) = \ln\left(\frac{dME}{dt}\right) = -k_1 \ln(me) + C \qquad \text{(Eq.3.3)}$$

$$\ln(\text{rate}) = \ln\left(\frac{dME}{dt}\right) = -Ae^{-E/RT} \ln(me) + C \qquad \text{(Eq. 3.4)}$$

$$k_1 = Ae^{-E/RT} \qquad \text{(Eq. 3.5)}$$

3.7 Summary of the procedures

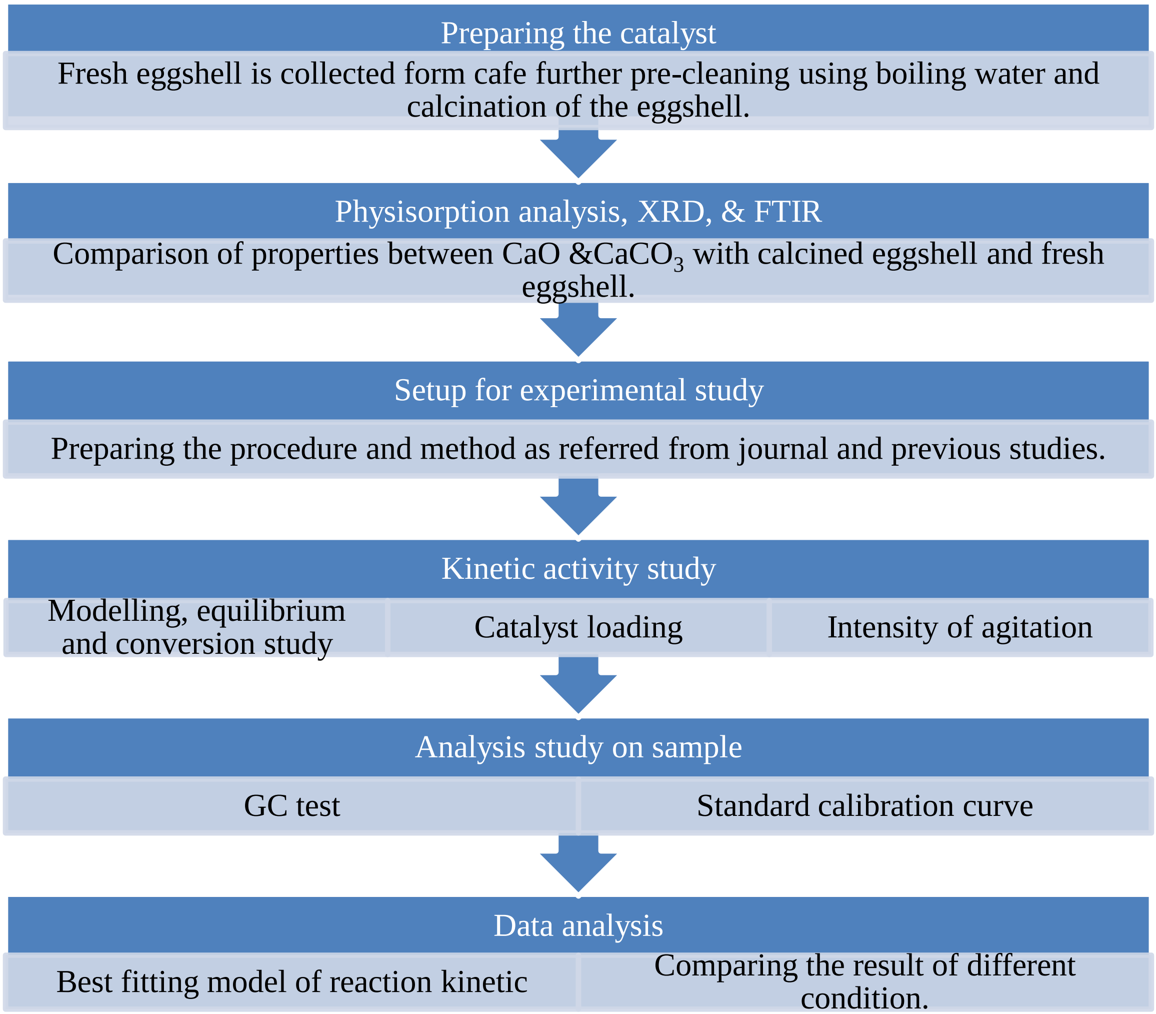


Figure 3.10 Summary of the procedures.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst characterization

Heterogeneous catalysts for transesterification of Refined palm oil (RPO) to fatty acid methyl ester (FAME). CaO catalyst was used in some of the previous studies due to its good activities in transesterification of palm oil, where more than 97.26 % methyl ester yield was obtained (Lichinda and Sudsakorn, 2006). Besides it's good activity, CaO can be easily converted from natural lime stone., natural waste, such as mollusk (Boro,2012). The conversion of waste to CaO could be enhanced by calcining the mollusk. The calcining process can be done under high temperature in range 800 to 1000 ^{0}C. In this study, chicken eggshell was converted as catalyst. Heeggshell was calcined at 900 degree Celsius under air. The eggshell was analyzed using FTIR, XRD and Physisorption analysis. The characteristics will be discussed in following subsection.

4.1.1 X-ray diffraction(XRD)

XRD pattern from powdered calcined eggshell, CaO(99% purity), and $CaCO_3$ and fresh eggshell are shown in Figure 4.1.

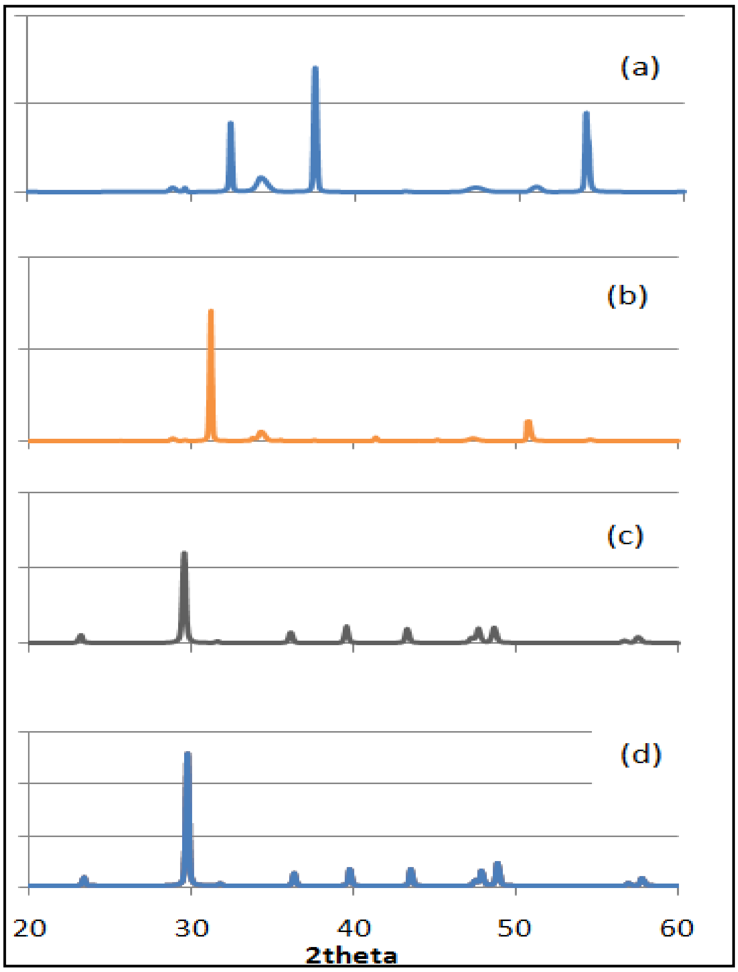


Figure 4.1 X-ray diffraction patterns for calcined eggshell (a), CaO(99% purity) (b), and $CaCO_3$(c) and fresh eggshell (d)

The results shown in the Figure 4.1 (a) & (b) have identical peak at 32.395^0, 34.272^0, 37.59 ^{0}, and 54.53^0.

On the other hand, the result shown in Figure 4.1 (c) & (d) have identical peak at *29.563^0, 36.086^0, 39.564^0, 43.288^0, 47.678^0, and 48.661^0 of 2theta.This proven that the fresh eggshell contains of Calcium carbonate in majority. In addition, as the intensity of the Calcium Carbonate is much higher than the fresh eggshell. This might due the concentration of the Calcium Carbonate is much higher than the concentration of calcium carbonate in sample of fresh eggshell (Connolly, 2012). Identification of each of samples is shown in Appendix B.

The diffractogram is identical with one reported from Engin, (2006) shows the same peak appearance as mentioned above except the commercial Calcium oxide. The results from Engin (2011) shown in Figure 4.2. The identical peaks are marked with 5 points star and 4 points star. Nevertheless, the diffractogram of commercial Calcium oxide was analysed as not much identical to the calcined eggshell. This might due to the irregular shape of the Calcium Oxide as it has not been activated under high temperature. Calcium oxide was not annealed until 900 degree Celsius and different crystal form of Calcium Oxide has been produced.

Figure 4.2 compared the X-ray diffraction pattern of Calcined Eggshell and Fresh Eggshell. The 5-points stars are $CaCO_3$ phase and 4-points stars are CaO phase. The figure shows that different of two samples before and after the calcinations process at 900 ^{0}C. The reduction in the intensity of Calcium Carbonate in the Calcined Eggshell has proven the conversion of $CaCO_3$ to CaO.

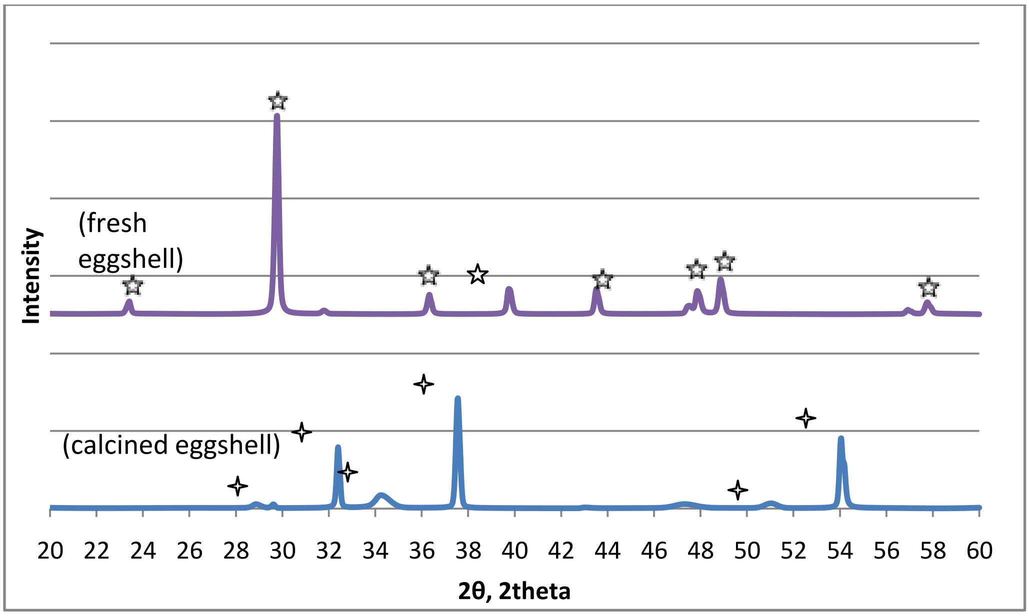


Figure 4.2 Comparison of XRD patterns for fresh eggshell and Calcined eggshell.

