OPTIMIZATION OF BIODIESEL FUEL USING EDIBLE VEGETABLE OIL

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DECLARATION

I declare that this project report entitled "Optimization of Biodiesel Fuel Using Edible Vegetable Oil" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

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APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Thermal-Fluids).

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ABSTRACT

Biodiesel produced by transesterification of triglycerides with alcohol, is the newest form of energy that has attracted the attention of many researches due to various advantages associated with its usages. Response surface methodology, based on a three level, three independent variables central composite design is used to analyze the interaction effect of the transesterification reaction variables in the experiment which consists of temperature, molar ratio of methanol to oil and catalyst concentration on biodiesel yield. The linear terms of methanol molar ratio, and also the quadratic terms methanol to oil ratio and temperature, had significant effects on the biodiesel production ($p<0.05$). Through optimization plot done in response surface design method, maximum yield for the production of methyl esters from corn oil was predicted to be 90.15 % under the condition of temperature of 50.85^{o}C, the molar ratio of methanol to corn oil of 7:1, and catalyst concentration of 0.722 wt%, with a fixed constant variable of stirring speed 300 rpm and a reaction time of 1hr.

ABSTRAK

Hasilan biodiesel melalui proses transesterifikasi trigliserida dan alkohol, merupakan suatu teknologi baru yang telah menarik perhatian golongna pengkaji disebabkan oleh pelbagai kelebihan berkaitan kegunaan minyak itu sendiri. Kaedah gerak balas permukaan, yang digunakan berdasarkan atas tiga peringkat, tiga pemboleh ubah bebas, memebentuk satu reka bentuk komposit pusat, bertujuan untuk mengkaji kesan dan hubungan di antara pemboleh ubah bebas tersebut yang digunakan di dalam eksperimen iaitu suhu, nisbah molar alkohol kepada minyak dan kepekatan pemangkin terhadap biodiesel yang dihasilkan. Istilah linear nisbah alkohol kepada minyak dan juga syarat kuadratik nisbah alkohol kepada minyak dan suhu, mempunyai pengaruh yang jelas terhadap penghasilan biodiesel melalui nilai p yang tidak melebihi 0.05. Melalui plot pengoptimuman yang telah dihasilkan melalui kaedah gerak balas permukaan juga, hasil maksimum yang dihasilkan melalui minyak sayur jagung yang digunakan adalah dijangkakan pada peratusan 90.15% dengan set pemboleh ubah suhu pada 50.85℃, nisbah metanol kepada minyak jagung pada 7:1 dan kepekatan pemangkin pada 0.722 peratusan berat%, berserta pemboleh ubah tetap kelajuan kacau 300 pusingan per minit dan masa reaksi selama sejam.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The energy policies in Malaysia are formulated by the Energy Section of the EPU under the Prime Minister's Department and these policies are renewed for every five years as part of the Five Year Malaysia Plan. An overall energy policy was established in 1979 (National Energy Policy 1979) with broad guidelines on long term energy objectives and strategies to ensure efficient, secure and environmentally sustainable supplies of energy (Jalal & Bodger, 2009). This is the main policy that governs the energy sector in Malaysia. Other energy policies were later formulated to support the objective and the implementations of this policy.

In 2000, the Four Fuel Policy was amended to become the Fifth Fuel Policy as formulated in the Eighth Malaysia Plan, where renewable energy was announced as the fifth fuel in the energy supply mix. When the Fifth Fuel Policy was introduced in 2001, renewable energy was targeted to be a significant contributor to the country's national grid with the generation mix of 5% of the total electricity demand by 2005 (Osman, 2006).

The target of 5% of renewable energy penetration was then later revised to be 350MW in the Ninth Malaysia Plan. Out of this 350 MW energy capacity, 245 MW was aimed to be achieved from the production of the biomass sector whereas the remaining 105 MW was from hydropower sources. Clearly from the statistics, biomass is expected to be one of the leading energy producers in the future.

Biomass in Malaysia generally can be seen of the production or development of organic matter available on a renewable basis, including forest and mill residues, wood wastes, agricultural crops and wastes, animal wastes and municipal solid waste. Malaysia is the world's second largest palm oil producer with 38% of the global market, and is the largest palm oil exporter, consisting of about 88% of the market's palm oil in 2011. As one

of the world's leading producers of palm oil, an average of 50 million tons of dry oil palm residues are produced each year and expected to reach 100 million tons by 2020.

Oil palm biomass emerges as a potential major contributor to renewable energy as the government has now shifted from conventional energy sources such as coal, oil and gas to promoting renewable energy sources in order to increase energy security (Umar, et.al, 2008). Table 1.1 depicts the expected renewable energy capacity in electricity generation in the future. In the table, biomass as highlighted to contribute one of the most energy capacities compared to other renewable resources in the country in the future.

Table 1.1 : Renewable energy capacity in electricity generation (source:Ministry of Plantation Industries and Commodities. 2006)

Year	Renewable energy installation capacity (MW)						Share in electricity generation capacity
	Biomass	Biogas	Small-hydro power	Solar PV	Solid waste	Total	
2015	330	100	290	55	200	975	6%
2020	800	240	490	175	360	2065	10%
2030	1340	410	490	854	390	3484	13%
2050	1340	410	490	8874	430	11,544	34%

Biodiesel was identified as one of the potential renewable energy sources for vehicle fuel, and based on the Fifth Fuel Policy, the government of Malaysia has launched the National Biofuel Policy in 2006 to encourage the use of environmentally friendly, sustainable and viable sources of biomass energy (Ministry of Plantation Industries and Commodities, 2006).

There is a renewed interest in considering crop species as a substitute in producing energy since fossil fuels are quickly being depleted over time (Ahmad, et.al, 2009). Regarding fuels, biodiesel is the most widely used biofuel nowadays. Biodiesel is a renewable alternative fuel for diesel engines with non-toxic and biodegradable characteristics consisting of Fatty Acid Methyl Esters (FAME) mainly of vegetable oils and animal fat origin. The reduction of the CO_2 emissions by its use is one of the main

advantages while the poor oxidation stability and contamination problem is a field still under investigation. (Basha, et.al, 2009; Dodos, et.al, 2009).

It is also manufactured from plant oils (soybean oil, cotton seed oil, canola oil), recycled cooking greases or oils (e.g., yellow grease), or animal fats (beef tallow, pork lard). Using crop species or products such as vegetable oils, transformation of vegetable oils into biodiesel can be realized using three different methods, which are pyrolysis or catalytic cracking, micro-emulsification and transesterification using low molecular alcohols.

Transesterification is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel. The purpose of the transesterification process is to lower the viscosity of the oil. There are various parameters affecting the production of alkyl esters or the biodiesel yield from the transesterification reaction. Temperature, alcohol to oil molar ratio, catalyst concentration, reaction time and stirring rate are influential factors to be considered in biodiesel production using vegetable oils. Different vegetable or feedstock oils also may have different 'recipe' in terms of optimum yield of biodiesel as each of these vegetable oils has different composition of fatty acids which are to be reacted with alcohol and catalyst in transesterification process.

1.2 PROBLEM STATEMENT

Expectancy of the biodiesel through the biomass energy is high towards ensuring the energy sustainability in the future but there are few drawbacks that may needed to be considered. Biodiesel production is facing several issues and challenges like tough global competition, feedstock issue, food *versus* fuel war, sustainability, and limited land for use and deforestation (Chong, et.al, 2015).

Other viable alternatives should have been sought out immediately as abundance of palm oil may cause setbacks such as mentioned above. Different vegetable oils possess different characteristics and should be experimented and explored on their usage and ability to produce other forms of oil. Methods of producing biodiesel vary from micro-emulsifications, pyrolysis and transesterification. Using feedstock oil,

transesterification process is best suited and most convenient method to perform production of biodiesel. Chemical process in transesterification reduces the fatty acid chain in reaction with alcohol with presence of catalyst to obtain biodiesel. However, various reaction parameters are monitored and controlled in ensuring that maximum yield (and/or conversion) and purity is achieved.

It is equally important that the process be optimized and cost reduced to the minimum so as to make biodiesel competitive in the market. The use of statistical method such as RSM, is sought after in determining the optimum parameters for yield production of biodiesel. However, the proper choice of factorial design and obtained regression model is very important in any response surface investigation. This is true because the quality of prediction, as measured by the size of the prediction variance, depends on the design matrix. Determination of an optimal value over the specified region of interest, for which in the case, the biodiesel yield, depends on the best fitted response model (Khuri & Mukhopadhyay, 2010).

1.3 OBJECTIVES

The objectives and the aim of the study are to study :

- The use of transesterification process for the conversion of the edible vegetable oils to biodiesel, and

- The process optimization of process parameters for maximum biodiesel yield

1.4 SCOPE OF PROJECT

In this experimental study, the scope that will be covered throughout the research are the factors that is considered in conducting transesterificiation which are methanol to oil molar ratio, reaction temperature and the concentration of catalyst. The limitations of the study goes as far as finding the optimum operating conditions of concerning factors mentioned above for the maximum yield of biodiesel production.

The concerns of other criterias such as other characteristics such as mixing intensity, and method production of biodiesel methods , are not discussed in details. In this case, corn oil was chosen for edible vegetable oil to be converted to the biodiesel after weighing on its cost, availability, and chemical properties of the oil itself. This study covers only the conversion of corn oil into biodiesel and other vegetable oil were only discussed in passing.

CHAPTER 2

LITERATURE REVIEW

2.1 VEGETABLE OIL

The use of vegetable oils as fuels dates back almost as far as the diesel engine itself. In the 1920s, soybean oil was used to fuel the early diesel engines (Kubičková & Kubička, 2010). The inexpensive, petroleum-derived, hydrocarbon-based fuels then dominated the market for decades. Research interest in vegetable oil- derived fuels decreased drastically, transitioning to petroleum derivatives. The use of vegetable oils as an alternative renewable fuel to compete with petroleum was re-introduced in the beginning of the 1980s (Bartholomew, 1981).

Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel and historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines (Zaher, 1990). In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. There are several advantages in the use of vegetable oils as diesel, which are: portability; ready availability; renewability; higher heat content, lower sulphur content and lower aromatic content than that of mineral diesel; and biodegradability (Demirbas, 2008).

But direct usage of the vegetable oils will be impractical for a long term run to be applied in the available diesel engines due to high viscosity, acid contamination, free fatty acid formation. Hence vegetables oils are processed through several means so as to achieve and acquire properties as similar to that of fossil fuels and the processed fuel can be directly used in the diesel engines available without damaging the mechanism.

2.1.1 Palm oil in Malaysia

Malaysia is the second palm oil producer in the world after Indonesia. Palm planted area is expected to expand to 6.0 million hectares in 2016/17 with expansion mainly in

East Malaysia, area harvested increased to 4.9 million hectares while fully matured hectare equivalent (MHE) area, plantation with palm trees that producing fruits at least 4 times a year, is estimated at 2.75 million hectares.

Yields are expected to drop in 2015/16 due to adverse weather condition and will rebound in 2016/17 as the weather improves in line with increases in mature hectare equivalent (MHE). Consequently, output is forecast to grow to 21.0 million tons. (Malaysia oil seeds and product annual, 2016).

As Malaysia is one of the biggest producing palm oil country in the world, palm oil itself is a known conflict in whether to be applied into a grand scale of producing biofuel or biodiesel. An issue of food versus energy can arise from the involvement of palm oil. Thus in the study, although palm oil is abundant and can be easily available for the use of the transesterication process, a different oil was chosen as the subject instead.

2.1.2 Corn oil

Biodiesel, is produced through a reaction known as transesterification. In a transesterification reaction, one mole of triglyceride in vegetable oils in this case will react with three moles of alcohol (molar ratio of methanol to vegetable oil of 3:1) to form one mole of glycerol and three moles of the respective fatty acid alkyl esters. The process is a sequence of three reversible reactions, in which the triglyceride molecule is broken down from diglyceride until it becomes monoglyceride and glycerol (Mittelbach and Remschmidt, 2004).

Several types of vegetable oils available, have different and various composition in fatty acids. They are all can be used in the production of a biodiesel. Four oil crops clearly dominate the feedstock sources used for world-wide biodiesel production such as soybean (Sensöz and Kaynar, 2006; Xie et al., 2006), rapeseed (Cvengros and Povazanec, 1996; Peterson et al., 1996), palm (Kalam and Masjuki, 2002) and sunflower (Antolín et al., 2002; Vicente et al., 2005). However, there are no obligations to use only these types of oil crops and no restrictions towards the use of other vegetable oils.

As we all know, maize or commonly known as corn is an abundant food and feed crop. Diverse use of any feed crop would add higher value to its cultivation and production. Corn for example is one such crop which yields several useful products. Hence it remains one of the favourite crops in industrial sector. Although relatively a new emergence, corn oil is becoming popular among edible oils owing to its unique health related benefits (Rajendran et.al, 2012). Table 2.1 shows the kinematic viscosity of different oils and biodiesel, obtained from different sources. It can be appreciated that the oil from which is obtained will affect in different ways the kinematic viscosity of the product.

Table 2.1 : Kinematic viscosity of different oils

Species	Kinematic viscosity of oil (centistokes, at 40°C)	Kinematic viscosity of biodiesel (centistokes, at 40°C)
Rapeseed	35.1	4,3-5,83
Soybean	32.9	4.08
Sunflower	32.6	4.9
Palm	39.6	4.42
Peanut	22.72	4.42
Corn	34.9	3.39
Canola	38.2	3.53
Cotton	18.2	4.07
Pumpkin	35.6	4.41

(source:Dennis et.al, 2010)

Apart from that, there are some other important factors in choosing the oil to be used in the transesterification process. For instance, the possibility of obtaining a kind of vegetable oil depending on the geographical location and, indeed, the suitability of the biodiesel obtained from that oil depending on the climate conditions. Based on Malaysia own weather and climates, corn oil is considered relatively a foreign concept of edible oil used into production of biodiesel.

The properties of the triglyceride and the biodiesel fuel are determined by the amounts of each fatty acid that are present in the molecules. Different type of vegetable would possess different amount of fatty acids, and thus affect the transesterification process in which the molar ratio needed to convert a mole of the triglyceride in the vegetable oils with three mole of alcohol would be of different quantity. Thus, it is important to specifically know the contents of the fatty acid of the experimented vegetable oil in a transesterification process in obtaining the most accurate result. Table 2.2 lists the fatty acids contained in a number of vegetable oils and corn oil is highlighted as a subject of the study.

Table 2.2 : Fatty acid composition (wt%) of vegetable oils

Fatty acid	Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
Lauric (C12:0)	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Myristic (C14:0)	0.7	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Palmitic (C16:0)	36.7	11.6	8.0	4.9	11.3	6.2	6.9	4.6	10.4	6.5
Palmitoleic (C16:1)	0.1	1.0	0.0	0.0	0.1	0.1	0.1	0.1	0.5	0.6
Stearic (C18:0)	6.6	3.1	1.8	1.6	3.6	3.7	4.0	3.4	2.9	1.4
Oleic (C18:1)	46.1	75.0	53.3	33.0	24.9	25.2	19.0	62.8	77.1	65.6
Linoleic (C18:2)	8.6	7.8	28.4	20.4	53.0	63.1	69.1	27.5	7.6	25.2
Linolenic (C18:3)	0.3	0.6	0.3	7.9	6.1	0.2	0.3	0.1	0.8	0.1
Arachidic (C20:0)	0.4	0.3	0.9	0.0	0.3	0.3	0.3	0.3	0.3	0.1
Gadoleic (C20:1)	0.2	0.0	2.4	9.3	0.3	0.2	0.0	0.0	0.3	0.1
Behenic (C22:0)	0.1	0.1	3.0	0.0	0.0	0.7	0.0	0.7	0.0	0.0
Erucic (C22:1)	0.0	0.0	0.0	23.0	0.3	0.1	0.0	0.0	0.1	0.1
Lignoceric (C24:0)	0.1	0.5	1.8	0.0	0.1	0.2	0.0	0.3	0.0	0.1
Nervonic (C24:1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0

(source:Ramos et.al, 2008)

Palm oil which is much more commonly used in the country is a rather conservative choice of producing biodiesel from vegetable oil available in Malaysia. Given the cultivation plan planned by the government, corn plantation would be a viable alternative towards a brand new biodiesel based fuel to be used by Malaysia.

2.1.3 Malaysia's corn market

With the weakening Malaysian ringgit, and the gloomy outlook of the national economy, it may as well retarded the potential growth of corn imports to 3.45 million tons in 2015/16 from 3.22 million tons in 2014/15. The trend was visible for marketing year 2014/15, when imports of corn dropped by 7.6 percent to 3.2 million tons from 3.4 million tons in 2013/14. For 2014/15 total value of import was US$779 million (Grain & Feed Annual Kuala Lumpur. 2016) as shown in Table 2.3.

Larger drawbacks towards the Malaysia's corn imports after the USA have been set after the presidency has been handed over to Donald Trump. Trump's policy of reducing US exports may have significant effect towards the import of corn in Malaysia. 45 percent tariff has been imposed on China from Boeing order to agricultural imports (Daniels.J, 2016). There is no predicting the future and assurance that Malaysia may or may not be included in the tariff as well.

Table 2.3 : Malaysia's corn imports (source:Grain & Feed Annual Kuala Lumpur. 2016)

Import Trade Matrix			
Country	Malaysia		
Commodity	Corn		
Time Period	Market Begin Oct	Units :	1000MT
Imports for:	2013/2014		**2014/2015**
United States	10	U.S	30
Others		**Others**	
Argentina	1,168		1,538
Brazil	1,345		1,437
India	792		129
Paraguay	40		75
Australia	0		2
Thailand	47		0
Ukraine	71		0
Total for others	3,473		3,211
Others not listed	3		10
Grand Total	3,476		3,221

(source:Grain & Feed Annual Kuala Lumpur. 2016)

The data above clearly depicts Malaysia as an importer for the corn crop market and Malaysia do not produce corn mostly on yearly basis. However, Malaysia is expanding its maize cultivation with the first commercial planting to start in Kemaman, Terengganu by month's end.

Malaysia has been importing up to four million metric tons of maize grains every year, costing RM33.33 billion. High cost of investment causes the rising maize prices, and to overcome this, efforts to plant maize in the country will be expanded (Datuk Seri Ahmad Shabery Cheek, June 2016). Federation of Livestock farmers' Association of Malaysia expressing their indignation against rising prices of maize grain imports also has been the catalyst in driving maize plantation to cultivate in Malaysia and the need to stop depending on imports from other countries such as Argentina.

2.2 TRANSESTERIFICATION AND ITS PARAMETERS

2.2.1 Transesterification or Alcoholysis

In the USA and Europe, the surplus edible oils like soybean oil, sunflower oil, and rapeseed oil are being used as feedstock for the production of biodiesel (Ramadhas et.al, 2004). However, vegetable oil is about ten times more viscous than diesel. As a result, vegetable oils can cause poor fuel atomization, incomplete combustion, and carbon deposition on the injector and valve seats (Sarin & Sharma, 2007).All of these implicaations can contribute to damaging the engine system. Common methods have been used by means of reducing the viscosity of vegetable oils include by blending with diesel, emulsification, pyrolysis, cracking, and also transesterification.

Among these, the transesterification of vegetable oils to alkyl esters is deemed to be the best method (Fangrui et.al, 1999). Transesterification is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel. The purpose of the transesterification process is to lower the viscosity of the oil. Generalized steps in transesterification process are displayed and visualized through Figure 2.1.

The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/ sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates.

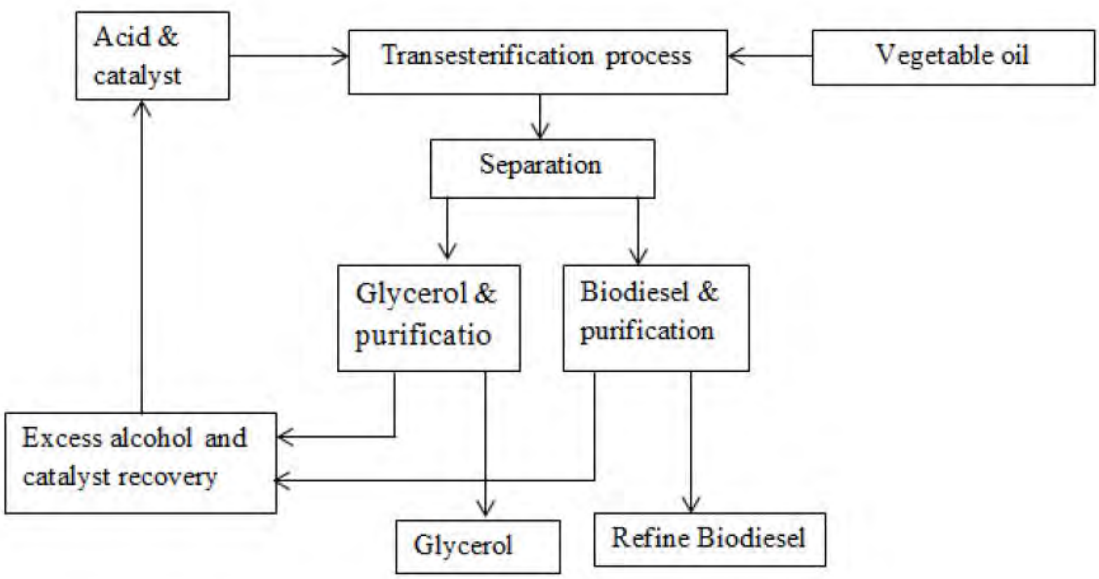

Figure 2.1 : Transesterification process

(source: Rajalingam et.al, 2016)

Transesterification also called alcoholysis which is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water (Murugesan et.al., 2009). The transesterification process can be represented in the form of a chemical reaction represented in Figure 2.2.

