UNIVERSITI MALAYSIA PAHANG

	BORANG PENGESAHA	AN STATUS TESIS*
JUDUL	: PRODUCTION OF BIODIES	EL FROM WASTE
	COOKING OIL AND RBD	
	TRANSESTERIFICATION	PROCESS
	SESI PENGAJIAN :	2008/2009
Saya	SITI FATIMA	AH ARIFIN
	(HURUF BE nbenarkan tesis (PSM/ Sarjana/Dokto aysia Pahang dengan syarat-syarat kegu	r Falsafah)* ini disimpan di Perpustakaan
 Perpu penga Perpu penga 	ijian sahaja. Istakaan dibenarkan membuat salinan te Ijian tinggi. a tandakan (√) SULIT (Mengandungi ma	dibenarkan membuat salinan untuk tujuan esis ini sebagai bahan pertukaran antara institusi uklumat yang berdarjah keselamatan atau ysia seperti yang termaktub di dalam
		aklumat TERHAD yang telah ditentukan adan di mana penyelidikan dijalankan)
	TIDAK TERHAD	Disahkan oleh
(TAN	DATANGAN PENULIS)	(TANDATANGAN PENYELIA)
Alamat Tetap	D-212, Felda Jengka 10,	
	26400 Bandar Jengka,	Nama Penyelia
	Pahang Darul Makmur	
Tarikh :		Tarikh:
CATATAN :	 * Potong yang tidak berkenaan. ** Jika tesis ini SULIT atau berkuasa/organisasiberkenaan der dikelaskan sebagai SULIT atau T 	ngan menyatakan sekali sebab dan tempoh tesis ini perlu
		esis bagi Ijazah Doktor Falsafah dan Sarjana secara agi pengajian secara kerja kursus dan penyelidikan, Auda (PSM).

PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL AND RBD PALM OIL USING BATCH TRANSESTERIFICATION PROCESS

SITI FATIMAH ARIFIN

UNIVERSITI MALAYSIA PAHANG

"I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Degree of Chemical Engineering"

Signature:Name of Supervisor: Madam Ruwaida Abdul RasidDate: 2 May 2009

PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL AND RBD PALM OIL USING BATCH TRANSESTERIFICATION PROCESS

SITI FATIMAH ARIFIN

A thesis submitted in fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering Universiti Malaysia Pahang

MAY 2009

I declare that this thesis entitled "Production of Biodiesel from Waste Cooking Oil and RBD Palm Oil Using Batch Transesterification Process" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

Signature	:
Name	: Siti Fatimah Binti Arifin
Date	: 2 May 2009

Dedicated especially to Father, Mother, Brothers and Sisters who give me inspiration and support that made this work possible.

ACKNOWLEDGEMENT

Firstly, I want to thank my supervisor Mrs. Ruwaida Abdul Rasid for her guidance towards this project. I also indebted to all the Technical Staff of Faculty of Chemical Engineering and Natural Resources for their help in finding all the material that was used in this project, giving their free time by opening the laboratory for me to do the experiment.

Besides that I also want to thank all my fellow colleagues for their support and their help in order to finish this project. I cannot mention all their names but their help are very much appreciated.

ABSTRACT

Waste Cooking Oil (WCO) has significant potential as the raw material or starting substance for biodiesel production. The objective of this research is to examine the performance of yield and purity of biodiesel from WCO as the starting material with different catalyst (NaOCH₃) concentration and reaction time via single step batch transesterification process. It is also to investigate the extent to which the sodium methoxide (NaOCH₃) as the catalyst and the effect of batch transesterification process on various parameters in production of biodiesel. The purity of methyl ester content in biodiesel is measured by Gas Chromatography. The exhaust emissions of biodiesel produced were evaluated by combustion test using Gas Combustion Unit. Results indicate that the higher conversion was obtained when RBD palm oil which is 98.2% yield and 97.5% purity instead of 96.8% yield and 94.7% purity in WCO used as the raw material. Biodiesel produced from WCO gives less exhaust emission of CO and CO_2 compared to commercial diesel thus contributed to the reduction of greenhouse gas that effect the global warming.

ABSTRAK

Minyak masak terpakai mempunyai potensi sebagai bahan mentah dalam penghasilan biodiesel. Objektif kajian adalah untuk memeriksa kadar hasil dan ketulenan biodiesel yang dihasilkan daripada minyak masak terpakai, dengan kepekatan mangkin sodium metoksida dan masa tindakbalas yang berbeza dalam satu langkah proses trasesterifikasi berkelompok. Kajian ini juga adalah untuk menyiasat takat kepekatan mangkin sodium metoksida dan kesan proses trasesterifikasi berkelompok ke atas pelbagai parameter dalam penghasilan biodiesel. Ketulenan metil ester di dalam biodiesel diukur dengan Gas Kromatografi. Pancaran buangan daripada biodiesel yang dihasilkan dinilai dengan ujian pembakaran menggunakan Unit Pembakaran Gas. Keputusan menunjukkan penukaran tertinggi diperolehi apabila minyak sawit digunakan sebagai bahan mentah yang mana memberi 98.2% kadar hasil dan 97.5% ketulenan, sebaliknya 96.8% kadar hasil dan 94.7% ketulenan diperolehi jika minyak masak terpakai diguanakan sebagai bahan mentah. Biodiesel yang dihasilkan daripada minyak masak terpakai memberi pancaran buangan karbon monoksida dan karbon dioksida yang kurang berbanding diesel komersial, seterusnya menyumbang kepada pengurangan kesan gas rumah hijau yang memberi kesan kepada pemanasan global.

TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	TITLE	iii
	DECLARATION	iv
	DEDICATION	v
	ACKNOWLEDGEMENT	vi
	ABSTRACT	vii
	ABSTRAK	viii
	LIST OF FIGURES	xiv
	LIST OF TABLES	XV
	LIST OF APPENDICES	xvi

1 INTRODUCTION

1.1	Background of study	1
1.2	Problem statement	2
1.3	Objectives	3
1.4	Scopes of study	3
1.5	Rationales and Significances	4

	LITE	RATURE REVIEW	5
2.1	Histo	rical Background on Biodiesel Production	5
2.2	Raw M	Material	7
	2.2.1	Straight Vegetable Oils (SVOs)	7
	2.2.2	Waste Cooking Oils (WCOs)	8
2.3	Solve	nt	8
2.4	Cataly	/st	9
	2.4.1	Homogeneous Catalyst	9
	2.4.2	Heterogeneous Catalyst	9
	2.4.3	Enzyme Catalyst	10
2.5	Proce	ess of Synthesizing Biodiesel	10
	2.5.1	Direct Use and Blending	11
	2.5.2	Micro-emulsion Process	11
	2.5.3	Thermal Cracking (Pyrolysis)	11
	2.5.4	Transesterification Process	12

3 METHODOLOGY

3.1	Intro	duction	13
3.2	Raw Material		15
	3.3	Equipment Selection	15
	3.4	Design of Experiment	17

3.5	Experi	ment procedure	18
	3.5.1	Pre-treatment	18
	3.5.2	Catalyst Preparation	18
	3.5.3	Transesterification Process	18
	3.5.4	Settling Process	19
	3.5.5	Methanol Recovery	19
	3.5.6	Purification Process	19
3.6	Analys	sis	20
	3.6.1	Biodiesel Yield	20
	3.6.2	Methyl Ester Purity	20
	3.6.3	Exhaust Emission of Biodiesel	21

4 RESULT AND DISCUSSIONS 22

4.1	Introduction	22
4.2	Effect of Catalyst Concentration	23
4.3	Effect of Reaction Time	26
4.4	Combustion Test	29

5 CONCLUSION AND RECOMMENDATION 31

5.1	Conclusion	31
5.2	Recommendation	32

REFERENCES 33

APPENDICES

11

36

LIST OF TABLES

TABLE NO.

TITLE

PAGE

4.1	Effect of NaOCH ₃ concentration for RBD	
	palm oil	23
4.2	Effect of NaOCH ₃ concentration for WCO	23
4.3	Effect of reaction time for RBD palm oil	26
4.4	Effect of reaction time for WCO	27
4.5	The exhaust emissions of biodiesel s	
	amples of RBD palm oil and WCO	
	compared to conventional diesel fuel	29
5.1	optimum condition of highest yield	
	and purity of biodiesel production	31

LIST OF FIGURES

FIGURE	TITLE	PAGE
3.1	Experimental Methodology	14
3.2	Filter Press	15
3.3	Shaking Water Bath	16
3.4	Hot Plate	16
3.5	Rotary Evaporator	16
3.6	Mechanical Stirrer	17
4.1	Effect of NaOCH3 concentrations on	
	biodiesel yield	24
4.2	Effect of NaOCH ₃ concentrations on	
	methyl ester purity	24
4.3	Effect of reaction time on biodiesel yield	27
4.4	Effect of reaction time on methyl ester purity	28

LIST OF APPENDICES

APPENDICH	ES TITLE	PAGE
А	Calculation of Methanol Needs	36
В	Effect of Catalyst Concentration and	
	Reaction Time	38
С	Results of Analysis from	
	Gas Chromatography	41
D	Results from Combustion Test	50

CHAPTER 1

INTRODUCTION

1.1 Overview of Research

With the exception of the hydroelectricity and nuclear energy, the majority of the world energy needs are supplied through petrochemical sources, coal and natural gas. All of these sources are finite and at current usage rates will be consumed in the future (Meher *et al*, 2006). The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum based fuels (Fukuda *et al*, 2001).

Biodiesel, derived from vegetable oil or animal fats by transesterification with alcohol like methanol and ethanol, is recommended for use as a substitute for petroleum based diesel mainly because biodiesel is an oxygenated, renewable, biodegradable and environmentally friendly biofuel with similar flow and combustion properties and also low emission profile (Altin and Selim, 2001). It helps to reduces global warming gas emissions such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur and contains 11% oxygen by weight. This characteristics of biodiesel reduce the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compared to petroleum based diesel fuels (Peterson and Hustrulid, 1998).

Currently, compared to petroleum based diesel, the high cost of biodiesel is a major barrier to its commercialization. It is reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (Fukuda *et al*, 2001). Use of low cost feedstocks such as waste cooking oil (WCO) should help make biodiesel competitive in price with petroleum diesel. Everywhere in the world, there is an enormous amount of waste lipids generated from restaurants, food processing industries and fast food shops everyday (Mittlebach and Gangl, 2001).

Because of the good properties and the environment improvement, many countries pay much attention to research and development (R&D) of biodiesel industry and constitute favorable legislation for it. More than 2.7 million tons biodiesel in 2003 was made in Europe, and 8-10 million tons is expected in 2010 (Altin and Selim, 2001).

Unfortunately, many of these feedstocks contain large amounts of free fatty acids (FFAs). These FFAs react with alkali catalysts to produce soaps that inhibit the fatty acid methyl esters (FAMEs) formation (Gerpen *et al*, 2004). In the case of the vegetable oils that contain up to 5% FFAs, the transesterification reaction can still be catalyzed with an alkali catalyst. However, additional catalyst must be added to compensate for the catalyst lost to soap. This soap can exhibit the separation of the methyl ester and glycerol and also contribute to emulsion formation during the washing step (Gerpen, 2005).

1.2 Problem Statement

The problem was to determine the extent to which the sodium methoxide (NaOCH₃) as the catalyst and the effect of batch transesterification process on various parameters where WCO and RBD palm oil are used as a raw material in production of biodiesel.

1.3 Objective of Study

The objective of this research is to examine the performance of yield and purity of biodiesel from WCO as the starting material with different catalyst (NaOCH₃) concentration and reaction time via single step batch transesterification process.

1.4 Scope of Study

The scopes of this research are:

- 1. To study the effect of catalyst concentration on yield and purity of biodiesel using batch transesterification process.
- 2. To study the combustion characteristic of biodiesel from both RBD palm oil and WCO using batch transesterification process and analyze the product using Gas Chromatography.

In the research that we conduct, we used the catalyst concentration of 0.25 to 1.5wt%. While the temperature range used is fixed at 40°C and the time that be conducted is between 20 to 50 minutes.