4.1.2 Fourier transform infrared (FTIR)

Through the FTIR analysis the appearance of carbonate ions and oxide ions in the samples can be identified. Besides identify, the analysis also can conclude the success of calcinations process through observing the changes of the chemical compound in the samples.

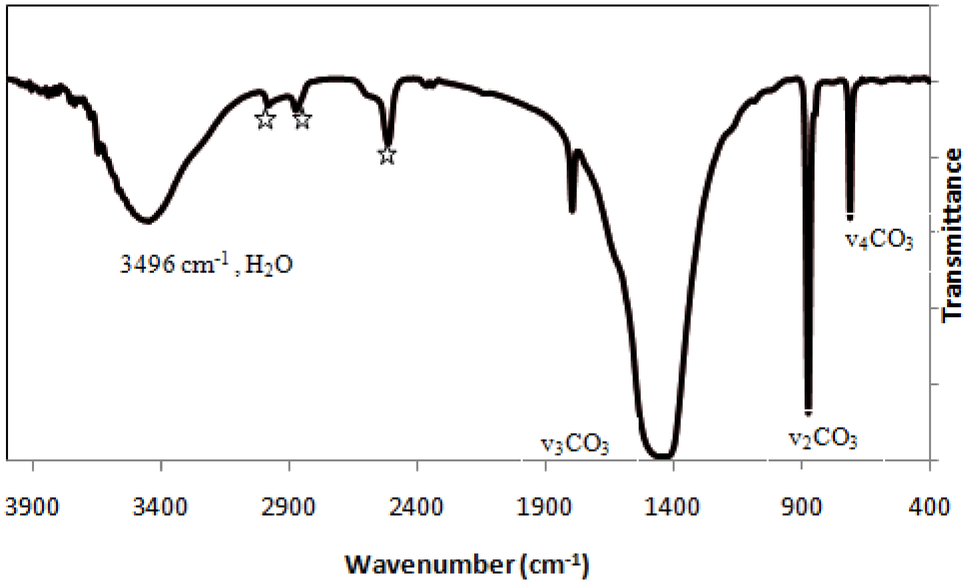


Figure 4.3 Infrared spectra of Calcium Carbonate

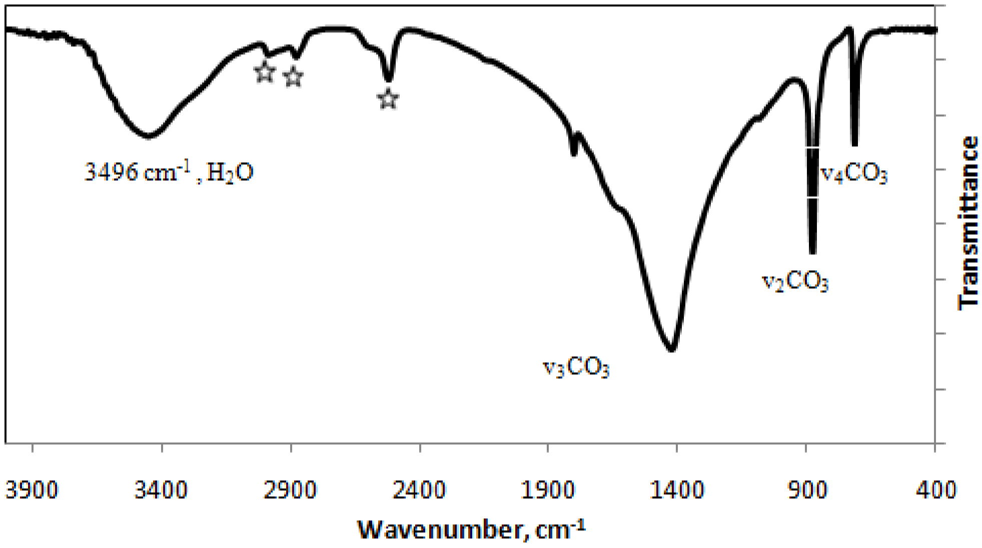


Figure 4.4 Infrared spectra of Fresh Eggshell

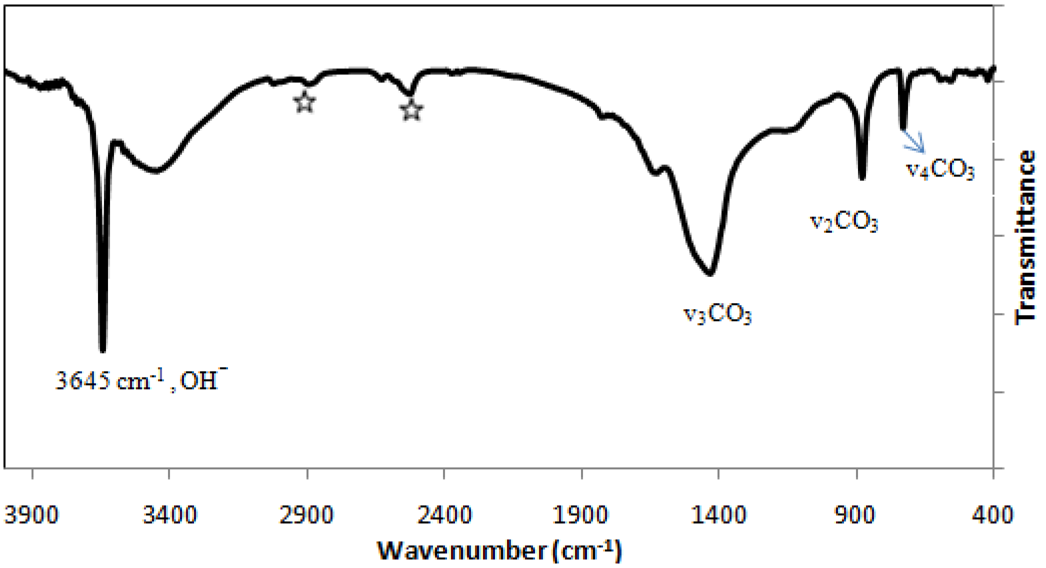


Figure 4.5 Infrared spectra of Calcium Oxide

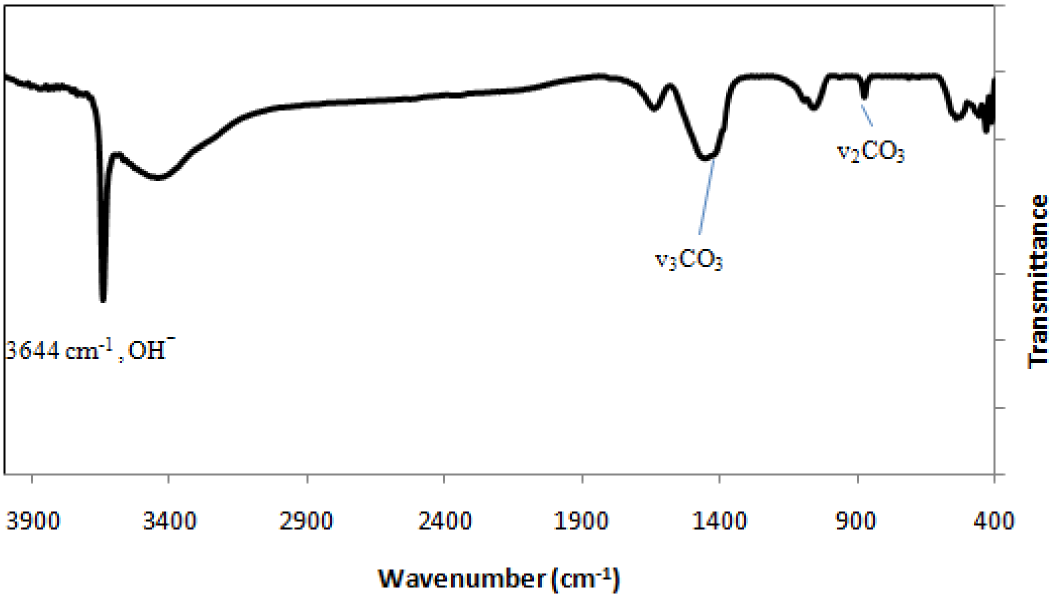


Figure 4.6 Infrared spectra of Calcined Eggshell

FTIR spectra of 4 samples, Calcium Carbonate, Fresh Eggshell, Calcium Oxide and Calcined eggshell are shown in Figure 4.6, 4.7, 4.8 and 4.9 respectively. All spectrums are taken in room temperature. The entire spectrums have adsorption bands at 1480 cm^{-1}, 876 cm^{-1}, and 731 cm^{-1}, named v_3CO_3, v_2CO_3, v_4CO_3. These 3 bands are represent the vibration of CO_3^{2-} molecules, as v_3 is asymmetric stretch, v_2 is out-of plane bend and v_4 is in-plane bend vibration modes.(LeGaros, 1970). For the Calcium Carbonate has highest absorption band for these 3 vibration bands. For Fresh Eggshell has identical background with sample of Calcium Carbonate. Besides that, both also have the same wavenumber at 3496 cm^{-1}. This wavenumber indicate that the sample is stretching with the water molecules in the atmosphere and cause vibration. 4 of these adsorption band decreases as the calcinations process applied.

As the Fresh Eggshell underwent to annealing process, the new absorption band appear at 3644 cm^{-1} for the Calcined eggshell spectra.. This absorption band is representing the vibration of OH^{-1} hydroxide ions. This is because the CaO is hygroscopic and interacted with the present of water and form ion of OH^{-1} and cause a very intense band. This band doesn't appear in carbonate samples. Calcium oxide sample also has the adsorption band at 3644 cm^{-1}.

5 points stars in the graph representing the organic matter in the samples. All spectrums contain the organic matter except Calcined eggshell. Where Calcined eggshell does not contain organic matter due to the annealing process had burned the organic material under high temperature. On the other hand, the Fresh Eggshell has highest adsorption intensity at the 5 points star (organic matter) amongst the samples.

4.1.3 Physisorption analysis.

The Physisorption analysis using BET method was done on two samples, which were Calcined eggshell and Calcium Oxide. Table 4.1 shows the result of physisorption analysis. From the analysis, Calcined eggshell has 5.745m^2/g of B.E.T surface area and pore-size of 6.58 nm. This shown the surface area of the catalyst used in this study is low. The improvement in surface area can be done such as hydration method as reported from Yoosuk (2010) using Calcium oxide react with water followed by calcinations process to regenerate a larger surface of catalyst. The catalyst of Calcium oxide formed after the hydration process increased double of its surface area as well as the basicity. Whereas the Calcium oxide has 5.4596 m^2/g B.E.T surface area. Compare with these two results, the surface area of Calcined Eggshell is slightly bigger than the Calcium oxide. The might be the organic substance in the eggshell was burned off and left the porous area and increased its surface area.

As reported from Birla, (2012) mesopores class of catalyst improved the diffusion rate of triglycerides molecule or methanol. In other word, rate of diffusion triglycerides is one of the important factors manipulated by the surface area of the catalyst.

Besides B.E.T. area analysis the analysis also involved the pore size analysis using *Barrett, Joyner, Halenda* (B.J.H.) method. The results were shown in the Table 4.1.