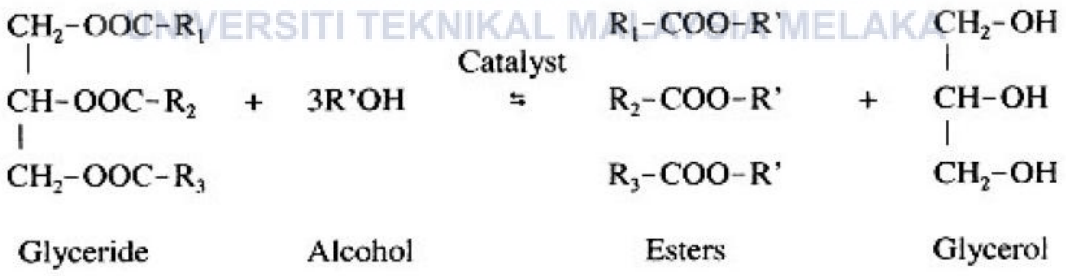

Figure 2.2 : Chemical reaction in transesterification

(source: Ma & Hanna, 1999)

The biodiesel manufacturing process converts oils and fats into long-chain mono alkyl esters, or biodiesel. (Paintsil, 2013). In the transesterification reaction, triglyceride is reacted with an alcohol (methanol, ethanol), in the presence of a catalyst to produce glycerol and fatty acid alkyl esters. The whole biodiesel production is summarized by this

reaction and hence various reaction parameters are monitored to ensure that maximum yield and purity is achieved.

Several other processes or methods of converting fatty acids into biodiesel can also be achieved through microemulsifications or thermal cracking also known as pyrolysis and microemulsification. Pyrolysis refers to chemical change caused by application of heat to get simpler compounds from a complex compound and this process is also known as cracking. In pyrolysis, vegetable oils can be cracked to reduce viscosity and improve cetane number (Ranganathan et.al, 2008).

Pyrolysis utilized a continuous system with a mechanically fluidized bed reactor at temperatures ranging from 400- 650°C (Gregory, 2015). Initial testing with soybean oil feedstock demonstrated that pyrolysis was the superior process for the application due to its greater severity. While microemulsions are clear, stable, two-phase nano-dispersions which readily form upon mixing water with an oil phase (Paintsil, 2013). Water-in-oil without microemulsions are comprised of a continuous nonpolar hydrocarbon phase and a discontinuous aqueous phase.

Microemulsion diesel fuel technology uses a microemulsifier to make a diesel or biodiesel fuel and a water phase compatible. The resulting microemulsion fuel, when utilized in conventional diesel engines, is “clean-burning”, thermal and shear stable in the fuel handling system. The purpose of the oxygenate is to help solubilize the surfactant in the fuel, adjust the properties for an example, viscosity of the fuel, and possibly contribute to improving the ignition properties of the water containing microemulsion fuel (Kesling, et. al, 2006).

2.2.2 Alcohol-to-oil molar ratio

The molar ratio of methanol to oil is very important factor as it affects the yield and also the cost of overall reaction. Higher molar ratio generates more esters than lower ratios in lesser time. The vegetable oils can be converted to biodiesel using 6:1 to 40:1 oil/alcohol molar ratio (Demirbas, 2002). According to stoichiometric ratio, 3 mol of alcohol and 1 mol of triglyceride produce 3 mol of ester and 1 mol of glycerol for the trans-esterification

reaction to occur. However, as transesterification is an equilibrium reaction, in practice, excess alcohol is required to move the reaction to forward direction (Akhtar et.al, 2014). This will induce an interference of the vegetable oil with the separation of glycerin because of the increase in solubility. When glycerin remains in solution, it helps to drive the equilibrium back to the left, lowering the yield of esters (Barnwal.P & Sharma.M, 2004).

In alkaline catalysed process, the yield of methyl ester increases with an increase in alcohol/oil ratio as the equilibrium shift towards the product (Verma *et al.* 2007). Methanol/ oil molar ratio is also associated with the type of catalyst used.An acid catalyzed reaction needed a 30:1 ratio of BuOH to soybean oil, while a alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time (Freedman et.al, 1986).

Higher molar ratios result in greater ester conversion in a shorter time. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated significantly more glycerine than a 3:1 molar ratio (Feuge and Grose, 1949). Rapeseed oil was methanolyzed using 1% NaOH or KOH (Nye & Southwell, 1983).They found that the molar ratio of 6:1 of methanol to oil gave the best conversion. When a large amount of free fatty acids was present in the oil, a molar ratio as high as 15:1 was needed under acid catalysis (Sprules and Price, 1950).

Many researchers have reported an alcohol to oil molar ration of 6:1 to be the optimal ratio. Since catalyst is required only in minute amounts, the primary cost would be only for alcohol. Therefore, if the use of alcohol can be reduced without significantly reducing the production of biodiesel, the biodiesel production cost would be lowered and the process would be more cost-effective (Hossain et.al, 2010).

A molar excess of alcohol to oil is needed for the transesterification reaction to proceed at a reasonable rate. Generally, the greater the molar ratio of alcohol to oil the faster the reaction rate, as long as the alcohol is soluble in the reaction mixture (Antczak et. al, 2009). When a portion of the alcohol remains insoluble (if in excess) it forms droplets which coat the enzyme causing ite deactivation. Thus, it is a proposition that a higher methanol to oil molar ratios was better than lower ratios in terms of soap formation (Singhet et.al, 2006).

2.2.3 Reaction temperature

It is only logical to assume that as the temperature increases, the rate of alcoholysis increases. The effect of temperature on the reaction yield was studied and It was found that the initial stages of the reaction is highly affected by temperature but after 1 hr of reaction, the ester formation was identical for 60˚C and 45˚C and only slighly lower for 32˚C. This explains the low effect of temperature on the yield in changing it from 30˚C to 60˚C.

However, an increase in reaction temperature beyond the optimal level led to decrease of biodiesel yield because higher reaction temperature accelerated the saponification process because of the triglycerides (Mathiyazhagan, 2011). Various studies have been conducted to study the reaction of temperature, to reach the optimization value as studies have also been done on optimizing the other parameters involved in a transesterification process.

Transesterification can occur at different temperatures, depending on the oil used. In methanolysis of castor oil to methyl ricinoleate, the reaction proceeded most satisfactorily at 20±35°C with a molar ratio of 6:1± 12:1 and 0.005±0.35% (by weight of oil) of NaOH catalyst (Smith, 1949). For the transesterification of refined soybean oil with methanol (6:1) using 1% NaOH, three different temperatures were used (Freedman et.al., 1984).

In the study done by Freedman (1984), transesterification using soybean oil, after 0.1 hour, ester yields were 94%, 87% and 64% for 60, 45 and 32°C, respectively. After an hour has passed, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters.

According to a study done by Abbah et.al (2016), an experiment of the transesterification using neem seed oil with methanol and KOH as the catalyst for the reaction parameters. Transesterification reaction was carried out at a range of temperatures of 30ºC until 65ºC . This is done in determining the influence of the temperature on the methyl ester production. Figure 2.3 shows the effect of the temperature on yield of neem seed oil.

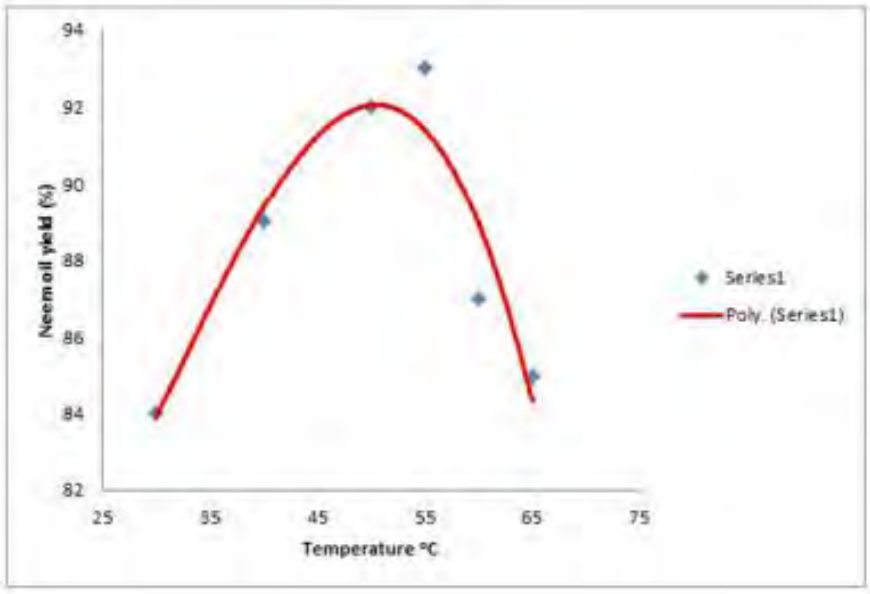

Figure 2.3 : Effect of temperature on yield of neem seed oil (source:Abbah et.al, 2016)

In general, the optimized temperature for transesterification using methanol as alcohol was 65ºC. Below and above this temperature, the yield of methyl ester would not reach at the maximum percentage that it could have been. Because at lower temperature, the reaction was not completed and at high temperature, methanol reaches its boiling point and vaporizes. Thus, decomposition of solvent results in ineffective conversion of oil to methyl ester.

2.2.4 Catalyst concentration

A catalyst functions to accelerate the reaction rates. For transesterification reaction, an increasing amount of heterogeneous catalyst caused the slurry too viscous giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring (Jagadale & Jugulkar, 2012). The same can be said likewise, when the catalyst concentration is not enough, the maximum production yield could not be achieved. Thus it is important to obtain an optimum amount of catalyst to be used in the transesterification process.

Catalysts can be classified into several types alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed (Freedman et al., 1984). However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed

transesterification is suitable (Freedman et al., 1984). Ester conversions at the 6:1 ratio for 1% NaOH and 0.5% $NaOCH_3$ were almost the same after 60 min (Freedman et. al, 1984).

Studies of conducting transesterification process with an acidic catalysts also have been done/ The transesterification of soybean oil with methanol, ethanol and butanol, using 1% concentrated sulfuric acid, was unsatisfactory when the molar ratios were 6:1 and 20:1 (Freedman et al., 1984). A 30:1 ratio resulted in a high conversion to methyl ester. More recently, an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of >98% (Jackson and King, 1996).

In general, the yield production of biodiesel will be significantly improving with the increasing amount of catalyst. This can be explained as followed: the solubility of alcohol in oil is limited so transesterification reaction can be able to carry out in the interface of two phases when catalyst loading is few. Reaction will be promoted by increasing catalyst load to increase the proton concentration in interface. Consequently, more methyl ester will be formed (Vicente et.al, 2004).

2.2.5 Mixing rate

Stirring has a positive effect on the yield of biodiesel even though it is not as pronounced as that of the other factors. Ma, et. al, (1999) mentions that the effect of stirring speed and time is only pronounced in the first 10 minutes. After a homogenous mixture is obtained, mixing does not affect the process that much. Stirring only has a linear relationship with the yield of biodiesel and a smaller coefficient compared to that of catalyst and free fatty acid amounts that vary accordingly to the designed alcohol to oil molar ratio. Thus, it can be justified on why increasing the mixing rate continuously after, will not influence the biodiesel yield significantly.

To achieve perfect contact between the catalyst and oil during transesterification ,they were mixed together in the process. Observations can be made during the transesterification reaction ,the reactants initially form a two phase liquid system .The mixing effect has been found to play a significant and influential role in cases of slow rate reactions .As phase separation ceases ,mixing on the movement of the particles of the

transesterification process forms the basis for process scale up and design. Thus, in case of slow rate reaction, stirring rate might have been more influential and significant to the output of the transsesterification process.

Methanolysis was conducted with stirring rates of 200, 400, 600, 800 and 1,000 revolutions per minute (rpm) and catalyst concentrations of 0.25%, 0.50%, 0.75%, 1% and 1.25% (Kumar, et.al, 2010). Kumar (2010) observed that 1wt% of catalyst give the best conversion, and the yield of methyl ester at different mixing intensities (rpm) with the amount of catalyst are investigated and the results are shown in Figure 2.4.

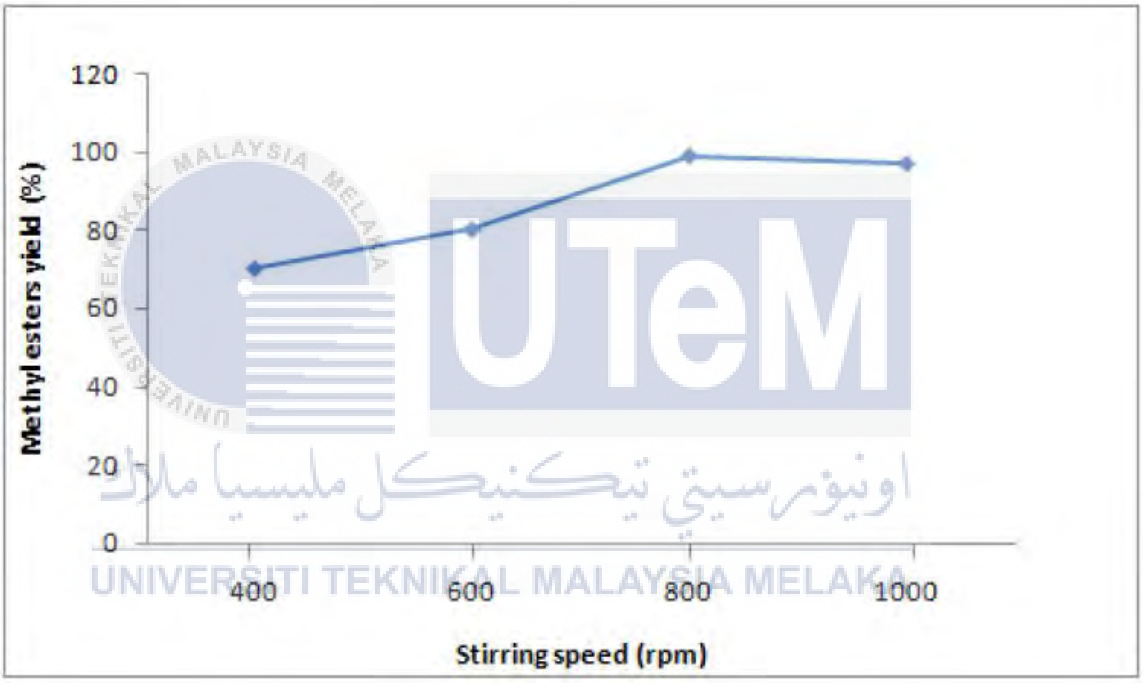

Figure 2.4 : Effect of stirring speed on biodiesel yield from coconut oil (source:Kumar et.al, 2010)

2.3 USAGE OF CATALYST

The conventional catalysts used for transesterification are acids and alkali, both liquid and heterogeneous, depending on the oil used for biodiesel production. The majority of biodiesel today is produced by alkali-catalyzed transesterification with methanol, with results in a relatively short reaction time. However the vegetable oil and alcohol must be substantially anhydrous and have low free fatty acid content, because the presence of water or free fatty acid or both promotes soap formation.

Table 2.4 lists in general, the type of catalyst available for the uses of transesterification reaction and process, along their advantages and disadvantages.

Table 2.4 : Summary of the catalysts in transesterification

Type of catalyst	Advantages	Disadvantages
Homogeneous base catalyst	Very fast reaction rate - 4000 times faster than acid-catalysed transesterification Reaction can occur at mild reaction condition and less energy intensive Catalysts such as NaOH and KOH are relatively cheap and widely available	Sensitive to FFA content in the oil Soap will form if the FFA content in the oil is more than 2 wt% Too much soap formation will decrease the biodiesel yield and cause problems during product purification especially generating huge amounts of wastewater
Heterogeneous base catalyst	Relatively faster reaction rate than acid-catalysed transesterification Reaction can occur at mild reaction condition and less energy intensive Easy separation of catalyst from product High possibility to reuse and regenerate the catalyst	Poisoning of the catalyst when exposed to ambient air Sensitive to FFA content in the oil due to its basicity property Soap will be formed of the FFA content in the oil is more than 2 wt % Too much soap formation will decrease the biodiesel yield and cause problems during product purification Leaching of catalyst active sites may result in product contamination
Homogeneous acid catalyst	Insensitive to FFA and water content in the oil Preferred method if low-grade oil is used Esterification and transesterification occur simultaneously Reaction can occur at mild reaction condition and less energy intensive	Very slow reaction rate Corrosive catalyst such as H_2SO_4 used can lead to corrosion on reactor and pipelines Separation of catalyst from product is problematic
Heterogeneous acid catalyst	Insensitive to FFA and water content in the oil Preferred method if low-grade oil is used Esterification and transesterification occur simultaneously Easy separation of catalyst from product	Complicated catalyst synthesis procedures lead to higher cost Normally, high reaction temperature, high alcohol to oil molar ratio and long reaction time are required Energy intensive Leaching of catalyst active sites may result to product contamination
Enzyme	Preferred method if low-grade oil is used Transesterification can be carried out at low reaction temperature, even lower than homogeneous base catalyst Only simple purification step is required	Very slow reaction rate, even slower than acid-catalysed transesterification High cost Sensitive to alcohol, typically methanol can deactivate the enzyme

(source:Gondra, 2010)

2.3.1 Alkaline based

Alkali catalyzed transesterification reaction is the most adopting methods for production of biodiesel because it is simple to extract the respective esters. This process is only applicable for oils that have low free fatty acid level (<4) and acid catalyst transesterification process is applicable only for high free fatty acid level (>4) oils.

Boiler ashes, potassium hydroxide (KOH) amongst other catalysts were successfully used in the ethanolysis and methanolysis of palm and coconut oils with yields as high as 90% (Ejikeme, 2008). It has also been reported that methyl and ethyl esters with 90% yield can be obtained from palm and coconut oil from the press cake and oil mill and refinery waste with the ashes of the wastes (fibers, shell, and husks) of these two oil seeds, and with lime, clay, zeolites. (Sasidharan & Kumar, 2004).

Variation of numerous researches and studies find that base-catalyzed transesterification of vegetable oils to proceed faster than the acid- catalyzed reactions. Because of this and the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts. Alkaline metal alkoxides are the most active catalysts. They give yields greater 98% in a relatively short reaction time of 30 min. even at low molar concentrations of about 0.5 mol% (Freedman, et.al, 1984).

Alkaline metal hydroxides such as KOH and NaOH are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol % However, the base catalyzed process still has two limitations: the base catalyzed transesterification of vegetable oil is sensitive to both moisture and to free fatty acids (FFA). This means that the raw materials must be refined; the moisture level must be no more than 0.06 wt% and FFA levels no more than 0.5 m wt% (Bandger, 2001). A small amount of moisture can initiate oil hydrolyzation to form soap and glycerol.

2.3.2 Acidic based

The transesterification process is catalyzed by Bronsted acids, preferably by sulphonic and sulphuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100°C and more than 3 hours to reach complete conversion.

Freedman et al (1984) showed that the methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65^{o}C, takes 50 hours to reach complete conversion of the vegetable oil (>99%), while the butanolysis (at 117^{o}C)

and ethanolysis (at 78ºC) using the same quantities of catalyst and alcohol take 3 hours and 18 hours, respectively.

Pryde et al. (1983) showed that the methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 hours to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 hrs., respectively.

Canakci and Van Gerpen (2001) used different amounts of sulphuric acid (1, 3 and 5 wt %) in the transesterification of grease with methanol and they discovered that a rate enhancement was observed with the increased amounts of catalyst and ester yield went from 72.7 to 95.0% as the catalyst concentration was increased from 1 to 5 wt%.

2.3.3 Enzyme based

Enzymatic catalyzed transesterification can also be used for the production of biodiesel from low grade feedstock like used cooking oil, animal fat, and so forth and this transesterification process is carried out in the presence of enzyme such as lipase (Math & Chandrashekhara, 2016). This process has many advantages over the conventional transesterification process like generation of zero byproduct, no difficulty in separation, and requiring moderate reaction conditions

Conventional chemical methods used for biodiesel production have many drawbacks such as high-energy consumption and intensive use of chemicals. Therefore, many researches focus on lipase-catalyzed transesterification for biodiesel, which is clean and effective (Liu et.al, 2012). The lipase-catalyzed transesterification can also eliminate the inherent problems associated with the use of chemical catalysts (Ting et.al, 2008). The major barrier to the wider use of enzymatic transesterification is the cost of lipases.

Although biodiesel is usually produced by chemical processes using basic or acid catalysts, it can also be obtained using enzymes as catalysts. The enzymatic processes may be advantageous because they do not promote secondary reactions, thereby reducing the number of purification steps, and the presence of enzyme in the glycerol phase can even

increase its value to produce foodstuff. Furthermore, the enzyme can be immobilized into solid supports and thus be used in continuous mode, which is economically advantageous for industrial purposes.

Lipase is commonly used to catalyse the reaction in mild conditions and, in last years, an increasing number of researches on this subject have been reported (Dizge & Keskinler, 2008). The yield of biodiesel through lipase-catalyzed transesterification is influenced by alcohol to oil ratio, alcohol type, reaction temperature, water content, purity of the triacyglycerol, and enzymes immobilisations. The quality of the source oil is also important for efficient conversion to biodiesel. However, yield, reaction times, and costs are still critical compared to alkaline catalyzed transesterification reaction (Canakci & Van Gerpen, 2001 & Hama et.al, 2004)

2.3.4 Heterogenous substance

Heterogeneous transesterification is considered a green process. The process requires neither catalyst recovery nor aqueous treatment steps and very high yields of ethyl esters can be obtained, close to the theoretical value (Kilonzi et.al, 2015). However, heterogeneously catalyzed transesterification generally requires more severe operating conditions, and the performance of heterogeneous catalysts is generally lower than that of the commonly used homogeneous catalysts.

