BIODIESEL PRODUCTION VIA SINGLE-STEP ALKALI CATALYST IN BATCH PROCESS

NURUL FARHA BINTI ABDUL RASHID

UNIVERSITI MALAYSIA PAHANG



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Tarikh	: 14 Mei 2008



BIODIESEL PRODUCTION VIA SINGLE-STEP ALKALI CATALYST IN BATCH PROCESS

NURUL FARHA BINTI ABDUL RASHID

A thesis submitted in fulfillment of the requirement for the award of the Degree of Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang

MAY 2008

"I declared that this thesis entitled "Biodiesel Production via Single-Step Alkali Catalyst in Batch Process" 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	:
Name of Candidate	: Nurul Farha Binti Abdul Rashid
Date	: 14 May 2008



Special dedication to my beloved parents, Haji Abdul Rashid Bin Haji Abdullah P.J.K, Wan Rihana Binti Haji Wan Ahmad and all my lovely family members, Kakak, Wieyn, Wa, Ijat, Ira, Adik, and Daniel.



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ABSTRACT

Biodiesel is an alternative fuel, produced from domestic and renewable resources. Biodiesel is biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel is made through a chemical process called transesterification whereby the glycerin, it's by product is separated from the fat or vegetable oil and sold to produce products such as soaps and grease. The main objective of this research is to produce the biodiesel from waste cooking oil and to optimize the production by using Design of Experiment (DOE). The single step alkali catalyzed process was adopted to prepare biodiesel by transesterification process by using the methanol and homogenous alkali catalyst, sodium hydroxide. The products was analyzed to determine the yield, concentration of methyl ester and moisture content to get the catalyst concentration and time at optimum condition by using DOE. From DOE it is found that the optimum condition to get the higher value of yield percentage was suggestion from RSM by the model equation is 56.31% with the reaction time is 30.37 minutes and catalyst concentration is 1.08%. For methyl ester concentration percentage, RSM suggested by the model equation is 77.96% with the reaction time is 30.24 minutes and catalyst concentration is 0.58%.



ABSTRAK

Biodiesel bermaksud bahan api alternatif yang diperolehi dari alam sekitar dan boleh diperbaharui. Biodiesel adalah mesra alam, tidak bertoksik dan mempunyai kandungan sulfur yang rendah. Biodiesel merupakan proses yang dihasilkan melalui proses kimia yang dipanggil transesterifikasi di mana gliserin, hasil sampingan dipisahkan dari minyak sayuran dan menghasilkan produk seperti sabun dan gris. Objektif utama untuk kajian ini adalah menghasilkan biodiesel daripada sisa minyak masak dan mengoptimumkan produk menggunakan Eksperimen Reka Bentuk (DOE). Proses pemangkin satu langkah telah diambil untuk menyediakan biodiesel dalam proses transesterifikasi dengan menggunakan metanol dan pemangkin alkali, natrium hidroksida. Hasil yang dapat (biodiesel) dianalisiskan untuk mengkaji peratus hasil, kepekatan metil ester dan kandungan air di dalam biodiesel untuk mendapatkan nilai kepekatan pemangkin dan masa tindak balas pada keadaan optimum dengan mengunakan Eksperimen Reka Bentuk (DOE). Dari keputusan DOE, keadaan optimum peratusan hasil yang dicadangkan oleh RSM melalui persamaan model adalah sebanyak 56.31% dengan kadar masa 30.37 minit dan kepekatan pemangkin sebanyak 1.08%. Manakala untuk kepekatan metil ester, RSM mencadangkan melalui persamaan model sebanyak 77.96% dengan kadar masa 30.24 minit dan kepekatan pemangkin sebanyak 0.58%.

TABLE OF CONTENTS

CHAPTER

TITLE

PAGE

DECLARATION	V
DEDICATION	vi
ACKNOWLEDGEMENT	vii
ABSTRACT	viii
ABSTRAK	ix
TABLE OF CONTENTS	Х
LIST OF FIGURE	xiii
LIST OF TABLE	xiv

1		INTRODUCTION	1
	1.1	Overview of Research	1
	1.2	Problem Statement	3
	1.3	Objective of Project	4
	1.4	Scope of Research Work	4
2		LITERATURE REVIEW	5

		-
2.1	Introduction	5
2.2	Biodiesel Production	5
2.3	The Possible Method of Biodiesel	9
	2.3.1 Pyrolisis	10
	2.3.2 Microemulsification	10
	2.3.3 Transesterification	11
2.4	The Transesterification Process of Biodiesel	13



2.5	Reaction Mechanism of Biodiesel Production	14
	2.5.1 Base Catalyzed Mechanism	15
2.6	Tranesterification Catalysis	17
	2.6.1 Acid-Catalyzed Transesterification	17
	2.6.2 Enzymatic Transesterification	18
	2.6.3 Alkali-Catalyzed Transesterification	19
2.7	The Advantages of Biodiesel	23
2.8	Comparison between Biodiesel and Diesel Fuel	23
2.9	Application of Factorial DOE and RSM	25

	METHODOLOGY	27
3.1	Introduction	27
3.2	Materials and Equipment for Biodiesel Production	28
3.3	Experimental Work	29
	3.3.1 Pre-Treatment WCO	29
	3.3.2 Transesterification Processing	30
	3.3.3 Separation Process	31
	3.3.4 Methanol Recovery	32
	3.3.5 The Washing Process	32
3.4	Analysis The Product	34
	3.4.1 Moisture Content	34
	3.4.2 Thin Layer Chromatography	34
	3.4.3 Yield	38
3.5	Design of Experiment (DOE)	38
	RESULT AND DISCUSSION	40
4.1	Introduction	40
4.2	Optimization of Biodiesel Purity	42
	4.2.1 Design Expert Plot	45
4.3	Optimization of Biodiesel Yield	48
	4.3.1 Design Expert Plot	51



5	CONCLUSION	55
5.1	Conclusion	54
5.2	Recommendation	55
REFEREN	CES	56
APPENDIX	ΧA	63
APPENDIX	K B	76



LIST OF FIGURES

FIGURE NO.

TITLE

PAGE

2.1	Transesterification of triglyceride using methanol and catalyst.	12
2.2	The reversible reactions between triglycerides and alcohol	13
2.3	The reaction mechanism by using strong base catalyst.	16
2.4	Flow diagram biodiesel production using the lipase catalyst.	18
2.5	Flow diagram biodiesel production using the alkali catalyst.	21
3.1	Research Methodology	27
3.2	Shaking Water Bath	28
3.3	Karl Fischer ASTM D789 (Moisture Content Test)	28
3.4	Rotary Evaporator	29
3.5	Pre-Treatment Process	30
3.6	Settling Process	31
3.7	Separation Process	31
3.8	Washing Process	32
3.9	Process Flow Schematic Biodiesel Production in Batch Process	33
3.10	TLC plate immersed in the n-Hexane and Chloroform Solution	35
3.11	TLC plate in the beaker filled with iodine pellet	36
3.12	Thin Layer Chromatography Calculation	36
3.13	Procedure of methyl ester concentration	37
4.1	Response surface plot of methyl ester production	46
4.2	Response surface plot of biodiesel yield	52



LIST OF TABLES

TABLE NO.

TITLE

PAGE

2.1	Physical and Chemical Properties of Biodiesel.	8
2.2	Effect of the catalyst on the biodiesel purity and yield	19
2.3	The comparison of alkali-catalysis, lipase-catalysis and	
	acid-catalysis methods for biodiesel production.	22
3.1	RSM model of experiment	39
4.1	Central composite design matrix Methyl Esters Content	41
4.2	The predicted and experimental value	42
4.3	ANOVA Methyl Esters Content	44
4.4	Coefficient Value of the equation	44
4.5	The Result of Optimization of Methyl Ester Concentration	47
4.6	Central composite design matrix biodiesel yield	48
4.7	ANOVA biodiesel yield	50
4.8	Coefficient Value of the equation	50
4.9	The Result of Optimization of Methyl Ester Concentration	53

CHAPTER 1

INTRODUCTION

1.1 Overview of Research

Biodiesel is easy-to-make, clean burning diesel alternative made from vegetable oil or fats, and has great promise as an energy industry that could be locally-produced, used, and controlled. Biodiesel is an alternative fuel that is relatively safe and easy to process when conscientiously approached. It is made from vegetable oil or animal fat that can be used in any diesel engine without any modifications. Chemically, it is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. It is thus distinguished from the straight vegetable oils (SVO) or waste vegetable oils (WVO) used as fuels in some diesel vehicles.

Biodiesel is biodegradable and non-toxic, and typically produces about 60% less net carbon dioxide emissions than petroleum-based diesel, as it is itself produced from atmospheric carbon dioxide via photosynthesis in plants. Biodiesel also produces fewer particulate matter, carbon monoxide, and sulfur dioxide emissions (all air pollutants under the Clean Air Act). Since biodiesel can be used in conventional diesel engines, the renewable fuel can directly replace petroleum products, reducing the country's dependence on imported oil.



Boasting an overall 92% reduction in toxic emissions compared to diesel, biodiesel is by far the best alternative fuel option at present. Biodiesel is the only alternative fuel currently available that has an overall positive life cycle energy balance. It is renewable, sustainable, and domestically produced. The only by-product of this form of biodiesel is glycerin, which can be easily used to make soap or other products. Biodiesel can also be produced from other biologically derived oils such as soybean oil, canola oil, sunflower oil, hemp oil, coconut oil, peanut oil, palm oil, corn oil, mustard oil, flaxseed oil, new or waste cooking oil, rapeseed oil, cottonseed oil, beef tallow, pork lard, as well as other types of animal fat.

In this research, biodiesel is produced through the reaction of the waste cooking oil with methanol in the presence of a catalyst to yield glycerin and biodiesel (chemically called methyl esters). The most common form uses methanol to produce methyl esters as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as isopropanol and butanol have also been used. The use of waste cooking oil to produce biodiesel can reduce the raw material cost because it is estimated to be about half the price of virgin oil. The most common way to produce biodiesel is by transesterification process and the common catalyst used is homogeneous basic catalysts usually used a strong base such as potassium hydroxide. The alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time.

1.2 Problem Statement

Biodiesel is needed for Malaysia future, toward the vision 2020. Since it's made domestically, it could reduce country's dependence on foreign oil. At present, the high cost of biodiesel is the major obstacle to its commercialization. Biodiesel usually have high cost than petroleum-based diesel. The criteria of pollutants like unburned hydrocarbon, carbon monoxide, and particulate matter were increased with diesel fuel used. The problem with processing waste oils is that they usually contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to formation of fatty acids salts (soap).



1.3 Objective of The Project

The main objective in this project is to produce the biodiesel from waste cooking oil by using alkali catalyst for replacement of diesel engine.

1.4 Scope of Research Work

The scopes of this research are to study the effect of catalyst concentration and reaction time at the optimum condition by using Design of Experiment (DOE) and to analyze the product by investigated the yield, methyl ester concentration content (TLC) and moisture content.

4



CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

"Bio" represents as a renewable and biological source in contrast to traditional petroleum-based diesel fuel; "diesel" refers to its use in diesel engines. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel defined as "a substitute for, or a additive to diesel fuel that is derived from the oils and fats of plants and animals" (Ma and Hanna, 1999) or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetables oil or animal fat. Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. It consists of the monoalkyl esters formed by a catalyzed reaction of the triglycerides in the oil or fat with a simple monohydric alcohol.

2.2 Biodiesel Production

Biodiesel production is the process of synthesizing biodiesel. Biodiesel is a liquid fuel source largely compatible with petroleum based diesel fuel. The most common method for its manufacture is synthesis by reacting glyceride-containing plant oil with a short chain alcohol such as methanol or ethanol in a step known as transesterification. The price of fossil diesel is soaring in these two years and it will be exhausted some day. Thus, looking for alterative way to develop a substitute for diesel



(biodiesel) is an imperious task for humans. Due to the increase in the price of the petroleum and the environmental concern about pollution coming from the car gases,

Rudolph Diesel, a German engineer, introduced the diesel engine over a century ago (Nitske and Wilson, 1965). He tested vegetable oil as the fuel for his engine (Shay, 1993). Many researchers have concluded that vegetable oils and their derivatives hold promises as alternative fuels for diesel engines rather than spark-ignited engines due to their low volatility and high cetane number (Wagner et al., 1984, Scholl and Sorenson, 1993; Bagby et al., 1987). However, using raw vegetable oils for diesel engines can cause numerous engine-related problems (Korus et al., 1982; Perkins and Peterson, 1991). The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking and piston ring sticking (Perkins and Peterson, 1991; Pestes and Stanislao, 1984; Clerk et al., 1984; Vellguth, 1983). However, these effects can be reduced or eliminated through transesterification of the vegetables oil to form alkyl ester (Perkins and Peterson, 1991; Zhang et al., 1988).

biodiesel is becoming a developing area of high concern (Ma and Hanna, 1999).