Table 4.1 B.E.T. surface area and pore size

Samples	B.E.T. surface area, m^2/g	Pore size, nm (B.J.H.)
Calcium Oxide	5.459	6.58
Calcined eggshell	5.745	10.986

From the Figure 4.7, Calcined Eggshell has the isotherms that of with the hysteresis after 0.95 of P/P_0. Thermo Surfer, (2011) reported that appearance of hysteresis beyond 0.95 or near to saturation region shows the sample had to be the macropores and porous size diameter shall more than 50 nm (Vannice, 2005). In order words, the hysteresis is to indicate the type of porosity of the sample. As the initial stage, the adsorption was at the stage of forming the multilayer; this was due to the formation of first layer or monolayer on top of the Calcined Eggshell was so rapid because of limited surface area available for the adsorption. The slope is flat because of the attraction between gasses is weaker and rate of adsorption of gases is relatively slow. Later followed by sharp inclined slope after the flatter slope, this is because of the capillary condensation happened and saturation of nitrogen gas in the capillary (Bel-Japan, 2012). However, as observe the hysteresis also appeared along the range of 0.33 to 0.95 of P/P_0 which is in the range of mesopores. This is same as the result from Table 4.1, pore side of Calcined eggshell is 10.986 nm (mesopores). Poljanjek, (2011) reported that the macropore is better for transesterification due to the large molecule of triglyceride is found difficult in mass transfer. Refer to Figure 4.8 and Table 4.1, the Calcium Oxide has smaller pore size if compared with the Calcined eggshell. From the isotherm of Calcium Oxide, the hysteresis appears before and after the 0.95 of $P/P_{0.}$ However, the larger gap of hysteresis is before the 0.95 value of P/P_0, which in the region of mesopores. The pore side of Calcium Oxide in Table 4.1 is match to the result in from the isotherm.

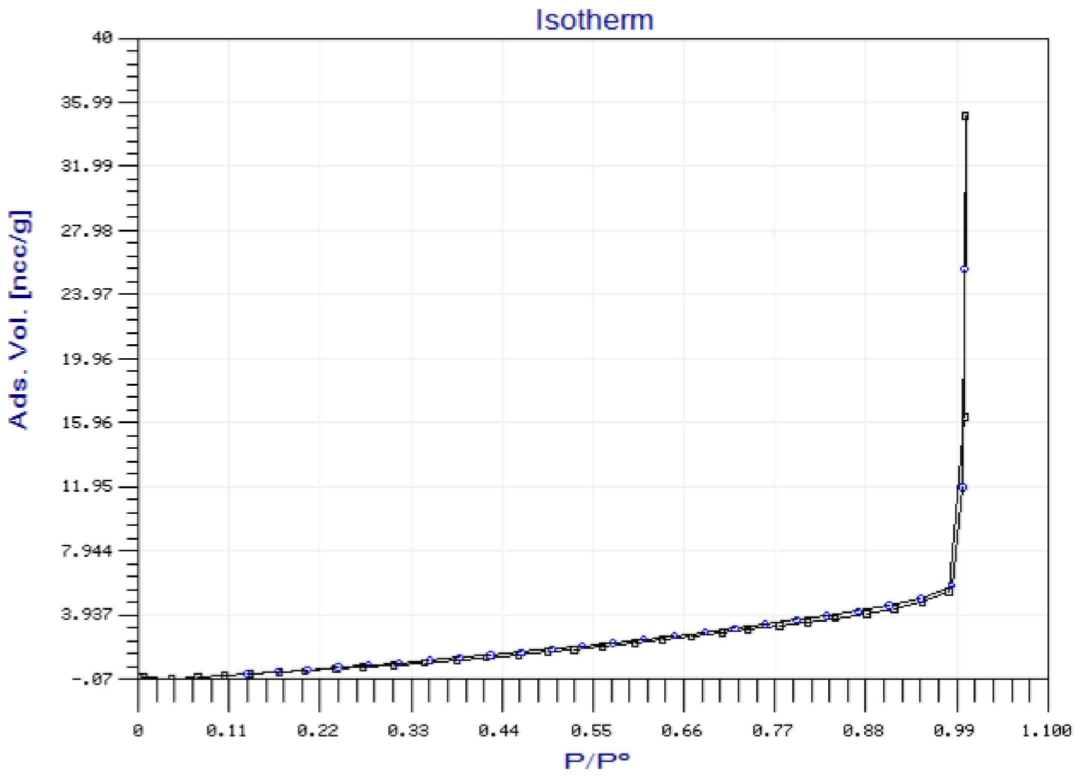


Figure 4.7 Calcined Eggshell Isotherm

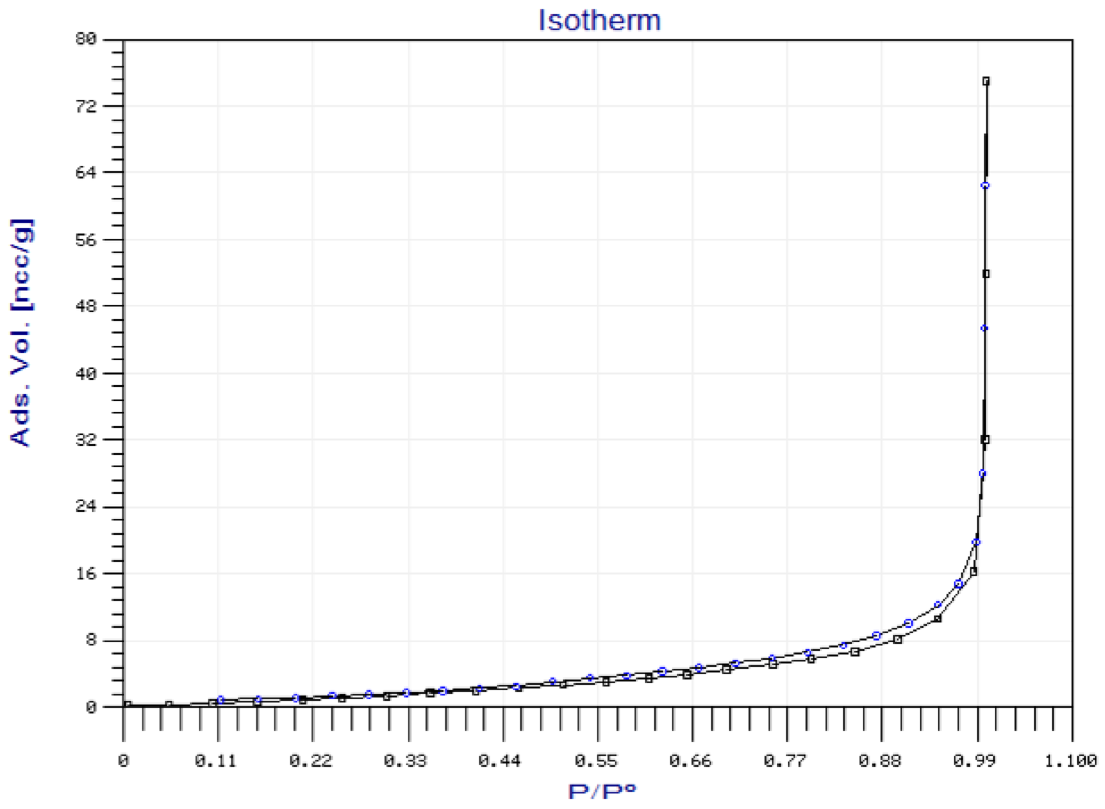


Figure 4.8 Calcium Oxide Isotherms

4.1.4. Catalyst size distribution

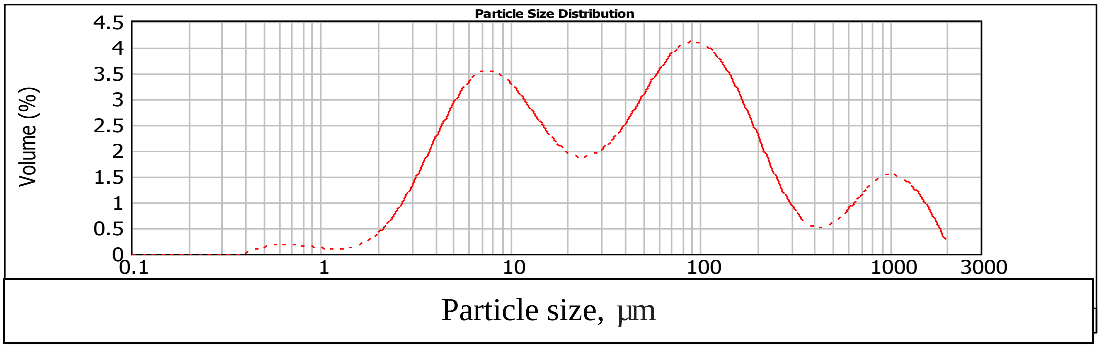


Figure 4.9 Particle Size Distributions of Calcined eggshell

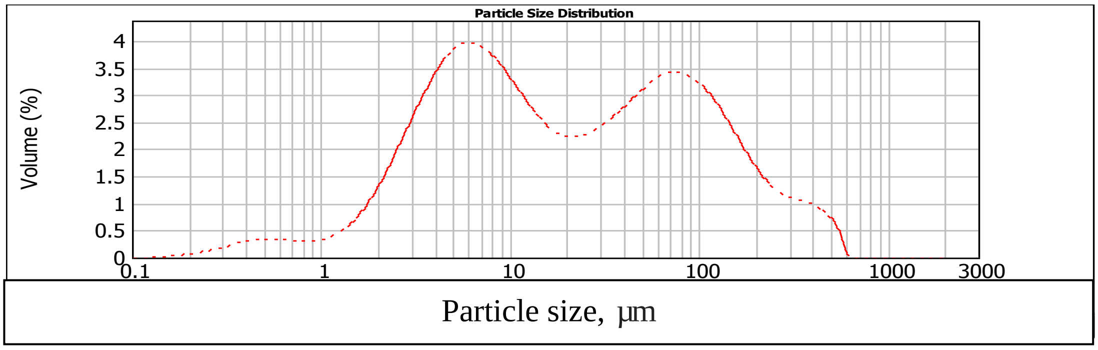


Figure 4.10 Particle Size Distributions of Calcium Oxide

The powdered catalyst (Calcined eggshell) was analysed using Mastersizer 2000. The size of the catalyst from the analysis is in the ranged of 0.4 µm to 2000 µm. From the Figure 4.9 has the highest number of distribution at 90 µm followed two smaller peaks at 7.5 µm and 1000 µm. During the process of filtration, the particle can fully be filtered out and left a small portion of catalyst left in each sample taken. As the result, samples taken would not affected by the catalyst remaining (very little if left) and safe for testing of the biodiesel. The commercial Calcium Oxide is ranged from 0.15 µm to 600 µm. Calcium oxide is produced using different of material and method that has different distribution from Calcined eggshell. However, results reported by Tangboriboon (2012) relatively smaller than the result obtained in this study. The results from the paper are 2.18, 9.14, 30.69 and 15 µm. This might due to the different method of crushing and obtain much finer powder for other purpose, such as using for Latex compound. In other paper from Verziu, (2011) reported that the calcium oxide particle size distribution is much identical with the analysis. Where the paper reported the size distribution of untreated Calcium oxide is 9 µm also.

4.2 Transesterification reaction

4.2.1 GC Analysis

By using four different of FAMEs, retention time of each molecular is identified. During the GC analysis some noise in the background are appeared but their present are ignored since insignificant. Each 4 FAMEs standards are generated five point's calibration series. Table 4.2 shows the retention of each sample.

Table 4.2 Different of methyl ester with retention time.

FAMEs	Retention time
Methyl Palmitate	16.771-16.878
Methyl Stearate	19.164-19.276
Methyl Oleate	19.394-19.476
Methyl Linoleate	19.920-20.010

4.2.2 Standard Calibration Curve of the Methyl Ester.

Four calibration curves were plotted for each of standard. The graphs plotted were linear and all were ranged from 500 ppm to 2500 ppm.