1.5 Rationale and Significances

The rationale of this research is to identify the important variables and to propose a suitable approach in scaling up the production of biodiesel from RBD palm oil and WCO using batch transesterification process. With the important variables such as catalyst concentration, reaction time, reaction temperature and ratio of methanol to oil used, we can produce high quality of biodiesel which have a high yield and high purity of methyl ester content. The high energy demand in the industrialized world as well as in the domestic sector, had caused pollution problems due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of smaller environmental impact than the fossil fuels such diesel fuels. The alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available that is familiar to biodiesel properties. Biodiesel also biodegradable, non-toxic and has low emission profiles as compare to diesel fuel.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background on Biodiesel Production

The first record of the use of vegetable oils as liquid fuels in internal combustion engines is from 1900 when Rudolf Diesel used peanut oil (Shay, 1993). However because of its low cost and easy availability, petroleum became the dominant energy source and petroleum diesel was then developed as the primary fuel for diesel engines. Nonetheless, petroleum and its derivatives fuels have periodically been through short supply and consequently, the search for alternative energy sources has emerged (Zanin *et al*, 2000). At that time the pyrolysis of different triglycerides was also used for liquid fuel supply in different countries. For example, hydrocarbons were produced in Chinaby a tung oil pyrolysis batch system used as liquid fuels (Chang and Wan, 1947). Another approach proposed at this time was the use of fatty acids ethyl or methyl esters, obtained by transesterification or alcoholysis of vegetable oils or esterification of fatty acids combined with transesterification of triglycerides (Keim, 1945).

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 (Marchetti *et al*, 2005). It is an alternatives fuel for diesel engines that is produced by chemical reaction of a vegetable oils or animal fats with an alcohol such as methanol. The product is called as methyl ester or biodiesel, which is receiving high attention as an alternative, nontoxic, biodegradable and renewable diesel fuels (Ma and Hanna, 1999). When biodiesel displaces petroleum diesel, it reduces global warming gas emission such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur and contains 11% oxygen by weight. These characteristics of biodiesel reduces the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compare petroleum-based diesel fuels (Peterson and Hustrulid, 1998).

Non-food product production from agricultural raw materials is more important than feed protein production in relation to the market economy of Malaysia, which are the biggest palm oil producer and exporter in the world. In 2000, export earnings from palm oil exceeded that from oil products (Malaysia exports some petroleum products after refining) and gas. That has made palm oil the biggest single export revenue earner for the country. Unlike oil and gas, which have a heavy foreign content, palm oil production is virtually 100% local. In 2000, the palm oil industry earned nearly US\$ 6.50 billion in exports and US\$ 7.5 billion in 2001. The Palm Oil Research Institute of Malaysia (PORIM) has taken an initiative since 1988 to look at the possibilities of converting oil palm products into fuels. One of the first products was the use of methyl ester of palm oil as diesel substitute. The use of methyl esters as fuel proved technically to be a very suitable substitute obtained by PORIM, Malaysia. The methyl ester of palm oil is known as palm oil diesel (POD) (Kalam *et. al.*, 2002).

Vegetable oils are widely available from various sources, and the glycerides present in the oils can be considered as a viable alternative for diesel fuel. Biodiesel, which is synthesized from bio-oil, is a realistic alternative of diesel fuel because it provides a fuel from renewable resources and has lower emissions than petroleum diesel. It is biodegradable and contributes a minimal amount of net greenhouse gases or sulfur to the atmosphere. More specifically, biodiesel cuts down on the amount of carbon dioxide, hydrocarbons, and particulate matter released into the environment (Dalai *et. al.*, 2003).

Biodiesel is defined as the monoalkyl esters of long chain fatty acids derived from renewable feed stocks like vegetable oils or animal fats. While most of the properties of biodiesel are comparable to petroleum based diesel fuel, improvement of its low temperature flow characteristic still remains one of the major challenges while using biodiesel as an alternative fuel for diesel engines. The biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher cloud points and pour points (Bhale *et al.*, 2008).

2.2 Raw Material

There are several sources that can be use as raw material for biodiesel production, such as non-edible oil, animal fats and vegetable oil. However, the vegetable oils extracted from plant that are composed of triglycerides was used because it contains similar fuel properties to diesel fuel except the higher viscosity and low oxidative stability that must be encountered before being converted into biodiesel. So, the vegetable oils that mostly used in transesterification reaction include pure plant oils (PPOs) or straight vegetable oils (SVOs) and waste vegetable oils (WVOs) (Knothe *et al.*, 2001).

2.2.1 Straight Vegetable Oils (SVO)

Pure plant oils (PPO) or commonly known as straight vegetable oils is not a byproduct of other industries either coming from domestic usage. Actually, the straight vegetable oils is a highly grade of oil extracted primarily from plant, usually, seeds of oilseed plants. In addition, these oils is the best starting material compare to waste cooking oils because of the conversion of triglyceride to fatty acid methyl ester is high and the reaction time is relatively short (Encinar *et al.*, 2006).

2.2.2 Waste Cooking Oils (WCO)

The feedstock coming from waste vegetable oils or commonly known as waste cooking oils is one of the alternative sources among other higher grade or refine oils. Waste cooking oil is easy to collect from other industries such as domestic usage and restaurant and also cheaper than other oils (refine oils). Hence, by using these oils as the raw material, we can reduce the cost in biodiesel production (Canakci and Van Gerpen, 2001). The advantages of using waste cooking oils to produce biodiesel are the low cost and prevention of environment pollution. These oils, need to be treat before dispose to the environment to prevent pollution. Due to the high cost of disposal, many individuals dispose waste cooking oils directly to the environment especially in rural area. Encinar (2006) conclude that use of waste cooking oils is an effective way to reduce the cost of biodiesel production

2.3 Solvent

Sprules and Price (1950), stated that alcohol is primary and secondary monohydric aliphatic alcohols having one (1) to eight (8) carbon atoms. In transesterification process, the main solvent use is alcohol. The examples of alcohol that can be used in the transesterification of triglycerides are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol is the most widely use because of its low price and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and sodium hydroxide and easily dissolved in it (Marchetti *et* al., 2005).