Vegetables oils, especially palm oil have become more attractive research recently because of their environmental benefits and the fact that it is made from renewable resources. Palm oils have the great potential for substitution of the petroleum distillates and petroleum based petrochemicals in the future. Others vegetable oil fuels are not now petroleum competitive fuels because they are more expensive than petroleum fuels (Demirbas, 2003). However, with the recent increase in petroleum prices and the uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in diesel engines. The diesel boiling range material is of particular interest because it has been shown to reduce particulate emissions significantly relative to petroleum diesel (Giannelos, Zannikos, Stournas, Lois, and Anastopoulos, 2002). There are more than 350 oil bearing crops identified, among which only palm oil, sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for diesel engines (Geoing, Schwab, Daugherty, Pryde, and Heakin, 1982).

From the viewpoint of chemical reaction, refined vegetable oil is the best starting material to produce biodiesel because the conversion of pure TG to FAME (fatty acid methyl ester) is high, and the reaction time is relatively short. Nevertheless, in China, the largest developing country with a population of over 1.3 billion, the limited refined edible oil must meet the need of consumers first. Waste cooking oil (WCO), if no suitable treatment is available, would be discharged and cause environmental pollution, but now, WCO is collected in Guangzhou, the third largest city in China, is over 20 thousand tons every year. This collected material is a good commercial choice to produce biodiesel due to its low cost (Wang et al, 2006).



Table 2.1 : Physical and Chemical Properties of Biodiesel
--

Vegetable oil methyl ester	Kinematic viscosity (mm ² /s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt %)
Peanut ^a	4.9 (37.8°C)	54.00	33.60	5.00	176.00	0.88	-
Soybean ^a	4.5 (37.8°C)	45.00	33.50	1.00	178.00	0.89	-
Soybean ^b	4.0 (40°C)	45.7-56	32.70	-	-	0.880 (15°C)	-
Babassu ^a	3.6 (37.8°C)	63.00	31.80	4.00	127.00	0.88	-
Palm ^a	5.7 (37.8°C)	62.00	33.50	13.00	164.00	0.88	-
Palm ^b	4.3-4.5 (40°C)	64.3-70	32.40	-	-	0.872- 0.877 (15°C)	-
Sunflower ^a	4.6 (37.8°C)	49.00	33.50	1.00	183.00	0.86	-
Tallow ^a	-	-	-	12.00	96.00	-	-
Rapeseed ^b	4.2 (40°C)	51-59.7	32.80	-	-	0.882 (15°C)	-
Used rapeseed ^c	9.48 (30°C)	53.00	36.70	-	192.00	0.90	0.00
Used corn oil ^c	6.23 (30°C)	63.90	42.30	-	166.00	0.88	0.00
Diesel fuel ^b	12-3.5 (40°C)	51.00	35.50	-	-	0.830- 0.840 (15°C)	-
JIS-2D ^c (Gas oil)	2.8 (30°C)	58.00	42.70	-	59.00	0.83	0.05
^a Ref.10.							

(American Standard Test Material, 2001)

^b Ref. 20. ^c Ref. 19.



2.3 The Possible Methods of Biodiesel

The quality of feed vegetable oil particularly FFA content plays an important role in identifying the suitable technology. The important factors to be considered for a biodiesel production plant include:

- i) Process ability of variety of vegetable oils without or minimum modifications
- ii) Process ability of high free fatty acid (FFA) containing oils/feed-stocks
- iii) Must be able to process raw both expelled and refined oil
- iv) Process should be environment friendly with almost zero effluent

Certain difficulties are experienced in the engines while using straight vegetable oil (SVO) or chemically unmodified vegetable oils. One major problem is the higher viscosity of vegetable oils. The triglycerals as present in vegetable oil are mostly associated with their high viscosities, low volatilities and polyunsaturated character. Thus property modifications by transesterification are required to impart properties similar to petroleum diesel to the vegetable oil. The selection of appropriate technology for production of biodiesel calls for careful selection of processing steps, catalyst and downstream process integration.

There are the various methods for processing of biodiesel as follows:

- i) Pyrolysis
- ii) Micro-emulsification
- iii) Trans-esterification

2.3.1 Pyrolysis

Pyrolysis refers to a chemical change caused by application of thermal energy in absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Many investigators have studied the pyrolysis of triglycerides with the aim of obtaining products suitable for diesel engines (Grossley et al, 1962; Schwab et al, 1988; Alencar et al, 1983; Billaud et al, 1995). Thermal decomposition of tri-glycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, aromatics, and carboxylicacids. Different types of vegetable oils reveal large differences in composition when they are thermally decomposed. Pyrolyzed soybean oil, for instance, contains 79% carbon and 12% hydrogen (Dykstra et al, 1988). It also has low viscosity and a highcetane number compared to pure vegetable oils. However, while pyrolyzed vegetable oils possess acceptable amounts of sulphur, water, and sediment, as well as giving accept-able copper corrosion values, they are unacceptable in terms of ash, carbon residues, and pour point. In addition, though the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during thermal processing also eliminates any environmental benefits of using an oxygenated fuel (Ma and Hanna, 1999).

2.3.2 Microemulsification

The formation of micro-emulsions (co-solvency) is a potential solution for reducing the viscosity of vegetable oil. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersions. The droplet in micro-emulsions ranges from 100 to 1000 Å. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. Water (from aqueous ethanol) may also be present in order to use lower-proof ethanol, thus increasing water tolerance of the micro-emulsions (Ziejewski, Kaufman, Schwab, and Pryde, 1984). The use of micro emulsions



with solvents such as methanol, ethanol, and 1-butanol has also been studied as a means of solving the problem of high viscosity of vegetable oils (Schwab, Bagby, and Freedman, 1987; Pryde, 1984; Ziejewski, Kaufman, Schwab, and Pryde, 1984). Micro emulsions are isotropic, clear or translucent thermodynamically stable dispersions of oil, water, a surfactant, and often a small amphiphilic molecule, called a co surfactant (Schwab, Bagby, and Freedman, 1987). Ziejewski et al. (Ziejewski, Kaufman, Schwab, and Pryde, 1984) prepared an emulsion of 53.3% (v/v) alkali-refined and winterized sunflower oil, 13.3% (v/v) 190-proof ethanol and 33.4% (v/v) 1-butanol. This non-ionic emulsion had a viscosity of 6.31 x 10^{-6} m²/s at 40°C, a cetane number of 25, a sulfur content of 0.01 %, free fatty acids of 0.01 %, and an ash content of less than 0.01%. Lower viscosities and better spray patterns were obtained by increasing the amount of 1-butanol. Schwab et al. (Schwab, Bagby, and Freedman, 1987) reported that 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. However, in a laboratory screening endurance test, irregular injector needle sticking, heavy carbon deposits, in complete combustion and an increase of lubricating oil viscosity were reported (Ziejewski, Kaufman, Schwab, and Pryde, 1984).

2.3.3 Transesterification

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 employed instead of water. The other suitable alcohols include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance (Clark, Wangner, S&rock, and Piennaar, 1984). Thus, fatty acid methyl esters (known as biodiesel fuel) obtained by transesterification can be used as an alternative fuel for diesel engines. Transesterification is a chemical process of reacting



vegetable oils with alcohol in the presence of a catalyst as shown in Figure 2.1 where R1, R2, and R3 are long hydrocarbon chains, called fatty acid chains.



Figure 2.1: Transesterification of triglyceride using methanol and catalyst. (Zhang et al, 2002)

There are three basic routes to biodiesel production from biolipids (biological oils and fats):

- Base catalyzed transesterification of the biolipid carried out under atmospheric pressure and at temperature ~60-700 C
- ii) Direct acid catalyzed transesterification of the biolipid
- iii) Conversion of the biolipid to its fatty acids and then to biodiesel

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, product of diglyceride monoglyceride and in the last step, from monoglycerides glycerin is obtained. In all these reactions esters are produced. The stoicheometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product:



Triglycerides (TG) + R'OH $\underset{k_2}{\overset{k_1}{\leftrightarrow}}$ Diglycerides (DG) + R'COOR₁, Diglycerides (DG) + R'OH $\underset{k_4}{\overset{k_3}{\leftrightarrow}}$ Monoglycerides (MG) + R'COOR₂, Monoglycerides (MG) + R'OH $\underset{k_6}{\overset{k_5}{\leftrightarrow}}$ Glycerin (GL) + R'COOR₃.

Figure 2.2: The reversible reactions between triglycerides and alcohol (Zhang et al, 2002)

2.4 The Transesterification Process of Biodiesel

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. Methanol is the most commonly used alcohol due to its low cost (Ma and Hanna, 1999 and Demirbas, 2003). Transesterification significantly reduces the viscosity of vegetable oils without affecting the heating value of the original fuel. Therefore, fuel atomization, combustion, and emission characteristics will display better results than pure vegetable oils are used in engines. Many researchers around the world agree that biodiesel making from transesterification process, does not need to modify diesel engine before using the biodiesel. Scientists Duffy and Patrick conducted this process as early as 1853 (Metzer, 1996).

Methanol is the most commonly used alcohol because it's low cost. Other alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. However, ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however methanol is used because of its low cost and its physical and chemical advantages (Wang et al, 2006).



In general, a large excess of methanol is used to shift the equilibrium far to the right, so the reaction will not go back to the triglyceride anymore. Chemically, transesterification also called alcoholysis that means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerine and creating an alcohol ester. The function of catalyst is usually used to improve the reaction rate and yield. Alcohols are primary or secondary monohydric aliphatic alcohols having 1-8 carbon atoms (Sprules, Price, 1950).

2.5 Reaction Mechanism of Biodiesel Production

The reaction mixture settles and separates into an ester phase and a glycerol phase. The ester phase contains glycerides, methyl esters and methanol which are purified by distillation to obtain the final biodiesel. The remaining unreacted glycerides are reintroduced in the transesterification reactor together with traces of esters which allow for a better mixture of the alcohol and oil phases. The glycerol phase which contains glycerol, water and methanol, is fed into a buffer tank which also contains the glycerol phase from the transesterification reactor. Once the two glycerol phases are well mixed, they are fed into an acidulation tank where FFA from the pre-esterification are added until having an alkaline pH to avoid the formation of soaps and emulsions. The remaining unreacted FFA is sent again into a FFA buffer tank to be reused in the preesterification reactor. The glycerol phase is neutralized and distilled to recuperate glycerol and methanol to be reused within the system. By this process, the transesterification takes place at moderate conditions and the biodiesel conversion reaches its highest rate, above 95% (Mittelbach, 2004).

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong <u>alkaline</u> (<u>NaOH</u>, <u>KOH</u> or <u>sodium silicate</u>). The main reason this process to produce biodiesel, is to find out how much alkaline is needed to ensure a complete transesterification. The alcohol reacts with the fatty acids to form



the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a <u>reversible reaction</u> so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion (Freedman et., 1984).

2.5.1 Base Catalyzed Mechanism

Base catalyzed reaction uses strong base such as NaOH, KOH, Sodium Methoxide and others. The base is dissolved in the alcohol to disperse solid catalyst into the oil. Any water in the process promotes the saponification reaction and inhibits the transesterification reaction.

The reaction equilibrium is far to the left. While KOH and NaOH are strong bases, such as methoxide can only be produced by reacting sodium metal in alcohol. However, the following reaction mechanism using methoxide as an example is common in the literature as methoxide is an excellent base catalyst for this reaction.