4.2.2.1 Methyl Palmitate Standard Preparation

Table 4.3 Methyl Palmitate Peak Area data

Concentration, ppm or mg/L	Peak area
500	1602.754
1000	2618.771
1500	5252.523
2000	6987.820
2500	8258.097

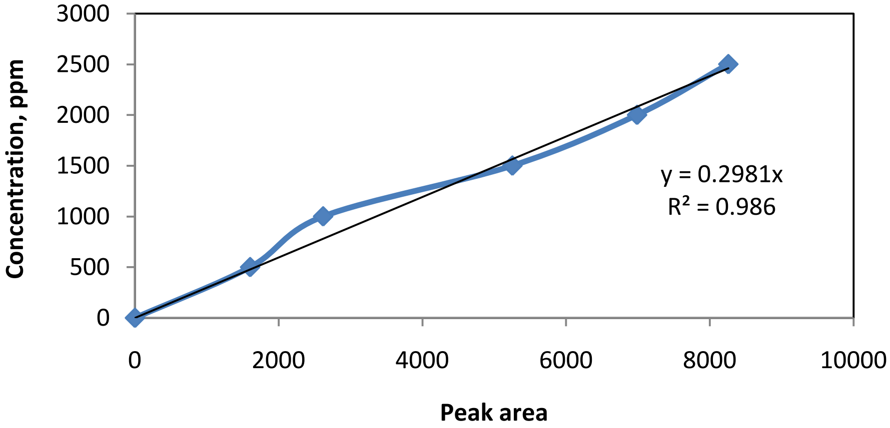


Figure 4.11 Methyl Palmitate calibration curve and equation

4.2.2.2 Methyl Stearate Standard Preparation

Table 4.4 Methyl Stearate Peak Area data

Concentration, ppm or mg/L	Peak area
500	1524.181
1000	2811.533
1500	4367.271
2000	6193.878
2500	7660.397

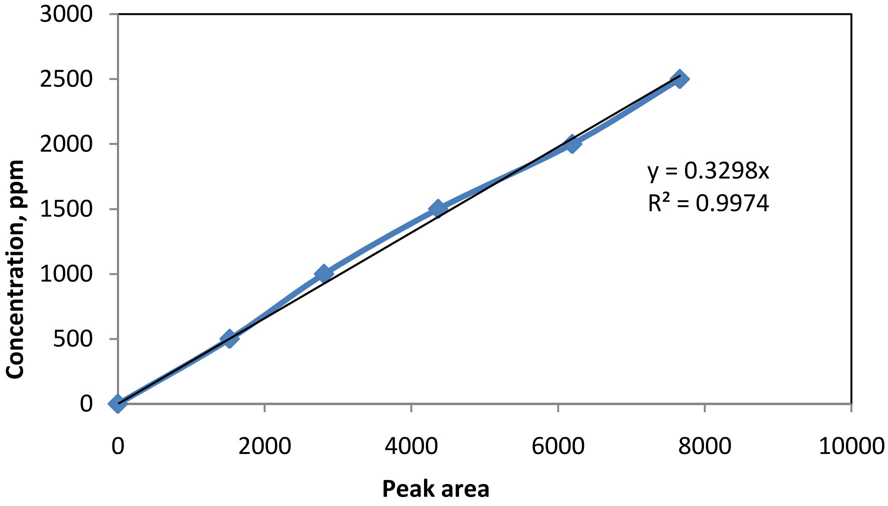


Figure 4.12 Methyl Stearate calibration curve and equation

4.2.2.3 Methyl Oleate Standard Preparation

Table 4.5 Methyl Oleate Peak Area data

Concentration, ppm or mg/L	Peak area
500	1943.928
1000	2224.774
1500	5395.711
2000	6662.387
2500	6857.810

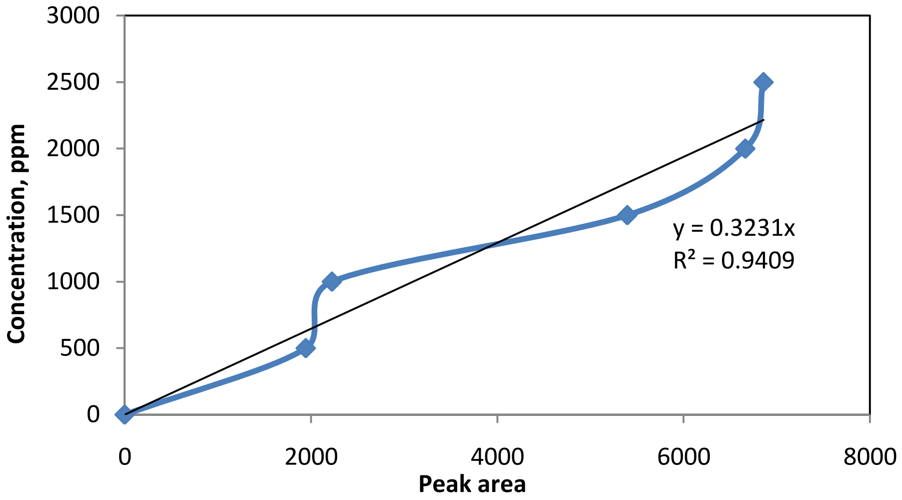


Figure 4.13 Methyl Oleate calibration curve and equation

4.2.2.4 Methyl Linoleate Standard Preparation

Table 4.6 Methyl Linoleate Peak Area data

Concentration, ppm or mg/L	Peak area
500	1804.288
1000	3283.551
1500	4983.063
2000	6486.321
2500	8113.545

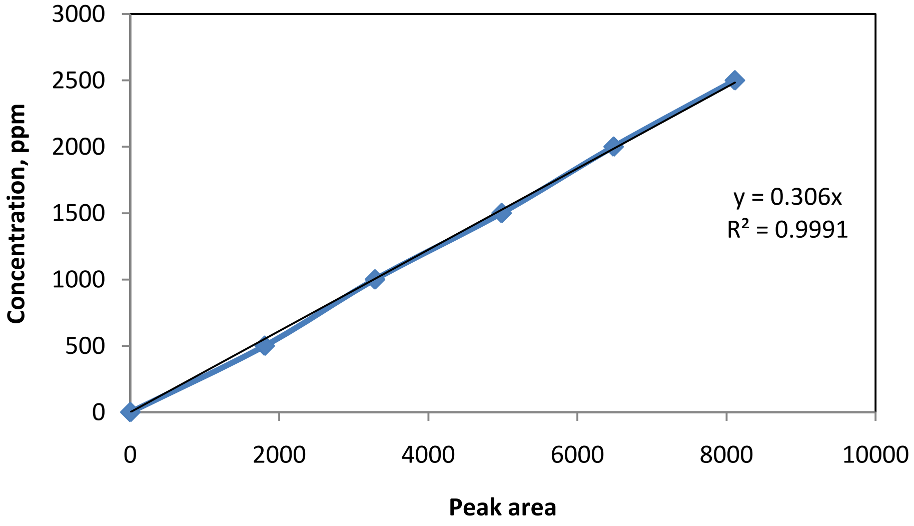


Figure 4.14 Methyl Linoleate calibration curve and equation.

4.3 Synthesis of biodiesel

From the previous part at Methodology, transesterification reactions at different parameters were carried out to analyse the yield percent of FAMEs at different condition.

4.3.1 Effect of variation of temperature

During the study of the effect of temperature, the molar to oil ratio was fixed at 12 to 1 and catalyst amount was fixed at 1.5 wt%. Samples were taken for 3.5 hours. From Figure 4.15, the increases of temperature will increase the yield %. Increasing temperature of a reaction process increases the kinetic energy content of the particles. Higher kinetic energy will tend to increase the number of collision in between particles. The higher energy means reactants have higher energy to overcome the activitation energy, which lead more successful collision and increase the reaction rate.

However, higher temperature will denature the triglyceride (major content in vegetable oil and animal fat) as stated by Kulkarni,(2006). Furthermore, the present of unsaturated fatty acid at high temperature will lead to form the undesired polymetric products. Above phenomenon, denaturation is assumed not happened since experiments were carried out at relatively low temperature.

In this study, the yield is lower if compared with the previous research using waste material that has high contains of calcium carbonate such in thparer of Boro (2012). This may due to few reasons,

i. The methanol and glycerol are actually partially soluble with FAME in the mixture (Doungsri, 2011). When samples been taken from oil after the samples formed two unmixable layers, small portion of FAME containing in the glycerol losses. This would affect the result of yield of FAME.

ii. Methanol in this study was removed that contains FAME.

Table 4.7 Yield at different of temperature.

Temperature, ^{0}C	**Yield, %**
65	9.920
60	2.873
55	2.733
50	0.555
45	0.172

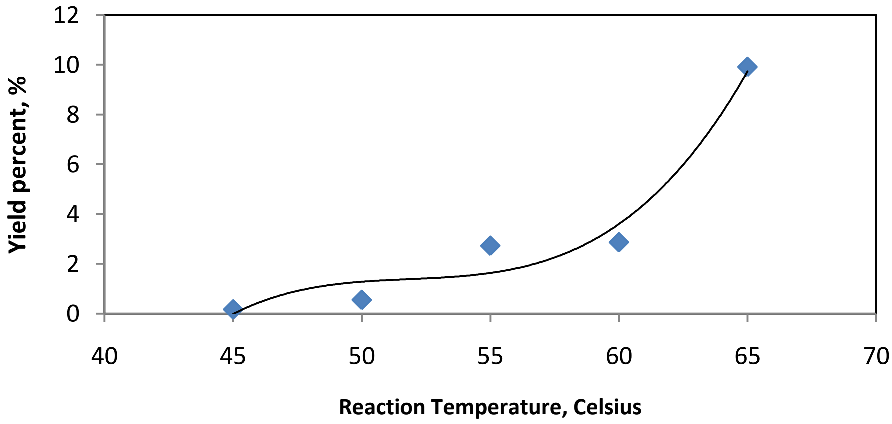


Figure 4.15 Influence of reaction temperature on yield %.

4.3.2 Effect of Catalyst Weight Percent Loading

The effect of the amount catalyst used was carried out at fixed temperature, molar ratio of methanol to oil, and agitation intensity respectively at 65 ^{0}C, 12:1 and 500 rpm. The different weight of catalyst loading varied at 1.5, 3.0 and 6.0 wt%. From the graph plotted in Figure 4.16, the predicted maximum yield was 82.82 % at catalyst loading 3.938 wt%. For the initial state, increases of the catalyst loading weight will increased the yield percent. This showed that more catalyst will provide higher surface for reaction and increase the rate of reaction. Nevertheless, after the 3.938 weight percent of catalyst, the yield percent started to get lower. This is due to the viscous of the mixture is increasing, make separation and mixing become problems (Zhang 2006). In order to avoid the lower yield and wasting the catalyst, the optimum catalyst amount should be determined.