2.4 Catalyst

A catalyst is a substance that accelerates the rate of reaction by lowering its activation energy. A catalyst recovered unchanged and it does not appear in the product. Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst. Fangrui Ma and Milford A. Hanna (1999), stated that excess amount of catalyst would lead to the higher amount of production cost and reduce product yield.

2.4.1 Homogeneous Catalyst

Homogeneous catalyst involves processes in which catalyst is in solution with at least one of the reactant. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst (H_2SO_4 or HCl) and alkali catalyst (KOH or NaOH). Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Du *et al.*, 2004).

2.4.2 Heterogeneous Catalyst

A heterogeneous catalytic process involves more than one phase, usually the catalyst is a solid and the reactant and product are in liquid or gaseous form. There are many advantages of using heterogeneous catalyst such as non-corrosive, environmental friendly present fewer disposal problems, easier in separation from liquid product and they can be design to give higher activity, selectivity and longer catalyst lifetime (Gryglewicz, 1999). There are many types of heterogeneous catalyst such as alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina and various type of zeolite that can be use in various type of chemical reaction

including transesterification process. However, most anion exchange resins and supported alkali metal catalyst are easily corroded by methanol and they exhibit short catalyst lifetime in catalyst transesterification. The alkaline earth metal oxides compound is very favorable used in transesterification process because it is slightly soluble in organic solvents (Supes *et al.*, 2004).

2.4.3 Enzyme Catalyst

There also have a different way of synthesizing biodiesel by using bio-catalyst such as lipase enzyme instead of chemically catalyst. Bio-catalyst such as enzyme is a high molecular weight protein or protein-like substance that acts on substrate (reactant molecule) to transform it chemically at a greatly accelerate rate than the uncatalyzed rate (Shuler nad Kargi, 2002).

2.5 Process of Synthesizing Biodiesel

There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process. However, there are a lot of methods can be done through transesterification process such as based-catalyzed transesterification, acid-catalyzed esterification, intergrated acid-catalyzed preesterification of FFAs and based-catalyzed transesterification, enzyme-catalyzed transesterification, hydrolysis and supercritical alcohol transesterification (Saka *et al.*, 2001).

2.5.1 Direct Use and Blending

The direct use of vegetable oils in diesel engine is not favorable and problematic because it has many inherent failings. Eventhough the vegetable oils have familiar properties as biodiesel fuel, it required some chemical modification before can be used into the engine. It has only been researched extensively for the past couple of decades, but has been experimented with for almost hundred years. Although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. For short term use, ratio of 1:10 to 2:10 oil to diesel has been found to be successful (Ma and Hanna< 1999).

2.5.2 Micro-emulsion Process

Schwab *et al.*, (1987) defined micro-emulsion as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1 ± 150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. Micro-emulsion with solvents such as methanol, ethanol and 1-butanol has been studied to solve the problem of the high viscosity of vegetable oils. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles.

2.5.3 Thermal Cracking (Pyrolysis)

Sonntag, (1979) defined pyrolysis as the conversion of one substance into another by means of heat or heating with the aid of a catalyst. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules (Weist et al., 1979(. Pyrolytic chemistry is difficult to characterize because of the variety of reaction path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil (Ma and Hanna, 1999).

2.5.4 Transesterification Process

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Srivatava and Prasad, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as in the following equation. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) will accelerate the conversion.

Catalyst
Triglycerides + Methanol
$$\leftarrow$$
 Glycerol + Methyl Ester (2.1)

Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. It was observed that transesterification is faster when catalyzed by alkali (Freedman *et al*, 1986).

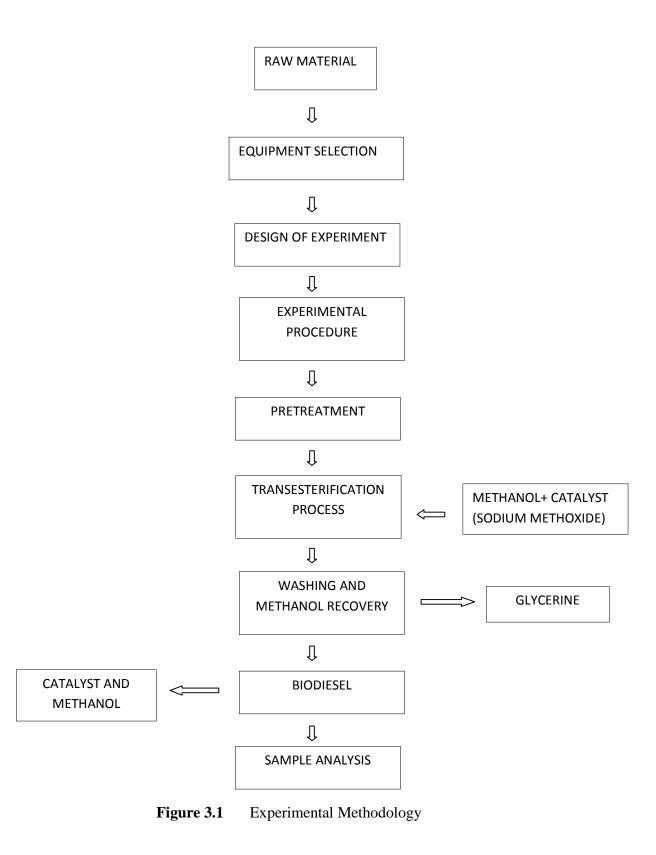
CHAPTER 3

METHODOLOGY

3.1. Introduction

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 conducted with Sodium Methoxide as the catalyst. Figure 3.1 shows the diagram of experimental methodology. This experimental methodology consists of five basic steps which are:

- 1. Raw material
- 2. Equipment selection
- 3. Design of experiment
- 4. Experimental procedure
 - a. Pre-treatment
 - b. Transesterification process
 - c. Settling
 - d. Washing and methanol recovery
- 5. Sample analysis



3.2 Raw Material

In this experiment, the raw material that used were WCO and RBD palm oil. WCO was collected from nearly restaurants, hostels and canteen while RBD cooking oil was supplied from Minyak Seri Murni. The chemical reaction specialist suggests that refined vegetable oil is the best start material in producing biodiesel. However, WCO is still valuable source because the price is much cheaper.