Once the alcohol mixture is made, it is added to the triglyceride. The reaction that follows replaces the alkyl group on the triglyceride in a series of reactions. The carbon on the ester of the triglyceride has a slight positive charge, and the oxygen have a slight negative charge, most of which is located on the oxygen in the double bond. This charge is what attracts the RO⁻ to the reaction site.







Figure 2.3: The reaction mechanism by using strong base catalyst

This yields a transition state that has a pair of electrons from the C=O bond now located on the oxygen that was in the C=O bond. These electrons then fall back to the carbon and push off the glycol forming the ester. Then two more RO groups react via this mechanism at the other two C=O groups. This type of reaction has several limiting factors. RO⁻ has to fit in the space where there is a slight positive charge on the C=O. So MeO- works well because it is small.

As the R on RO- gets bigger, reaction rates decrease. This effect is called steric hindrance. That is why methanol and ethanol are typically used. There are several competing reactions, so care must be taken to ensure the desired reaction pathway occurs. Most methods do this by using an excess of RO⁻. The acid catalyzed method is a slight variant that is also affected by steric hindrance.



2.6 Transesterification Catalysis

The transesterification reaction can be catalyzed by alkali, acids or enzymes. The first two types have received the greatest attention and are the focus of many of the researchers. As for the enzyme-catalyzed system, it is requires a much longer reaction time than the other two systems (Nelson et al., 1996; Watanabe et al., 2001).

Chemically catalyzed processes, including alkali catalyzed and acid catalyzed ones have proved to be more practical nowadays. An alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time (30-60min) (Muniyappa et al., 1996; Antolin et al., 2002). However, it is very sensitive to the purity of the reactants. Only well refined vegetable oil with less than 0.5 wt% of free fatty acid (FFA) can be used as the reactants in this process (Zhang, Dube, McLean, 2003). The most commonly preferred acid catalyst is sulfuric, sulphonic and hydrochloric acids. Sodium hydroxide, sodium methoxide and potassium hydroxide are preferred as alkaline catalyst. For transesterification reactions the concentration of catalyst ranges from 0.5 to 1.5 wt% (Freedman et., 1984).

2.6.1 Acid-Catalyzed or In-Situ Transesterification

Acids used for transesterification include sulfuric, phosphoric, hydrochloric, and organic sulfonic acids. Although transesterification by acid catalysts is much slower than that alkali catalysis (Ma and Hanna; Srivastava and Prasad; and Freedman et al., 1984), acid-catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid contents and more water (Freedman et al., 1984; Aksoy et al, 1988).



In situ transesterification differs from the conventional reaction in that the oilbearing material contacts acidified alcohol directly instead of reacting with purified oil and alcohol. In the transesterification of waste cooking oil with acidified methanol produces fatty acid methyl ester is produced significantly greater than those obtained from the conventional reaction (Harrington and D'Arcy-Evans, 1985).

2.6.2 Enzymatic Transesterification by Lipase

Both extracellular and intracellular lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems. In particular, it should be noted that the by-product, glycerol, can be easily recovered without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to methyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater that of an alkali one.



Figure 2.4: Flow diagram biodiesel production using the lipase catalyst. (Fukuda et al, 2001)



2.6.3 Alkali-Catalyzed Transesterification

Alkali used for transesterification includes NaOH, KOH, carbonates, and alkoxides such as sodium methoxide, sodium propoxide, and sodium butoxide. Alkalicatalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst (Formo, M.W, 1954), and is thus most often used commercially.

Catalyst				
	Sodium	Potassium	Sodium	Potassium
	hydroxide	hydroxide	methoxide	methoxide
Biodiesel				
purity	99.7	99.69	99.7	99.4
(wt%)	99.75	99.8	99.69	99.5
	99.72	99.8	99.72	99.65
	99.65	99.74	99.75	99.53
	99.71 ±0.04	99.76 ± 0.05	99.72 ± 0.03	99.52 ± 0.1
Biodiesel yield	86.33	91.67	99.17	98.33
(wt%)	86.67	91.67	99.33	98.5
	87	91.33	99.83	98.33
	86.71	92	99	98.67
	$86.71{\pm}0.28$	91.67 ± 0.27	99.33 ± 0.36	98.46 ± 0.16

Table 2.2: Effect of the	catalyst on the	biodiesel purity	and yield
(G.	Vicente et al,	2004)	

Temperature = $65 \degree C$, molar ratio = 6, catalyst = 1%



2.6.3.1 Effects of Moisture and Free Fatty Acids

For alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water causes a partial reaction change to saponification, which produces the soap (Wright et al., 1944). The soap consumes the catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation glycerol. (Ma *et al.*, 1998) suggested that the free fatty acid content of the refined oil should be as low as possible, below 0.5%, and Feuge and Grose (Feuge and Grose, 1949) also stressed the importance of oils being dry and free of free fatty acids. Freedman *et al.* (Freedman, Pryde, and Mounts, 1984) reported that the products were significantly reduced if the reactants did not meet these requirements; sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, diminishing their effectiveness.

2.6.3.2 Effect of Molar Ratio of Alcohol to Vegetable Oil (WCO)

Another important variable affecting the ester yield is the molar ratio of alcohol to waste cooking oil. The stoichiometry of the transesterification reaction requires 3 mol alcohol per mol of triglyceride to yield 3 mol of fatty esters and 1 mol glycerol (see Fig.1). Higher molar ratios result in greater ester conversion in a shorter time. Freedman *et al.* (Freedman, Pryde, and Mounts, 1984) studied the effect of molar ratios (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, palm, sunflower, peanut and cotton seed oils behaved similarly, with the highest conversion being achieved at a 6:1 molar ratio. Thus, a molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% on a weight basis (Feuge and Grose, 1949; Fillieres et al., 1995).



2.6.3.3 Effect of Catalyst Type

Sodium methoxide has been found to be more effective than sodium hydroxide, presumably because a small amount of water is produced upon mixing NaOH and MeOH (Freedman, Pryde, and Mounts, 1984; and Hartman, 1956). Alcantara *et al.* (Alcantara, Amores, Canoira, Fidalgo, France, and Navarro, 2000) transformed three fatty materials- bean oil, used frying oil, and tallow- with sodium methoxide into two different types of products by transesterification and amidation reaction with methanol and diethylamine, respectively. Amides enhance the ignition properties of petrochemical diesel fuel. However, sodium hydroxide and potassium hydroxide (Nye et al., 1983) are also able to catalyze transesterification, and because of their low cost, are widely used in industrial biodiesel production.



Figure 2.5: Flow diagram biodiesel production using the alkali catalyst. (Fukuda et al, 2001)



Table 2.3: The comparison of method between alkali-catalysis, lipase-catalysis and acid-catalysis for biodiesel production.

	Alkali-catalysis process	Lipase-catalysis process	Acid-catalysis process
Reaction temperature	60-70°C	30-40°C	55-80°C
Free fatty acids in raw material	Saponified products	Methyl esters	Esters
Water in raw materials	Interference with the reaction	No influence	Interference with the reaction
Yield of methyl esters	Normal	Higher	Normal
Recovery of glycerol	Difficult	Easy	Difficult
Purification of methyl esters	Repeated washing	None	Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Cheap

(Marchetti et al., 2007)


2.7 The Advantages of Biodiesel

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development, such as provides a market for excess production of vegetable oils and animal fats, decreases the country's dependence on imported petroleum although will not eliminate. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel (Sheehan, Camobreco, Duffield, Graboski, and Shapouri, 1998). The exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower than with regular diesel fuel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NO₂). When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel (Canakci, Van Gerpen, 2001).

2.8 The Comparison between Biodiesel and Diesel Fuel

There are a number of ways in which a comparison between conventional fuels and biodiesel can be made. For overall ozone forming potential of biodiesel is less than diesel fuel. The ozone forming potential of the speculated hydrocarbon emissions was nearly 50 percent less than that measured for diesel fuel (Bala BK., 2005). Sulfur emissions are essentially eliminated with pure biodiesel. The exhaust emissions of sulfur oxides and sulfates from biodiesel were essentially eliminated compared to sulfur oxides and sulfates from diesel. Criteria pollutants are reduced with biodiesel use. The use of



biodiesel in an unmodified Cummins N14 diesel engine resulted in substantial reductions of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides however were slightly increased. The exhaust emissions of carbon monoxide from biodiesel were 50 percent lower than carbon monoxide emissions from diesel (A. Demirbas, 2003). Breathing particulate has been shown to be a human health hazard. The exhaust emissions of particulate matter from biodiesel were 30 percent lower than overall particulate matter emissions from diesel. The exhaust emissions of total hydrocarbons were 93 percent lower for biodiesel than diesel fuel (Bala BK., 2005). NO₂ emissions from pure (100%) biodiesel increased in this test by 13 percent. However, biodiesel's lack of sulfur allows the use of NO₂ control technologies that cannot be used with conventional diesel. So, biodiesel NO₂ emissions can be effectively managed and efficiently eliminated as a concern of the fuel's use.

Biodiesel degrades about four times faster than petroleum diesel. Within 28 days, pure biodiesel degrades 85 to 88 percent in water (Korbitz.W, 1999). The flash point of a fuel is defined as the temperature at which it will ignite when exposed to a spark or flame. Biodiesel's flash point is over 300 deg. Fahrenheit, well above petroleum based diesel fuel's flash point of around 125 deg. Fahrenheit. Testing has shown the flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore, biodiesel and blends of biodiesel with petroleum diesel are safer to store, handle, and use than conventional diesel fuel (Korbitz.W, 1999)

2.9 Application of the Factorial Design of Experiment and Response Surface Methodology.

There are several types of software that can be used in modeling. One of the easiest and favourable method use is Design of Experiment; Response Surface Methodology. Design of experiment is a technique to make product, process or investigation more robust. Design of Experiment (DOE) is a structured, organized method that is used to determine the relationship between the different factors (Xs) affecting a process and the output of that process (Y). This method was first developed in the 1920s and 1930, by Sir Ronald A. Fisher, the renowned mathematician and geneticist. Design of Experiment involves designing a set of ten to twenty experiments, in which all relevant factors are varied systematically. When the results of these experiments are analyzed, they help to identify optimal conditions, the factors that most influence the results, and those that do not, as well as details such as the existence of interactions and synergies between factors. Design of Experiments (DOE) is widely used in research and development, where a large proportion of the resources go towards solving optimization problems and minimizing optimization costs by conducting as few experiments as possible. DOE requires only a small set of experiments and thus helps to reduce costs.

Response surface methodology (RSM) explores the relationships between several explanatory variables and one or more response variables (G. E. P. Box and K. B. Wilson,1951). The main idea of RSM is to use a set of designed experiments to obtain an optimal response. Box and Wilson suggest using a first-degree polynomial model to do this. They acknowledge that this model is only an approximation, but use it because such a model is easy to estimate and apply, even when little is known about the process. The response surface methodology, which includes factorial design and regression analysis, can build models to evaluate the effective factors and study their interaction and select optimum conditions in limited number of experiments (McBride, 1999). A prior knowledge and understanding of the parameters involved is necessary for achieving a more realistic model. An easy way to estimate a first-degree polynomial model is to use a factorial experiment or a fractional factorial designs. This is sufficient to determine which explanatory variables have an impact on the response variable(s) of interest. Once it is suspected that only significant explanatory variables are left, and then a more complicated design, such as a central composite design can be implemented to estimate a second-degree polynomial model, which is still only an approximation at best. However, the second-degree model can be used to optimize (maximize, minimize, or attain a specific target for) a response. Some extensions of response surface methodology deal with the multiple response problem. Multiple response variables create difficulty because what is optimal for one response may not be very optimal for other responses. Other extensions are used to reduce variability in a single response while targeting a specific value, or attaining a near maximum or minimum while preventing variability in that response from getting too large.