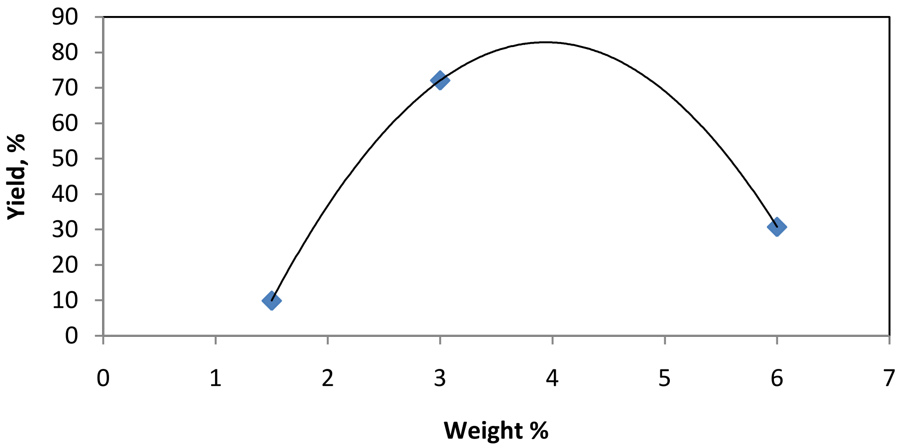


Figure 4.16 Influence of catalyst weight loading on yield %.

4.3.3 Effect of Agitation Intensity

In this study was carried out at fixed temperature, molar ratio of methanol to oil, and weight % of catalyst respectively at 65 ^{0}C, 12:1 and 1.5 wt%. Figure 4.17 showed the yields % increases as agitation intensity increases. Reason was the agitation increasing the amount of collisions in between molecules make with one another, therefore speeding up the overall reaction rate. Besides that, methanol and palm oil were immiscible. In order to reduce the effect of mass transfer limitation, it is needed to increase the agitation speed until the mixture has to be mixed in homogeneous stage. This is allowed the thin layer of absorbed methanol on the catalyst would able to react with the triglyceride.

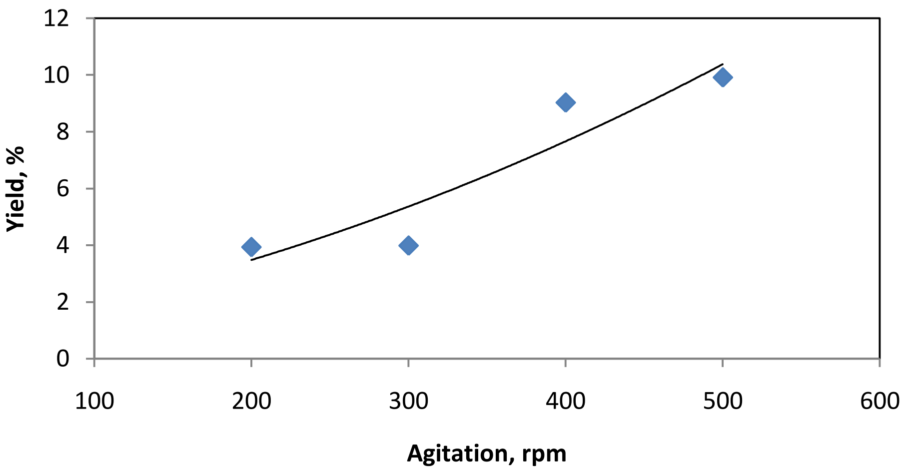


Figure 4.17 Influence of Agitation Intensity on yield %.

4.3.4 Effect of Molar Ratio

Temperature, agitation intensity, and weight % of catalyst were fixed respectively at 65 ^{0}C, 12:1 and 1.5 wt%. Figure 4.18 showed the yields % increases as Molar ratio increases. Methanol was varied from 12:1, 9:1 and 6:1 molar ratio. Methanol as an important element in this reaction, its present was significant changes the rate of reaction. From Figure 4.18, as increasing the molar ratio of methanol to oil, the yield% percent increases. As stated earlier, the transesterification reaction is reversible. According to Le Chatelier's, the equilibrium system will change to a newly state of equilibrium if an external factor affecting or new element tend to changes the system. Therefore, the higher amount of methanol forced the reaction forward and produced more FAME.

However, Zhang (2010) reviewed that the Methanol used excessively would dilute the concentration of oil and cause the oil molecule difficult to dissolve through the catalyst.

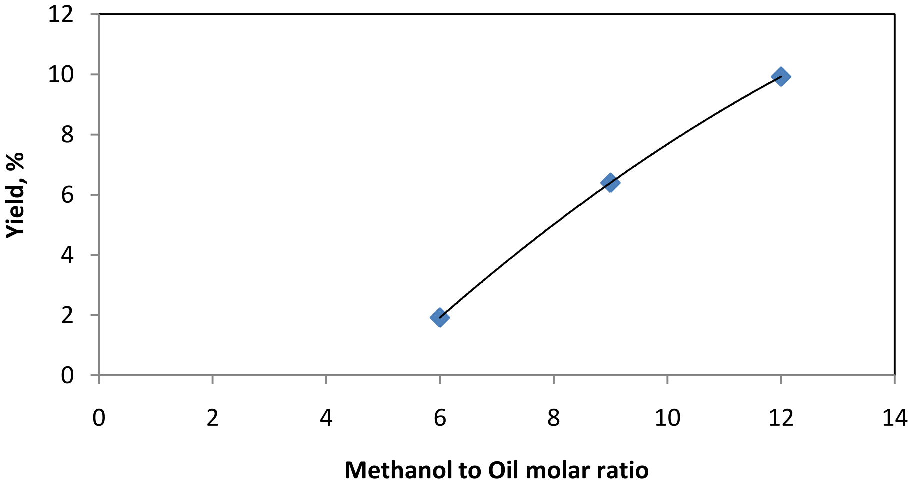


Figure 4.18 Influence of molar ratio on yield %.

4.4 Kinetics of transesterification

For last two decades, utilization of biodiesel is still increasing. This is true especially at Europe country. However, chemical kinetics of transesterification catalyzed by Calcined eggshell remains doubt and uncertainty. Kinetics in this study was to describe the rate of chemical reaction. In the real situation the formation of FAMEs are for 3 consecutive reactions. The three consecutive reactions as shown in Figure 2.1. However, in this overall reaction was assumed to be a single reaction.

The reaction kinetics and model were developed based on the experimental data obtained at three different temperatures which are 55, 60 and 65 degree Celsius. Figure 4.19 showed the relation between Yield percent vs. Reaction time. The graph of each different temperature showed the yield percent gradually increased as the time passed.

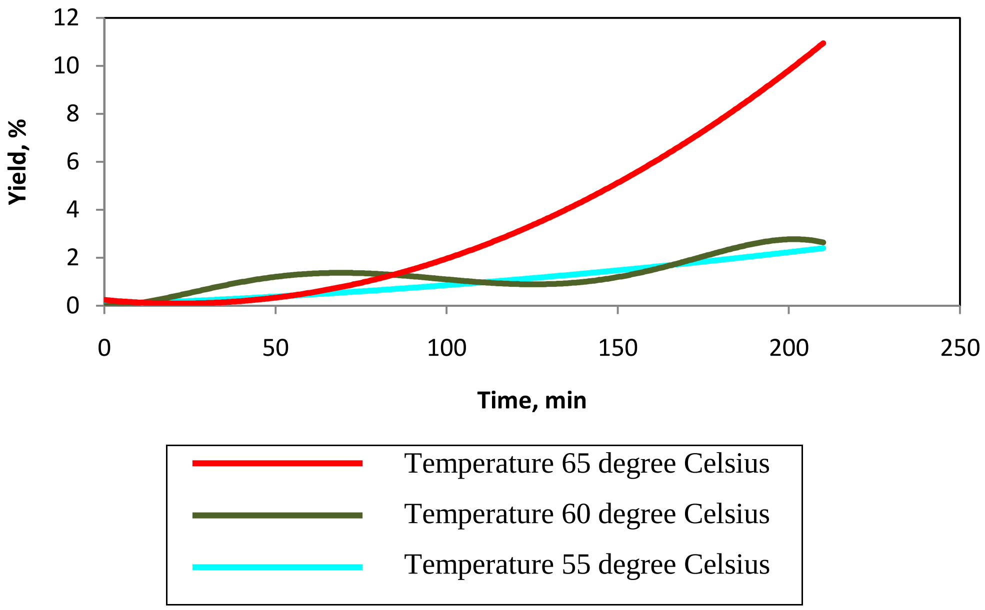


Figure 4.19 Effect of temperature with condition: 12:1 (Methanol to oil molar ratio), catalyst wt% (1.5 wt %), reaction time 3.5 hours.

The kinetics model used was pseudo-first order, as proposed by Jain (2010). In her paper, the reaction is assumed first order and the model of rate to concentration of FAME was such that, where $\frac{dME}{dt}$ is the rate of formation of FAME.

$$\ln(\text{rate}) = \ln\left(\frac{dME}{dt}\right) = -k_1 \ln(me) + C \qquad \text{(Eq. 4.1)}$$

Since, $k_1=Ae^{-E/RT}$ ` (Eq. 4.2)

After combination of Arrhenius' equation and equation of 4.1, obtained,

$$\ln(\text{rate}) = \ln\left(\frac{dME}{dt}\right) = -Ae^{-E/RT} \ln(me) + C \qquad \text{(Eq. 4.3)}$$

Polynomial equation for each different temperature are found using POLYMATH and further differential of the polynomial equation to obtained the rate of formation of FAME at different temperature. The calculated concentration FAME and rate of formation FAME are in the POLYMATH result spreadsheet. In each of different temperature, constant value k_1 are calculated and found the activitation energy of the reaction as 65.77 Kj/mol and A is 1.02 X 10^{10} min^{-1}.

The results of the each temperature and its k_1 and C value were in the table below,

Table 4.8 Values of constant k_1, C and R^2 at different of Temperature.

Temperature, ^{0}C	k_1	C	R^2
65	0.698	-3.23	0.91
60	0.491	-3.23	0.91
55	0.342	-3.23	0.91

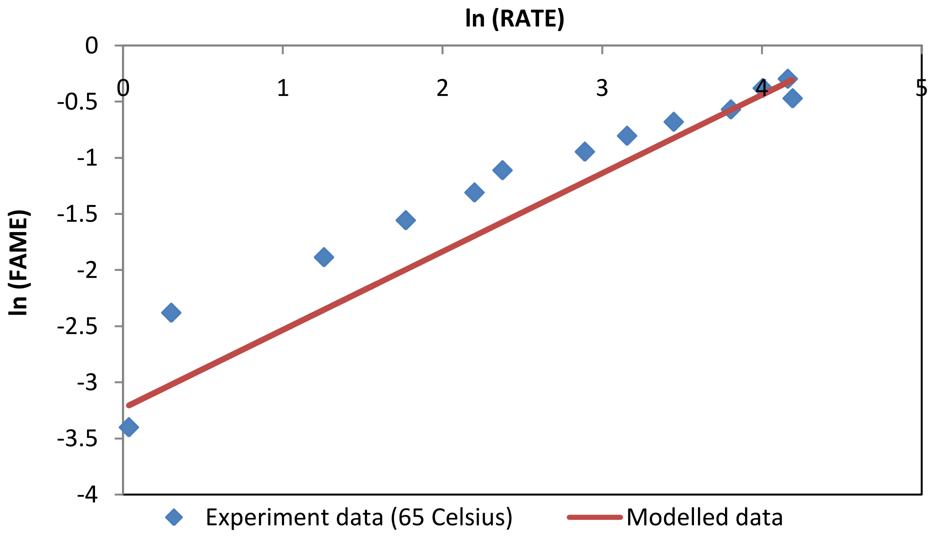


Figure 4.20 Plot of FAME versus reaction rate on logarithmic graph (65 ^{0}C)