2.4 USAGE OF ALCOHOL

In the case of the alcohol, probably the most important reason is the money. Ethanol and methanol are the most commonly used alcohols, but methanol is usually preferred because it is cheaper (Carter et.al, 2005). Moreover, ethanol has a lower transesterification reactivity than methanol (Dennis et.al, 2010). Of course, other alcohols could be considered, but their higher prices make them unsuitable, except for the cases when there is a cheap source available elsewhere.

Based on the result obtained, the amounts of biodiesel produced by using different types of alcohol decreased in the following order: Methanol > Ethanol > Butanol. This

result obtained was slightly different with the finding of Nye et al. (1983). They reported that methanol was the alcohol that can give the highest biodiesel yield, followed by butanol and then ethanol. According to Meher et.al, (2006), the production of biodiesel by using ethanol in alkali-catalyzed transesterification is more difficult than that by using methanol due to the formation of stable emulsion during ethanolysis.

For methanolysis, the emulsions formed would break down easily to form a lower glycerol rich layer and upper methyl ester rich layer. While in ethanolysis, the emulsions formed are more stable due to the presence of larger non-polar group in ethanol, making the separation and purification of biodiesel more difficult (Zhou et.al, 2003). This explained why the biodiesel yield from ethanolysis was lower than methanolysis in this study.

Although methanol is the most suitable alcohol for alkali-catalyzed biodiesel production, the reported result obtained from biodiesel production catalyzed by lipase suggested otherwise. Mittelbach (1990) reported that the ethanol- and butanol catalyzed transesterification gave much higher yields than methanol-catalyzed transesterification. The same result was also reported by Abigor et.al, (2000).

2.5 USAGE OF RESPONSE SURFACE METHODOLOGY

Response surface methods (RSM) are information based techniques and perform well when there is a rich tapestry of accurate information provided. They have gained immense popularity due to their ease of use as well as dexterity of being applied across the board of industrial applications.

RSM offers techniques for mapping multidimensional patterns of responses to varying levels of control factors that are identified to govern physical processes. RSM is dependent on the use of regression analysis on data from experiments carried out at multiple levels and can be used to find approximate minima or maxima in response patterns provided such optima are within the design space of regressed points.

Optimization study for biodiesel production is crucial to assist researchers to develop a more efficient and cost-effective system in biodiesel industry (Wong et.al, 2015).

Generally, the reaction parameters such as reaction time, reaction temperature, catalysts loading and methanol to oil molar ratio, are being manipulated to optimize the biodiesel yield. Previously, optimization study was done with the variation of one parameter at a time which is tedious and time consuming (Bezerra et.al. 2008).

Besides, this technique does not show interactive effects among the reaction variables and overall effects of the variable (Bas & Boyacl, 2007). Development of response surface methodology (RSM) had simplified the optimization study where multiple parameters can be studied simultaneously. By establishing three-dimensional plot from the experimental data, the overall behavior of the reaction system can be easily understood and the interactions between reaction variables would be more visible.

2.5.1 RSM as a tool

Research further sought to use statistical methods to determine the optimum parameters for the production of biodiesel. Montgomery (2003), mentioned that by designed experiments, engineers can determine which subset of the process variables has the greatest influence on process performance.The use of statistical methods greatly reduced the time spent on experiments as a few experiments were used to arrive at a meaningful conclusion, thereby reducing the cost of production.

RSM is proved to be useful tool for the analysis of problems during which a certain response of concern. In which this concern that we aimed to find will usually be influenced by several different reaction parameters with the purpose to optimizing defined response of interest. Modeling of experimental response was the main objective of using RSM but later on applications of RSM were extended to develop models for the optimization of numerical experiments (Box & Norman, 1987). In fact, RSM is aimed at topographical understanding of response surfaces and region finding where we can find optimal response (Montgomery, 2005).

2.5.2 Advantages and application of RSM

A factorial experiment is recommended to study the variables and factors better to understand the effects that each variables may has on the response. It is an experimental strategy in which factors are varied together, instead of one at a time. In this method, two levels of the factors are considered and several experiments run. The effects of each factor and the possibility of different factors to interact are investigated.

Response surface methods usually accompany factorial designs. These are a collection of mathematical and statistical techniques that are useful for modeling and analysis in applications where a response of interest is influenced by several variables and the objective is to optimize this response. The response surface of the response variable is mapped out and the process is moved as close to the optimum as possible, taking into account all constraints. Thus, it is convenient to study the optimization of different available parameters in a transesterification process using the RSM method.

Vicente et. al (1998), investigated the application of these methods to the optimisation of biodiesel. They experimented using Sunflower Oil and methanol. Stirring was fixed at 600 rpm, time at 4 minutes, methanol-oil ratio fixed at 6:1 at atmospheric pressure. The factors investigated were temperature and catalyst concentration. They found that the conversion of trans-glycerides was strongly dependent on these two factors with the conversion increasing at low temperatures and high catalyst concentrations.

They further noted that the conversion decreased at very high temperature and pressures. This they explained to be a result of an increase in side reactions at these elevated conditions. Similar results were obtained by Joshi et. al (2008), when they investigated how the catalyst (KOH) concentration affects, ethanol oil ratio and temperature affects the yield of biodiesel. In their report, catalyst and Ethanol-Oil molar ratio were found to be the main factors that affect the yield using the response surface design.

2.5.3 Limitations of RSM

RSM is still in an early stage and has not been widely accepted and treated as a design tool. The wide range of RSM application in designing experiments is indeed convenient but it lacks mathematical formalism and basis with which the physical continuum is tied to model. The dimension of discreteness needs to be addressed as part of the response surface approach and this is a prevalent challenge to the capability of the procedure being universally accepted as a design tool.

The nature of the physical system sometimes cannot be adequately captured by the response surface approximation. Stability, multiple load paths, bifurcations and mode jumping phenomena are very common non smooth phenomena that RSM finds difficulty in dealing with. This restriction limits the range of applicability as well as the variety of problems that can be solved using RSM.

CHAPTER 3

METHODOLOGY

Because of its high viscosity and low volatility, the direct use of feedstock in diesel engines can cause problems including: high carbon deposits, scuffing of engine liner, injection nozzle failure, gum formation, lubricating oil thickening and high cloud and pour points (Fukuda et al., 2001). In order to avoid these recurring problems that may damage the engine, the feedstock goes through a chemical modification chemically modified which enables them to have properties more similar to conventional diesel (Fukuda et al., 2001).

The objectives of the study can be achieved through several means, the first being the transesferication process to convert the edible vegetable oil or in this case, corn oil into biodiesel. Recently, biodiesel is mostly produced by a transesterification reaction of oil with an alcohol in the presence of a catalyst, to produce esters and glycerol, which are then separated, and purified to obtain pure biodiesel as the end product and the flow process of the reaction is illustrated through Figure 3.1.

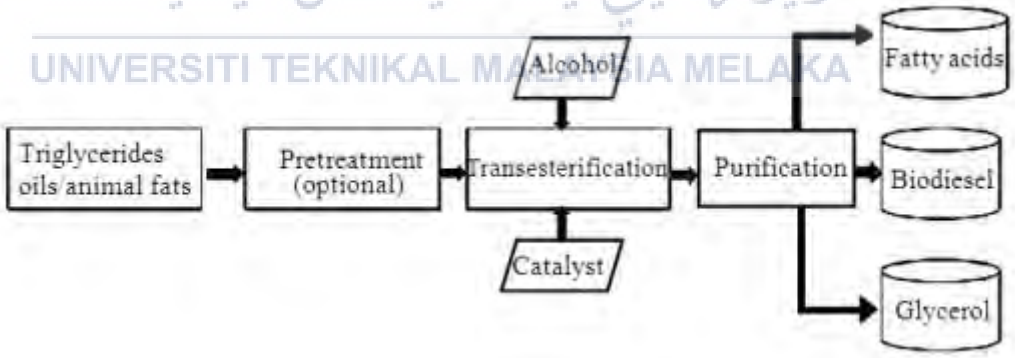

Figure 3.1 : Flow process of transesterication reaction
(source:Jagadale & Jugulkar, 2012)

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Meher et al. 2006).

3.1 TRANSESTERIFICATION

3.1.1 Material and apparatus preparation

Corn oil was obtained through the purchase of the product at a local supermarket as shown in Figure 3.2. Chemicals such as Potassium Hydroxide to act as the alkaline catalyst and the alcohol, methanol to form a methoxide solution with the catalyst will be obtained at chemical stores. The variation of catalyst concentration and the alcohol to oil molar ratio used in the experiment will be repeated according to each run of the experiment on the apparatus. Each experiment was conducted in a 100 ml beaker, and the mixture was agitated though the use of a hot plate stirrer at a constant stirring speed at 300 rpm.

Figure 3.2 : Mazola's virgin corn oil

Preparation of methyl hyroxide

Chemicals used for the experiment such as methanol and potassium hydroxide solution was obtained and bought from Poly-Scientific Enterprise. Two litres of methanol and one

kilogram of potassium hydroxide pellets have been purchased to complete the experimental design. To prepare for the correct usage of alcohol-to-oil molar ratio, fatty acids composition of corn oil will be needed to be considered. Based on Table 3.1, the contents of the fatty acid in the corn oil will be vital to estimate the amount of alcohol and catalyst to be used accordingly to the design parameters.

Table 3.1 : Corn fatty acid composition

Fatty acid	**Corn**
Lauric (C12:0)	0.0
Myristic (C14:0)	0.0
Palmitic (C16:0)	6.5
Palmitoleic (C16:1)	0.6
Stearic (C18:0)	1.4
Oleic (C18:1)	65.6
Linoleic (C18:2)	25.2
Linolenic (C18:3)	0.1
Arachidic (C20:0)	0.1
Gadoleic (C20:1)	0.1
Behenic (C22:0)	0.0
Erucic (C22:1)	0.1
Lignoceric (C24:0)	0.1
Nervonic (C24:1)	0.0

(source:Ramos.M.J, et.al, 2008)

Equation 3.1 is used to calculate for the amount of methanol to be used accordingly to the designed molar ratio in the experimental table.

$$\frac{MolOfFattyAcid}{100\%} xoilweight \tag{3.1}$$

Depending on the molar ratio to be used, for an example at alcohol to oil molar ratio of 3:1, Equation 3.1 will be multiplied with one as one mol of methanol will react with one

mol of fatty acid which consists of three chains of glycerol. To obtain the weight of methanol to be used, the equation 3.1 which has been multiplied with a value to satisfy the molar ratio will then be multiplied with the molecular mass of methanol which is 32 g/mol. Figure 3.3 shows one litre of methanol to be used for the remaining of the experiments and the process of breaking KOH pellets into smaller pieces in the crucible lid.

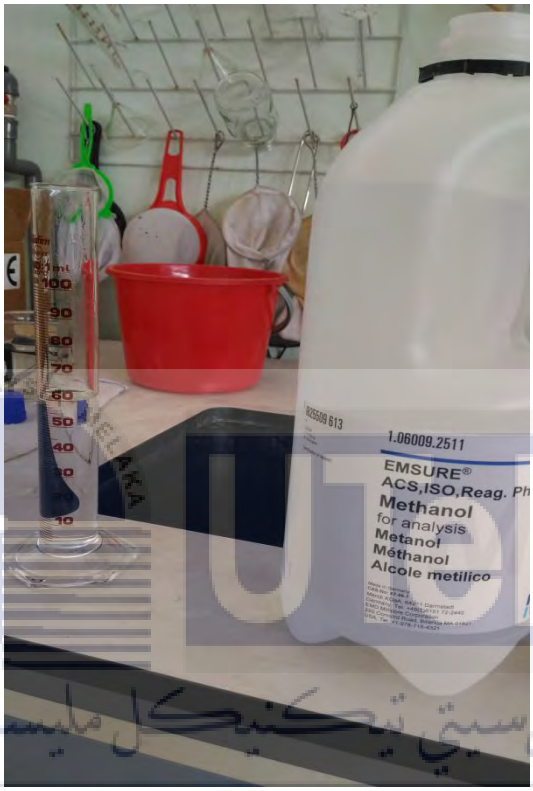

Figure 3.3 : One litre of methanol

Amount of catalyst which varies from 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt% and 0.9 wt% will be divided by each time of the run of the weight of the oil. First potassium hydroxide (KOH) pellets were first broken into smaller pieces in the crucible as shown in Figure 3.4.

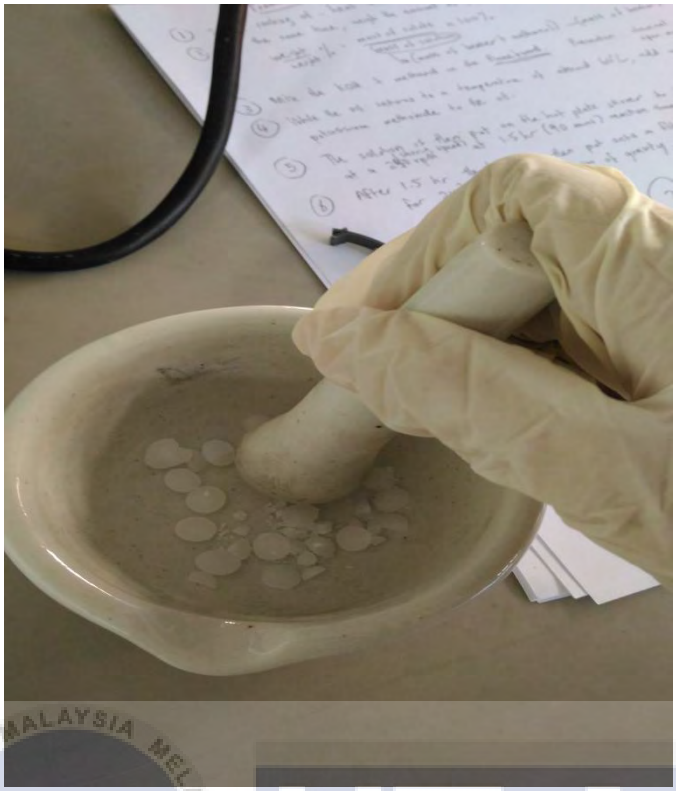

Figure 3.4 : Breaking down the KOH pellets

3.1.2 Transesterification reaction

The transesterification reactions are performed in various conditions to determine the optimum conditions of transesterification. Procedures in transesterification is done in a sequential order, and involves meticulous and cautious steps in order to reduce error from affecting the outcomes of the experiment.

First, 20 ml of corn oil will be poured in the beaker and first be weighted. This will allow to measure the amount of methanol and the base catalyst, potassium hydroxide (KOH) to be used as the oil weight varies in each of the run. Beaker containing corn oil later will be allowed to equilibrate to the temperature of reaction at 300 rpm as shown in Figure 3.5. Hot water circulated in the jacket of the reactor provided the necessary heat for the reaction.

The prepared potassium methoxide solution (a mixture of methanol and potassium hydroxide) will later be added into the hot beaker containing 20 ml of corn oil. Reaction

time is only started then and apparatus set will be left for experiment for an hour as shown in the set of apparatus seen in Figure 3.5.

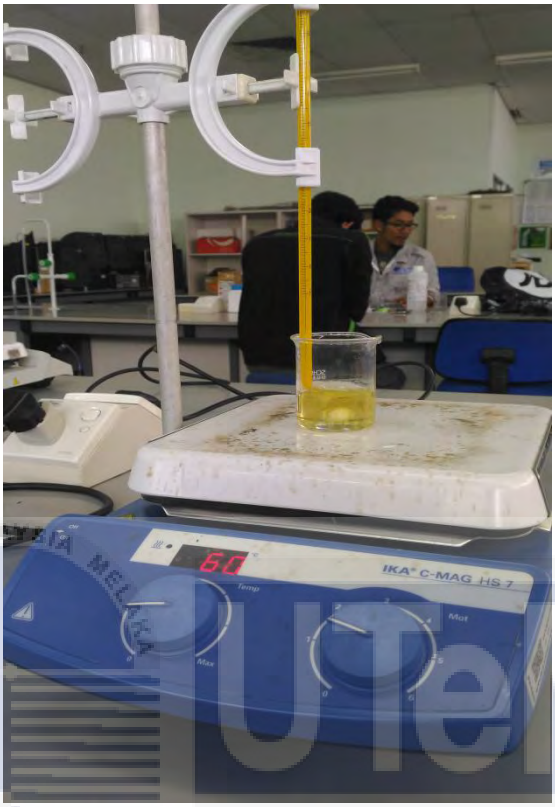

Figure 3.5 : Set apparatus was left for one hour reaction time

After one hour, which is the constant reaction time that is used. Hot plate stirrer is then stopped and the mixture is then stored into a glass container. The glass container is left for a day to allow separation of biodiesel and glycerin.

3.1.3 Biodiesel washing

Once glycerin layer can visibly be seen at the bottom of the glass container shown in Figure 3.6, the mixture is then be allowed to be poured into the separatory funnel for washing purposes. Glycerin can be described as the viscous sediment that will settle at the bottom of the container and it is undesirable to consider glycerin in the biodisesl mixture. Thus, washing process is very vital in order to obtain the biodiesel which in the aim in the process.

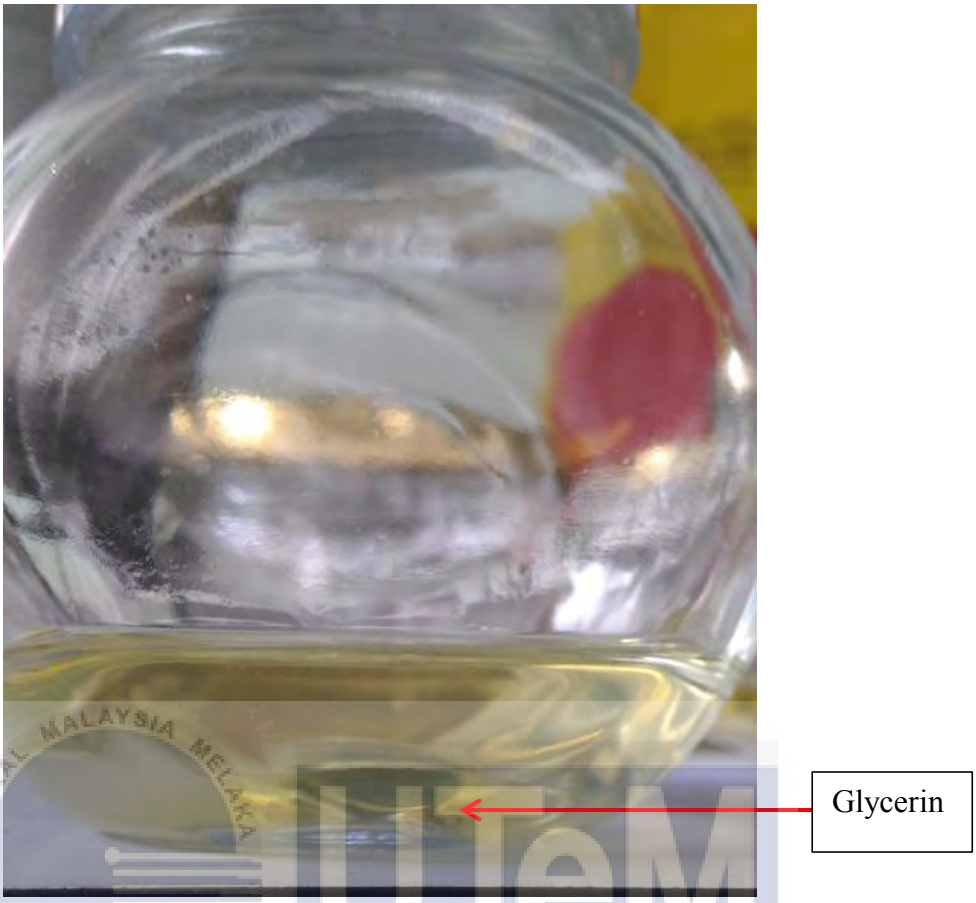

Figure 3.6 : Sediment of glycerin at bottom of glass container

Once the mixture is poured into the separatory funnel, hot water heated up to 60 - 70ºC will be added into the mix. Addition of hot water will cause the mixture to separate into three different layers, which consist of biodiesel at the top layer, soap in the middle layer, and glycerin which is the most dense to be at the bottom layer. These different layers in the separatory funnel can be seen in Figure 3.7.