3.3 Equipment Selection

There are several type of equipment that are used in this experiment. Figure 3.2 to 3.6 shows the picture of some of the equipment. The examples of the equipment are such as:

- a. Filter press: to filter solid compound in waste cooking oil.
- b. Hot palate: to remove water by pre-heating the waste cooking oil.
- c. Shaking water bath with stirrer: use during transesterification process.
- d. Rotary evaporator: to recover methanol after transesterification process.



Figure 3.2 Filter Press



Figure 3.3 Shaking Water Bath



Figure 3.4 Hot Plate



Figure 3.5 Rotary Evaporator



Figure 3.6 Mechanical Stirrer

3.4 Design of Experiment

Design of experiment is a technique to make product, process or investigation more robust. It consists of a set of experiment to run. In this design of experiment, three stages method was used to evaluate and study the effects of variables on biodiesel production which are:

- a. Catalyst concentration (0.25 1.5 wt%)
- b. Reaction time (20 50 minutes)

The three stages method has generated a model of experiment with different condition of variable. The model of experiment consists of 22 trials and the samples of every trial were used to determine its biodiesel yield and methyl ester purity. The first stages is used to determine optimum value of catalyst concentration at fixed temperature 40°C and fixed reaction time which is at 40 minutes. The second stages are used to determine optimum value of time. Lastly, the third stages is used to examine the exhaust emission of biodiesel from the optimum value of temperature and time that results from first and second stages of the experiment and compare with conventional diesel.

3.5 Experimental Procedure

In this experiment procedure, it shows the step by step procedure to be followed during the experiment. It consists of five basic steps which are pre-treatment, catalyst preparation, transesterification process, settling process and washing process.

3.5.1 Pre-treatment

Filter press was used in this pre-treatment process to removed solid compound in the WCO. Then, filtrated WCO was heated around 80°C to 90°C to removed water. The oil was left to cool before it can be proceeds to the next steps.

3.5.2 Catalyst Preparation

Sodium methoxide catalyst was weighted accordingly to its concentration due to the data provided by the three stages of experiment and fed into a 1liter conical flask. Put the conical flask into the batch reactor (water bath). 0.209 liter of methanol was added into the flask. The solution mixed within few minutes using mechanical stirrer.

3.5.3 Transesterification Process

1 liter WCO was added into the conical flask with molar ratio of methanol to WCO fixed at 6:1. In the meantime, the temperature and reaction time also fixed at 40°C and 40 minutes respectively. Make sure the conical flask mouth covered by aluminum foil to prevented methanol from vaporized as its boiling point was at 65°C. After the

reaction completed, the sample settled out over one night in order to get two layers which make it easier to separate.

3.5.4 Settling Process

After one night it settled down, glycerine and catalyst residue were settled at the bottom while biodiesel and residue of methanol at the top layer. At the top layer, separator funnel was used to separated biodiesel from glycerine by gravitational forces.

3.5.5 Methanol Recovery

Rotary evaporator was used to remove methanol from both crude biodiesel and glycerine. The temperature set was around 60°C to 70°C. At this temperature methanol vaporized while biodiesel and glycerine remains in liquid form. The methanol was collected and stored properly.

3.5.6 Purification Process

For the purification process, water was boiled at 80°C. It was used to washed out the sample for about half to one hour. This process was repeated twice in order to get the better result. After that, the sample was heated-up from 100°C to 110°C using stirring hot plate to removed any residual of moisture content. Continued from the heating process, sample was stored tightly in the sample bottle in order to prevent any residue or particulate moisture from surrounding.

3.6 Analysis

In this experiment, there are three parameters that need to be analyzed which are biodiesel yield, methyl ester content and the emission profile from the biodiesel produced. Every sample from each experiment produced from different condition will be analyzed to find the optimum condition of the experiment.

3.6.1 Biodiesel Yield

Product yield is defined as the weight percentage of the final product (purified biodiesel) relative to the weight of oil at the beginning process. The biodiesel yield (% wt) calculated by the following equation:

$$Product \ yield = \frac{\text{Weight of product}}{\text{Weight of raw material}} \times 100\%$$
(3.1)

3.6.2 Methyl Ester Purity

A Gas Chromatography (GC) method for determination of the purity of methyl ester in the biodiesel has been developed. Samples have been prepared by mixing 100 mg biodiesel from each experiment with 5000 μ l methyl ester standard solution. Finally, 1 ml samples will be added into a 1 ml vial and the mixture was shaken vigorously and 2 μ l aliquots were injected in the GC after at least 10 minutes. The following equation used to calculate the methyl ester purity in biodiesel.

$$Product purity = \frac{[\Sigma A] - A EI}{A ei} x \frac{C ei x V ei}{m} x 100\%$$
(3.2)

Where, [ΣA] = Total peak area for methyl ester
A ei = Corresponding area for methyl ester
C ei = Concentration of methyl ester standard solution, mg/ml
V ei = Volume of methyl ester standard solution, ml
m = Mass of samples, mg

3.6.3 Exhaust Emission of Biodiesel

Gas combustion unit is an instrumental method for emission test. Exhaust gas emission of CO_2 and CO were measured by an exhaust gas analyzer. The experimental value for each gas was taken from the average value of three measurements.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

Homogeneous catalytic reaction is one of the conventional ways to produce biodiesel. In this study, the raw materials used for production of biodiesel are RBD palm oil and WCO with aid of sodium methoxide (NaOCH₃) as the catalyst and .methanol as the solvent. In order to optimize and compare the performance WCO towards optimum condition of biodiesel production with RBD palm oil, two parameters were studied which is catalyst concentration and reaction time. As mention previously, the volume of raw material is fixed to 11iter, the catalyst concentration used is in the range 0.25 to 1.5 wt% and the reaction time is varied from 20 to 50 minute. In this batch transesterification process, the molar ratio of methanol to raw material is fixed at 6:1 while the temperature also fixed at 40°C. When the optimum value of catalyst concentration and reaction time was showed, which consumed highest yield and highest purity of methyl ester content for both source of raw material, the next step of experiment was conducted, which is combustion test. The combustion test performed to compare the emission of biodiesel and commercial diesel fuel. After all reaction was completed, results were obtained from analysis data which is the effect of catalyst concentration and reaction time towards biodiesel yield and purity of methyl ester content were studied.