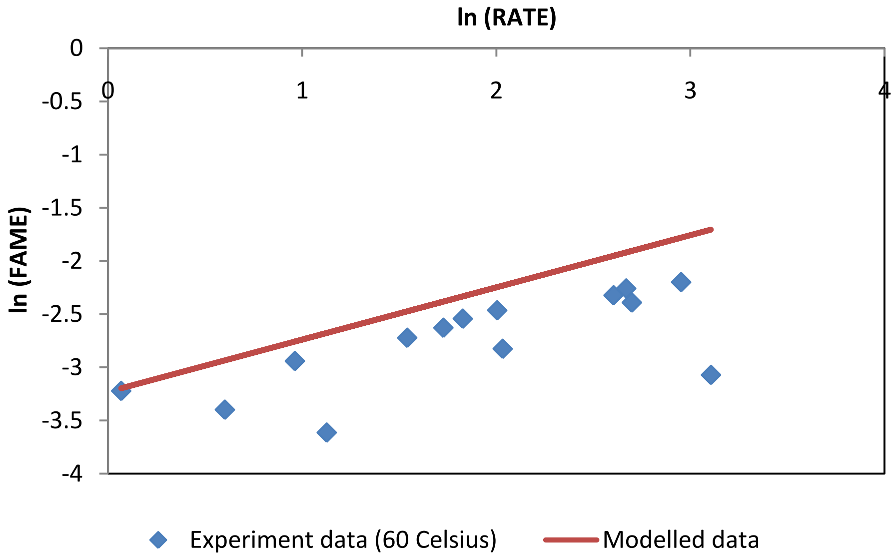


Figure 4.21 Plot of FAME versus reaction rate yield on logarithmic graph (60 ^{0}C)

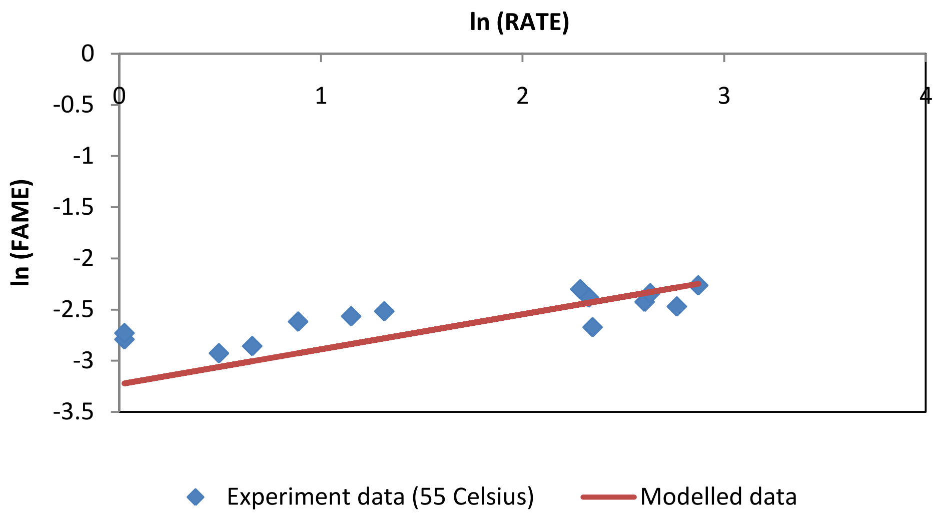


Figure 4.22 Plot of FAME versus reaction rate on logarithmic graph (55 ^{0}C)

Based on the result above, the model obtained 0.91 of R^{2}value for all the temperature. However, the accuracy of this model is small. Darnoko, (2000) using the model of pseudo-homo 2nd order respective to formation of FAME. The model has obtained highest R^2 value of 0.9974. Birla (2012) using model of pseudo-first order kinetic by ignore the intermediate product, (i.e. diglyceride and monoglyceride.) and based on concentration of Triglyceride and rate of consumption of Triglyceride has obtained 0.98 of R^2 value.

$$\ln K = \ln A - \frac{E}{R}\frac{1}{T} \qquad \text{(Eq. 4.4)}$$

Where, A, E, R & T are reactivlely,Pre-exponential factor or frequency factor, Activitation energy, Gas constant=8.314 J/mol.K, T=Absolute temperature, K

Rearranged, the Arrhenius equation for this study was,

$$k = 1.072 \text{ X } 10^{10} \exp\left(-\frac{65770}{T}\right)$$

The activation energy calculated is at normal range. The typical energy activitation E_a is in the range of 33.6-84 KJ/mol (Freedman, 1986). However the activation energy is depending on the reactant used as reported by Zhang. (2010), where the activitation energy for his study was 65.77 Kj/mol, Zhang used the DMC (Dimethyl Carbonate) instead of methanol.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Calcined eggshell contains of Calcium Oxide. Calcium Oxide is basic and good activity in transesterification process as discussed in the literature review. In this study, 3 methods of analysis such as FTIR, physical adsorption analysis and XRD were conducted. It is found out that the Calcined eggshell is identical to the physical properties of Calcium Oxide.

Throughout this study, transesterification catalysed by Calcined Eggshell in 3.5 hours were influenced by,

a. Reaction temperature
b. Molar ratio of methanol to oil
c. Amount of catalyst or weight percent of catalyst.
d. Agitation speed/ intensity.

It was observed that increase in operating temperature will increases the yield % of FAME. However, the highest operating temperature was only 65 degree Celsius. This due to the methanol has boiling point of 65 ^{0}C and will vaporise at atmospheric pressure. Higher temperature will favor to produce more FAME. Besides temperature, the catalyst weight percent was also influenced the most in this study. Higher the weight percent of catalyst contribute more surface area and allowed the equilibrium reached earlier. Negative effect of too much catalyst will increase the viscosity in the mixture and reduce yield of FAME. Followed by the molar ratio of methanol to oil will increase the yield percent. The results behave like the Le' Chatelier's principle. On the other hand, the agitation intensity or agitation speed will rise up the yield percent as well. The agitation plays important role in minus the mass transfer limitation.

In kinetic study, the model was used is Pseudo-homogeneous model as below,

$$\ln(\text{rate}) = \ln\left(\frac{dME}{dt}\right) = -Ae^{-E/RT}\ln(me) + C$$

The accuracy or R^2 value is 0.91. The model developed is fitted to the experimental data.

The derived equation of Arrhenius equation is shown below,the equation is developed through the kinetic study in chapter 4.

$$k = 1.07 \text{ X } 10^{10} \exp\left(-\frac{65770}{T}\right)$$

5.2 Recommendation

Based on the previous study, some of the recommendation can be done to avoid the mistakes and getting good data.

i. Methanol and glycerol taken from sample is partially containing the FAME. The studies of phase equilibrium should be investigated before start the analysis of biodiesel.

ii. Methanol of each sample should be dried at advanced and left the FAME before further analysis.

iii. The analysis of by-products contains such as glycerol, triglyceride, diglyceride and monoglyceride should be calculated in order to get better result in kinetics study.

iv. The process can be analysed using continues type of reactor that commonly used in the industry.

v. For GC test, each pre-run will blank before inject the samples. This is because the column was contaminated by previous samples. Also inject as internal standard in each sample to analyse the accuracy of the analysis.

vi. Futher investigate can be done in the optimization in the yield of biodiesel.

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Appendix A

Reactant calculation for URP 1&2

If 12:1 methanol to oil optimum condition (molar ratio) in 500 ml OR $cm^3 = 5 \times 10^{-4}$ m^3

If 450 ml ,Molar mass/ density=volume per mole

Reactant	Amount
Palm oil	888.17 g/mol / 0.880 g/cm^3 = 1009.284 cm^3/mol
Methanol	34.02 g/mol / 0.7918 g/cm^3 =42.96 cm^3/mol

n (42.96 cm^3/mol x 12 mol + 1009.284 cm^3/mol x 1mol)=450 cm^3

n= 0.295 mol (should be used)

Example: 0.295 mol of oil + 3.541 mol of methanol in the beaker.

For each experiment

Reactant	Amount
Palm oil	0.295 mol x 888.17 g/mol =262.01g (277.46 ml)
Methanol	3.541 mol x 32.04 g/mol = 113.45 g of methanol (172.54 ml)

Designated experiment

Experiment	Unit parameter	Times
Agitation intensity	50 100, 200,300, and 400 rpm	5
Kinetic study	45, 50, 55, 60 and 65	5
Methanol :oil ratio	12:1, 9:1, 6:1	3
Weight of catalyst study	3wt%, 5 wt% and 6 wt%	3

Estimated experiment with runs plus 4 trials. Total is 20 runs.

Total reactants needed for URP

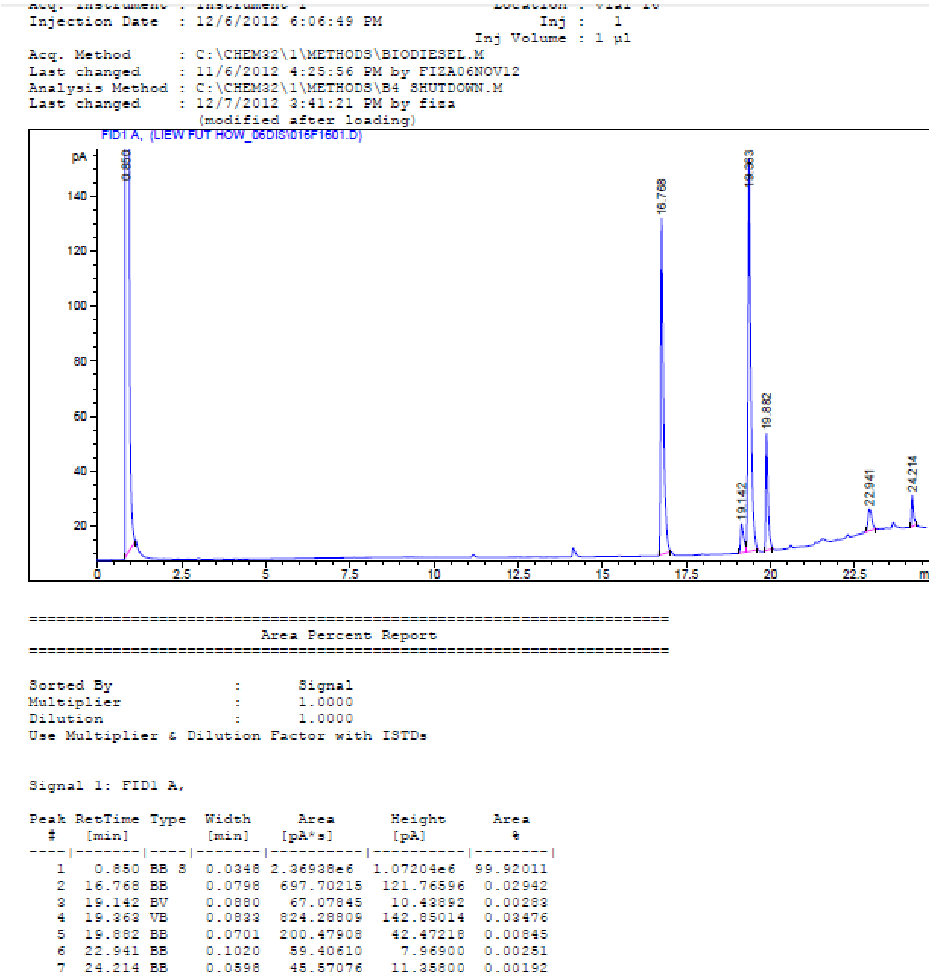
Reactant	Amount
Palm oil	20 x 262.01 of oil =5240.2 g
Methanol	20 x 113.45 g of methanol=2269 g