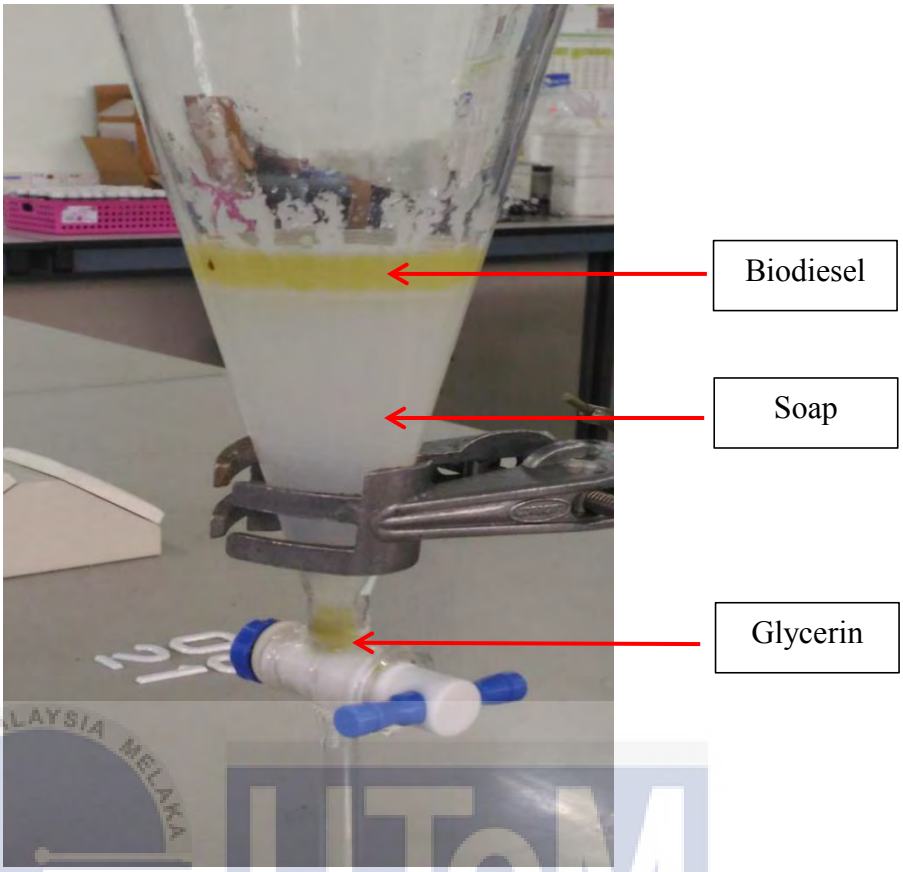

Figure 3.7 : Different layers present after warm water is added

Glycerin and excess soap will be removed and filtered out until the soap content can be eliminated as much as possible. An acceptable amount of washing will be needed to ensure that all the soapy part of the water to be removed as can be seen through the Figure 3.8. In this figure, the layer of water below the biodiesel in the upper layer should be clear in order to finally stop the washing process.

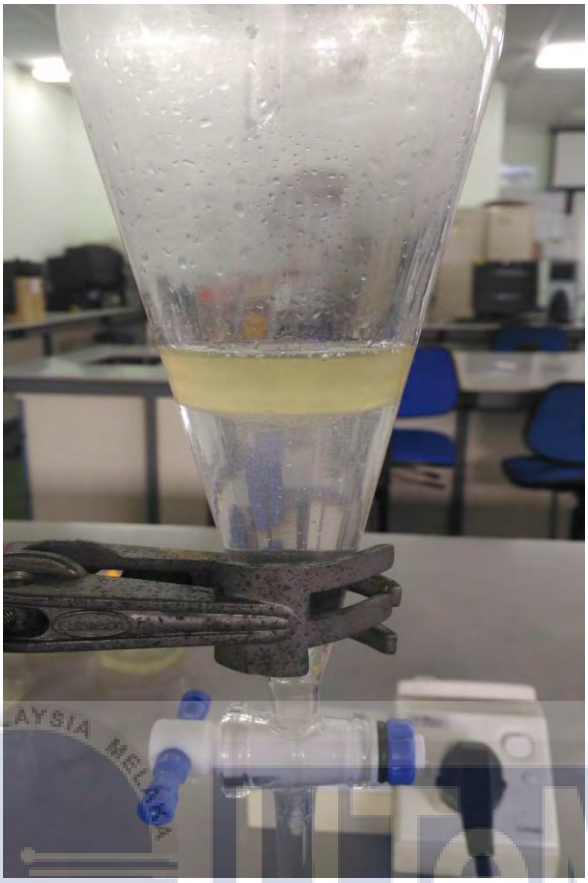

Figure 3.8 : Desired condition after adequate washing

Soap content is vital in this case in which it could affect the yield. Repeated washing will be ensured to obtain the clearest colour of the biodiesel. The remaining biodiesel will stored inside a glass container and sealed properly.

3.1.4 Output of biodiesel yield

There are several different methods in obtaining the yield of biodiesel, in this case because the sample is small in scale, it is thus more suitable and convenient to use the biodiesel analyzer. The recently published ASTM method D7861 for measuring biodiesel blend ratios enables users to take full advantage of the speed, convenience and durability provided by portable infrared analyzers, such as those offered by Wilks—a Spectro Scientific Company as shown in Figure 3.9.

Figure 3.9 : Biodiesel analyzer

The analyzers provide a fast, easy-to-use and inexpensive infrared method alternative for measuring biodiesel blend percentages. The analyzer available in the laboratory can analyze up to 30% of the biodiesel blends put onto the infrared analyzer.

In the experiment, once the washing proces is completed, the biodiesel sample is to be put onto the biodiesel analyzer. To extract only a little of the sample of the biodiesel, an apparatus is utilized in this case, an Eppendorf micropipette, 100 micron with only 0.1 ml intake of solution as shown in Figure 3.10.

Figure 3.10 : Eppendorf 100 microns micro-pipette

The sample is later run and analyzed to obtain the percent yield. Each run is repeated from the very first step in weighing the correct molar ratio of methanol and catalyst according to the oil weight. Transesterification reaction is set and fixed during an hour reaction time with a constant stirring rate at 300 rpm. Then, biodiesel mixture is left to separate and washing process occurs. Finally, the remaining biodiesel that has been washed will be analyzed using the biodiesel analyzer in order to obtain the yield percentage.

3.2 DESIGN EXPERIMENT USING RESPONSE SURFACE METHODOLOGY (RSM)

Response surface methodology (RSM) with central composite design (CCD) was the applied method or the design tool aimed to find the optimization value of the involving parameters. The products of transesterification will be analyzed according to the involving parameters which has been outlined in the scope of study. Three independent parameters that will be included are alcohol to oil molar ratio, catalyst concentration and temperature whilst the dependent variable of the experiment is the methyl ester production or the biodiesel yield. (Note:Temperature design of the experiment should not exceed 65^{o}C as the temperature is the boiling point temperature for methanol).

RSM is one the most commonly used in predicting the value of optimization based on several variables and factors in experiments. The method includes a full or fractional factorial design with center points that are augmented with a group of star points. As the distance from the center of the design space to a factorial point is defined as ±1 unit for each factor, the distance from the center of the design space to a star point is ±α with $|\alpha|>1$.

The RSM was employed to evaluate the effect of reaction temperature, catalyst concentration or loading and oil: alcohol ratio on FAMEs yield. The coded values for the variables are shown in Table 3.2. In order to avoid bias, 20 runs will be performed in a random set of order.

Table 3.2 : Experimental range and levels of independent process variables

Symbols	Independent variable	Coded levels				
		-α	-1	0	+1	+α
X_1	Temperature (°C)	30	40	50	60	65
X_2	Alcohol:oil molar ratio	3:1	6:1	9:1	12:1	15:1
X_3	Catalyst loading (wt.%)	0.5	0.6	0.7	0.8	0.9

Temperature, methanol-to-oil ratio, catalyst concentration were chosen as independent variables, and the production of methyl esters and glycerol were the dependent variables. The experimental range and levels of independent variables for biodiesel production are given in the Table 3.2 above.

For this study, a set of 20 experiments will be run which including the 2^3 factorial experiments, 6 star points and 6 replicates of center points. The center points are made up of all variables at zero level which are crucial in determination of experimental error and the reproducibility of the data. On the other hand, combination of variables consisting of one at its lowest (-a) level or highest (a) level with other variables at zero level constitutes the axial points.Since a full factorial is used, value of α, is calculated by $\alpha=(2n)^{1/4}$, where n is the factor numbers (in this study, n is three so α is equal to 1.68).

Each response obtained from the transesterification process was used to develop a mathematical model that correlates the biodiesel yield to the independent reaction variables via second-order polynomial Eq. (3.2) as given from (Montgomery 2001):

$$Y = \beta_o + \sum_{j=1}^{k} \beta_j x_j + \sum \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \varepsilon \quad (3.2)$$

By depending on the p-value obtained for each of the models plotted, the suitable model such as linear, square or cubic can be chosen to best portray the obtained regression model from the simulated response surface design. Table 3.3 outlines the parameters conditions in each run and the production of biodiesel yield or the dependent variable.

Table 3.3 : Full factorial central composite design matrix for biodiesel production.

Experiment	Independent variables			Biodiesel yield (%)
	X_1 : Temperature (°C)	X_2 : Alcohol : oil molar ratio	X_3 : Catalyst loading (wt.%)	
1	-1	-1	-1	
2	+1	-1	-1	
3	-1	+1	-1	
4	+1	+1	-1	
5	-1	-1	+1	
6	+1	-1	+1	
7	-1	+1	+1	
8	+1	+1	+1	
9	-α	0	0	
10	+α	0	0	
11	0	-α	0	
12	0	+α	0	
13	0	0	-α	
14	0	0	+α	
15	0	0	0	
16	0	0	0	
17	0	0	0	
18	0	0	0	
19	0	0	0	
20	0	0	0	

The optimum values of selected variables were obtained by solving the regression equation and also by analyzing the response surface contour plots by solving the equation Eqn. (3.2) where Y is the predicted response; β_o, β_j, β_{ij} and β_{jj} as the constant coefficients; x_i and x_j are the coded independent variables or factors;ε is random error. This is only a draft of the expected experimental design of the RSM optimization on corn oil with the

varying process parameters. The value for the responses are still not available due to the absence of the suitable software in the computer to complete the regression equation.

The results obtained from the biodiesel analyzer was repeated for eight times, in order to get the most accurate value of each run of experiment. The eight figures of biodiesel yield shown through the apparatus would later be constructed into a box plot. Box plot is a diagram that gives a visual representation to the distribution of the data, highlighting where most values lie and those values that greatly differ from the norm, called outliers. The box plot is also referred to as box and whisker plot or box and whisker diagram

The bottom side of the box represents the first quartile, and the top side, the third quartile. Therefore the vertical width of the central box represents the inter-quartile deviation. The horizontal line inside the box is the median. The vertical lines protruding from the box extend to the minimum and the maximum values of the data set, as long as these values are not outliers. The median value of each run will be chosen as the value of the biodiesel yield.

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 REGRESSION MODEL

The complete design matrix of the experiments as can be seen in the methodology section is presented here in Table 4.1 along with the experimental yield. From the table, it can be seen that the biodiesel yield obtained was in the range of 38.8 to 89.4%. The center points replicated six times which is indicated from run 15-20 were used to determine the experimental error (pure error) and the reproducibility of the data.

The RSM software that is utilized is used to generate and model a series of model equations (linear, two factor interaction (2FI), quadratic that fitted to the response as well as to suggest the best fitted model. Table 4.1 shows the experimental design matrix, according to each of their coded levels for each parameters, and along with their respective experimental output of biodiesel yield.

Table 4.1: Design matrix of experiments and their respective experimental yield

Experiment	Independent variables			Biodiesel Yield(%)
	A : Temperature (°C)	B : Alcohol : oil molar ratio	C : Catalyst loading (wt.%)	
1	-1	-1	-1	79.9, 80.0,80.1,80.3, 80.3, 80.5, 80.6, 80.9
2	+1	-1	-1	83.7, 83.8, 84.0, 84.1, 84.3, 84.3, 84.5, 84.5
3	-1	+1	-1	39.8, 39.9, 40.0, 40.0, 40.2, 40.3, 40.4, 40.5
4	+1	+1	-1	42.9, 42.9, 43.2, 43.3, 43.6, 43.6, 43.7, 43.8
5	-1	-1	+1	84.8, 84.9, 85.0, 85.1, 85.1, 85.2, 85.5, 85.6
6	+1	-1	+1	89.0, 89.1, 89.3, 89.3, 89.4, 89.5, 89.6, 89.8
7	-1	+1	+1	38.1, 38.1, 38.2, 38.6, 39.0, 39.1, 39.1, 39.2
8	+1	+1	+1	50.9, 50.9, 51.0, 51.1, 51.1, 51.2, 51.4, 51.4
9	-α	0	0	49.9, 50.0, 50.1, 50.1, 50.1, 50.2, 50.3, 50.3
10	+α	0	0	50.8, 50.9, 50.9, 50.0, 50.0, 50.1, 50.4, 50.4
11	0	-α	0	50.2, 50.2, 50.4, 50.5, 50.6, 50.7, 50.7, 50.9
12	0	+α	0	45.4, 45.5, 45.6, 45.7, 45.8, 45.8, 45.9, 46,0
13	0	0	-α	44.0, 44.2, 44.4, 44.7, 45.1, 45.2, 45.2, 45.4
14	0	0	+α	60.8, 60.9, 61.4. 62.9, 62.9, 63.0, 63.0,63.1
15	0	0	0	80.8, 80.9, 81.0, 81.2, 81.2, 81.3, 81.4, 81.6
16	0	0	0	87.2, 87.3, 87.4, 87.8, 87.8, 87.9, 87.9, 88.0
17	0	0	0	89.0, 89.1, 89.1, 89.2, 89.6, 89.6, 89.8, 89.9
18	0	0	0	86.9, 87.2, 87.2, 87.4, 87.5, 87.5, 87.7, 87.8
19	0	0	0	86.5, 86.6, 86.8, 86.8, 87.0, 87.1, 87.2, 87.2
20	0	0	0	84.1, 84.3, 84.4, 84.6, 84.7, 84.7, 84.8, 84.9

A box plot graph was plotted using all eight obtained values, each of this box plot graph was plotted using the SigmaPlot software. In Figure 4.1, box plot for run 9 was drawn, and the median was highlighted as the final value for that run of the experiment.

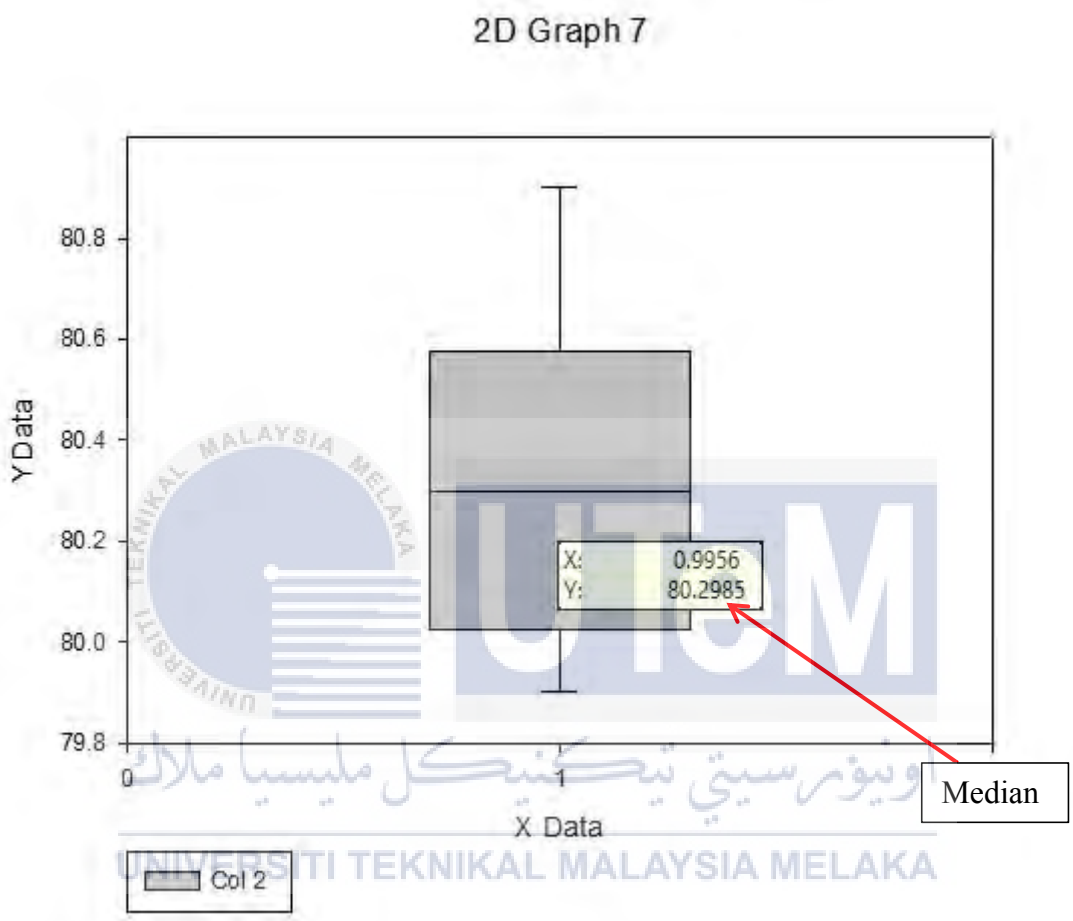

Figure 4.1 : Plotting box plot to obtain median

As it is highlighted in Figure 4.1, the median that is obtained for run 1 is 80.29, two decimal points are taken into consideration in order to be more precise and accurate. These steps are then repeated for the remaining runs, in order to get the experimental yield. Recorded value of yields are tabulated in Table 4.2. Table 4.2 displays all experimental biodiesel yield obtained for every 20 runs that have been conducted for transesterification reaction.

Table 4.2 : Complete results of experimental biodiesel yield

Experiment	Independent variables			Biodiesel Yield(%)
	A : Temperature (°C)	B : Alcohol : oil molar ratio	C : Catalyst loading (wt.%)	
1	-1	-1	-1	80.30
2	+1	-1	-1	84.20
3	-1	+1	-1	40.20
4	+1	+1	-1	43.45
5	-1	-1	+1	85.05
6	+1	-1	+1	89.35
7	-1	+1	+1	38.80
8	+1	+1	+1	51.10
9	-α	0	0	50.05
10	+α	0	0	51.00
11	0	-α	0	50.90
12	0	+α	0	45.75
13	0	0	-α	44.90
14	0	0	+α	61.75
15	0	0	0	81.20
16	0	0	0	87.60
17	0	0	0	89.40
18	0	0	0	87.45
19	0	0	0	86.90
20	0	0	0	84.65

Later, all the experimental runs are simulated along with their respective yields using the Minitab software. Figure 4.2 shows the experimental design table with their respective yield. The table is first constructed using the factorial, 2^3 to obtain 6 center points, and the +α and -α is given value at +1.68 and -1.68 respectively. 20 unblocked runs will be chosen from the available design option, and thus lead to a formation full factorial design with 8 cube points, 6 replicates of center points

Table 4.3 : Experimental design table in Minitab

StdOrder	RunOrder	PtType	Blocks	A	B	C	Yield (%)
1	1	1	1	-1.00000	-1.00000	-1.00000	80.30
2	2	1	1	1.00000	-1.00000	-1.00000	84.20
3	3	1	1	-1.00000	1.00000	-1.00000	40.20
4	4	1	1	1.00000	1.00000	-1.00000	43.45
5	5	1	1	-1.00000	-1.00000	1.00000	85.05
6	6	1	1	1.00000	-1.00000	1.00000	89.35
7	7	1	1	-1.00000	1.00000	1.00000	38.80
8	8	1	1	1.00000	1.00000	1.00000	51.10
9	9	-1	1	-1.68179	0.00000	0.00000	50.05
10	10	-1	1	1.68179	0.00000	0.00000	51.00
11	11	-1	1	0.00000	-1.68179	0.00000	50.90
12	12	-1	1	0.00000	1.68179	0.00000	45.75
13	13	-1	1	0.00000	0.00000	-1.68179	44.90
14	14	-1	1	0.00000	0.00000	1.68179	61.75
15	15	0	1	0.00000	0.00000	0.00000	81.20
16	16	0	1	0.00000	0.00000	0.00000	87.60
17	17	0	1	0.00000	0.00000	0.00000	89.40
18	18	0	1	0.00000	0.00000	0.00000	87.45
19	19	0	1	0.00000	0.00000	0.00000	86.90
20	20	0	1	0.00000	0.00000	0.00000	84.65

Option DOE is chosen for analyze purposes, and through given scope of the project, Response Surface Methodology will be adapted to analyze the data obtained. By clicking on the analyze option, a regression equation will be simulated and analysis of variance will display output of the activity.

In the regression equation analysis obtained, model summary of the analysis obtained also shows the value of R-squared for the simulation. R-squared is a statistical term or measure of how close the data are to the fitted regression line. It is the percentage of the response variable variation that is explained by a linear model.

R-squared in this case visualizes how close the data fit the regression equation obtained that has been simulated in Minitab. As it can be seen through the value of R-squared in Figure 4.2 , it shows that 72.73% of the data analysis will accurately depicts the regression equation.

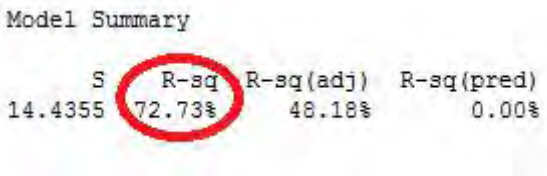

Figure 4.2 : Value of R-squared from regression model

For such a meticulous and critical experiment such as transesterification in which surrounding factors may needed to be considered, it is prone enough for errors to happen. These systematic and human errors will be discussed further later after each parameters and its influence on the biodiesel yield is discussed first.

From the design of analysis and through the formulated regression equation, expected and predicted of the value of the biodiesel yield can be obtained. Value of predicted biodiesel yield is tabulated in Table 4.4 in comparison with the experimental biodiesel yield that has been obtained through the process of transesterification.