In the transesterification process, several factors such as reaction temperature, reaction time, and catalyst concentration may affect the yield of biodiesel. Their affect can be either independent or interactive to each other. Triveni *et al.*, (2001) stated that, many factors affect the desired response. However response surface methodology (RSM) becomes an effective tool for optimizing the process. The advantages of using RSM are reported to reduce the number of experimental trials needed to evaluate multiple parameters, and the ability of the statistical tool to identify interactions (Lee, Ye, Landen, and Eitenmiller, 2000). In addition to analyzing the effects of the independent variables, the experimental methodology also generates a mathematical model that accurately describes the overall process. RSM provide more information per experiment than unplanned experiment. Other advantages of using RSM are in terms of organize data collection and analysis information, asses the information reliability in the light of experimental and analytical variation, and provide a good interaction during the experiment.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Basically, there are two steps in this experimental work. The first step is how to produce biodiesel in batch process by manipulating the amount of methanol and sodium hydroxide as the alkali-catalyzed. For the first step, the batch experiment will be conduct by using the transesterification process to produce a good product. The washing of the biodiesel will be included in this method. The second step is to analyze the product that is biodiesel itself. Here, the parameters to study of biodiesel are the moisture content, thin layer chromatography (methyl ester) and yield of product. The overall step to this research is summarized in the Figure 3.1 shown.



Figure 3.1: Research methodology



3.2 Materials and Equipment for Biodiesel Production

In this research, the materials that used to produce biodiesel are waste cooking oil (WCO), methanol, and sodium hydroxide (NaOH) as the alkali catalyst. The equipments for biodiesel production are the 500 ml beaker, 50 ml beaker, magnetic stirrer for the mixing process, funnel separator, rotational evaporator, shaking water bath, the hot plate, conical flask, temperature, aluminium coil, and filter paper. For the analysis, the materials are hexane and chloroform as the solvent for TLC test, and iodine pellet and for equipment, used the 1000 ml beaker, aluminium plate, capillary forces, Karl Fischer ASTM D789 for moisture content test, and 10 ml of syringe.



Figure 3.2: Shaking Water Bath



Figure 3.3: Karl Fischer ASTM D789 (Moisture Content Test)





Figure 3.4: Rotary Evaporator

3.3 Experimental Work

There are several methods in synthesizing of biodiesel. The most and preferred method is transesterification process with the aid of catalyst. In this experiment, single step transesterification were implemented with Sodium hydroxide is use as catalyst. This experimental methodology consists of five basic steps which are:

3.3.1 Pre-Treatment of Waste Cooking Oil (WCO)

The care must be taken to monitor the amount of water and <u>free fatty acids</u> in the incoming biolipid (WCO). If the free fatty acid level or water level is too high it may cause problems with soap formation (<u>saponification</u>) and the separation of the glycerin by-product downstream. Before preceding the process transesterification, the 200 gram of WCO was pre-heated at 75° C to remove the water.





Figure 3.5: Pre-treatment process

3.3.2 Transesterification Process.

In this process, the certain ratio of sodium hydroxide as alkali catalyst was dissolved to the 38.44 gram of methanol into the mixer. The mixed of the methanol and sodium hydroxide is then charged into a closed beaker and the 200 gram of WCO was added after the temperature WCO was decreased to 65 °C. The reaction was carried out with a 6:1 molar ratio of methanol to oil. The system from here on is totally closed to the atmosphere to prevent the loss of the alcohol. The reaction mixture was kept around 65°C until well mixed. Then the beaker was placed into the shaking water bath to maintain the temperature at 65 °C for the certain time.



3.3.3 Separation Process

The mixture was left for 1 day for settling until get two layers for separation process. The upper layer was the FAME (crude biodiesel) with lighter color and the bottom layer was the glycerol. The glycerin phase is much denser than the biodiesel phase and the two can be <u>separated</u> by settling process. The biodiesel was separate from the glycerol by using the paper filter to get the pure biodiesel without glycerol.



Figure 3.6: Settling process



Figure 3.7: Separation process



3.3.4 Methanol Recovery

Then, the excess of methanol was recovered under vacuum $(10\pm1 \text{ mmHg})$ at 65 °C with a rotational evaporator. Care must be taken to ensure no water accumulates in the recovered alcohol stream. The distillations were performed in a 500 ml round bottom one neck flask. The equipment includes a temperature controller, a receiver flask connected to a vacuum gauge and a condenser. A pump connected to the condenser provided vacuum.

3.3.5 The Washing Process

The crude biodiesel was washed by warm water at 80 $^{\circ}$ C to remove soap which was produced by reaction of the alkali and FFA. The volume should be 50:50 of biodiesel and warm water and let it for 1 hour. Repeat this step for 3 times. Then separate the biodiesel from water by using funnel separator. The wet crude biodiesel was dried at 100 $^{\circ}$ C by using hot plate to remove excess water in the biodiesel.



Figure 3.8: Washing process





Figure 3.9: Process flow schematic biodiesel production in batch process.



3.4 Analysis of the Product

In this research, the product was analyzed by 3 response variables there are moisture content, thin layer chromatography that is to determined the methyl ester in the biodiesel and the yield of the product. Every sample from each experiment produce from different condition will be analyzed to find the optimum condition of the reaction.

3.4.1 Moisture Content

The moisture content test was determined the water in the biodiesel by using the Karl Fischer. The 10ml of the sample in the syringe was weighed and then insert the sample into the vessel Karl Fischer and weighed again the syringe. After that key in the value of weight, press ENTER and then START. Then wait for 5 minutes until the result in % come out. The results must be lower than 0.05% that means the water content in the sample is too small and the biodiesel is more purity.

3.4.2 Thin Layer Chromatographhy

Thin-layer chromatography (TLC) is a very commonly used technique in synthetic chemistry for identifying compounds, determining their purity and following the progress of a reaction. In this experiment, the thin layer chromatography is to determine the concentration of methyl ester in biodiesel. The TLC plate on the side with the white surface do not touched. In order to obtain an imaginary start line, two notches on each side of the TLC plate was made. Draw a thin line with pencil. The start line should be 0.5-1 cm from the bottom of the plate was made. Then drop the sample at the start line by using the capillary forces. Try to avoid spotting too much biodiesel, because this will deteriorate the quality of the separation considerably ('tailing'). The spots should be far enough away from the edges and from each other as well.



Then, placed the plate into the container which is the mixed of the hexane and chloroform (ratio 1:1) as the solvent (mobile phase). The solvent level has to be below the starting line of the TLC, otherwise the spots will dissolve away. The lower edge of the plate is then dipped in a solvent. The solvent (eluent) travels up the matrix by capillarity, moving the components of the samples at various rates because of their different degrees of interaction with the matrix (=stationary phase) and solubility in the developing solvent. Non-polar solvents will force non-polar compounds to the top of the plate, because the compounds dissolve well and do not interact with the polar stationary phase. Allow the solvent to travel up the plate until ~1 cm from the top. Take the plate out and mark the solvent front immediately. Do not allow the solvent to run over the edge of the plate. Next, let the solvent evaporate completely. Then, put the plate into the container which is containing iodine pellet to see the concentration of methyl ester clearly. After a few minutes, a spot of methyl esters, mono-, di- and triglyceride will appear on the plate.



Figure 3.10: TLC plate immersed in the n-Hexane and Chloroform solution



Figure 3.11: TLC plate in the beaker filled with iodine pellet



Figure 3.12: Thin Layer Chromatography calculation





Figure 3.13: Procedure of methyl ester concentration



3.4.3 Yield of Biodiesel

The yield of the samples was determined by the weighing of the final biodiesel after drying process over the 200 gram of waste cooking oil (WCO). The yield of the biodiesel must be in the percent.

$$Yield(\%) = \frac{Mf - Mi}{Mi} (100\%)$$
(3.1)

$$\label{eq:mass} \begin{split} & \text{Yield} = \text{conversion of biodiesel} \\ & \text{M}_i = \text{initial mass} \ (\text{WCO}) \\ & \text{M}_f = \text{final mass} \ (\text{biodiesel}) \end{split}$$

3.5 Design of Experiment (DOE)

In this design of experiment, Response Surface Methodology (RSM) was use to evaluate and study the effects of variables on biodiesel production which are:

- i) Catalyst concentration (0.5 % 1.5%)
- ii) Reaction time (30minute 90minute)

The RSM have generated a model of experiment with different condition of variable. The model of experiment consists of 13 trials and the samples of every trial will need to determine its biodiesel yield, methyl ester content, and moisture content. Table 3.1 shows the RSM model of experiment.



Std	Run	Block	Factor 1	Factor 2	Response 1	Response 2	Response 3
			Time (min)	Catalyst (Conc.)	Moisture Content (%)	Yield (%)	TLC (%)
8	1	Block 1	60	1.5			
12	2	Block 1	60	1			
9	3	Block 1	60	1			
7	4	Block 1	60	0.5			
10	5	Block 1	60	1			
6	6	Block 1	90	1			
13	7	Block 1	60	1			
4	8	Block 1	90	1.5			
1	9	Block 1	30	0.5			
11	10	Block 1	60	1			
3	11	Block 1	30	1.5			
2	12	Block 1	90	0.5			
5	13	Block 1	30	1			

Table 3.1: RSM model of experiment

CHAPTER 4

RESULTS AND DISCUSSION OF RESEARCH WORK

4.1 Introduction

In this research, two variables factor will be manipulated based on the 13 trials of Design of Experiment (DOE). Design of Experiment (DOE) involves designing a set of 13 experiments, in which all relevant factors, time and catalyst concentration are varied systematically. Both of these parameters showed the characteristic that can affects the purity of the biodiesel (methyl esters content) and biodiesel yield. The value of moisture content cannot to be analyzed by using DOE because the moisture content result was affected by environmental factor and raw material factor. So the moisture content result was unpredictable.

For the homogenous catalyst process, we used NaOH as the alkali catalyst and methanol as the alcohol. The temperature was fixed at 65 °C and methanol to oil was fixed at the ratio 6:1. According to the journal for the alkali process, a short time between 30 to 90 minutes can achieve high purity and yield of biodiesel product and typical concentrations for transesterification reactions range are between 0.5 wt% to 1.5 wt%. Optimization of methyl esters content and yield of biodiesel was carried out using Response Surface Methodology (RSM). By using Central Composite Design (CCD), a total of 13 trials of experiments with different combination of reaction time and catalyst concentration were performed. The experiment sequences arranged by the Design Expert Software with experimental result are shown in Table 4.1.



Std	Run	Block	Factor 1	Factor 2	Response 1	Response 2	Response 3
			Time (min)	Catalyst (Conc.)	Moisture Content (%)	Yield (%)	TLC (%)
8	1	Block 1	60	1.5	0.02	49.201	73.323
12	2	Block 1	60	1	0.05	52.011	74.711
9	3	Block 1	60	1	0.09	54.271	76.214
7	4	Block 1	60	0.5	0.05	46.232	75.082
10	5	Block 1	60	1	0.09	53.741	76.032
6	6	Block 1	90	1	0.06	48.922	75.341
13	7	Block 1	60	1	0.08	55.863	74.664
4	8	Block 1	90	1.5	0.03	51.256	76.322
1	9	Block 1	30	0.5	0.05	47.452	77.863
11	10	Block 1	60	1	0.02	55.863	75.111
3	11	Block 1	30	1.5	0.04	54.721	76.394
2	12	Block 1	90	0.5	0.07	44.513	74.182
5	13	Block 1	30	1	0.04	55.924	77.082

 Table 4.1: Central composite design matrix



4.2 Optimization of Biodiesel Purity (Methyl Esters Content) Using Response Surface Methodology.

Optimization of methyl esters content was carried out using response surface methodology (RSM). By using central composite design (CCD), the experiment of biodiesel purity was performed. This experiment arranged by Design Expert Software is listed in Table 4.2

Table 4.2: Central composite design matrix, the predicted and experimental value obtained for the expression of biodiesel production by TLC

Standard Order	Actual value (%)	Predicted Value (%)	Residual
1	77.86	77.99	-0.13
2	74.18	74.36	-0.18
3	76.39	75.83	0.56
4	76.32	75.8	0.52
5	77.08	77.51	-0.43
6	75.34	75.68	-0.34
7	75.08	74.77	0.31
8	73.32	74.40	-1.08
9	76.21	75.19	1.02
10	74.66	75.19	-0.53
11	74.70	75.19	-0.49
12	75.10	75.19	-0.086
13	76.03	75.19	0.84



The result was analyzed using analysis of variance (ANOVA) as it is appropriate to the experimental design used. The regression equation 4.1 was obtained from analysis of variance and all terms regardless of their significant are included in the equation.

$$TLC = 75.19 - 0.92A - 0.18B + 1.41A^{2} - 0.60B^{2} + 0.90AB$$
(4.1)

Where A is the reaction time, B is the catalyst concentrations and TLC is the methyl esters content in percent (%). The designed model were performed consist of 1 offset, 2 linear, 2 quadratic and 1 interaction terms. That means reaction time and catalyst concentration give more affect to optimize the methyl ester concentration in biodiesel. From the experimental data, the highest methyl esters content were recorded at 77.86 % at Standard 1 with the condition 0.50 wt% of catalyst concentration and 30 minutes in reaction time.