Catalysts and Calcium Oxide

Materials	Amount
Calcined eggshell	5 weight percents of oil for each reaction =5240.2 x 0.05 =262.01 grams +60 gram x 3 tests (FTIR, XRD, S_{BET}) =323.417grams
Calcium oxide	100 grams
Calcium carbonate	100grams

Appendix B

GC analysis result, XRD &Physisorption test



```
Acq. Instrument : Instrument 1                    Location : Vial 16
Injection Date  : 12/6/2012 6:06:49 PM                 Inj :    1
                                                Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\BIODIESEL.M
Last changed    : 11/6/2012 4:25:56 PM by FIZA06NOV12
Analysis Method : C:\CHEM32\1\METHODS\B4 SHUTDOWN.M
Last changed    : 12/7/2012 3:41:21 PM by fiza
                  (modified after loading)
```

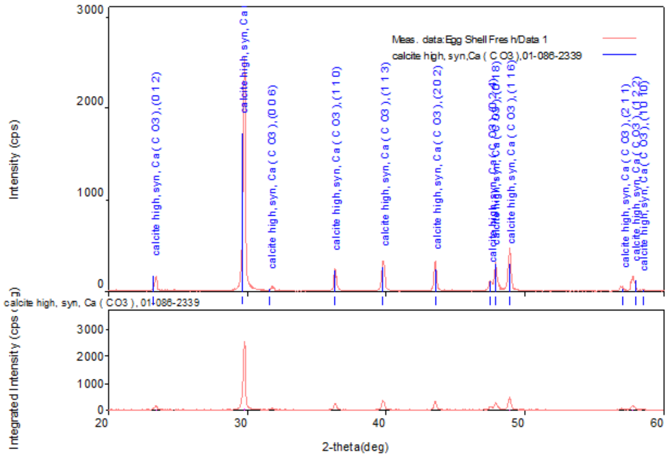
```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   0.850 BB S  0.0348 2.36938e6  1.07204e6  99.92011
   2  16.768 BB    0.0798  697.70215  121.76596  0.02942
   3  19.142 BV    0.0880   67.07845   10.43892  0.00283
   4  19.363 VB    0.0833  824.28809  142.85014  0.03476
   5  19.882 BB    0.0701  200.47908   42.47218  0.00845
   6  22.941 BB    0.1020   59.40610    7.96900  0.00251
   7  24.214 BB    0.0598   45.57076   11.35800  0.00192
```

Figure B1 Example of analysis in GC at 3 wt % of catalyst.



FigureB2 X-ray diffraction patterns for fresh eggshell

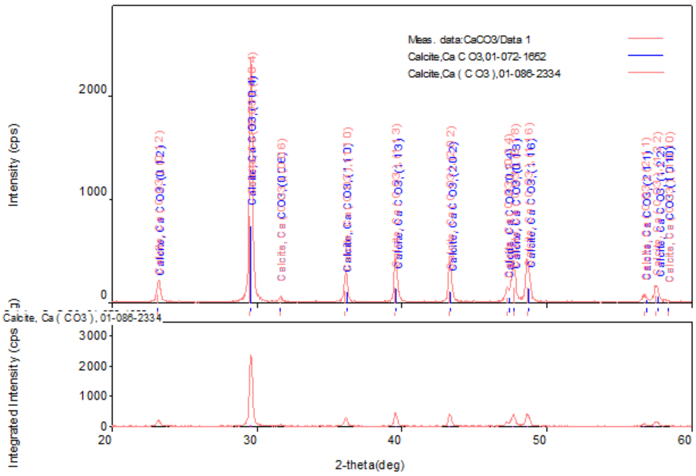


Figure B3X-ray diffraction patterns for $CaCO_3$

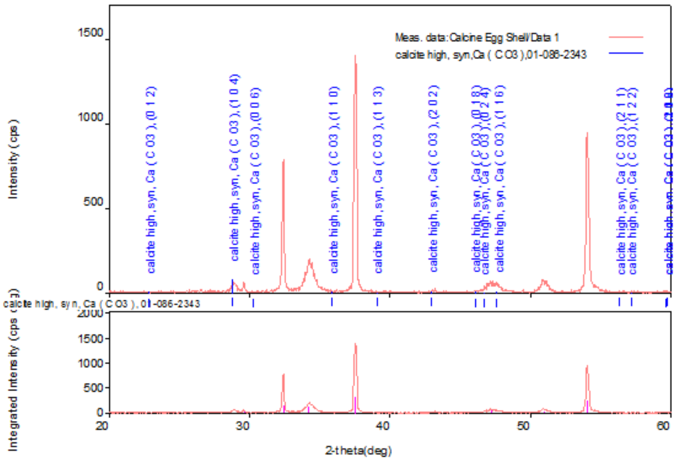


Figure B4 X-ray diffraction patterns for calcined eggshell.

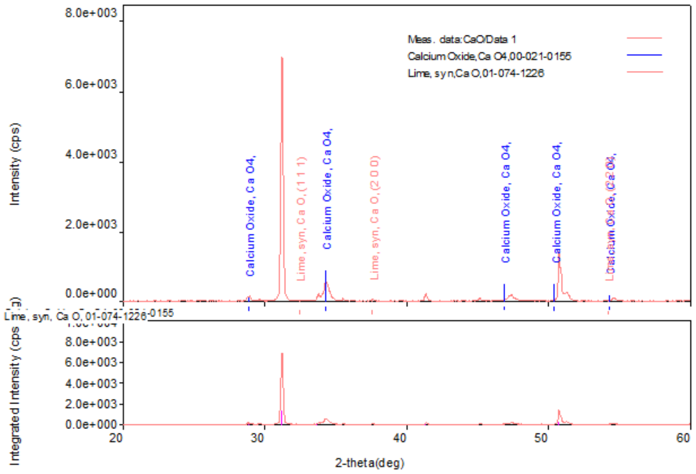
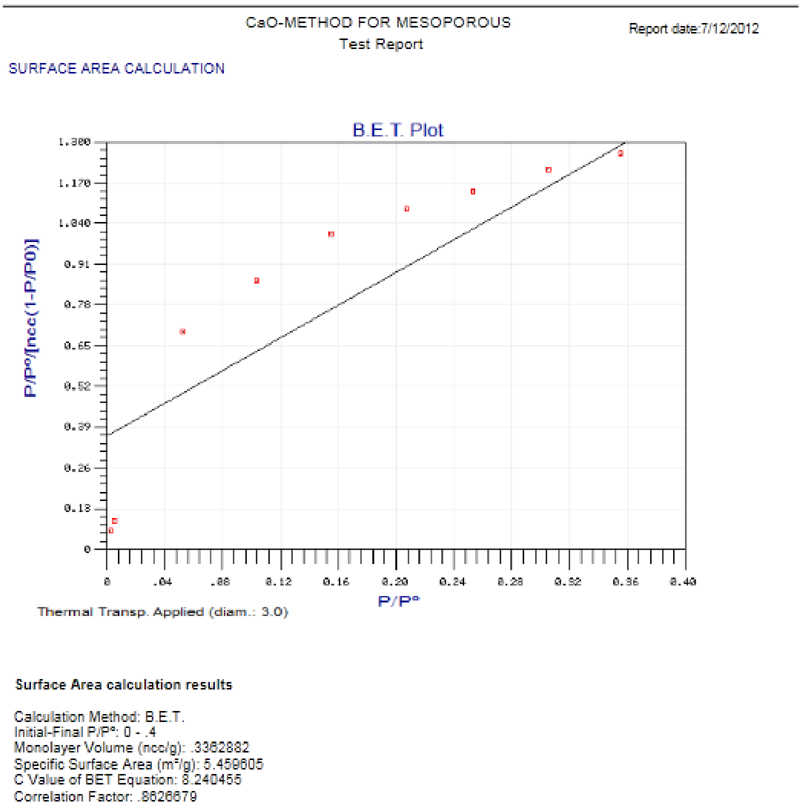


Figure B5 X-ray diffraction patterns forCaO.



CaO-METHOD FOR MESOPOROUS
Test Report

Report date:7/12/2012

SURFACE AREA CALCULATION

Thermal Transp. Applied (diam.: 3.0)

Surface Area calculation results

Calculation Method: B.E.T.
Initial-Final P/P°: 0 - .4
Monolayer Volume (ncc/g): .3362882
Specific Surface Area (m^2/g): 5.459605
C Value of BET Equation: 8.240455
Correlation Factor: .8626679

Figure B6 Example of analysis for BET.

Appendix C

FAME content calculation

A calibration curve plotted as shown in chapter 4 was concentration, ppm vs peak area. Let's use methyl Palmitate and 6 wt % gc analysis data as the example,

From figure 4.13, y= mx or y=0.2981x

Obtained the peak area from Figure B1, for methyl Palmitate is equal to 697.70215.

Hence, y (ppm)= 697.70215 x 0.2981 = 207.985 mg/l or ppm

Using the same method above, calculate each of concentration of FAME.

Get,

FAME	**ppm**
Methyl Palmitate	207.985
Methyl Stearate	22.12
Methyl Oleate	266.33
Methyl Linoleate	12.996
TOTAL	509.431

Yield, % = $\frac{mass\ of\ FAME\ obtained\ \ from\ \ GC\ with\ help\ of\ standard\ \ curve}{Theoretical\ \ mass\ of\ FAME} \times 100\%$

Theoretical weight=

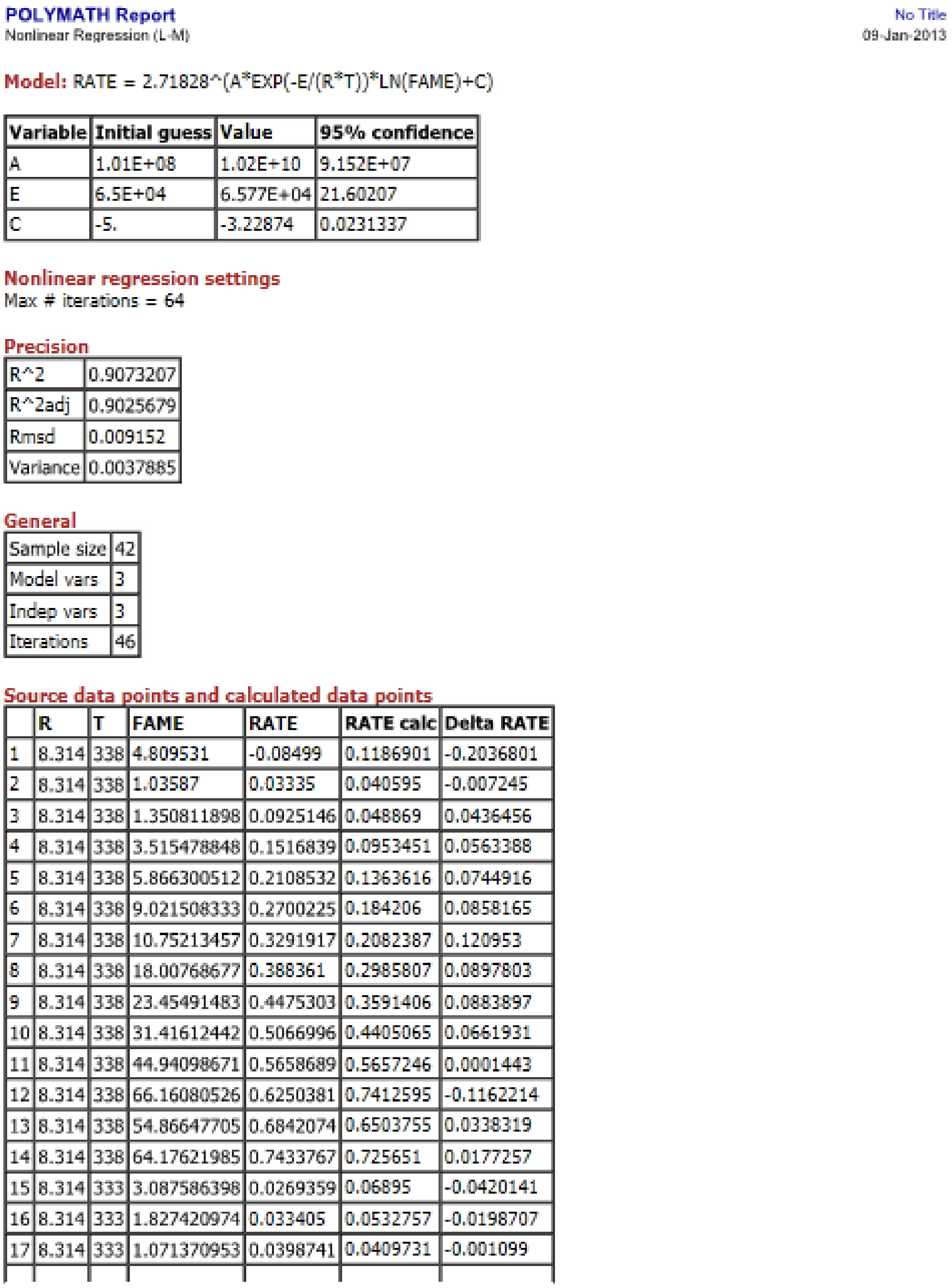
$\frac{weight\ of\ the\ oil\ (initial\ \ oil\ used)}{molecul\ ar\ formula\ \ weight\ of\ oil}$ X (3 mol FAME/ mol oil) X Molecular weight of FAME.(average).