Table 4.4 : Resulf of experimental yield along with predicted yield

Experiment	Independent variables			Biodiesel Yield (%)	
	A : Temperature	B : Alcohol-to-oil molar ratio	C : Catalyst loading	Experimental	Predicted
1	-1	-1	-1	80.30	67.15
2	+1	-1	-1	84.20	66.66
3	-1	+1	-1	40.20	40.74
4	+1	+1	-1	43.45	43.93
5	-1	-1	+1	85.05	72.21
6	+1	-1	+1	89.35	76.45
7	-1	+1	+1	38.80	43.98
8	+1	+1	+1	51.10	51.89
9	-α	0	0	50.05	56.15
10	+α	0	0	51.00	62.39
11	0	-α	0	50.90	78.50
12	0	+α	0	45.75	35.64
13	0	0	-α	44.90	56.59
14	0	0	+α	61.75	67.55
15	0	0	0	81.20	85.70
16	0	0	0	87.60	85.70
17	0	0	0	89.40	85.70
18	0	0	0	87.45	85.70
19	0	0	0	86.90	85.70
20	0	0	0	84.65	85.70

The predicted values of the biodiesel yield vary from the experimental results as R-squared discussed does not fully satisfied the regression equation obtained through the response surface design method. It only agrees with 72.73% of the result, and thus certain factors should be accounted for those difference in the results between experimental and prediction.

Each independent parameters used as variables in the experiment and their influences on the dependent variable which in this case, the biodiesel yield, can be obtained through the simulation of the response surface design. Figure 4.3 shows the coded coefficients of each term constant consisting of temperature (A), alcohol molar ratio (B) and catalyst loading (C). The interaction between different sets of parameters such as A-B and B-C can also be analyzed.

Coded Coefficients

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		85.70	5.89	14.56	0.000	
A	3.71	1.86	3.91	0.48	0.645	1.00
B	-25.48	-12.74	3.91	-3.26	0.009	1.00
C	6.52	3.26	3.91	0.83	0.424	1.00
A*A	-18.69	-9.35	3.80	-2.46	0.034	1.02
B*B	-20.25	-10.12	3.80	-2.66	0.024	1.02
C*C	-16.71	-8.36	3.80	-2.20	0.053	1.02
A*B	1.84	0.92	5.10	0.18	0.861	1.00
A*C	2.36	1.18	5.10	0.23	0.822	1.00
B*C	-0.91	-0.46	5.10	-0.09	0.931	1.00

Figure 4.3 : Coded coefficients for design variables

The regression equation obtained through the simulation are the main equation that dictate the prediction value discussed previously and indicates the most significant parameter in influencing the biodiesel yield. The regression equation of the transesterification reaction based on the experimental result , is as shown in Eqn. (4.1).

$$Y = 85.70 + 1.86A - 12.74B + 3.26C - 9.35A^2 - 10.12B^2 - 8.36C^2 + 0.92AB + 1.18AC - 0.46BC \quad (4.1)$$

From Eqn. (4.1), it can be seen that in this case, methanol to corn oil ratio displays the biggest value of coefficient on the biodiesel yield, signifies the biggest influence on the biodiesel yield compared to other parameters. Analysis of variance can be obtained through the simulation done from the response surface design option in Minitab which is shown in Figure 4.4.

The data displays in the analysis of variance can be seen in Table 4.4, which shows the value of sum of squares, degree of freedom, mean of square, F-value and P-value for sources of data and each parameters. The parameter which possesses least P-value and higher F-value are considered the most significant towards the output of the result.

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	5556.86	617.43	2.96	0.053
Linear	3	2409.17	803.06	3.85	0.045
A	1	47.05	47.05	0.23	0.645
B	1	2217.20	2217.20	10.64	0.009
C	1	144.92	144.92	0.70	0.424
Square	3	3128.11	1042.70	5.00	0.023
A*A	1	1258.71	1258.71	6.04	0.034
B*B	1	1476.95	1476.95	7.09	0.024
C*C	1	1006.17	1006.17	4.83	0.053
2-Way Interaction	3	19.58	6.53	0.03	0.992
A*B	1	6.75	6.75	0.03	0.861
A*C	1	11.16	11.16	0.05	0.822
B*C	1	1.67	1.67	0.01	0.931
Error	10	2083.83	208.38		
Lack-of-Fit	5	2042.18	408.44	49.03	0.000
Pure Error	5	41.65	8.33		
Total	19	7640.69			

Figure 4.4 : Analysis of variance

Table 4.4 : Sequential model sum of squares

Source	Sum of squares	Degree of freedom	Mean of square	F-value	P-value
Model	5556.86	9	617.43	2.96	0.053
Linear	2409.17	3	803.06	3.85	0.045
Square	3128.11	3	1042.70	5.00	0.023
2-Way Interaction	19.58	3	6.53	0.03	0.992
Error	2083.83	10	208.38		
Total	7640.69	19			

The best fitted model in this case, is indeed the quadratic or square equation that has been shown through Equation 4.1 as it has the least p-value. Small p values indicate that the null hypothesis can be rejected and it displays significant result compared to other models. Despite that, in making sure that the regression equation obtained earlier is good

enough to be analyzed throughout, Figure 4.5 which displays residuals versus the fitted values and Figure 4.6 shows the normal probability plot were first obtained, to verify the equation to be used.

For a verified result of data, residuals should always be in a similar pattern throughout the whole experiment. In this case, as seen in Figure 4.5, the randomized pattern of data can be seen through the positive and negative residuals plotted in the graph.

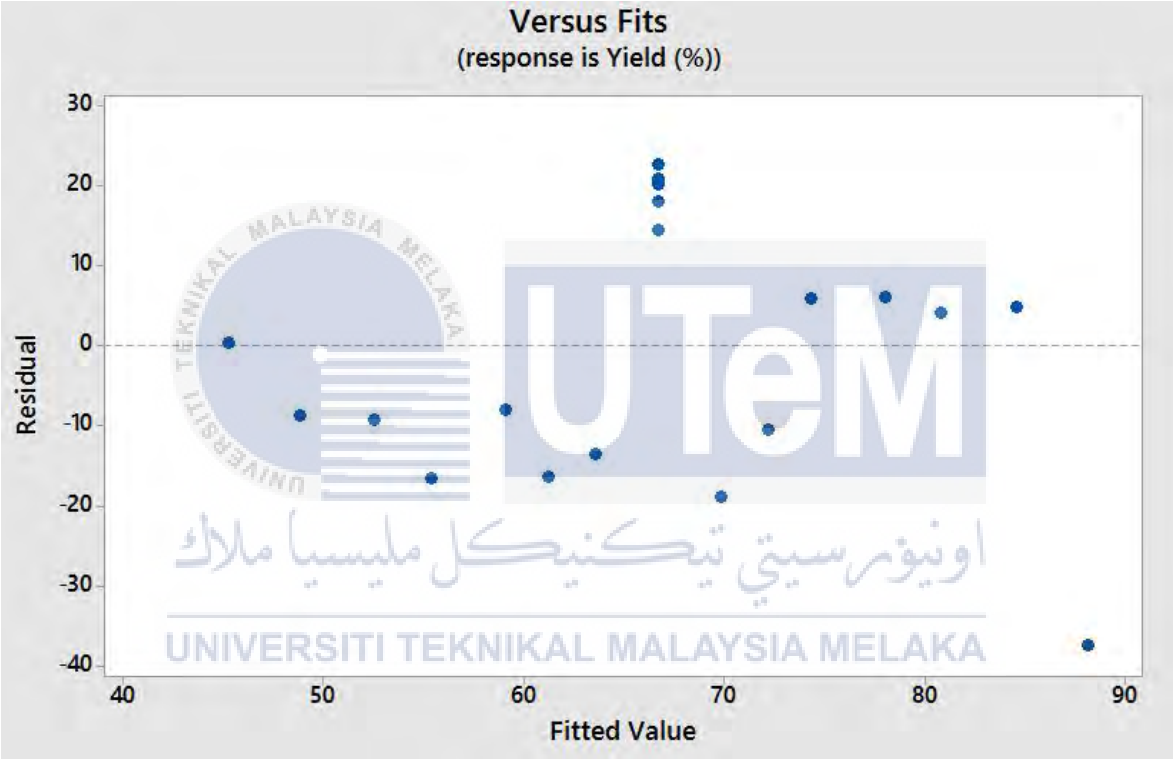

Figure 4.5 : Graph of residuals versus fits

Errors encountered during the experimentation process affect the result obtained and thus may cause misalignment from the most accurate representation of the fitted model. From Figure 4.7, it can be seen that result of the runs conducted does not scatter far away from the expected probability line for the residuals obtained. It shows a similar pattern of an increase in the value of residuals as the yield percent increase.

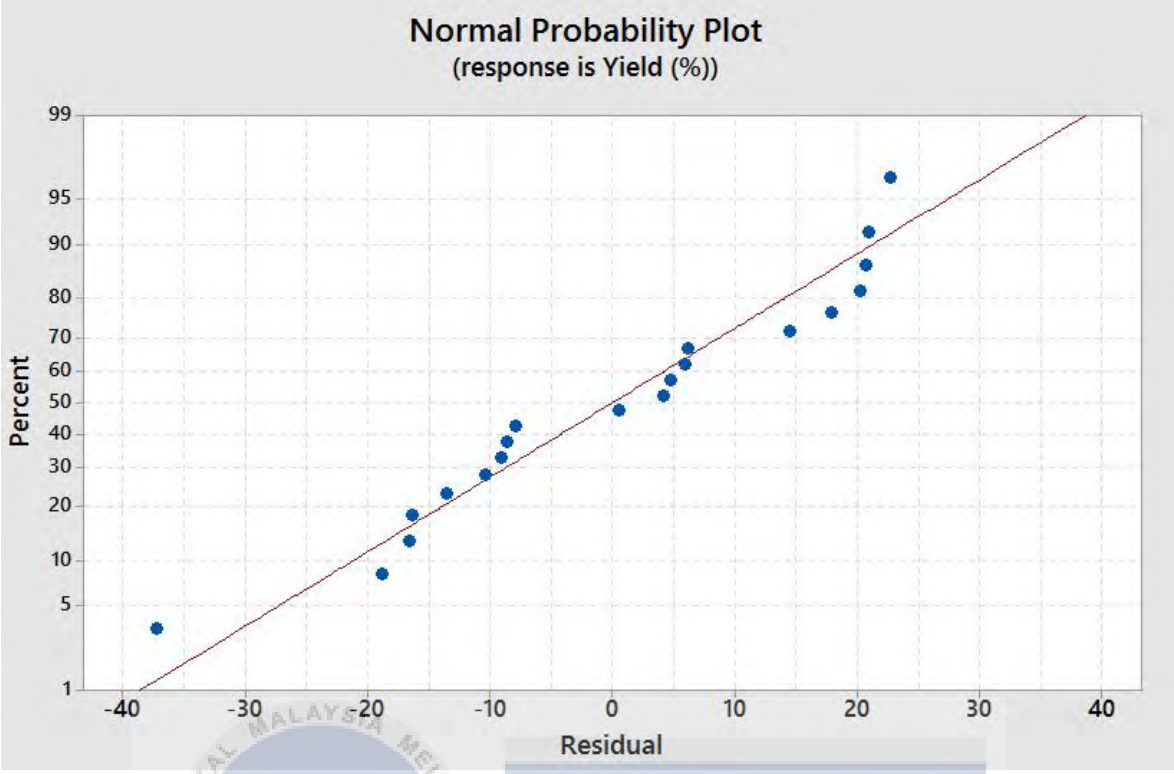

Figure 4.6 : Normal probability plot of yield

Figure 4.7 shows the probability plot for yield with a confidence interval set at 95 percent. Lower grouped runs are located around mostly at 40 % to 50 % while the higher grouped runs are located around mostly around 80 percent. The mean of all the runs is displayed as 66.7. The difference of the value of the lower and the higher runs can also be contributed to the difference set of washing done in the transesterification process.

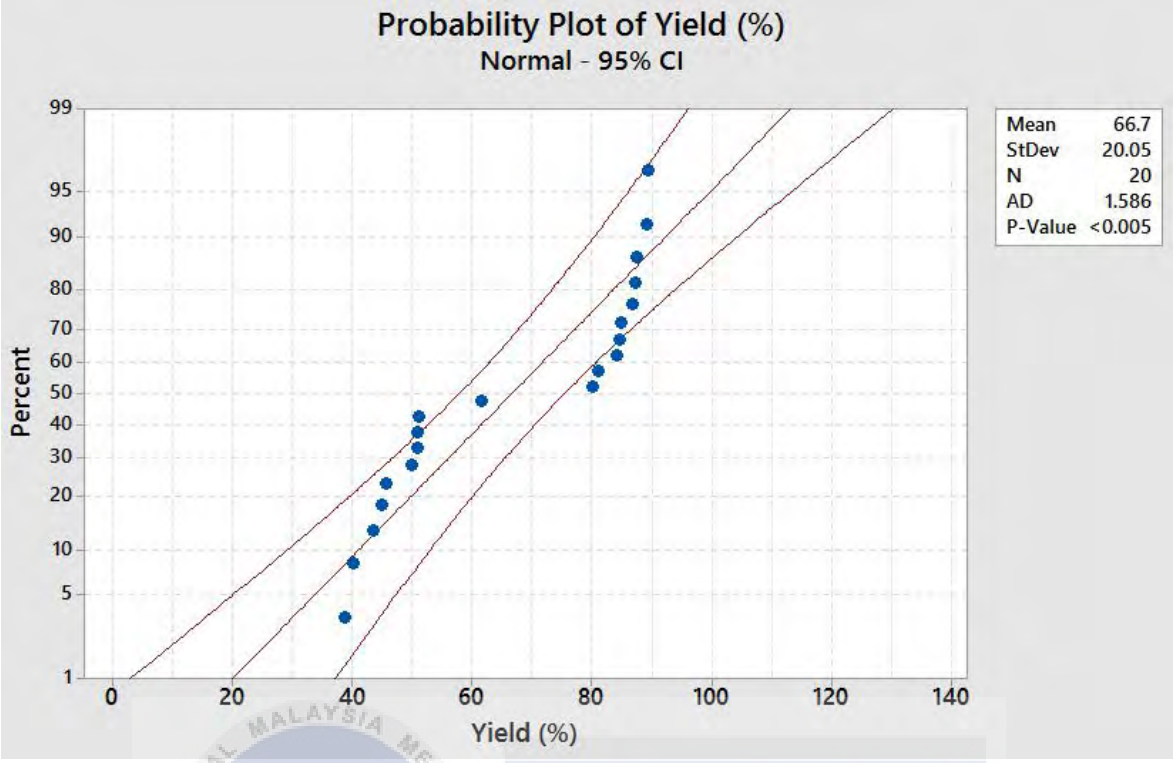

Figure 4.7 : Probability plot of yield

4.2 INFLUENCE OF PARAMETERS

4.2.1 Temperature of reaction

According to studies that have been cited in the literature review in Chapter 2, an effect of an increasing temperature of reaction in the transesterification process will cause an increase in the biodiesel yield as well. The increase of the yield will reach at the maximum percentage until a limiting value of the temperature which is the boiling point temperature of the methanol.

Further experiment conducted at temperature above the boiling point temperature of the methanol will cause a decrease in the biodiesel yield. For the result obtained in the transesterification experiment that has been done to obtain biodiesel, the result of the experiment is later analyzed using Response Surface Design in Minitab.

In the data analysis, it has been found out that temperature indeed has a positive influence on the yield. Figure 4.8 shows the relation of parameter A (which is temperature)

on the biodiesel yield. Through the figure, the results that have been obtained displayed similar trend and pattern throughout the study and the experiment.

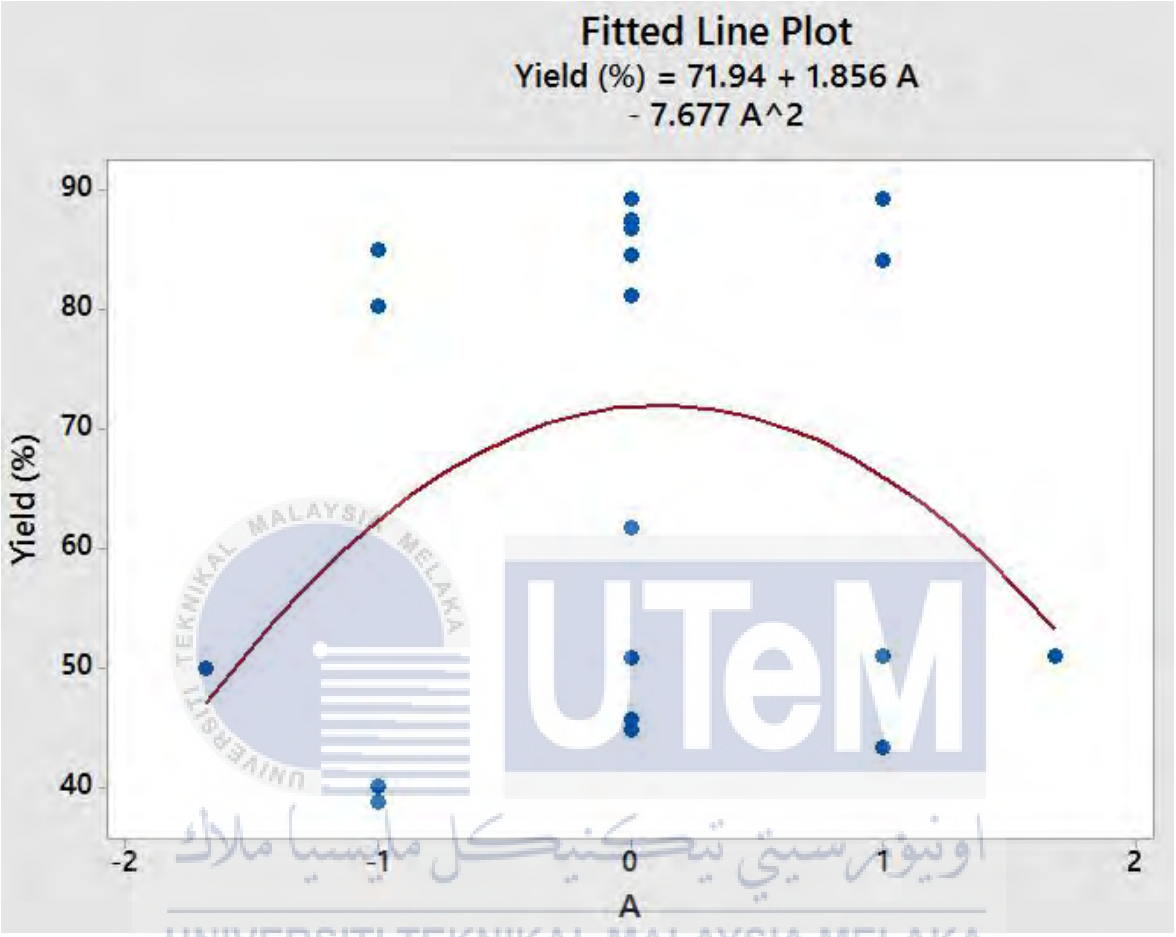

Figure 4.8 : Fitted line plot of yield against temperature

An increase in temperature will subsequently results in an increase in the biodiesel yield, but a maximum point is reached before the maximum coded level (α or 1.68) and the percent of yield start to decrease by then. Figure 4.9 displays graph concerning the probability plot of parameter A (temperature). Based on the figure, the set of runs conducted according to their design coded levels are randomized around the same percent and the percent increase accordingly with an increase in temperature used.

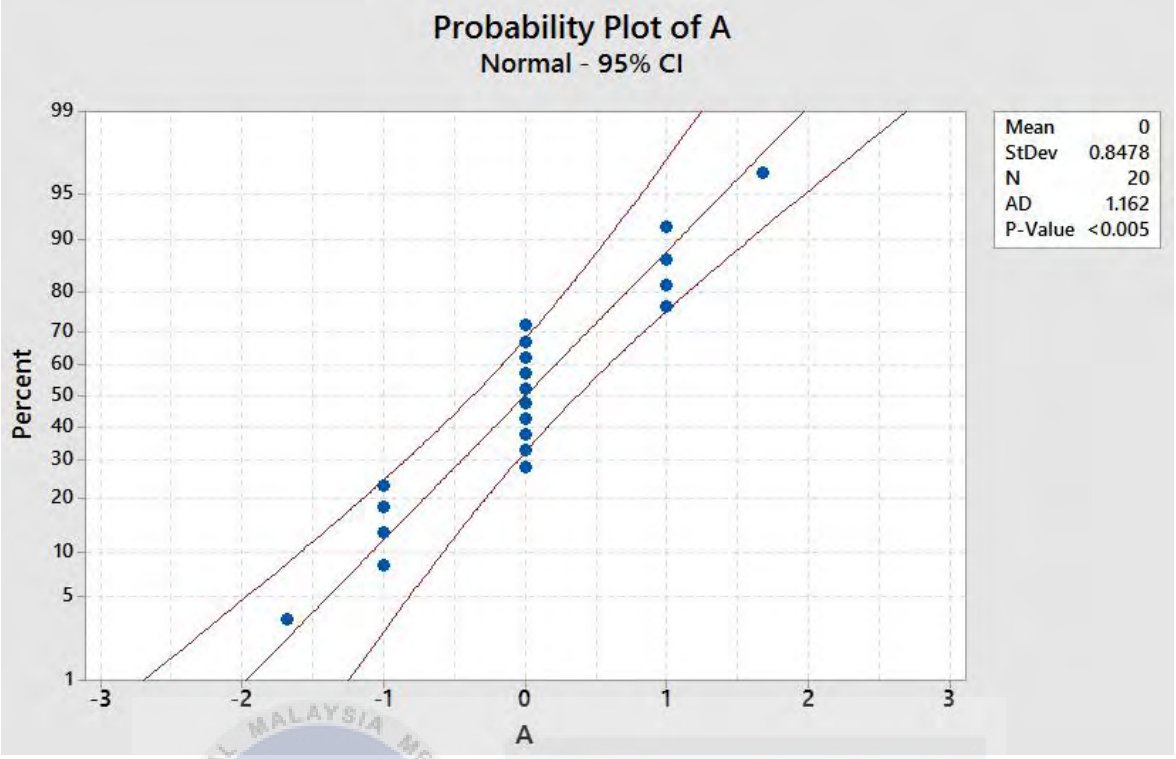

Figure 4.9 : Probability plot of temperature

4.2.2 Methanol to corn oil molar ratio

Based on previous studies and experiments cited in the literature review section, each of them shows a similar pattern throughout the output of the biodiesel yield in terms of the difference in alcohol-to-oil molar ratio. An increase in alcohol used for transesterification, for in this case, will cause an increase in biodiesel yield obtained nevertheless it does not pass the limiting value of the boiling point of methanol, which is 65.4 %. Temperature past the boiling point temperature, will cause the methanol to vaporize and less yield is expected as less alcohol is present to react with the used catalyst.