Table 4.3 shows the ANOVA for Response Surface Reduce Quadratic Model Analysis of methyl esters content in the biodiesel. It is noted that, P-value less than 0.05 are significance model terms that influence the methyl esters content in the biodiesel production and P-value grater than 0.1000 indicate the model terms are not significant. Based on the table, the model terms that are significant are the linear term of the reaction time (A), squared terms of reaction time (A^2). The linear and squared terms of catalyst concentration (B) and (B^2) are seemed to be insignificant to this model as its P-value is 0.5959 and 0.2529 for each. Interaction terms of reaction time and catalyst concentration (AB) also insignificant with the value 0.0589. From the model (Equation 4.1) it is founded that the P-values obtained were small, which is 0.0403 (in Table 4.3) below to the maximum significance value, 0.05. Thus it indicates that the regression model was accurate in predicting the pattern of significance for methyl esters content in biodiesel production from waste cooking oil. The Lack of Fit F- value of 1.44 implies the Lack of Fit is not significant relative to the pure error. There is a 35.68 % chance that a Lack of Fit F- value this large could occur due to noise.



Saumaa	Sum of	Dogree of	Mean	F	Duch > F	
Source	Square	Freedom	Square	Value	Pro d > F	
Model	13.98	5	2.8	4.36	0.0403	significant
А	5.02	1	5.02	7.83	0.0266	
В	0.2	1	0.2	0.31	0.5959	
A2	5.49	1	5.49	8.55	0.0222	
B2	1	1	1	1.55	0.2529	
AB	3.26	1	3.26	5.08	0.0589	
Residual	4.49	7	0.64			
Lack of Fit	2.33	3	0.78	1.44	0.3568	not significant
Pure Error	2.16	4	0.54			
Correlation Total	18.47	12				

Table 4.3: Response Surface Reduced Quadratic Model Analysis of Methyl Esters

Content

Table 4.4: Coefficient value of the equation

Std. Dev.	0.8	\mathbf{R}^2	0.7568
Mean	75.56	Adjusted R ²	0.583
C.V.	1.06	Predicted R ²	-0.2984
PRESS	23.99	Adequate Precision	6.6790



The precision of the model can be checked by the determination coefficient (\mathbb{R}^2). The lists of the coefficient valued are listed in the Table 4.4. Based on the table, the determination coefficient (\mathbb{R}^2) value was 75.68 %, which indicates that 75.68 % of the sample variation was attributed to the independent variable tested and only 24.32 % of the total variation was not explained by the model. The regression model having a \mathbb{R}^2 value higher than 70% is considered to have a very high correlation. The adjusted \mathbb{R}^2 was valued at 58.30 % and predicted \mathbb{R}^2 was valued at -29.84 %. A negative predicted \mathbb{R}^2 implies that the overall mean is a better predictor of this response than the current model. The adjusted \mathbb{R}^2 value indicates not so good understanding existed between experimental and predicted values of purity of biodiesel

Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In this experiment, the adequate signal ratio indicates 6.679. This model can be used to navigate the design space.

4.2.1 Design Expert Plot of Methyl Ester Concentration (TLC)

To investigate the effect of methyl ester concentration in biodiesel, the response surface methodology was used and the three dimensional (3D) plot was drawn. In Figure 4.1 indicate the response surface curve for methyl ester concentration in biodiesel. The response surface representing the methyl ester concentration was a function of two response variable. The reaction time at X axis and Y axis is catalyst concentration.





Figure 4.1: Response surface plot of methyl ester production from waste cooking oil catalyst concerntration versus reaction time.

From the graph, it can be shown that the time and catalyst concentration gave the significant effect to optimize the methyl ester concentrationas. Longer reaction time increased the reaction rate of transesterification process and thus increases the yield of methyl esters content in the biodiesel. However, when reaction time was increased, the reaction rate of methyl ester concentration was decreased. The higher of methyl ester concentration just occurred at the beginning but then decreased drastically after a few minutes and then increased slightly at the last time. The result was not consistent. This error occurred maybe of the effect of using raw material during the experiment. The sources or suppliers of waste cooking oil were not consistent. So, the extending reaction time gives the negative effect to the methyl ester concentration in biodiesel. For catalyst concentration, the methyl ester concentration was decreased when increasing catalyst concentration. This is because higher catalyst concentration enhances the hydrolysis of esters which is reverse reaction of transesterification, resulted in the loss of methyl esters and hence causing more fatty acids to form soap. So, the extending the catalyst concentration also gives the negative effect to the methyl ester concentration in biodiesel.



Solutions No	Time	Catalyst	Response 1	Desirability	
1	30.30	0.62	77.9530	1	
2	<u>30.24</u>	<u>0.58</u>	<u>77.9610</u>	<u>1</u>	<u>Selected</u>
3	30.52	0.63	77.9082	1	
4	30.25	0.70	77.9062	1	
5	30.64	0.62	77.8928	1	
6	30.09	0.74	77.9004	1	
7	30.61	0.59	77.9063	1	
8	30.60	0.65	77.8874	1	
9	30.36	0.73	77.8716	1	
10	90.00	1.28	75.8960	1	

 Table 4.5:
 The result of optimization of methyl ester concentration

The optimum condition to get the higher value of methyl ester concentration (TLC) percentage as suggested by RSM is condition 2 which the reaction time is 30.24 minutes and catalyst concentration is 0.58%. The result that is predicted is 77.961% of methyl ester concentration.

47

4.3 Optimization of Biodiesel Yield Using Response Surface Methodology.

Optimization of yield of biodiesel was carried out using response surface methodology (RSM), using central composite design (CCD). This experiment arranged by Design Expert Software is listed in Table 4.6

Standard Order	Actual value	Predicted Value	Residual
1	47.45	48.30	-0.85
2	44.51	43.83	0.68
3	54.70	53.95	0.75
4	51.26	49.49	1.77
5	55.92	56.03	-0.10
6	48.92	51.57	-2.65
7	46.23	46.06	0.17
8	49.20	51.72	-2.52
9	55.86	53.80	2.07
10	54.27	53.80	0.47
11	55.86	53.80	2.07
12	53.74	53.80	-0.056
13	52.00	53.80	-1.80

Table 4.6: Central composite design matrix, the predicted and experimental value obtained for the expression of biodiesel production by yield



The results were analyzed using analysis of variance (ANOVA) as it is appropriate to the experimental design used. The regression Equation 4.2 was obtained from analysis of variance and all terms regardless of their significant are included in the equation.

$$YIELD = 53.80 - 2.23A + 2.83B - 4.91B^2$$
(4.2)

Where A is the reaction time, B is the catalyst concentrations and TLC (Thin Layer Chromatography) is the methyl esters content in percent (%). The designed model were performed consist of 1 offset, 2 linear and 1 quadratic. That means catalyst concentration gives more affect to optimize the yield of biodiesel than the reaction time. From the experimental data, the highest yield of biodiesel was recorded at 55.92 % at Standard 5 with the condition 1.0 wt% of catalyst concentration and 30 minutes in reaction time.

Table 4.7 shows the ANOVA for Response Surface Reduce Quadratic Model Analysis of yield in the biodiesel. It is noted that, P-value less than 0.05 are significance model terms that influence the yield in the biodiesel production and P-value grater than 0.1000 indicate the model terms are not significant. Based on the table, the all model terms are significant, that are the linear reaction time (A) 0.0154, linear catalyst concentration (B) 0.0044 and the square catalyst concentration (B^2) 0.0010. From the model (equation 4.2) it is founded that the P-values obtained were very small, which is 0.0007 (in table 4.7) below to the maximum significance value, 0.05. Thus it indicates that the regression model was accurate in predicting the pattern of significance for yield in biodiesel production from waste cooking oil. The Lack of Fit F- value of 1.51 implies the Lack of Fit is not significant relative to the pure error. There is a 35.56 % chance that a Lack of Fit F- value this large could occur due to noise.



		Degree	Mean	F		
Source	Sum of Square	of Freedom	Square	Value	Prob > F	
Model	155.58	3	51.86	15.43	0.0007	significant
А	29.86	1	29.86	8.89	0.0154	
В	47.96	1	47.96	14.27	0.0044	
B2	77.76	1	77.76	23.14	0.001	
Residual	30.24	9	3.36			
Lack of Fit	19.77	5	3.95	1.51	0.3556	not significant
Pure Error	10.48	4	2.62			
Cor Total	185.82	12				

Table 4.7: ANOVA for response surface reduced quadratic model analysis of yield

Table 4.8: Coefficient value of the equation

Std. Dev.	1.83	\mathbf{R}^2	0.8372
Mean	51.53	Adjusted R ²	0.7830
C.V.	3.56	Predicted R ²	0.6511
PRESS	64.83	Adequate Precision	11.993



The precision of the model can be checked by the determination coefficient (R^2). The lists of the coefficient valued are listed in the Table 4.8. Based on the table, the determination coefficient (R^2) value was 83.72 %, which indicates that 83.72 % of the sample variation was attributed to the independent variable tested and only 16.28 % of the total variation was not explained by the model. The regression model having a R^2 value higher than 70% is considered to have a very high correlation. The adjusted R^2 was valued at 78.30% and predicted R^2 was valued at 65.11%. The adjusted R^2 value indicates good understanding existed between experimental and predicted values of purity of biodiesel. The predicted R^2 of 0.6511 is in reasonable agreement with the adjusted R^2 of 0.7830. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In this experiment, the adequate signal ratio indicates 11.993. This model can be used to navigate the design space.

4.3.1 Design Expert Plot of Yield.

To investigate the effect of methyl ester concentration in biodiesel, the response surface methodology was used and the three dimensional (3D) plot was drawn. In Figure 4.2 indicate the response surface curve for yield in biodiesel. The response surface representing the yield was a function of two response variable. The reaction time at X axis and Y axis is catalyst concentration.



Figure 4.2: Response surface plot of biodiesel yield from waste cooking oil; catalyst concerntration versus reaction time.

From the graph, it can be shown that the catalyst concentration gave the significant effect and major influence to optimize the yield of biodiesel than the reaction time. As the catalyst concentration increased, the amount of biodiesel yield also increased because of the conversion of triglycerides was increased. But in sufficient amount of catalyst resulted in incomplete conversion of triglycerides and thus reduced the esters yield. This is because addition of excess alkaline catalyst, sodium hydroxide caused more triglycerides to participate in the saponification reaction, producing more soap and thus reducing the biodiesel yield. So, that mean the extending catalyst concentration give the positive effect for optimization of yield but after one limit it changed to be the negative effect to optimize the biodiesel yield.



Solutions No	Time	Catalyst	Response 1	Desirability	
1	33.87	1.24	55.9630	1	
2	31.50	1.03	56.0566	1	
3	35.17	1.18	56.0317	1	
<u>4</u>	<u>30.37</u>	<u>1.08</u>	<u>56.3146</u>	<u>1</u>	<u>Selected</u>
5	35.79	1.11	55.9785	1	
6	33.01	1.05	56.0283	1	
7	34.50	1.17	56.0849	1	
8	36.18	1.14	55.9759	1	
9	33.01	1.21	56.1199	1	
10	36.47	1.16	55.9495	1	

Table 4.9: The result of optimization of methyl ester concentration

The optimum condition to get the higher value of biodiesel yield percentage was suggestion from RSM is condition 4 which the reaction time is 30.37 minutes and catalyst concentration is 1.08 %. The result that is predicted is 56.3146 % of biodiesel yield.