4.2 Effect of Catalyst Concentration

The first parameter studied in this batch transesterification process is catalyst concentration. The concentration of sodium methoxide (NaOCH₃) used in the first stage of experiment was varied from 0.25 to 1.5 wt% while the reaction temperature and reaction time were fixed at 40°C and 40 minute respectively. The volume of raw material of both RBD palm oil and WCO also fixed at 1 liter. Table 4.1 and Table 4.2 shows result for the first stage of experiment for both type of raw material used.

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(wt %)	(g)	Biodiesel (g)	(%)	
0.25	860	761.62	88.56	86.84
0.5	860	776.06	90.24	96.82
0.75	860	745.96	86.74	83.10
1.0	860	686.80	79.86	80.82
1.5	860	668.05	77.68	78.33

Table 4.1: Effect of NaOCH₃) concentration for RBD palm oil

Table 4.2: Effect of NaOCH₃) concentration for WCO

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(wt %)	(g)	Biodiesel (g)	(%)	
0.5	920	644.37	70.04	76.84
0.75	920	693.96	75.43	80.04
1.0	920	780.16	84.80	94.56
1.5	920	739.68	80.40	93.42

The amount of catalyst is one of the most important variables that effects conversion efficiency as well as production cost of biodiesel and the results is given in Figure 4.1 and Figure 4.2.

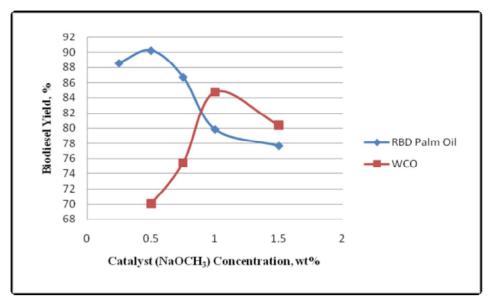


Figure 4.1: Effect of NaOCH₃ concentrations on biodiesel yield

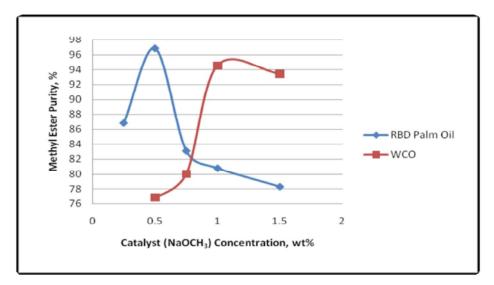


Figure 4.2: Effect of NaOCH₃ concentrations on methyl ester purity

It is not only to determine the reaction rates, but the catalyst also causes the hydrolysis and saponification. Both reactions interfere with the separation of the glycerol rich phase and the methyl ester purification (Felizardo et al, 2006). In Figure 4.1, for RBD palm oil shows that, when the NaOCH₃ concentration increased from 0.25wt% to 0.5 wt%, the yield of biodiesel produced will be increased slightly from about 88.56% to almost 90.24% and tend to decreased to 77.68% when NaOCH₃ concentration increased further to 1.5 wt%. Meanwhile, for WCO, when catalyst concentration increased from 0.5 wt% to 1.0 wt%, the product yield of biodiesel will increased slowly from 70.04% up to 84.80%, but it start to decreased slightly to 80.40% when the NaOCH₃ concentration increased to 1.5 wt%. The 3% value of free fatty acids (FFAs) required completing a base catalyzed transesterification process. The higher the acidity of the oil used, the smaller the conversion efficiency. Excess of both FFAs and moisture content in the oil within insufficient amount of catalyst, may cause soap formation (Meher et al, 2006). RBD palm oil content less than 3% FFAs thus yield 90.24% of biodiesel compare to WCO that contains quite large amount of water and FFAs contents which resulted just 84.80% biodiesel yield.

In Figure 4.2, for RBD palm oil, it is shows that, the increasing in NaOCH₃ concentration will decrease the methyl ester purity contents as well as decreased in biodiesel yield. It also can be seen that, the optimum value of methyl ester purity content occurred at 0.5 wt% of NaOCH₃ concentration and decreased if an excess catalyst was added. Meanwhile, for WCO, when we increased the NaOCH₃ concentration, the methyl ester purity content also will increased as well as biodiesel yield and start to decreased when it's reached its optimum NaOCH₃ concentration. The starting materials or raw materials used for the base catalyzed transesterification process should meet certain specification. The triglycerides or vegetable oils should have lower acid value and all material should substantially anhydrous. The addition of more catalyst compensates for higher acidity, but the resulting soap formation causes an increase in viscosity or formation of gels that interferes in the reaction as well as with separation of glycerol (Meher *et al*, 2006). When we used RBD palm oil, the biodiesel yields are significantly reduced. This happened maybe because of the prolonged contact with air that will

diminish the effectiveness of this catalyst through interaction with moisture and carbon dioxide. However, when WCO was used as starting material, pretreatment was performed such as filtration and water removal. Within these pretreatment processes, the biodiesel yields increased slightly with increasing of catalyst concentration.

From this optimum catalyst concentration results for both type of starting material used, the experiment was proceed to the next stage which to determine the effect of reaction time. The optimum value of NaOCH₃ concentration for RBD palm oil is 0.5 wt% while for the WCO is 1.0 wt%.

4.3 Effect of Reaction Time

Effect of reaction time was studied in the second stage of experiment. Reaction time will be conducted within range from 20 to 50 minutes while the other parameter setting such as catalyst concentration will be taken from the optimum value from the previous experiment which is 0.5 wt% for RBD palm oil and 1.0 wt% for WCO, reaction temperature fixed at 40°C, volume of both raw material also fixed at 1 liter and so for methanol to oil ratio which is 6:1. Table 4.3 and Table 4.4, shows result for the second stage of experiment for both type of raw material used.