In this case, as it can be seen through Figure 4.10, which displays the fitted line plot of parameter B (methanol molar ratio), molar ratio at design level (-1.68 or α) increases and slowly declining at (0), and eventually decreases at a steady rate at the final level which at design level (1.68 or α). Thus, it can be concluded from the analysis of data that methanol concentration to oil weight has a negative influence on the biodiesel yield, in this case.

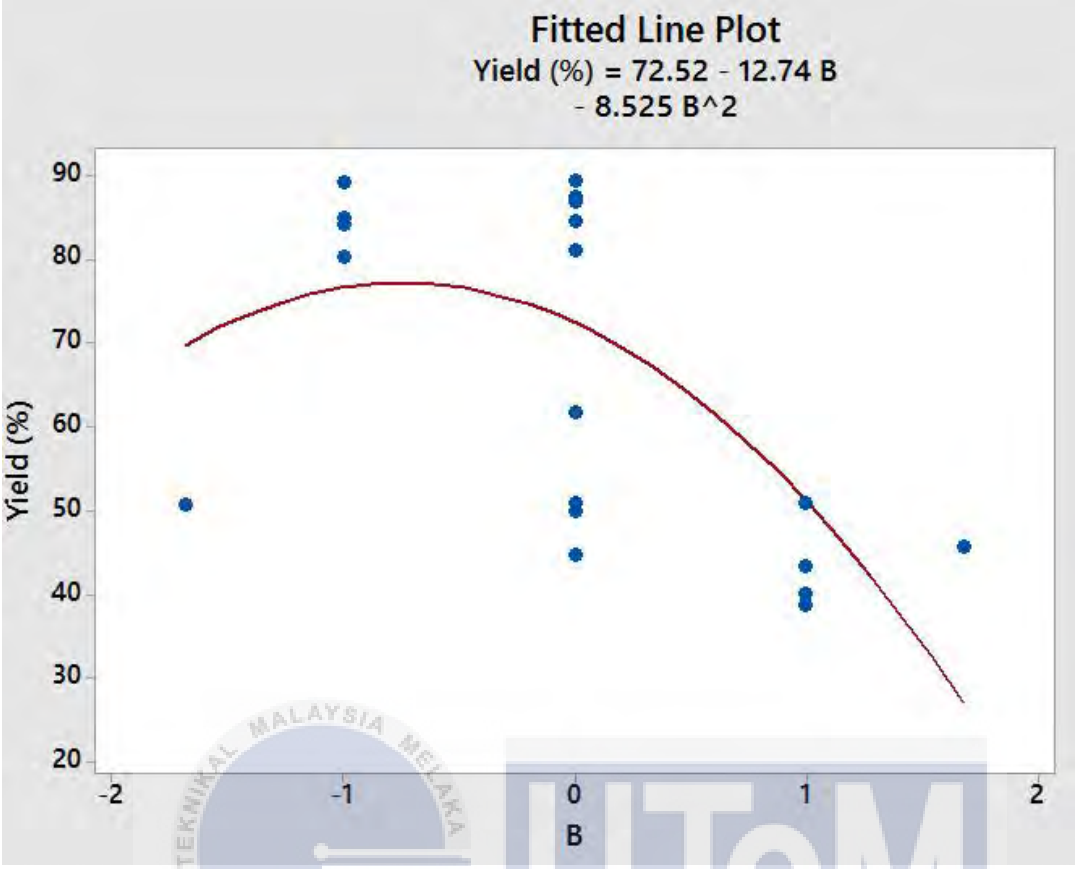

Figure 4.10 : Fitted line plot of yield against alcohol molar ratio

The probability plot of parameter B (methanol molar ratio) which is described in Figure 4.11 shows the trends of runs conducted according to their designated coded levels ranging from -1.68 to +1.68. As it can be seen through the graph, experiment that is operated on the same coded levels show almost similar percent and it increases accordingly from -1.68 to the maximum level at 1.68.

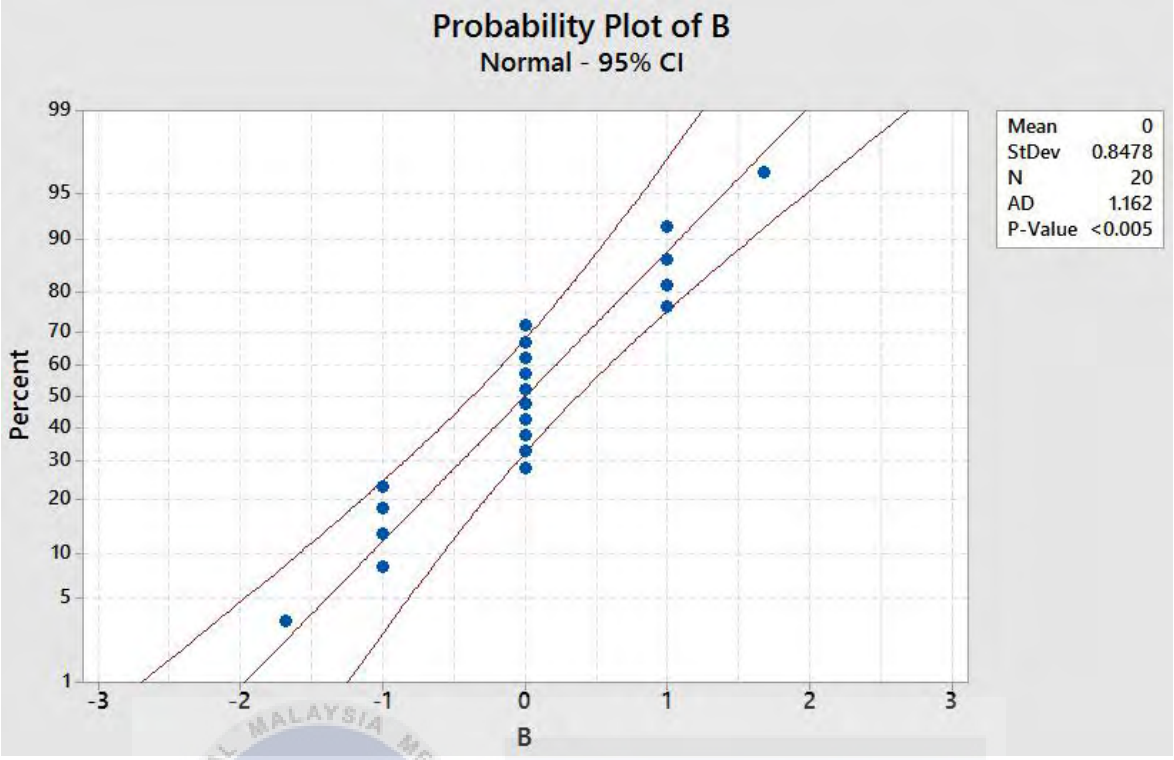

Figure 4.11 : Probability plot of alcohol molar ratio

4.2.3 Concentration of Potassium Hydroxide (KOH) (wt%)

Past studies that have been discussed in the literature review section has shown similar pattern and trends for the effects of catalyst loading on the biodiesel yield. Based on the researches done, an increment in catalyst concentration will cause an increment in the biodiesel yield simultaneously. However, once the optimum value has been achieved, the biodiesel yield will start to decrease as an increase in base catalyst in this case increases the risk of saponification and increases the content of soap.

In the data analysis, it has been found out that catalyst loading also has a positive influence on the yield based on the positive coefficient obtained from the regression plot. Figure 4.12 shows the relation of parameter C, indicating the catalyst concentration on the biodiesel yield. Through the figure, the results that have been obtained displayed similar trend and pattern and complies the nature of the past researches that has been done.

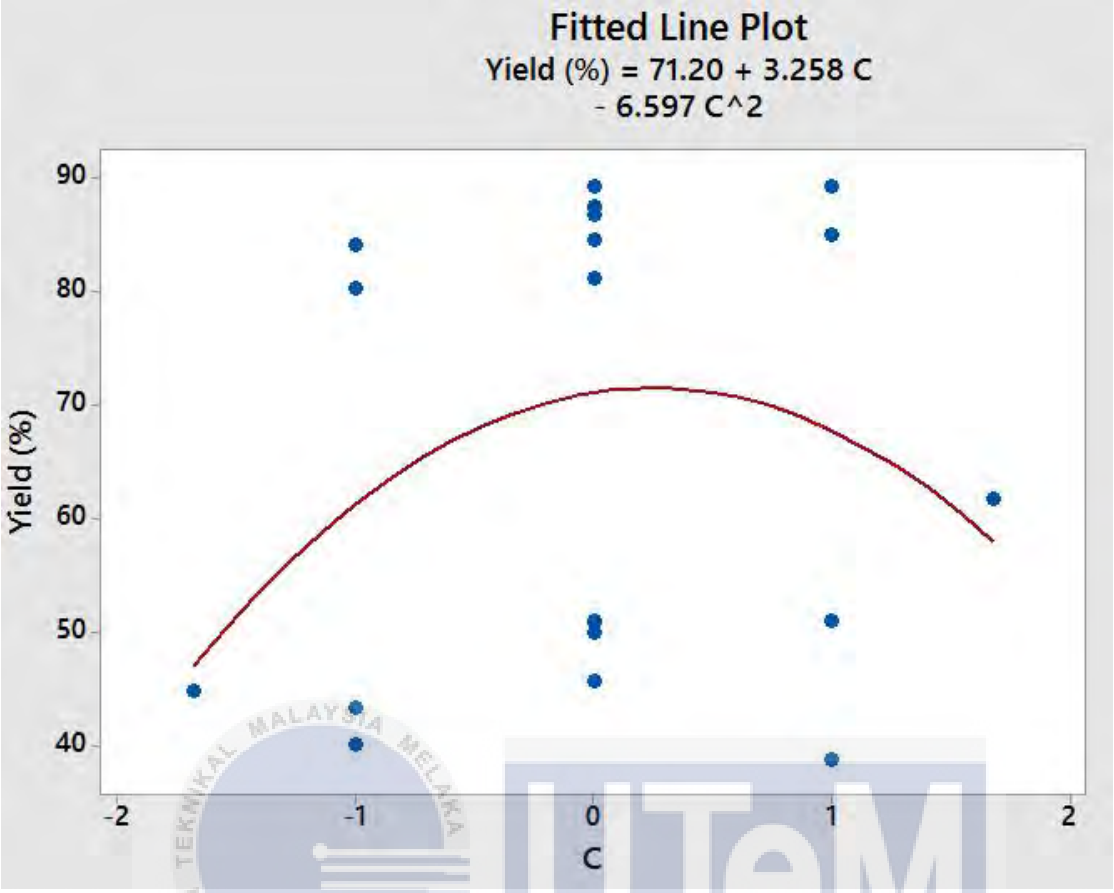

Figure 4.12 : Fitted line plot of yield against catalyst loading

From the graph plotted, it can be seen that amount of potassium hydroxide (KOH) used in the transesterification reaction has a positive impact and influence on the biodiesel yield. The relation increases linearly from -1.68 to value of almost 1 then it started to decrease again reaching the maximum coded level at 1.68. For the probability plot of data of parameter C (catalyst loading) shown in Figure 4.13, the groups of runs conducted at each of their designated levels show similar amount of percent and it increases accordingly along the increase of the designated parameters.

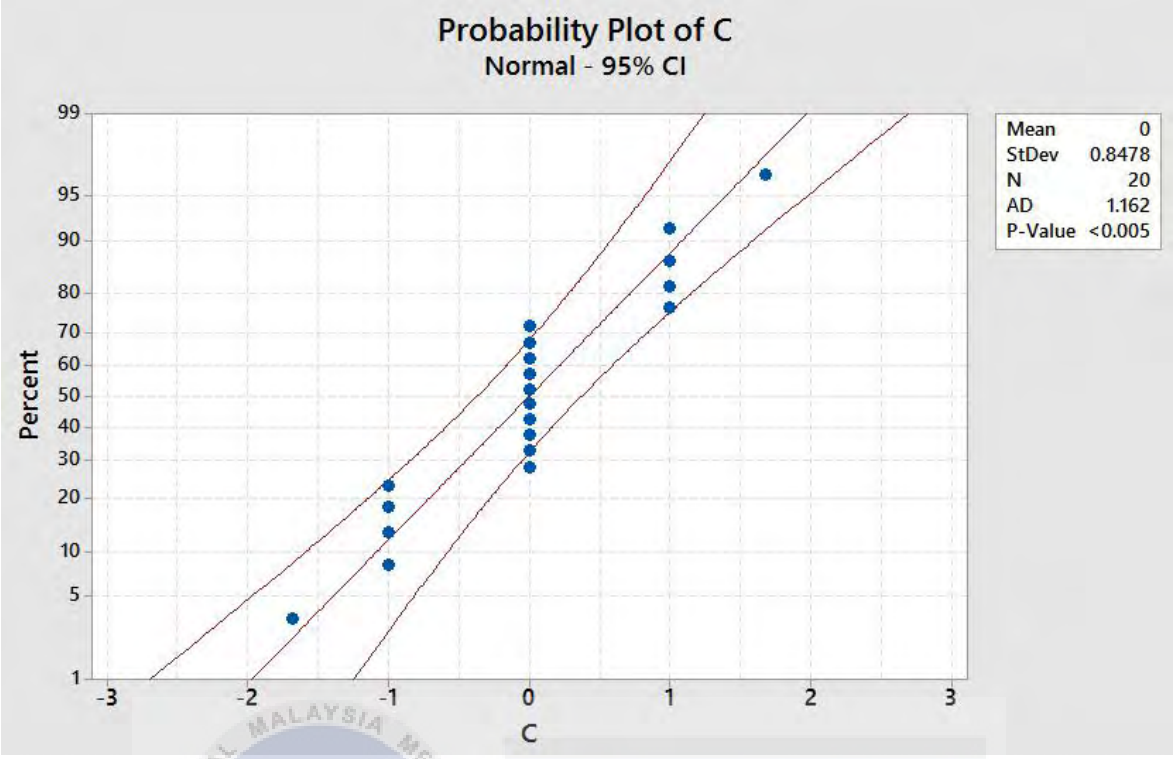

Figure 4.13 : Probability plot of catalyst loading

4.3 INTERACTION BETWEEN PARAMETERS

Besides studying each parameters significance on the biodiesel yield, from the regression model obtained, the relationship between parameters can also be studied. In the study, three variables has been chosen as the independent parameters which are temperature, methanol to oil molar ratio and catalyst concentration. In order to know the relationship between each of the pair parameters used, interaction plot such as described in Figure 4.14 has been plotted.

From the interaction plot in the figure, temperature (A)-alcohol molar ratio (B) has a similar bell-shaped relationship. With an increase in both temperature and alcohol molar ratio, an expected increase of biodiesel yield will be obtained for all design levels used. Similar can be said for the relationship between temperature (A) and catalyst loading (C), which also possess similar bell-shaped pattern in the interaction plot. A rise in temperature and catalyst loading will result in biodiesel yield. Both A-B and A-C show positive influence on the biodiesel yield.

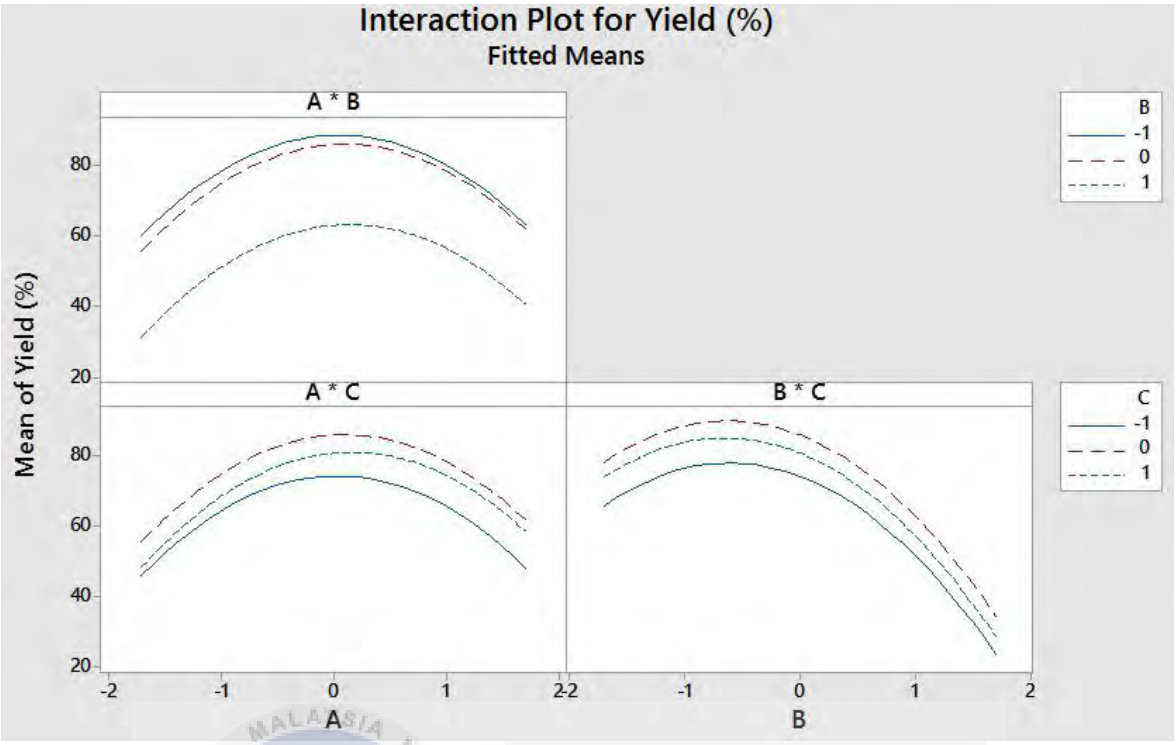

Figure 4.14 : Interaction plot of fitted means against experimental variables

However, for the relationship between alcohol molar ratio (B) and catalyst loading (C), the graph display different pattern in which from the smallest design coded levels, both parameters increase slightly and start to decrease linearly along the remaining design coded levels. From the coded coefficients obtained from the regression model simulated using response surface design, B-C indicates negative influence on the biodiesel yield. Thus, an increase on both the parameters first show slight increment, but overall decreases the output of the experiment.

Figure 4.15 displays the main effects of individual parameters A, B and C on the biodiesel output. In the figure, parameter temperature and parameter catalyst loading show similar bell-shaped pattern on the biodiesel output. An increase on both of these parameters will cause an increase in the biodiesel yield until it reaches the peak of the bell graph. Meanwhile, for parameter B, after a slight raise in the early designated levels, it shows a steady decline for the remaining higher coded levels.

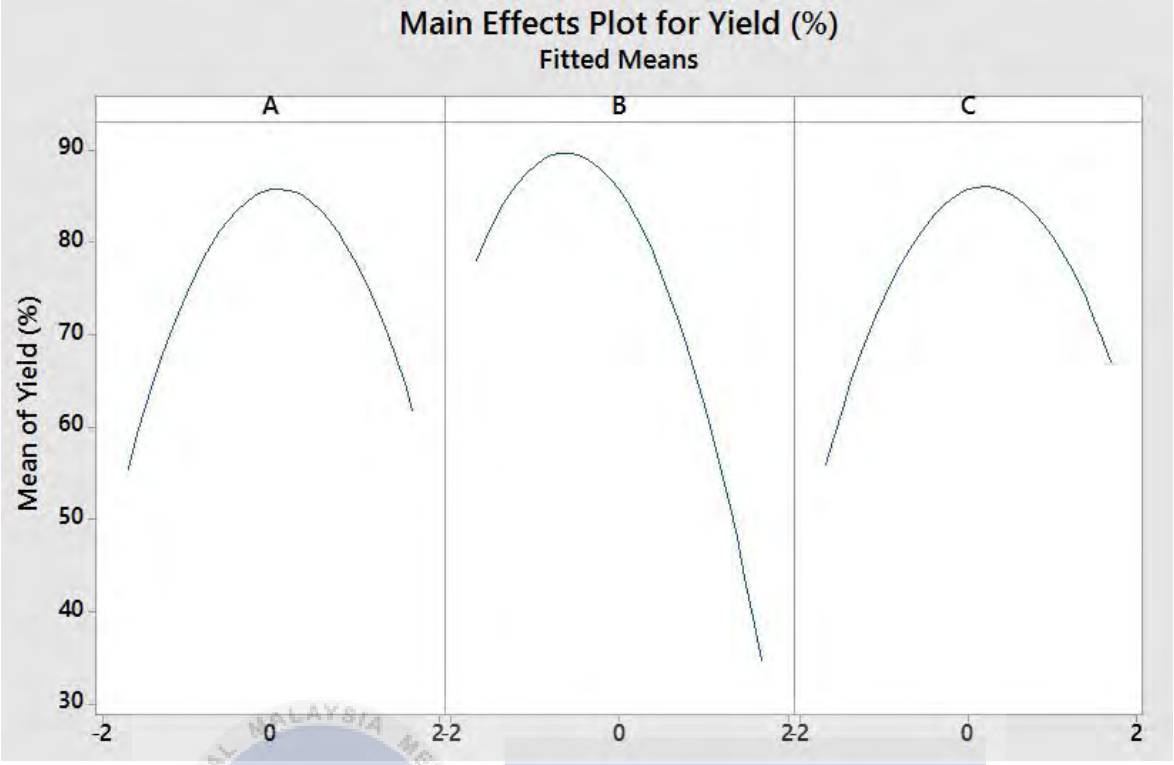

Figure 4.15 : Main effects plot for yield against experimental variables

To further emphasize on the relationship between parameter A (temperature) and parameter B (alcohol molar ratio), a contour plot of yield for both of the parameters has been plotted through the Figure 4.16. In the figure, maximum biodiesel yield which is indicated by area of dark green is obtained when temperature vary from -0.5 to 0.5 with alcohol molar ratio varying from coded levels at -1.5 to 0. Too high or too low of a temperature, along with a too high of alcohol molar ratio indicates less biodiesel yield.