CHAPTER 5

CONCLUSION AND RECOMENDATION

5.1 Conclusion

In recent years, biodiesel has become more attractive as an alternative fuel for diesel engines because of its environmental benefits and the fact that it is made from renewable resources. As the conclusion from this research, waste cooking oil can be utilized for making biodiesel fuel, thus helping to reduce the production cost. In the homogenous alkali catalyzed (sodium hydroxide) reaction, it is very good process of production of biodiesel with relatively high conversion rate. In transesterification reaction, the maximum of alkali catalyst concentration is 1.5 wt% and it is to avoid the saponification process occur that produce the soap. This single step catalyzed process provides a simple and economic method to produce biodiesel from waste cooking oil.

From this experiment the methyl esters content in the final product which indicates the purity of the biodiesel exhibited tendency with both of the parameters which is the reaction time and catalyst concentration. The optimum condition to get the higher value of methyl ester concentration percentage was suggestion from RSM by the model equation is reaction time at 30.24 minutes and catalyst concentration is 0.58 %. The result that is predicted is 77.96 % of methyl ester concentration. For the biodiesel yield percentage, catalyst concentration gives a major influence for yield percentage in producing biodiesel than the reaction time. Excess reaction time could not promote the conversion but favors the reverse reaction to occurred resulting in a reduction in the product yield. In this experiment, catalyst concentration shows clear influence factors



in the biodiesel yield. High concentration result in formation of soap and low catalyst concentration caused not all triglycerides were not converted to methyl esters. Therefore it would reduce the yield of the product. The optimum condition to get the higher value of yield percentage was suggestion from RSM by the model equation is condition 4 which the reaction time is 30.37 minutes and catalyst concentration is 1.08 %. The result that is predicted is 56.31 % of biodiesel yield.

5.2 Recommendation

In this research work, it is recommended that noise during experiment is eliminated. First of all, the raw material are used in biodiesel production, WCO are not consistent. The sources of WCO came from many places and it can give the big affect of the FFA in the WCO. So, for the future the pre-treatment is very important to do like checking the conversion of FFA in waste oil before starting the experiment. The temperature of WCO also must maintain at room temperature, 25 °C. The equipments must be standardized for all 13 samples to make sure all the reading of the result is reliability. All the equipment like shaking water bath, beaker, and others and also procedure like washing step and time to settling must be same and maintain for all the 13 samples. Used the other waste oil like waste lubricant oil or something frying oil that used for two or three times to get the higher yield of biodiesel.



REFERENCES

A.Demirbas (2002). Energy Conversion and Management 44/2093-2109

- Aksoy, Kahraman, Karaosmanoglu, and Civelekoglu (1988). *Evaluation of Turkish* sulphur olive oil as an alternative diesel fuel. J. Am. Oil Chem. Soc., 65, 936-938.
- Alcantara, Amores, Canoira, Fidalgo, France, and Navarro (2000). *Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow*. Biomass Bioenerg., 18, 515-527.
- Alencar, J.W., Alves, P.B., and Craveiro (1983). A Pyrolysis of tropical vegetable oils.J.Agric. Food Chem., 31, 1268-1270
- American Society for Testing and Materials, Standard Specification for Biodiesel Fuel (b100) (2002).Blend Stock for Distillate Fuels, Designation D6751-02, ASTM International, West Conshohocken, PA.
- Antolý n G, Tinaut FV, Bricen; o Y, et al. (2002). *Optimisation of biodiesel production* by sunflower oil transesterification. Bioresour Technol ;83:111–4
- Bagby, M.O., Freedman, B., Schwab, A.W., (1987). Seed oils for diesel fuels sources and properties. ASAE Paper 87-1583.



- Bala B.K. (2005) Studies On Biodiesel From Transformation Of Vegetable Oils For Diesel Engines. Energy Edu Sci Technol; 15:1-43
- Billaud, Dominguez, Broutin, and Busson (1995). Production of hydrocarbons by pyrolysis of methyl esters from rapeseed oil. J. Am. Oil Chem. Soc., 72, 1149-1154.
- Canakci M, Van Gerpen J. (2001) *Biodiesel production from oils and fats with high free fatty acids*. Trans ASAE; 44:1429–36.

Chand N. (2002) Plant oils-fuel of the future. J Sci Ind Res; 61:7-16.

- Clark, S.J., Wagner, L., Schrock, M.D., Piennaar, P.G., (1984). Methyl and ethyl soybean esters as renewable fuels for diesel engines. JAOCS 61(10), 1632–1638. Conference on Plant and Vegetable Oils as Fuels, ASAE Publication 4-82, Fargo, ND, USA, pp. 117–122.
- Demirbas A. (2003). Biodiesel fuels from vegetable oils via catalytic and noncatalytic supercritical alcohol transesterifications and other methods: a survey. Energy Converse Manage; 44:2093–109.
- Dykstra, Selke, Sorenson, and Pryde (1988). Vegetable oil methyl ester as a diesel substitute. Chem. Ind. 21, 863-865.
- Fargo, ND, USA, *Triglycerides-based diesel fuels in transesterification process* pp. 218–223.

- Feuge, R. 0. and Grose, T.: (1949). Modification of vegetable oils. VII. Alkali catalyzed interesterilication of peanut oil with ethanol. J. Am. Oil Chem. Sot., 26,97-102
- Fillieres, Benjelloun-Mlayah, and Delmas (1995). *Ethanolysis of rapeseed oil: quantitation of ethyl esters, mono-, di-, and triglycerides and glycerol by high performance size exclusion chromatography.* J. Am. Oil Chem. Soc., 72, 427-432.
- Freedman, B., Pryde, E. H., and Mounts, T. L.: (1984). Variables affecting the yields of fatty esters from transesteritied vegetable oils. J. Am. Oil Chem. Sot., 61, 1638-1643
- Freedman, B., Pryde, E.H., (1982). Fatty esters from vegetable oils for use as a diesel fuel. In: Vegetable Oils Fuels—Proceedings of the International
- Fukuda H, Kondo A, Noda H. (2001) *Biodiesel fuel production by transesterification* of oils. J Biosci Bioeng; 92(5):405–16.
- <u>G. E. P. Box</u> and <u>K. B. Wilson</u>, (1951). *Central composite designs*. J.R. Stat. Soc X111 (1), 1-35
- G. Vicente et al. (2004). Bioresource Technology 92 297-305
- Grossley, Heyes, and Hudson (1962). *The effect of heat on pure triglycerides*. J. Am. Oil Chem. Soc., 39, 9-14.

Harrington KJ, DA' rcy-Evans C. (1985). Ind Eng Chem Prod Res Dev 24:314.


J. Metzer (1996) Pulse of the Planet.

- Korbitz W. (1999) Biodiesel production in Europe and North America, an encouraging prospect. Renew Energy; 16:1078–1083.
- Korus, R.A., Mousetis, T.L., Lloyd, L., (1982). Polymerization of vegetable oils. In: Vegetable Oils Fuels—Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, ASAE Publication 4-82,

Krawczyk, T., (1996). Biodiesel. INFORM 7 (8), 801-822.

- Lee, Ye, Landen, and Eitenmiller (2000). Optimization Production Of Ethyl Esters Of Grease Using 95% Ethanol By Response Surface Methodology. J. Am. Oil Chem. Soc., 76, 517-521 (1999)
- M. Canakci and J.H. Van Gerpen (1999). "Biodiesel Production via Acid Catalysis," Transactions of the ASAE, 42(5):1203-1210

Ma F, Hanna MA. (1999) Biodiesel production: a review. Bioresour Technol; 70:1–15.

- McBride, N., (1999). Modeling the production of biodiesel from waste frying oil.B.A.Sc. thesis, Department of Chemical Engineering, University of Ottawa.
- Muniyappa PR, Brammer SC, Noureddini H. (1996) *Improved conversion of plant oils* and animal fats into biodiesel and co-product. Bioresour Technol; 56:19–24.



- Nelson et al., (1996) Watanabe et al., (2001) Producing Biodiesel from esterificatin method 299-55.
- Nelson LA, Folgia TA, Marmer WN. JAOCS (1996); *Triglycerides-based diesel fuels* 73(8):1191–5.
- Nitske, R.W., Wilson, C.M., (1965). *Rudolph Diesel, Pioneer of the Age of Power*. University of Oklahoma Press, Norman, OK.139.
- Nye, Williamson, Deshpande, Schrader, Snively, Yurkewich, and French (1983). *Conversion of used frying oil to diesel fuel by traneseterification*: preliminary test. J. Am. Oil Soc. Chem. 60 (8), 1598-1601.
- Perkins, L.A., Peterson, C.L., (1991). Durability testing of transesteriWed winter rape oil (Brassica napus L.) as fuel in small bore, multi-cylinder, DI, CI engines. SAE Paper 911764.
- Peterson, C. L., Auld, D. L., and Korus, R A. (1983). *Winter rape oil fuel for diesel engines*: recovery and utilization. J. Am. Oil Chem. Sot., 60, 1579-1587.
- Peterson, C.L., Feldman, M., Korus, R., Auld, D.L. (1991). *Batch type transesterification process for winter rape oil*. Appl. Eng. Agric. 7(6), 711–716.
- Pryde, E. H. (1983): Vegetable oil as diesel fuel overview. J. Am. Oil Chem. Sot., 60, 1557-1558.
- Schmidt, K., Van Gerpen, J.H., (1996). *The effect of biodiesel fuel composition on diesel combustion and emissions*. SAE Paper 961086.



- Scholl, K.W., Sorenson, S.C., (1993). Combustion of soybean oil methyl ester in a direct injection diesel engine. SAE Paper 930934.
- Schwab et al (1988). Diesel fuel from thermal decomposition of soybean oil. J. Am. Oil Chem. Soc., 65, 1781-1786.
- Schwab, A. W., Bagby, M. O., and Freedman, B.: *Preparation and properties of diesel fuels from vegetable oils*.
- Sheehan, Camobreco, Duffield, Graboski, and Shapouri (1998). Life cycle inventory of biodiesel and petroleum diesel for use in an urban bus, final report for U.S.
 Dept. of Energy's Office of Fuel Development.

Sprules FJ, Price D (1950). Production of fatty esters US Patent 2, 366–94.

- Srivastava, A. and Prasad, R (2000). *Triglycerides-based diesel fuels*. Renew. Sust. Energ. Rev., 4, 111-133
- Triveni et al., (2001) *Optimization Of Alkali-Catalyzed Transesterification Of Brassica Carinata Oil For Biodiesel Production*. Energy fuel; 18:77-83.
- Vicente, G., (2001). *Study of the biodiesel production*. PhD Thesis, Faculty of Chemistry. Complutense University of Madrid.
- Wagner, L.E., Clark, S.J., Schrock, M.D., (1984). *Effects of soybean oil esters on the performance, lubrication oil, and water of diesel engines.* SAE Paper 841385.
- Wright, Segur, Clark, Coburn, Langdon, and DuPuis (1944). A report on ester interchange. Oil Soap, 21, 145-148.

- Y. Zhang, M.A. Dube, D.D. McLean, M. Kates, (2003). *Biodiesel production from* waste cooking oil: economic assessment and sensitivity analysis, Bioresour. Technol. 90 229–240.
- Zhang Y, Dube' MA, McLean DD, et al. (2003). Biodiesel production from waste cooking oil: 1. process design and technological assessment. Bioresour Technol; 89:1–16.
- Zhang, Q., Feldman, M., Peterson, C., (1988). *Diesel engine durability when fueled with methyl ester of winter rapeseed oil*. ASAE Paper88-1562.
- Zhang, Y., Van Gerpen, J.H., (1996). *Combustion analysis of esters of soybean oil in a diesel engine*. SAE Paper 960765.
- Ziejewski, Kaufman, Schwab, and Pryde, (1984) *Preparation and properties of biodiesel from vegetable oils*. ASAE; 44:1429–36.