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(min)	(g)	Biodiesel (g)	(%)	
20	860	775.72	90.2	83.4
30	860	800.66	93.1	94.7
40	860	844.52	98.2	97.5
50	860	807.54	93.9	93.2

Table 4.3: Effect of reaction time for RBD palm oil

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(min)	(g)	Biodiesel (g)	(%)	
20	920	699.20	76.0	90.2
30	920	728.64	79.2	93.1
40	920	830.56	96.8	94.7
50	920	798.56	86.8	93.9

Table 4.4: Effect of reaction time for WCO

Effects of reaction time on biodiesel yield and methyl ester purity are shown in Figure 4.3 and Figure 4.4.

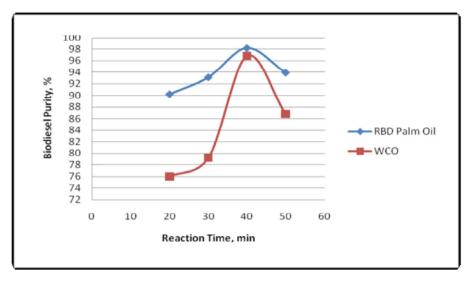


Figure 4.3: Effect of reaction time on biodiesel yield

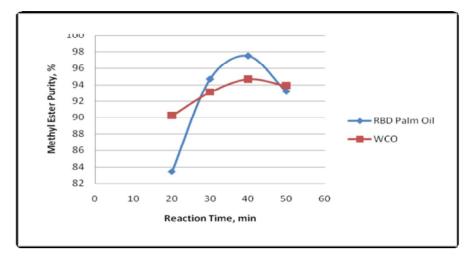


Figure 4.4: Effect of reaction time on methyl ester purity

To achieve perfect contact between the reagents and the oil during reaction, they must be stirred well at constant rate and well mixed together (Xiangmei et al, 2008). In Figure 4.3 and Figure 4.4, for RBD palm oil, it can be observed that increasing in reaction time from 20 to 40 minutes, will also increased the reaction rate as well as product yield (biodiesel yield), but it start to decreased slightly when the reaction time further increase up to 50 minutes. The product yield reached an optimum value about 98.2% within reaction time of 40 minutes. However, slightly reduction in biodiesel yield occurred after 40 minute is due to longer reaction time thus enhanced the hydrolysis of ester which is reverse reaction of transesterification that could result in loss production. Meanwhile, for WCO, it is shown that the optimum value of reaction time also reached at 40 minutes but consumed low biodiesel yield and methyl ester purity compared with the batch transesterification process of RBD palm oil which is 96.8% and 94.7% respectively. It is indicated that, an extension of reaction time had no significant effect on conversion of triglycerides (waste cooking oil) to methyl ester (biodiesel), but slightly decreased after 40 minutes reaction time due to soap formation resulted from high amount of FFAs contained in WCO. The optimum value of reaction time for both type of raw material used is 40 minutes.

4.4 Combustion Test

Since biodiesel is produced within two different types of oil which is RBD palm oil and WCO, it was necessary to identified and studied the qualified standardization of fuel quality to guarantee engine performance without any difficulties either to consumers and environment. Within fixed reaction temperature at 40°C, raw material volume at 1 liter and also methanol to oil ratio at 6:1, the batch alkali catalyzed transesterification process were performed together with the optimum value of catalyst concentration (NaOCH₃) and reaction time that obtained from the first and second stage of experiment respectively, resulted highest biodiesel yield and methyl ester purity for basically two different types of raw material used. From this result, we proceed to the last stage of the experiment which is to identify combustion characteristic of exhaust emissions of biodiesel produced from RBD palm oil and WCO and compared with the commercial diesel fuel. Table 4.5 shows the comparison characteristic of RBD palm oil, WCO and commercial diesel fuel.

Emission	RBD Palm Oil	WCO	Commercial Diesel Fuel
O ₂ (%)	10.1	9.8	9.3
CO (ppm)	65	44	376
CO ₂ (%)	8.1	8.21	8.7
NO (ppm)	0	0	0.021
NO _X (ppm)	0	0	0.07
H ₂ S (ppm)	0	0	0.03

 Table 4.5: The exhaust emissions of biodiesel samples of RBD palm oil and WCO compared to conventional diesel fuel

Biodiesel is biodegradable, non-toxic and has low emission profile compare to petroleum diesel. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter compare to emission from diesel fuel (Meher *et al*, 2006). From Table 4.5, it can be seen

that, the content of carbon monoxide (CO) in biodiesel is typically less than those for diesel fuel which is 65 ppm for biodiesel from RBD palm oil and 44 ppm for biodiesel that made from WCO compare to 376 ppm for conventional diesel fuel. This result is due to higher combustion efficiency of biodiesel than conventional diesel fuel. Because carbon monoxide is the product of incomplete combustion, the lower the concentration of carbon monoxide results in higher tendency to form ignitable mixture.

In this test, the production of CO_2 of biodiesel is lower than those in diesel fuel, and this has a neutral effect on the greenhouse effect, because the gas released in the combustion is the same absorbed and fixed by the plant for its growth. Besides that, biodiesel produced had almost no nitrogen oxides (NO) rather than diesel fuels that released for about 0.021 ppm nitrogen oxides when burned. Nitrogen oxide effects on human health, plants and also materials such as respiratory illness, injury to vegetation and greenhouse effects. Then, in commercial diesel, it contains high content of sulfur than in biodiesel that will produce SO_2 , SO_3 and SO_4^{2-} in the combustion, source of acids rains, corrosive and irritation. H₂S is released and converted to SO_2 . Essentially, sulfur emissions are completely eliminated compare to diesel fuel. So, if the resulted majority of the emission from biodiesel is less than those in diesel fuel, means it is better to used biodiesel rather than diesel to reduced respiratory diseases and control pollution that damage our natural environment

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Scale up production of biodiesel was conducted before commercialization of the product could be realized in order to fulfill the market demand of the products. The production of 1L of raw material which is RBD palm oil and WCO respectively was successfully carried out at constant temperature of 40°C and methanol to oil ratio at 6:1. In the experiment, for RBD palm oil, it gives the optimum value of catalyst concentration at 0.5 wt% and 40 minutes reaction time while 1.0 wt% catalyst concentration within 40 minutes reaction time for WCO as the raw material to produce biodiesel. It also shows that the higher conversion was obtained when RBD palm oil used as raw material which is 98.2% biodiesel yield and 97.5% methyl ester purity instead of 96.8% biodiesel yield and 94.7% methyl ester purity in WCO. Table 5.1 showed the optimum condition from first and second stage of experiment for both types of raw material to produced biodiesel.