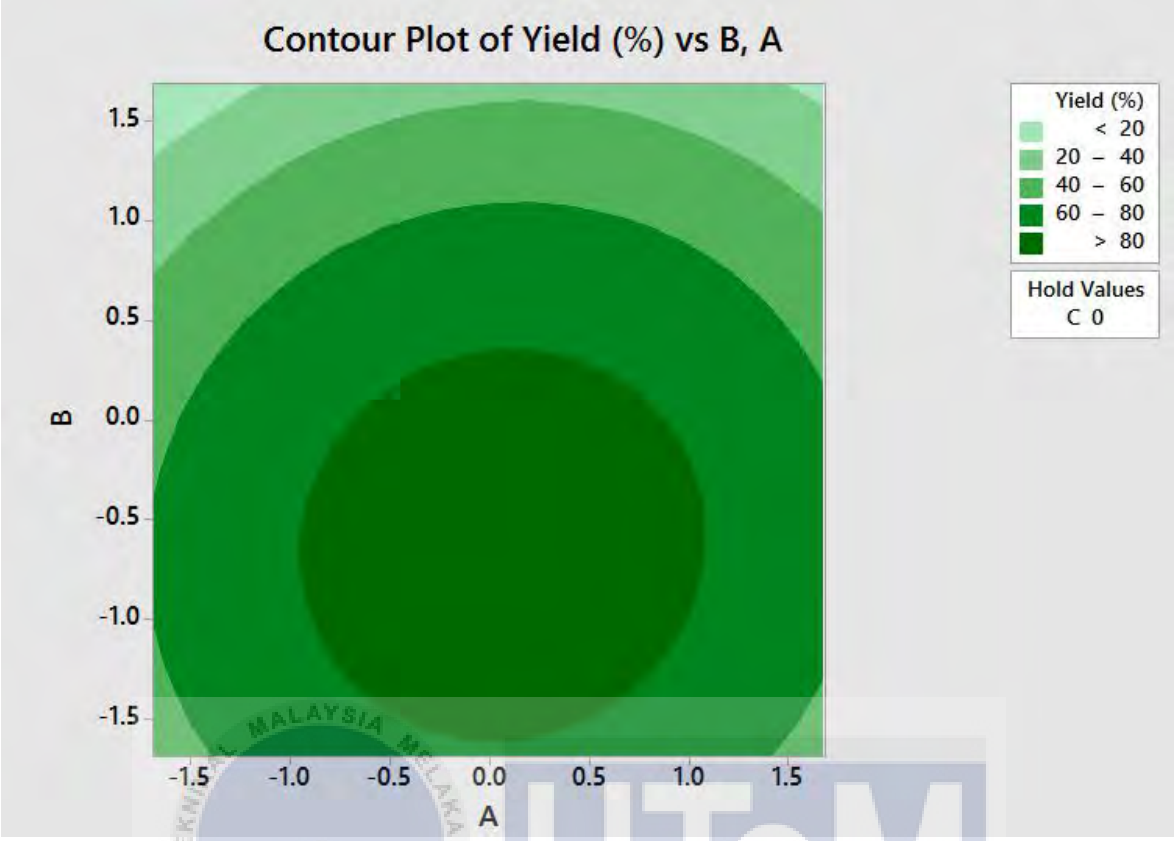

Figure 4.16 : Contour plot of yield versus temperature-alcohol molar ratio

For paired parameters of temperature (A) and catalyst loading (C), a contour plot of yield for both of the parameters has been plotted through the Figure 4.17. Through the contour plot obtained, maximum biodiesel which indicates 80% percent yield, is obtained when temperature vary from -0.5 to 0.5 with alcohol molar ratio varying from coded levels at -0.5 to 0. The area of large percent of biodiesel yield revolves mostly around the center points of the designated coded levels.

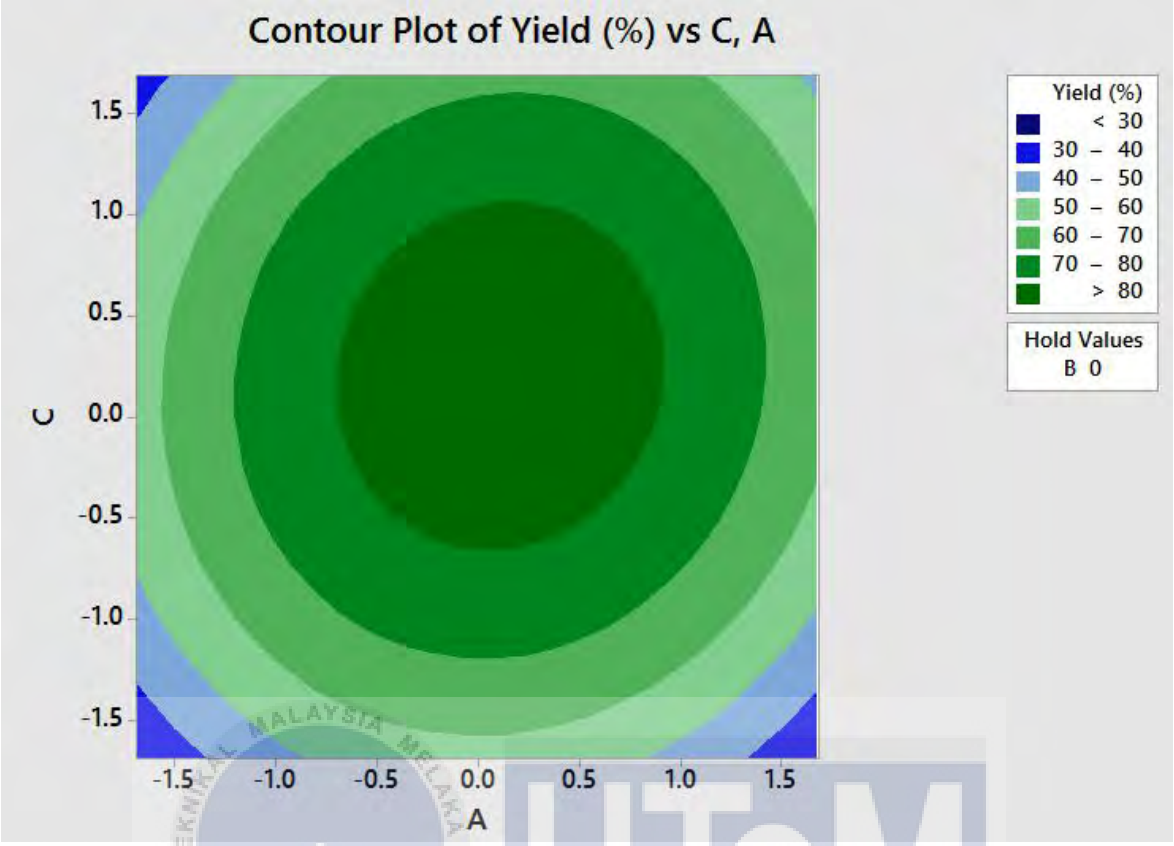

Figure 4.17 : Contour plot of yield versus temperature-catalyst loading

The relationship between parameter B (alcohol molar ratio) and also parameter C (catalyst concentration) can be summarized through the contour plot obtained in Figure 4.18. In the figure, maximum biodiesel yield is produced when alcohol molar ratio vary from -1.5 to 0 coded levels, and when catalyst loading vary from -0.5 to 1 design levels. Rise after design coded level 0 for parameter B produces less biodiesel yield with catalyst loading is most productive around the center points of the design levels.

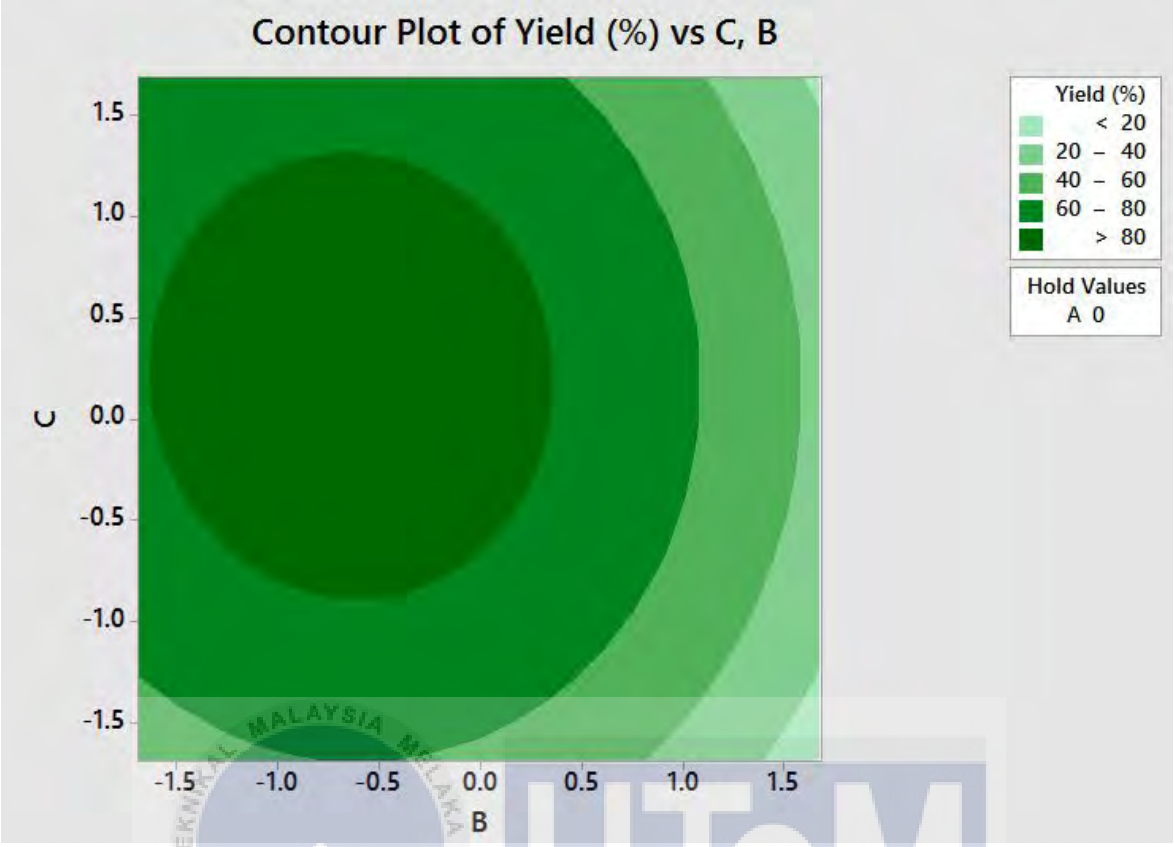

Figure 4.18 : Contour plot of yield versus alcohol molar ratio-catalyst loading

Besides contour graphs and plots that have been shown through the figures previously, 3D surface plot have been plotted to give further emphasize and insights into each paired parameters on the output of transesterification which is the biodiesel yield. In Figure 4.19, it can be seen that both temperature which is indicated by A and alcohol molar ratio symbolized by B, display similar bell-shaped graph in which they increase linearly and reaches the highest amount of yield at the middle part of the plot. After it passes the peak optimum value, it started to decrease linearly until it reaches the maximum designated coded levels.

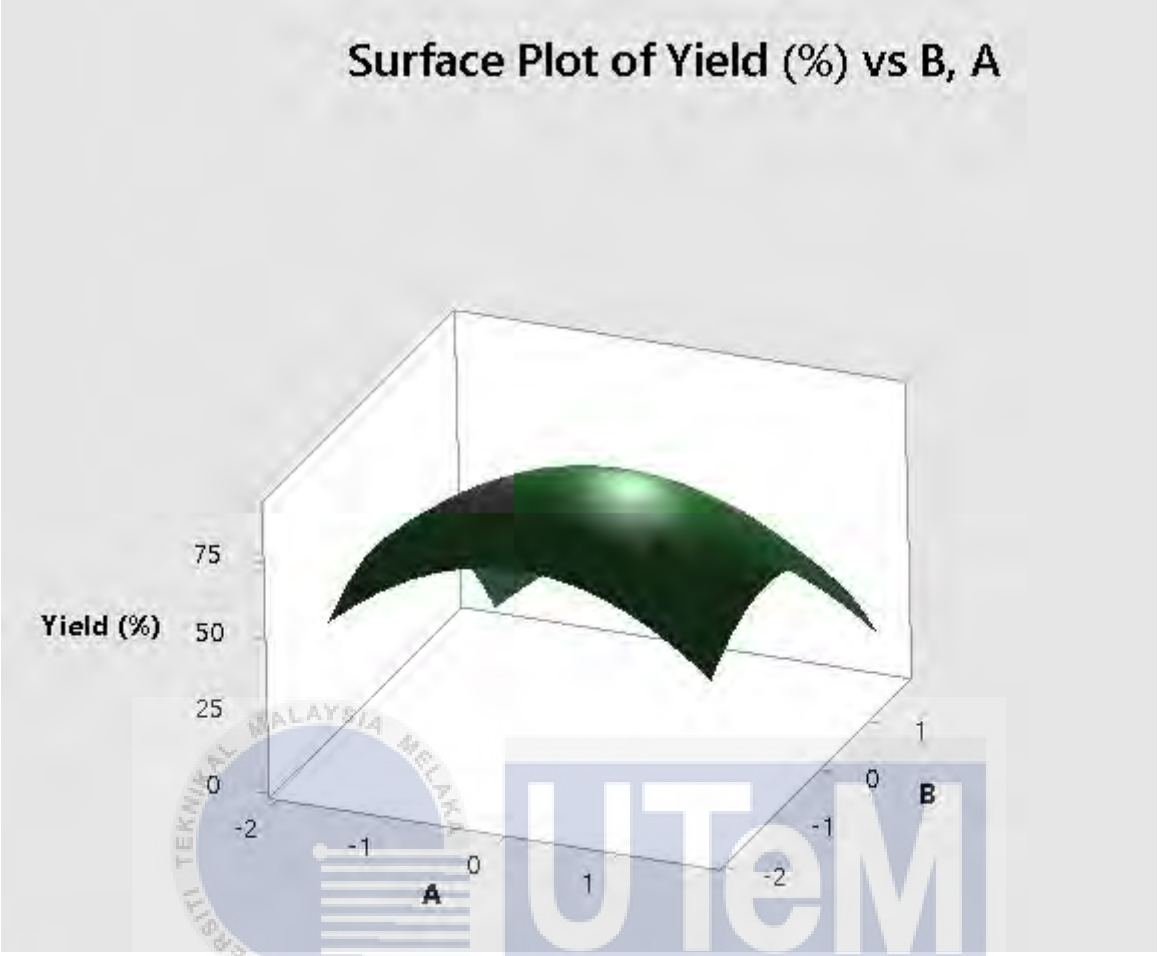

Figure 4.19 : Surface plot of yield versus temperature-alcohol molar ratio

For other paired parameters such as temperature (A) and catalyst concentration (C), 3D surface plot has also been simulated to portray the relationship between these two variables through the Figure 4.20. From the figure, both temperature and catalyst loading display similar trends as the paired parameters A-B although A-C contains steeper slope than in A-B.

Thus, an increase of temperature and an increase of catalyst concentration results in a more dramatic and bigger difference of biodiesel yield in comparison to A-B. Both variables will increase until a certain peak value, and past the peak value, the biodiesel yield start to decrease along the remaining coded levels.

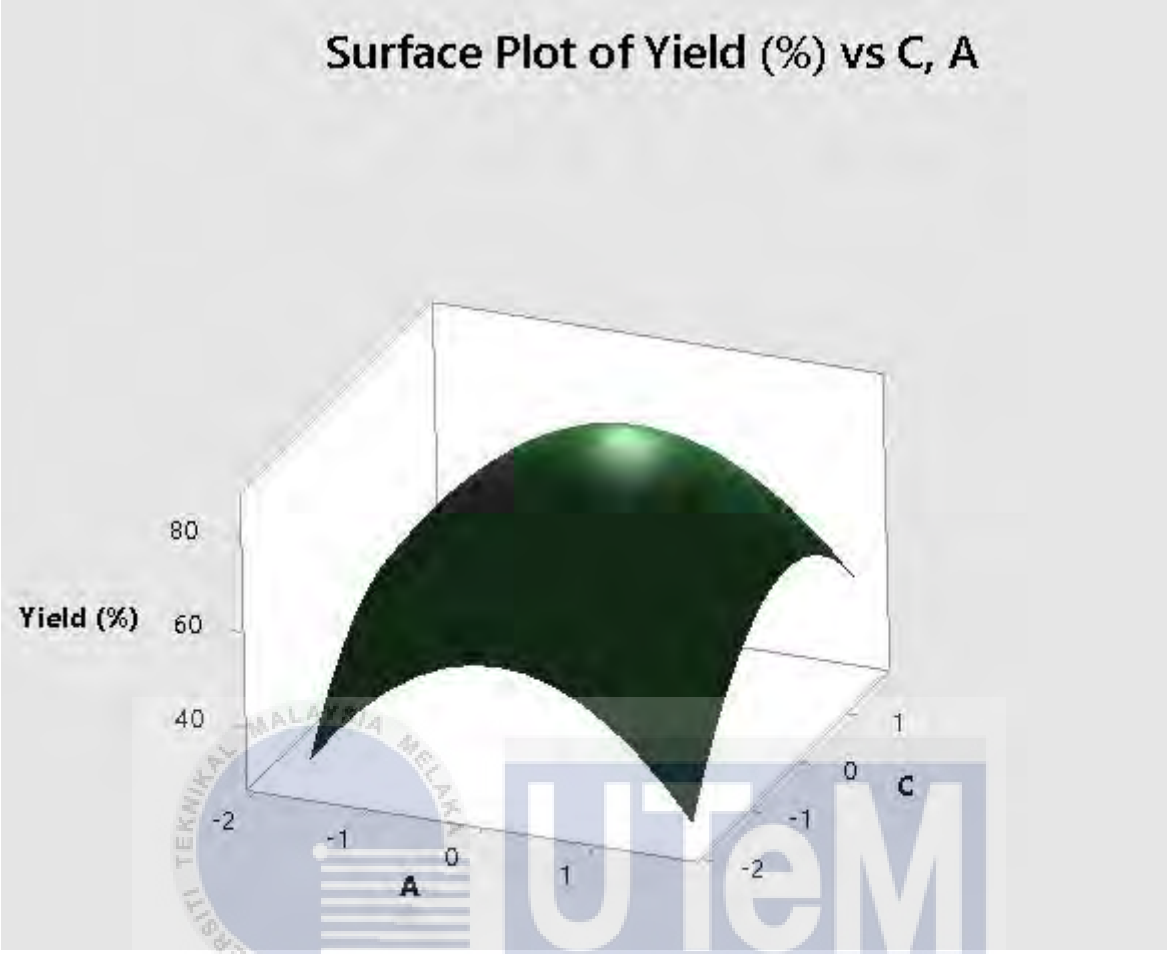

Figure 4.20 : Surface plot of yield against temperature-catalyst loading

Although, the same pattern for pairs of A-B and pairs of A-C for the paired parameters of B and C which consist of alcohol molar ratio and catalyst loading respectively. The relationship of B-C is shown here through surface plot in Figure 4.21, in which alcohol molar ratio mostly has a negative influence on the biodiesel yield, and only affects positively in the early stages of the coded levels.

Eventhough alcohol molar ratio has negative effect on the yield, but catalyst loading display otherwise in which an increase in catalyst concentration used will cause an increase in the output of methyl esters although it will only increase until it reaches a certain peak point in the graph.