Mass of methyl ester obtained from GC=

(509.431 mg/l) x dilution factor x total mass of (oil+ methanol) at initial state.

Appendix D

POLYMATH RESULT



POLYMATH Report
Nonlinear Regression (L-M)

No Title
09-Jan-2013

Model: RATE = 2.71828^(A*EXP(-E/(R*T))*LN(FAME)+C)

Variable	Initial guess	Value	95% confidence
A	1.01E+08	1.02E+10	9.152E+07
E	6.5E+04	6.577E+04	21.60207
C	-5.	-3.22874	0.0231337

Nonlinear regression settings
Max # iterations = 64

Precision

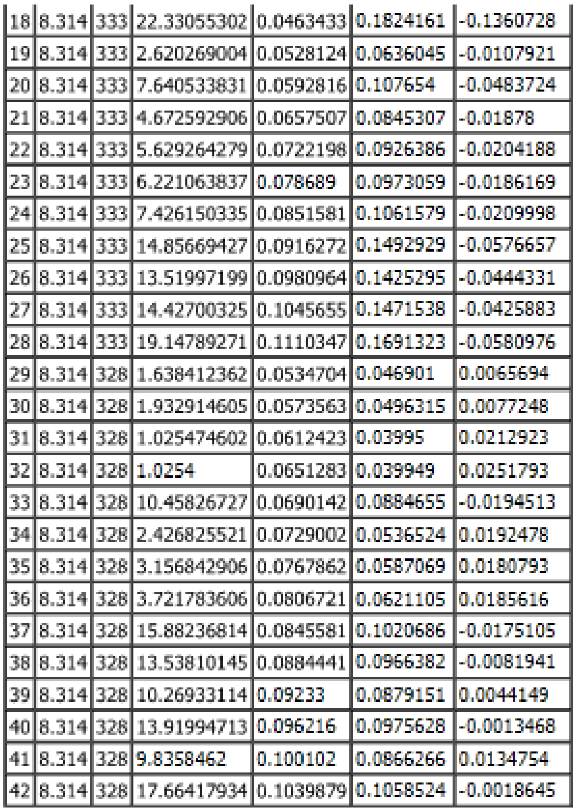
R^2	0.9073207
R^2adj	0.9025679
Rmsd	0.009152
Variance	0.0037885

General

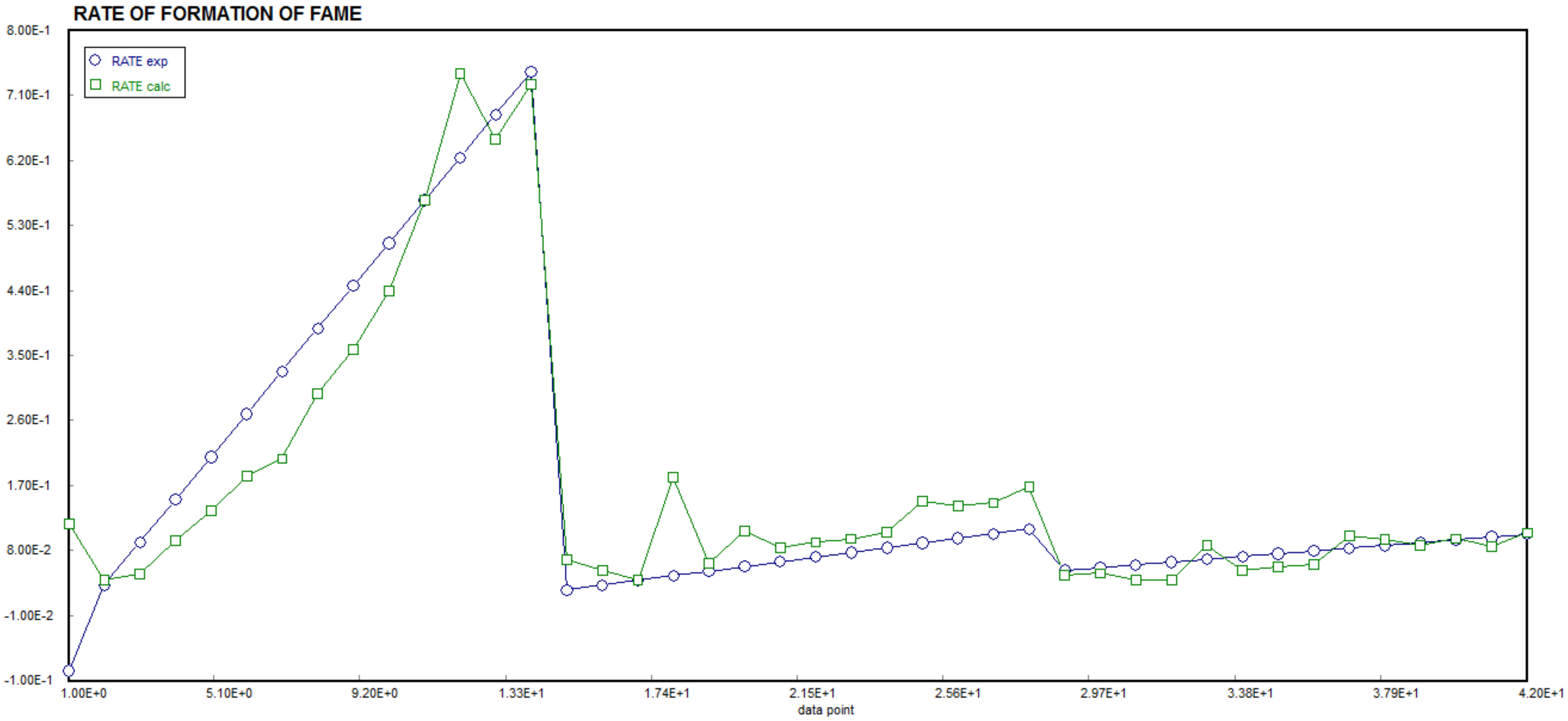
Sample size	42
Model vars	3
Indep vars	3
Iterations	46

Source data points and calculated data points

	R	T	FAME	RATE	RATE calc	Delta RATE
1	8.314	338	4.809531	-0.08499	0.1186901	-0.2036801
2	8.314	338	1.03587	0.03335	0.040595	-0.007245
3	8.314	338	1.350811898	0.0925146	0.048869	0.0436456
4	8.314	338	3.515478848	0.1516839	0.0953451	0.0563388
5	8.314	338	5.866300512	0.2108532	0.1363616	0.0744916
6	8.314	338	9.021508333	0.2700225	0.184206	0.0858165
7	8.314	338	10.75213457	0.3291917	0.2082387	0.120953
8	8.314	338	18.00768677	0.388361	0.2985807	0.0897803
9	8.314	338	23.45491483	0.4475303	0.3591406	0.0883897
10	8.314	338	31.41612442	0.5066996	0.4405065	0.0661931
11	8.314	338	44.94098671	0.5658689	0.5657246	0.0001443
12	8.314	338	66.16080526	0.6250381	0.7412595	-0.1162214
13	8.314	338	54.86647705	0.6842074	0.6503755	0.0338319
14	8.314	338	64.17621985	0.7433767	0.725651	0.0177257
15	8.314	333	3.087586398	0.0269359	0.06895	-0.0420141
16	8.314	333	1.827420974	0.033405	0.0532757	-0.0198707
17	8.314	333	1.071370953	0.0398741	0.0409731	-0.001099



18	8.314	333	22.33055302	0.0463433	0.1824161	-0.1360728
19	8.314	333	2.620269004	0.0528124	0.0636045	-0.0107921
20	8.314	333	7.640533831	0.0592816	0.107654	-0.0483724
21	8.314	333	4.672592906	0.0657507	0.0845307	-0.01878
22	8.314	333	5.629264279	0.0722198	0.0926386	-0.0204188
23	8.314	333	6.221063837	0.078689	0.0973059	-0.0186169
24	8.314	333	7.426150335	0.0851581	0.1061579	-0.0209998
25	8.314	333	14.85669427	0.0916272	0.1492929	-0.0576657
26	8.314	333	13.51997199	0.0980964	0.1425295	-0.0444331
27	8.314	333	14.42700325	0.1045655	0.1471538	-0.0425883
28	8.314	333	19.14789271	0.1110347	0.1691323	-0.0580976
29	8.314	328	1.638412362	0.0534704	0.046901	0.0065694
30	8.314	328	1.932914605	0.0573563	0.0496315	0.0077248
31	8.314	328	1.025474602	0.0612423	0.03995	0.0212923
32	8.314	328	1.0254	0.0651283	0.039949	0.0251793
33	8.314	328	10.45826727	0.0690142	0.0884655	-0.0194513
34	8.314	328	2.426825521	0.0729002	0.0536524	0.0192478
35	8.314	328	3.156842906	0.0767862	0.0587069	0.0180793
36	8.314	328	3.721783606	0.0806721	0.0621105	0.0185616
37	8.314	328	15.88236814	0.0845581	0.1020686	-0.0175105
38	8.314	328	13.53810145	0.0884441	0.0966382	-0.0081941
39	8.314	328	10.26933114	0.09233	0.0879151	0.0044149
40	8.314	328	13.91994713	0.096216	0.0975628	-0.0013468
41	8.314	328	9.8358462	0.100102	0.0866266	0.0134754
42	8.314	328	17.66417934	0.1039879	0.1058524	-0.0018645


RATE OF FORMATION OF FAME
RATE exp
RATE calc
8.00E-1
7.10E-1
6.20E-1
5.30E-1
4.40E-1
3.50E-1
2.60E-1
1.70E-1
8.00E-2
-1.00E-2
-1.00E-1
1.00E+0
5.10E+0
9.20E+0
1.33E+1
1.74E+1
2.15E+1
2.56E+1
2.97E+1
3.38E+1
3.79E+1
4.20E+1
data point