APPENDIX A

Result in DOE and Graph of the Methyl Ester Concentration



DESIGN OF DOE

6	1	Block 1	90.00	1.00	75.34
4	2	Block 1	90.00	1.50	76.32
5	3	Block 1	30.00	1.00	77.08
1	4	Block 1	30.00	0.50	77.86
11	5	Block 1	60.00	1.00	74.7
8	6	Block 1	60.00	1.50	73.32
3	7	Block 1	30.00	1.50	76.39
9	8	Block 1	60.00	1.00	76.21
2	9	Block 1	90.00	0.50	74.18
13	10	Block 1	60.00	1.00	76.03
10	11	Block 1	60.00	1.00	74.66
12	12	Block 1	60.00	1.00	75.1
7	13	Block 1	60.00	0.50	75.08

DESIGN SUMMARY

Study Type Response Surface Initial Design Central Composite Design Model Quadratic				Experiments 13 Blocks No Block		
Response	Name	Units	Obs	Minimum	Maximum	
Trans Y1 None	Model Response 1 Quadratic	TLC	13	73.32	77.86	
Factor Low Coded	Name High Coded	Units	Туре	Low Actual	High Actual	
A Time	Numeric	30.00	90.00	-1.000	1.000	
BCatalyst	Numeric	0.50	1.50	-1.000	1.000	



EVALUATION RESULT

2 Factors: A, B

Design Matrix Evaluation for Response Surface Quadratic Model

No aliases found for Quadratic Model

Degrees of Freedom for Evaluation Model 5 Residuals 7 Lack Of Fit 3 Pure Error 4 Corr Total 12

			Power	at 5 % alpha	level for effe	ct of
Term	StdErr**	VIF	Ri-Squared	1/2 Std. Dev.	1 Std. Dev.	2 Std. Dev.
А	0.41	1.00	0.0000	8.3 %	18.6 %	55.9 %
В	0.41	1.00	0.0000	8.3 %	18.6 %	55.9 %
A^2	0.60	1.17	0.1451	11.2 %	30.1 %	81.2 %
\mathbf{B}^2	0.60	1.17	0.1451	11.2 %	30.1 %	81.2 %
AB	0.50	1.00	0.0000	7.2 %	14.0 %	40.8 %
**Basi	s Std. Dev. =	= 1.0				

Measures Derived From the (X'X)⁻¹ Matrix

Std	Leverage	Point Type
1	0.7902	Fact
2	0.7902	Fact
3	0.7902	Fact
4	0.7902	Fact
5	0.4943	Axial
6	0.4943	Axial
7	0.4943	Axial
8	0.4943	Axial
9	0.1724	Center
10	0.1724	Center
11	0.1724	Center
12	0.1724	Center
13	0.1724	Center
Average =	0.4615	

Maximum Prediction Variance (at a design point) = 0.790 Average Prediction Variance = 0.462

Condition Number of Coefficient Matrix = 2.231

G Efficiency (calculated from the design points) = 58.4 %

Scaled D-optimality Criterion = 2.571

Determinant of $(X'X)^{-1} = 5.987E-5$ Trace of $(X'X)^{-1} = 1.480$

Correlation Matrix of Regression Coefficients

	Intercept	А	В	A^2	\mathbb{B}^2	AB
Intercept	1.000					
А	0.000	1.000				
В	0.000	0.000	1.000			
A^2	-0.414	0.000	0.000	1.000		
\mathbb{B}^2	-0.414	0.000	0.000	-0.381	1.000	
AB	0.000	0.000	0.000	0.000	0.000	1.000

Correlation Matrix of Factors [Pearson's r]

	А	В	A^2	\mathbf{B}^2	AB
А	1.000				
В	0.000	1.000			
A^2	0.000	0.000	1.000		
\mathbb{B}^2	0.000	0.000	0.381	1.000	
AB	0.000	0.000	0.000	0.000	1.000

FIT SUMMARY

Response: Response 1

*** WARNING: The Cubic Model is Aliased! ***

Sequenti	al Model Sum of	f Squares				
	Sum of		Mean	\mathbf{F}		
Source	Squares	DF	Square	Value	Prol	b
> F						
<u>Mean</u> 742	<u>219.57</u>	<u>1</u>	<u>74219.57</u>			Suggested
Linear	5.22	2	2.61	1.97	0.1899	
2FI	3.26	1	3.26	2.93	0.1209	
<u>Quadratic</u>	<u>5.50</u>	<u>2</u>	<u>2.75</u>	4.28	<u>0.0609</u>	Suggested
Cubic	1.47	2	0.73	1.21	0.3716	Aliased
Residual	3.02	5	0.60			
Total 742	238.04	13	5710.62			

"Sequential Model Sum of Squares": Select the highest order polynomial where the additional terms are significant and the model is not aliased.



Lack of Fit Tests

	Sum of		Mean	F	
Source	Squares	DF	Square	Value	Prob > F
Linear	11.09	6	1.853.42	0.1272	
2FI	7.83	5	1.572.90	0.1624	
Quadratic	<u>2.33</u>	<u>3</u>	0.781.44	<u>0.3568</u>	Suggested
Cubic	0.86	1	0.861.59	0.2755	Aliased
Pure Erro	or 2.16	4	0.54		

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Model Su	mmary	Statistics			
	Std.	Adjusted	Predicted		
Source	Dev	R-Squared	R-Squared R-Squared	PRESS	
Linear	1.15	$0.\bar{2}827$	0.1392 -0.5042	27.79	
2FI	1.05	0.4590	0.2787 -0.6453	30.39	
<u>Quadratic</u>	0.80	<u>0.7568</u>	<u>0.5830</u> <u>-0.2984</u>	23.99	Suggested
Cubic	0.78	0.8363	0.6071 -4.5887	103.24	Aliased

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared"

and the "Predicted R-Squared".

ANOVA

Use your mouse to right click on individual cells for definitions.

Response:	Response 1
------------------	------------

ANOVA for Response Surface Quadratic Mode	ł
Analysis of variance table [Partial sum of squares]	

	Sum of		Mean	F		
Source	Squares	DF	Square	Value	Prob > F	
Model	13.98	5	2.80	4.36	0.0403	significant
A	5.02	1	5.02	7.83	0.0266	
В	0.20	1	0.20	0.31	0.5959	
A^2	5.49	1	5.49	8.55	0.0222	
B^2	1.00	1	1.00	1.55	0.2529	
AB	3.26	1	3.26	5.08	0.0589	
Residual	4.49	7	0.64			
Lack of Fit	2.33	3	0.78	1.44	0.3568	not significant
Pure Error	2.16	4	0.54			
Cor Total	18.47	12				

The Model F-value of 4.36 implies the model is significant. There is only a 4.03% chance that a "Model F-Value" this large could occur due to noise.



Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, A^2 are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy),

model reduction may improve your model.

The "Lack of Fit F-value" of 1.44 implies the Lack of Fit is not significant relative to the pure

error. There is a 35.68% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.80	R-Squared	0.7568
Mean	75.56	Adj R-Squared	0.5830
C.V.	1.06	Pred R-Squared	-0.2984
PRESS	23.99	Adeq Precision	6.679

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your

ratio of 6.679 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		S	Standard	95% CI	95% CI
Factor	Estimate	DF	Error	Low	High	VIF
Intercept	75.19	1	0.33	74.40	75.97	
A-Time	-0.92	1	0.33	-1.69	-0.14	1.00
B -Catalyst	-0.18	1	0.33	-0.96	0.59	1.00
A^2	1.41	1	0.48	0.27	2.55	1.17
\mathbf{B}^2	-0.60	1	0.48	-1.74	0.54	1.17
AB	0.90	1	0.40	-0.045	1.85	1.00

Final Equation in Terms of Coded Factors:

Response 1	=
+75.19	
-0.92	* A
-0.18	* B
+1.41	* A ²
-0.60	* B ²
+0.90	* A * B



Final Equation in Terms of Actual Factors:

=
* Time
* Catalyst
* Time ²
* Catalyst ²
* Time * Catalyst

Diagnostics Case Statistics

Standar	d Actual	Predicte	ed	Student	Cook's	Outlier	Run	
Order	Value	Value	Residual L	Leverage	Residual	Distance	e t	Order
1	77.86	77.99	-0.13	0.790	-0.365	0.084	-0.341	4
2	74.18	74.36	-0.18	0.790	-0.488	0.149	-0.460	9
3	76.39	75.83	0.56	0.790	1.538	1.485	1.750	7
4	76.32	75.80	0.52	0.790	1.415	1.258	1.551	2
5	77.08	77.51	-0.43	0.494	-0.755	0.093	-0.730	3
6	75.34	75.68	-0.34	0.494	-0.597	0.058	-0.568	1
7	75.08	74.77	0.31	0.494	0.549	0.049	0.520	13
8	73.32	74.40	-1.08	0.494	-1.902	0.589	-2.533	6
9	76.21	75.19	1.02	0.172	1.405	0.069	1.535	8
10	74.66	75.19	-0.53	0.172	-0.722	0.018	-0.694	11
11	74.70	75.19	-0.49	0.172	-0.667	0.015	-0.638	5
12	75.10	75.19	-0.086	0.172	-0.118	0.000	-0.109	12
13	76.03	75.19	0.84	0.172	1.158	0.047	1.193	10

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

1) Normal probability plot of the studentized residuals to check for normality of residuals.

- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Outlier t versus run order to look for outliers, i.e., influential values.
- 4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

NUMERICAL

Constraints

		Lower	Upper	Lower	Upper	
Name	Goal	Limit	Limit	Weight	Weight	Importance
Time	is in ra	nge 30	90	1	1	3
Catalyst	is in ra	nge 0.5	1.5	1	1	3
Response 1	maxim	ize 73.32	77.86	1	1	3



Solutions	5				
Number	Time	Catalyst	Response 1	De	sirability
1	<u>30.30</u>	<u>0.62</u>	<u>77.943</u>	<u>1.000</u>	Selected
<u>2</u>	<u>30.24</u>	<u>0.58</u>	<u>77.961</u>	<u>1.000</u>	
<u>3</u>	<u>30.52</u>	<u>0.63</u>	<u>77.9082</u>	<u>1.000</u>	
<u>4</u>	<u>30.25</u>	<u>0.70</u>	77.9062	1.000	
<u>5</u>	<u>30.64</u>	0.62	77.8928	1.000	
<u>6</u>	<u>30.09</u>	<u>0.74</u>	<u>77.9004</u>	<u>1.000</u>	
<u>7</u>	<u>30.61</u>	<u>0.59</u>	<u>77.9063</u>	<u>1.000</u>	
<u>8</u>	<u>30.60</u>	<u>0.65</u>	<u>77.8874</u>	<u>1.000</u>	
<u>9</u>	<u>30.36</u>	0.73	77.8716	<u>1.000</u>	
10	<u>90.00</u>	<u>1.28</u>	<u>75.896</u>	0.567	

10 Solutions found

Number of Starting Points 10

<u>Time</u>	<u>Catalyst</u>
<u>57.26</u>	<u>1.43</u>
<u>31.78</u>	<u>1.29</u>
<u>84.33</u>	<u>1.49</u>
<u>36.52</u>	0.73
38.69	<u>1.33</u>
<u>41.07</u>	<u>0.81</u>
<u>65.21</u>	<u>1.08</u>
<u>47.32</u>	<u>0.74</u>
<u>45.95</u>	1.25
<u>59.54</u>	0.90

POINT PREDICTION

Factor	Name	Level	Low]	Level	High Level Std. Dev.
Α	Time		60.00	30.00	90.00
0.000					
В	Catalyst		1.00	0.50	1.50
0.000					

Prediction SE Mean95% CI low95% CI high SE Pred 95% PI low 95% PI high Response 1 75.1859 0.33 74.40 75.97 0.87 73.13 77.24





Graph of TLC vs Time



Graph of TLC vs Catalyst





Graph of TLC vs Time and Catalyst



Graph of Residual vs Lambda (Box- Cox)





Graph of Predicted vs Actual



Graph of Residual vs Predicted





Graph of Outlier T vs Run Number



Graph of Cook's Distance vs Run Number





Graph of Catalyst vs Time



Graph of Catalyst vs Time



APPENDIX B

Result in DOE and Graph of the Yield



DESIGN OF EXPERIMENT

13	1	Block 1	60.00	1.00	52
3	2	Block 1	30.00	1.50	54.7
6	3	Block 1	90.00	1.00	48.92
2	4	Block 1	90.00	0.50	44.513
10	5	Block 1	60.00	1.00	54.271
5	6	Block 1	30.00	1.00	55.924
1	7	Block 1	30.00	0.50	47.45
12	8	Block 1	60.00	1.00	53.741
11	9	Block 1	60.00	1.00	55.863
7	10	Block 1	60.00	0.50	46.23
4	11	Block 1	90.00	1.50	51.256
8	12	Block 1	60.00	1.50	49.2
9	13	Block 1	60.00	1.00	55.863