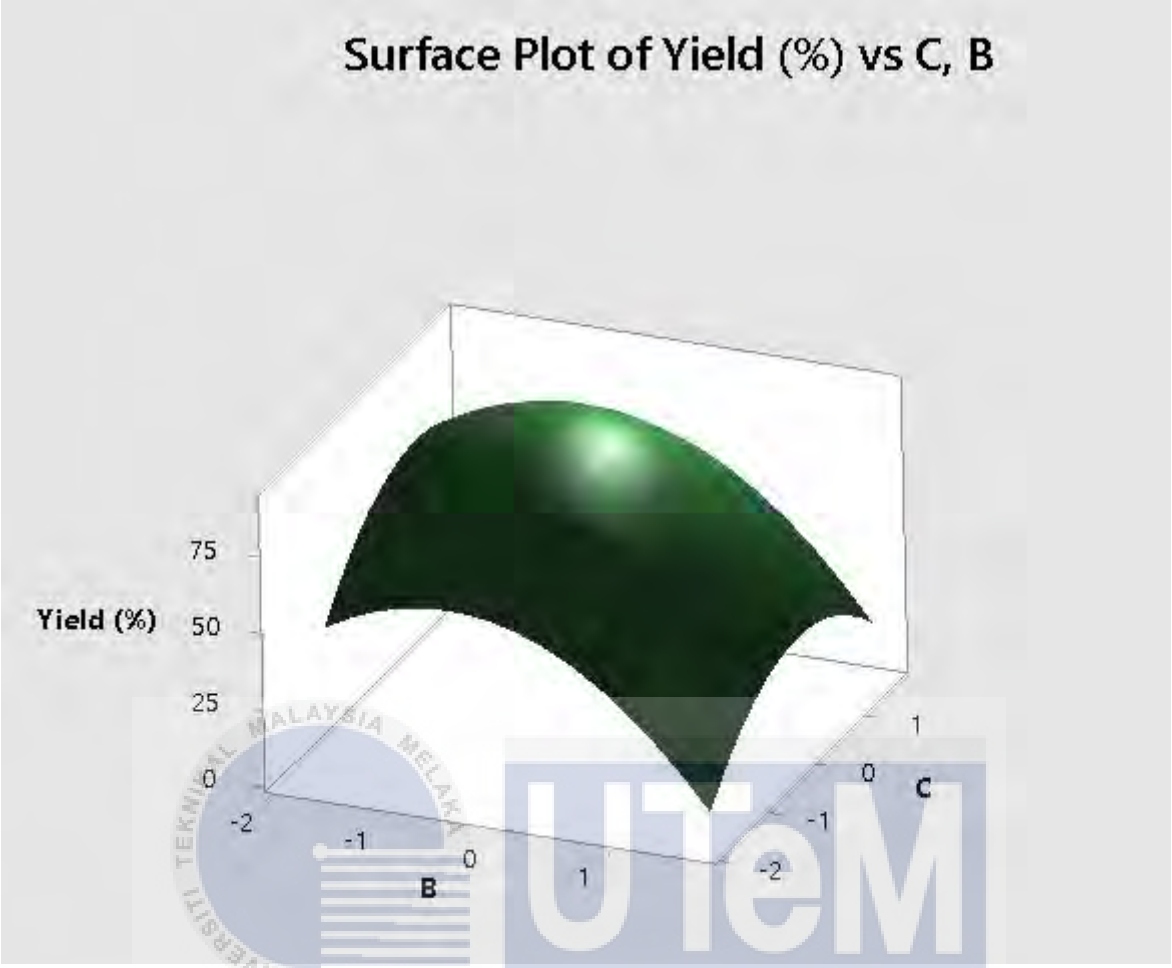

Figure 4.21 : Surface plot of yield against alcohol molar ratio-catalyst loading

4.4 OPTIMIZATION OF PARAMETERS

In obtaining the best design parameters based on the regression model and equation used, optimization option is used to establish the designated parameters (temperature, alcohol molar ratio and catalyst loading) to get the maximum biodiesel yield. Figure 4.22 depicts the condition of parameter along an increase in the design coded levels.

It can be seen through the graph plotted in the figure, the optimum values that is used to produce the maximum biodiesel yield. For parameter A which is the reaction temperature, the value of design coded level proposed is 0.085, for parameter B, alcohol to oil molar ratio shows the value of -0.629 and finally for parameter C which indicates the concentration of catalyst used, is 0.221.

Figure 4.22 : Design optimization plot

The parameters designed are first obtained through the optimization option, by setting the minimum value of the yield according to the result at 38.8 % and the highest value of the yield at 89.4 %. Through interpolation of the data, the parameters needed to produce the maximum biodiesel yield in terms of the regression equation are reaction temperature at 50.85ºC, 7:1 methanol to corn oil molar ratio and 0.722 wt% of potassium hydroxide (KOH) respectively.

Through the optimization plot, options can be chosen on whether to display how many solutions needed to optimize the regression equation to produce the maximum biodiesel yield. In Figure 4.23, three different solutions have been provided in optimizing the equation to obtain maximum methyl ester. However, only option 1 will be chosen as it produces the highest amount of expected yield which is 90.15 %.

Parameters

Response	Goal	Lower	Target	Upper	Weight	Importance
Yield (%)	Maximum	38.8	89.4		1	1

Solutions

Solution	A	B	C	Yield (%) Fit	Composite Desirability
1	0.0849390	-0.628549	0.220841	90.1479	1.00000
2	0.878086	-1.07255	1.07238	76.8005	0.75100
3	1.38785	-1.47209	0.335265	66.1444	0.54040

Figure 4.23 : Provided solutions for optimization

4.5 PRESENCE OF ERRORS

In this study, large part of the project research revolves mainly around the experimental process of transesterification in obtaining the data of biodiesel yield for each designated runs. Thus, it is unavoidable for errors to not happen or occur during the experimental process of transesterification. As discussed in the results section, from the experimental data of yield obtained, a regression model has been simulated through response surface design.

However, the obtained regression model equation does not fully portray the regression line as it can be deciphered through the value of R-squared that is produced which is 72.73%. The residuals that are plotted against the fitted value also show randomized patterns between negative and positive values across the plot. This is all due to the experimental data that is obtained from the runs that had been conducted in the laboratory.

The errors that had most significant effect on the transesterication output in this case is the systematic errors and human errors. Systematic errors are present as all the available hot plate stirrer used in the laboratory had a problem with its thermostat. In this case, it affects the temperature that is needed to be constant throughout the 1 hour reaction time. Temperature does indeed have a significant effect on the biodiesel yield.

Temperature needed to be constant at 65^{o}C signified critical temperature, and in theory should produce the highest amount of biodiesel yield. However, the results display otherwise, run conducted at 65^{o}C produced one of the least yield among the 20 runs conducted. Maximum biodiesel yield can only be achieved at the critical temperature if the transesterification process is done in a tightly-close beaker and environment in avoiding the affecting variables present in the surrounding.

Besides that, one of the most contributing factors in deviating the results from achieving total 100% fitted regression plot is the washing process of biodiesel. As it can be seen, certain runs have been grouped first and washed accordingly at that time, and remaining runs are washed later. The second process of washing affects the biodiesel yield by a significant amount of value as it ranges from 38% to 61% compared to the higher values that are obtained during the first set of washing.

Improper and excessive washing process contributes to a larger amount of moisture content in the separatory funnel during the washing process. Separatory funnel should always be made sure to be dry in order moisture content does not affect the biodiesel yield. Moisture or water content in this case is highly reacted with methanol as chemical properties of methanol is hydrophilic, in which it reacts with water, and soluble in it. The base catalyst also has the same chemical properties, in which it is also hydrophilic.

Errors that cause the biodiesel yield to vary from one sets of wash to another sets are mainly caused by the human errors during the washing process of the biodiesel. Thus, toa improvise on the errors, heating of biodiesel should have been done to remove the moisture content to obtain better yield of biodiesel. Other than that, the transesterification process is a highly meticulous that needed crucial amount of details especially through the amount of methanol and catalyst to be used.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

As an overall, after successfully completing all the different chapters leading up to this final chapter, transesterification is indeed an easy, convenient and cheap way of producing raw biodiesel. Parameters such as temperature, alcohol molar ratio, catalyst loading, reaction time and also stirring rate act as independent parameters and display different significance that may atrribute towards the output of the transesterification process, which is the biodiesel yield.

Objectives of the project, which was to apply the use of transesterification process in making biodiesel and also to optimize the involved parameters which in this case, the temperature, methanol molar ratio and concentration of potassium hydroxide (KOH) through the use of response surface design method have also been realized. Through the experimental process, 20 runs have been conducted with the designed coded levels of parameters, and a simulated response surface design has been used to analyze and optimize the resultant biodiesel from the experimental runs.

The quadratic regression model obtained through RSM displayed different influence of the parameters based on the coded coefficients obtained through the analysis of variance. In summary, alcohol molar ratio plays the most significant part in the biodiesel yield, as errors occuring during the washing process affect the output of the data. Catalyst loading plays the second most influential parameter in the study followed eventually by temperature.

Temperature often show the biggest influence based on the studies that had been done by the past researches. However, as systematic errors involving the apparatus are present during the experimentation, in which thermostat are not working functionally, temperature had to be adjusted manually in the experimentation process thus random flunctuations of temperature kept affecting the result of the transesterification experiment. Thus, in this case temperature show the least effect on the regression model obtained.

The relationship between parameters and variables involved also show similar patterns or trends in which for A-B and A-C, both parameters tend to increase until a certain peak value of the bell shaped graph has been achieved. However, the same cannot be said for paired B-C, in which they have a slight rise in the early stage of the design coded levels, and started to decline on a steady pace reaching the higher value of the design levels.

Thus, for reference for future work to be done, errors whether caused by apparatus or human, should be avoided at all costs as they do affect the result of the data. Inaccuracy of the data produces less accurate regression model, and it is harder to analyze the response surface design simulated as it does not really portray the regression plot obtained. The output of the biodiesel yield in overall also influence the optimization process of the parameters to produce the maximum biodiesel yield.

In summary, the optimized parameters for the virgin Mazola corn oil that is used for the study to produce the largest biodiesel yield are 50.85^{o}C, 7:1 methanol to oil molar ratio with 0.722 wt% concentration of potassium hydroxide (KOH). Different brand of virgin corn oil may need different set of parameters depending on the nutrition content of the oil itself. Eventhough, corn oil is still an unfamiliar oil to be used for the production of biodiesel, it is hoped that from this study, an insight and a detailed analysis on the production of biodiesel using the edible vegetable oil, which is corn for future references.

REFERENCES

A. Demirbas, Biodiesel from vegetable oils via transesterification in supercritical methanol, Energ. Convers. Manage. **43** (2002) 2349–2356.

Abbah.E.C., Nwandikom G.I., Egwuonwu C.C., Nwakuba N.R. Effectof Reaction Temperature on the Yield of Biodiesel From Neem Seed Oil. American Journal of Energy Science. Vol. 3, No.3, 2016, pp. 16-20.

Agensi Innovasi Malaysia. National Biomass Strategy 2020: New Wealth Creation for Malaysia's Biomass Industry; AIM: Selangor, Malaysia, 2013.

Ahmad.M, Rashid.S, Khan.A.M, Zafar.M, Sultana.S, Gulzar.S, 2008. African Journal of Biotechnology Vol. 8 (3), pp. 441-446, 4 February, 2009.

Ambika Rajendran. R, Nirupma Singh, Vinay Mahajan, D.P. Chaudhary, Sapna & R. Sai Kumar. Corn Oil: An emerging industrial product. 2012. Directorate of Maize Research, New Delhi, *Technical Bulletin*, No. 8: 36 p.

Amita.N & Susan.J. A Study on Castor Oil and Its Conversion into Biodiesel by Transesterification Method. *Nepal Journal of Science and Technology Vol. 15, No.1 (2014) 45-52*

Anjana Srivastava, Ram Prasad, "Triglycerides –Based Diesel fuels", Renewable and sustainable energy reviews (2002).Pp.111-133.

Barnwal. B.K, M.P.Sharma, "Prospect of Biodiesel Production from vegetable oil in India", Renewable and sustainable energy reviews (2004) Pp. 238-246.

Bas, D. & Boyacl, I.H. 2007. Modeling and optimization I: Usability of response surface methodology. *Journal of Food Engineering* 78: 836-845.

Bandger B P, Uppalla L S and Sadavarte V S, *Green Chem.,* 2001, **3**, 39-41.

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S. & Escaleira, L.A. 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* 76: 965-977.

Box, G.E.P.; Norman, R.D. *Empirical Model-Building and Response Surfaces*; Wiley: Hoboken, NJ, USA, 1987; p. 424.

Canakci M and Van Garpen J, *Trans ASAE*, 1999, **42(5),** 1203-1210.

Canakci M and Van Garpen J, *Trans ASAE*, 2001a , **44(6),** 1429-1436.

Carter D., Darby D., Hallé J., Hunt P. (2005), *How to make biodiesel*, Milton Keynes, Great Britain: Lightening Source. ISBN: 0-9549171-0-3.

Chong, C.; Ni, W.; Ma, L.; Liu, P.; Li, Z. The Use of Energy in Malaysia: Tracing Energy Flows from Primary Source to End Use. Energies 2015, 8, 2828-2866.

Crabba E, Nolasco-Hipolito C, Kobayashi G, Sonomoto K and Ishizaki A, Biodiesel Production from Crude Palm Oil and Evaluation of Butanol Extraction and Fuel Properties, Process Biochemistry, 2001, **37(1),** 67-71; DOI: 10.1016/S0032-9592(01)00178-9.

Demirbas A. (2008), *Biodiesel: A realistic fuel alternative for diesel engines,* London, Great Britain: Springer. ISBN: 978-1-84628-994-1.

Demirbaş A (2003). Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. Energy Conv. Manage., 44: 2093-2109.

Dennis Y.C. Leung, Xuan Wu, M.K.H. Leung, *A review on biodiesel production using catalyzed transesterification*, Applied Energy 87 (2010), 1083-1095.

Economics and Industry Development Division of Malaysian Palm Oil Board, Overview of the Malaysian Oil Palm Industry. Available online:

http://bepi.mpob.gov.my/imagesoverview/Overview_of_Industry_2013.pdf (accessed on 18 October 2016).

Ejikeme P M, *J Chem Soc Nigeria,* 2008, **33(1),** 145-149.

F.M Kilonzi, A. Kumar, S. S. Namango, H.K Kiriamiti & D.K Some. *Optimization of Transesterification of Sunflower Oil with Ethanol using Eggshell as Heterogeneous Catalyst*, 2015.

Akhtar. F.H, Yasir A. Elsheikh, M. Bassyouni, Monazza Kaukab, Ayyaz Muhammad, Nadeem Feroze, An alkali catalyzed transesterification of rice bran, cottonseed and waste cooking oil, *Hem. Ind.* **68** (3) 347–355 (2014).

Fangrui, M.; Milford, A. Hannab, Biodiesel production: A review. *Bioresource Technol*. **1999**, *70*, 1-15.

Freedman B, Butterfield R O and Pryde E H, *J Am Oil Chem Soc.,* 1986, **63**, 1375.

Freedman B, Pryde E H and Mounts T L, *J Am Oil Chem Soc.,* 1984, **61(10)**, 1638-1643.

Feuge, R. O. & Gros, A. T., 1949. Modification of Vegetable Oils. VI. Alkali Catalyzed Interesterification of Peanut Oil with Ethanol. *Journal of the American Oil Chemists Society ,* 26(3), pp. 97-102.

Fukuda H, Kondo S, Noda H. Biodiesel fuel production by transesterification of oils. J Biosci Bioeng 2001;92(5):405–16.

G. Knothe, J. Krahl, J. Van Gerpen (Eds.): *The Biodiesel Handbook*. AOCS Press, Champaign, IL (USA) 2005.

G.Kumar, D. Kumar, Shailandra.S, S. Kothari, Sumit.B & Chandra.P.S. Continuous Low Cost Transesterification Process for the Production of Coconut Biodiesel. *Energies **2010**, 3, 43-56; doi:10.3390/en3010043*

Dodos. G.S, V.Perdiou, F.Zannikos, 2009. Effect of Biodiesel in the Microbiological Growth in the Diesel Fuel Supply Chain, 7th Pan-Hellenic Scientific Conference on Chemical Engineering,Patras, Greece.

Gregory, Jamie A., "Thermal Conversion of Triglycerides of Vegetable Oil for Production of Renewable Lamp Fuel" (2015). *Electronic Thesis and Dissertation Repository.* Paper 2786.

Griffin, W.; Michalek, J.; Matthews, H.; Hassan, M. Availability of Biomass Residues for Co-Firing in Peninsular Malaysia: Implications for Cost and GHG Emissions in the Electricity Sector. Energies 2014, 7, 804–823.

Hossain ABMS, Aishah S, Boyce AN, Salleh A, Chandran S (2010). Impacts of alcohol type, ratio and stirring time on the biodiesel production from waste canola oil. *African Journal of Agricultural Research Vol. 5(14), pp. 1851-1859, 18 July, 2010*

Jagadale S. S., Jugulkar L. M. Review of Various Reaction Parameters and Other Factors Affecting on Production of Chicken Fat Based Biodiesel. *Vol.2, Issue.2, Mar-Apr 2012 pp-407-411.*

Khuri.A Mukhopadhyay.S. John Wiley & Sons, Inc. WIREs Comp Stat 2010, 2, 128–149, March/April, 2010.

Knothe G, Dunn R O and Bagby M O "Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels" in Fuels and Chemicals from Biomass, ACS**,** Washington**,** DC, USA,1997, 172–208

Kuo, P.-C.;Wu,W. Design, Optimization and Energetic Efficiency of Producing Hydrogen-Rich Gas from Biomass Steam Gasification. Energies 2014, 8, 94–110.

L. Meher, D.V. Sagar, S. Naik, Technical aspects of biodiesel production by transesterification – a review, Renew. Sust. Energ. Rev. **10** (2006) 248–268.

Liu CH, Huang CC, Wang YW, Lee DJ, Chang JS. Biodiesel production by enzymatic transesterification catalyzed by *Burkholderia* lipase immobilized on hydrophobic magnetic particles. *Appl Energ*. 2012, 100:41-46.

M.J. Ramos et. al (2008). Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*, no.100, pp. 261-268

Ma F, Hanna MA (1999). Biodiesel production: a review. Biores. Technol., 70:1-15.
M. Canakci and J. H. Van Gerpen, "Biodiesel production from oils and fats with high free fatty acids," *Transactions of the American Society of Agricultural Engineers*, vol. 44, no. 6, pp. 1429–1436, 2001.

Mansourpoor M, Shariati A (2012) Optimization of Biodiesel Production from Sunflower Oil Using Response Surface Methodology. J Chem Eng Process Technol 3:141. doi:10.4172/2157-7048.1000141

Mathiyazhagan, M., Ganapathi, A., Jaganath, B., Renganayaki, N. And Sasireka, N. (2011). "Production of biodiesel from non-edible plant oils having high FFA content" *International Journal of Chemical and Environmental Engineering. 2:119-122.*

Mekhilef, S.; Saidur, R.; Safaria, A.; Mustaffaa, W.E.S.B. Biomass energy in Malaysia: Current state and prospects. Renew. Sustain. Energy Rev. 2011, 15, 3360–3370.

Mittlebach, M. Worgetter M., Pernkopf J., Junek H., *Energ. Agr*., 2, 369–384 (1983).
National Biofuel Policy. Available online: http://www.greentechmalaysia.my/Pages/ pages.aspx?View=GreenBiofuel (accessed on 24 November 2014).

Montgomery, D.C. *Design and Analysis of Experiments: Response Surface Method and Designs*; John Wiley and Sons, Inc.: Hoboken, NJ, USA, 2005.

N.Dizge, B. Keskinler, Enzymatic production of biodiesel from canola oil using immobilized lipase. Biomass and Bioenergy, 32 (2008), pag. 1274.

Osman, Z.: 'Renewable Energy Development in Malaysia', Universiti Tenaga Nasional, 2006.

Paintsil, Arnold, "Optimisation of the Transesterification Stage of Biodiesel Production using statistical methods" (2013). *Electronic Thesis and Dissertation Repository.* Paper 1693.

Ramadhas, A.S.; Jayaraj, S.; Muraleedharan, C. Use of vegetable oils as C.I. engine fuels: A Review. *Renewable Energy* **2004**, *29*, 727-742.

S.A.Basha, K.R.Gopal, S.Jebaraj, 2009. A review on biodiesel production, combustion, emissions and performance, Renewable and Sustainable Energy Reviews, 13, 1628–1634.

S. Hama, H. Yamaji, M. Kaieda, M. Oda, A. Kondo, and H. Fukuda, "Effect of fatty acid membrane composition on wholecell biocatalysts for biodiesel-fuel production," *Biochemical Engineering Journal*, vol. 21, no. 2, pp. 155–160, 2004.
Sasidharan A and Kumar R, *J Mol Catal A Chem.,* 2004, **210**, 93-98.

Sarin, R.; Sharma, M. Jatropha palm biodiesel blends: An optimum mix for Asia. *Fuel* **2007**, *86*, 1365-1371.

Sengupta A, Pal M, SilRoy S, Ghosh M. Comparative Study of Sterol Ester Synthesis using *Thermomyces lanuginosus* Lipase in Stirred Tank and Packed-Bed Bioreactors. *J Am Oil Chem Soc*. 2010; 87(9): 1019- 1025.

Ting WJ, Huang CM, Giridhar N, Wu WT. An enzymatic/acid-catalyzed hybrid process for biodiesel production from soybean oil. *J Chin Inst Chem Eng*. 2008; 39: 203-210.

Umar, M.S.; Jennings, P.; Urmee, T. Generating renewable energy from oil palm biomass in Malaysia:2008 The Feed-in Tariff policy framework. Biomass Bioenergy 2014, 62, 37–46.

Verma, M. N. and G. Madras. 2007. Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids. *Industrial & Engineering chemistry Research* **46(1)**: 1-6.

Vicente G, Martinez M, Aracil J. ―Integrated biodiesel production: ―acomparison of different homogeneous catalysts systems‖ BioresourTechnol 2004;92:297–305. http://dx.doi.org/10.1016/j.biortech.2003.08.014

Wong, Y.C, Tan, Y.P, Taufiq-Yap, Y.H. & Ramli.I, 2015. An Optimization Study for Transesterification of Palm Oil using Response Surface Methodology (RSM). Sains Malaysiana 44(2)(2015): 281–290

Zaher, F.A. *Grasas y Aceites* **1990**, *41*, 82.