Design Summary

Study Type Initial Desig Design Mod	Response Su gn Central Con el Quadratic	rface nposite	Experiments Blocks	s 13 No Blocks	
Response Trans	Name Model	Units	Obs	Minimum	Maximum
Y1 None	Response 1 RQuadratic	yield	13	44.51	55.92
Factor	Name	Units	Туре	Low Actual	High Actual
Low Coded	High Coded				
A Time		Numeric	30.00	90.00	-1.000
B Catalyst 1.000		Numeric	0.50	1.50	-1.000



EVALUATION

2 Factors: A, B

Design Matrix Evaluation for Response Surface Quadratic Model

No aliases found for Quadratic Model

Degrees of Freedom for Evaluation

Model5Residuals7Lack Of Fit3Pure Error4Corr Total12

Power at 5 % alpha level for effect of

Term	StdErr**	VIF	Ri-Squared	1/2 Std. Dev.	1 Std. De	v. 2Std.Dev.
А	0.41	1.00	0.0000	8.3 %	18.6 %	55.9 %
В	0.41	1.00	0.0000	8.3 %	18.6 %	55.9 %
A^2	0.60	1.17	0.1451	11.2 %	30.1 %	81.2 %
\mathbb{B}^2	0.60	1.17	0.1451	11.2 %	30.1 %	81.2 %
AB	0.50	1.00	0.0000	7.2 %	14.0 %	40.8 %
**Basis S	Std. Dev. = 1.0					

Measures Derived From the (X'X)⁻¹ Matrix

Std	Leverage	Point Type	
1	0.7902	Fact	
	2	0.7902	Fact
	3	0.7902	Fact
	4	0.7902	Fact
	5	0.4943	Axial
	6	0.4943	Axial
	7	0.4943	Axial
	8	0.4943	Axial
	9	0.1724	Center
	10	0.1724	Center
	11	0.1724	Center
	12	0.1724	Center
	13	0.1724	Center
	Average =	0.4615	

Maximum Prediction Variance (at a design point) = 0.790 Average Prediction Variance = 0.462



Condition Number of Coefficient Matrix = 2.231 G Efficiency (calculated from the design points) = 58.4 %

Scaled D-optimality Criterion = 2.571

Determinant of (X'X)⁻¹ = 5.987E-5 Trace of (X'X)⁻¹ = 1.480

Correlation Matrix of Regression Coefficients

	Intercept	А	В	A^2	\mathbb{B}^2	AB
Intercept	1.000					
А	0.000	1.000				
В	0.000	0.000	1.000			
A^2	-0.414	0.000	0.000	1.000		
\mathbb{B}^2	-0.414	0.000	0.000	-0.381	1.000	
AB	0.000	0.000	0.000	0.000	0.000	1.000

Correlation Matrix of Factors [Pearson's r]

	А	В	A^2	\mathbf{B}^2	AB
А	1.000				
В	0.000	1.000			
A^2	0.000	0.000	1.000		
\mathbb{B}^2	0.000	0.000	0.381	1.000	
AB	0.000	0.000	0.000	0.000	1.000

FIT SUMMARY

Response: Response 1 *** WARNING: The Cubic Model is Aliased! ***

Sequen	tial Model S	um of Squa	res			
	Sum of		Mean	\mathbf{F}		
Source	Squares	DF	Square	Value	Prob > F	1
Mean	34523.66	1	34523.66			
Linear	77.82	2	38.91	3.60	0.0663	
2FI	0.064	1	0.064	5.358E-003	0.9432	
Quadratic	77.82	<u>2</u>	<u>38.91</u>	<u>9.04</u>	0.0115	Suggested
Cubic	10.25	2	5.13	1.29	0.3534	Aliased
Residual	19.87	5	3.97			
Total	34709.48	13	2669.96			

"Sequential Model Sum of Squares": Select the highest order polynomial where the additional terms are significant and the model is not aliased.





it Tests					
Sum of		Mean	F		
Squares	DF	Square	Value	Prob > F	ז
97.52	6	16.25	6.21	0.0494	
97.46	5	19.49	7.44	0.0373	
<u>19.64</u>	<u>3</u>	<u>6.55</u>	<u>2.50</u>	<u>0.1986</u> b	Suggested
9.39	1	9.39	3.59	0.1312	Aliased
10.48	4	2.62			
	t Tests Sum of Squares 97.52 97.46 <u>19.64</u> 9.39 10.48	It Tests Sum of Squares DF 97.52 6 97.46 5 <u>19.64</u> <u>3</u> 9.39 1 10.48 4	It TestsSum ofMeanSquaresDFSquare 97.52 616.25 97.46 519.49 $\underline{19.64}$ $\underline{3}$ $\underline{6.55}$ 9.39 1 9.39 10.48 4 2.62	It TestsSum ofMeanFSquaresDFSquareValue 97.52 616.256.21 97.46 519.497.44 19.64 36.552.50 9.39 19.393.59 10.48 42.62	Sum ofMeanFSquaresDFSquareValueProb > H97.52616.256.210.049497.46519.497.440.0373 $\frac{19.64}{9.39}$ $\frac{3}{1}$ $\frac{6.55}{9.39}$ $\frac{2.50}{3.59}$ $\frac{0.1986b}{0.1312}$ 10.4842.62 $1000000000000000000000000000000000000$

"*Lack of Fit Tests*": Want the selected model to have insignificant lack-of-fit. **Model Summary Statistics**

	Std.		Adjusted	Predicted		
Source	Dev.	R-Squar	ed R-Square	d R-Squared	PRESS	
Linear	3.29	0.4188	0.3025	0.0154	182.95	
2FI	3.46	0.4191	0.2255	-0.6154	300.17	
Quadratic	2.07	0.8379	0.7221	<u>0.0114</u>	<u>183.69</u>	Suggested
Cubic	1.99	0.8931	0.7434	-4.9557	1106.68	Aliased

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared"

and the "Predicted R-Squared".

ANOVA

Use your mouse to right click on individual cells for definitions.

Response: Response 1

ANOVA for Response S	Surface Reduced Quadratic Model
Analysis of variance table [H	Partial sum of squares]

	Sum of		Mean	F		
Source	Squares	DF	Square	Value	Prob > F	
Model	155.58	3	51.86	15.43	0.0007	significant
A	29.86	1	29.86	8.89	0.0154	
В	47.96	1	47.96	14.27	0.0044	
B^2	77.76	1	77.76	23.14	0.0010	
Residual	30.24	9	3.36			
Lack of Fit	19.77	5	3.95	1.51	0.3556	not significant
Pure Error	10.48	4	2.62			
Cor Total	185.82	12				

The Model F-value of 15.43 implies the model is significant. There is only a 0.07% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, B^2 are significant model terms.



Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy),

model reduction may improve your model.

The "Lack of Fit F-value" of 1.51 implies the Lack of Fit is not significant relative to the pure

error. There is a 35.56% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	1.83	R-Squared	0.8372
Mean	51.53	Adj R-Squared	0.7830
C.V.	3.56	Pred R-Squared	0.6511
PRESS	64.83	Adeq Precision	11.993

The "Pred R-Squared" of 0.6511 is in reasonable agreement with the "Adj R-Squared" of 0.7830.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your

ratio of 11.993 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI	
Factor	Estimate	DF	Error	Low	High	VIF
Intercept	53.80	1	0.69	52.23	55.36	
A-Time	-2.23	1	0.75	-3.92	-0.54	1.00
B -Catalyst	2.83	1	0.75	1.13	4.52	1.00
\mathbf{B}^2	-4.91	1	1.02	-7.21	-2.60	1.00

Final Equation in Terms of Coded Factors:

Response 1	=
+53.80	
-2.23	* A
+2.83	* B
-4.91	* B ²

Final Equation in Terms of Actual Factors:

Response 1	=
+32.98105	
-0.074361	* Time
+44.90176	* Catalyst
-19.62371	* Catalyst ²

81



Diagnostics Case Statistics

Standard	Actual	Predicted	Student	Cook's	Outlier	Run		
Order	Value	Value	Residual	Leverage	Residual	Distance	t	Order
1	47.45	48.30	-0.85	0.500	-0.652	0.106	-0.630	7
2	44.51	43.83	0.68	0.500	0.524	0.069	0.502	4
3	54.70	53.95	0.75	0.500	0.579	0.084	0.556	2
4	51.26	49.49	1.77	0.500	1.364	0.465	1.444	11
5	55.92	56.03	-0.10	0.310	-0.068	0.001	-0.065	6
6	48.92	51.57	-2.65	0.310	-1.737	0.338	-2.009	3
7	46.23	46.06	0.17	0.333	0.111	0.002	0.104	10
8	49.20	51.72	-2.52	0.333	-1.683	0.354	-1.916	12
9	55.86	53.80	2.07	0.143	1.217	0.062	1.255	13
10	54.27	53.80	0.47	0.143	0.279	0.003	0.264	5
11	55.86	53.80	2.07	0.143	1.217	0.062	1.255	9
12	53.74	53.80	-0.056	0.143	-0.033	0.000	-0.031	8
13	52.00	53.80	-1.80	0.143	-1.059	0.047	-1.067	1

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

1) Normal probability plot of the studentized residuals to check for normality of residuals.

2) Studentized residuals versus predicted values to check for constant error.

3) Outlier t versus run order to look for outliers, i.e., influential values.

4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

NUMERICAL

Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Time	is in range	30	90	1	1	3
Catalyst	is in range	0.5	1.5	1	1	3
Response	maximize	44.513	55.924	1	1	3



Solutions

Number	Time	Cat	talyst	Response 1	Desirability
1	<u>33.87</u>	<u>1.24</u>	<u>55.963</u>	<u>1.0</u>	<u>00</u>
<u>2</u>	<u>31.50</u>	<u>1.03</u>	<u>56.0566</u>	<u>i 1.0</u>	<u>00</u>
<u>3</u>	<u>35.17</u>	<u>1.18</u>	<u>56.0317</u>	<u> </u>	<u>00</u>
<u>4</u>	<u>30.37</u>	1.08	<u>56.3146</u>	<u>i</u> <u>1.0</u>	00 Selected
<u>5</u>	<u>35.79</u>	<u>1.11</u>	<u>55.9785</u>	<u>1.0</u>	<u>00</u>
<u>6</u>	<u>33.01</u>	1.05	<u>56.0283</u>	<u>1.0</u>	<u>00</u>
<u>7</u>	<u>34.50</u>	<u>1.17</u>	<u>56.0849</u>	<u>1.0</u>	<u>00</u>
<u>8</u>	36.18	<u>1.14</u>	<u>55.9759</u>	<u>1.0</u>	<u>00</u>
<u>9</u>	<u>33.01</u>	1.21	<u>56.1199</u>	<u>1.0</u>	<u>00</u>
<u>10</u>	<u>36.47</u>	<u>1.16</u>	<u>55.9495</u>	<u>1.0</u>	<u>00</u>

10 Solutions found

Number of Starting Points 10

<u>Time</u>	<u>Catalyst</u>
<u>62.37</u>	<u>0.92</u>
<u>78.75</u>	<u>1.19</u>
86.92	<u>1.29</u>
<u>33.37</u>	0.90
<u>83.79</u>	<u>0.91</u>
67.51	<u>1.47</u>
70.50	<u>1.10</u>
56.80	<u>0.92</u>
<u>51.01</u>	0.84
<u>63.47</u>	<u>0.71</u>

POINT PREDICTION

Factor	Name	Level	Low Lo	evel High L	evel Std. Dev.
Α	Time		60.00	30.00	90.00
0.000					
В	Catalyst		1.00	0.50	1.50
0.000					

 Prediction
 SE Mean9
 5% CI low
 95% CI high
 SE Pred 95% PI low
 95% PI high

 Response 1
 53.7974
 0.69
 52.23
 55.36
 1.96
 49.36
 58.23





Graph of Yield vs Time



Graph of Yield vs Catalyst



Graph of Residual vs Lambda (Box-Cox)



Graph of Normal vs Residual





Graph of Predicted vs Actual



Graph of Residual vs Predicted





Graph of Catalyst vs Time