	1	e :	1 2	1
Sample	Catalyst	Reaction Time	Biodiesel Yield	Methyl Ester
	Concentration	(min((%)	Purity (%)
	(%)			
RBD Palm oil	0.5	40	98.2	97.5
WCO	1.0	40	96.8	94.7

Table 5.1: The optimum condition of highest yield and purity of biodiesel production

Biodiesel produced both from RBD palm oil and WCO contained less CO, CO_2 and contain no NO, NO_X and H₂S respectively, compared to commercial diesel thus contributed to the reduction of greenhouse gas that effect the global warming.

5.2 Recommendation

In order to get higher conversion and purity of biodiesel, it is recommended to use two step heterogeneous catalyzed reactions instead of single step homogeneous alkali catalyzed. An alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time. However it is very sensitive to the purity of the reactants. Only well refined vegetable oil with less than 0.5 wt% FFAs can be used as the reactant in this process (Yong Wang *et al*, 2007). The high cost of raw material is the major obstacle to its commercialization. High amount of FFAs contained in WCO is the major problem towards of transesterification reaction because it was favored to soap formation rather than selectivity of triglycerides on methyl ester conversion. Hence, a process with acid catalyzed pretreatment was developed to synthesized biodiesel from WCO that can reduced the FFAs content thus increased the purity of methyl ester.

The homogeneous alkali catalyst will be replaced by the heterogeneous alkali catalyst which contribute to the easier separation form product as well as increase the production yield. Heterogeneous alkali catalyst also showed good result and favorable because this type of catalyst presence fewer disposal problems and also easier to separate from liquid product. The byproduct of glycerol and soap stock in this process can be easily handled. The catalyst used will give the higher activity and selectivity, more economical and ecological thus contributed to the environmental friendly and also give longer catalyst lifetime which can be regenerated or recover after reaction process.

REFERENCES

- Altin R., Selim C., *The Potential of using vegetable oil fuels as diesel engines*, Energy Convers. Manag. 42 (2001) 529-538.
- Bhale P. V., Deshpande N.V., Thombre S.B., 2008. Improving the low temperature properties of biodiesel fuel. Renewable Energy (2008) 1-7.
- Canakci M., Van Gerpen J. Trans. ASAE 44(2001)1429.
- Chang C. C., Wan S. W. *China's motor fuels from tung oil* Industrial and Engineering Chemistry Research, 1947; 39:1543-1548.
- Dalai A. K., Dmytryshyn S.L., Chaudhari S.T., Mishra H.K., Reaney M.J., 2004. Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties. Bioresource Technology 92 (2004) 55–64.
- Du W., Xu Y. Y., Jing Z., Liu D. H., Biotechnol. Appl. Biochem. 40(2004)187.
- Encinar J. M., Gonzalez J. F., Podrlguez-Reinares A., *Ethanolysis of Used Frying Oil: Biodiesel preparation and characterization*. Fuel Processing Technology Universidad de Extremadura, Spain. 88(2006) 512-513.
- Felizardo P., Joana Neiva Correia M. Raposo I., Mendes J. F., Berkemeier R., Bordado J. M. Production of biodiesel from waste frying oils, Waste Manage. 26(2006)487-494.
- Freedman B., Butterfield R. O., Pryde E. H., *Transesterification kinetics of soybean oil*.J. Am. Oil Chem. Soc. 1986;63(10):80-1375.
- Fukuda H., Kondo A., Noda H., *Biodiesel fuel production by transesterification of oils*, J. Biosci. Bioeng. 92 (2001) 405-416.
- Gerpen J. V., *Biodiesel processing and production*, Fuel Process. Technol. 6 (2005) 1097-1107.

.

- Gerpan J. V., Shanks B., Pruszko R., Clemento D., Knothe G., *Biodiesel production* technology, NREL/SR-510-36244, National Renewable Energy Laboratory, 2004
- Grylewicz S. Rapeseed oil methyl ester preparation using heterogeneous catalyst. FUEL. 70(1999)249-253.
- Kalam M. A., Masjuki H.H., 2002. *Biodiesel from palm oil an analysis of its properties and potential*. Biomass and Bioenergy 23 (2002) 471-479.
- Keim G. I. Fat acid slkyl esters from low grade oils and fats. US patent 2,383-601, 1945; 40: 4617.
- Knothe G., Krahl J., Van Gerpen J., *The biodiesel handbook*. Campaign (IL) AOCS Press (2005).
- Ma F and Hanna M. A. *Biodiesel Production a Review*. Bioresource Technology 1999. 70, 1-15
- Marchetti J. M., Miguel V. U., Errazu A. F. *Possible methods for biodiesel production*, Renew. Sust. Energy Rev., 2005; 11:1300-1311.
- Meher L. C., Vidya Sagar D., Naik S. N., *Technical aspects of biodiesel production by transesterification- a review*, Renew. Sustain. Energy Rev. 10 (2006) 248-268.
- Mittlebach M., Gangl S., Long storage stability of biodiesel made from rapeseed and used frying oil, J. Am. Oil Chem. Soc. 78 (2001) 573-577.
- Peterson C., Hustrulid T., *Carbon cycle for rapeseed oil biodiesel fuels*, Biomass Bioenerg. 14 (1998) 91-101.
- Saka S., Kusdiana D., FUEL. 80(2001)275.
- Schwab A. W., Bagby M. O., Freedman B., *Preparation and properties of diesel fuel from vegetable oils*. FUEL. 66(1987)1372-1378.
- Shay E. G., *Diesel Fuel from Vegetable- opportunities* Biomass Bioenergy 4 (1993) 227-242.
- Shuler M. L., Kargi F., *Bioprosess Engineering Basic Concept*. 2nd edition Prentice Hall. (2002).
- Sonntag N. O. V., *Reaction of fats and fatty acids. Bailey's Industrial Oil and Fats Product*, vol. 1, 4th editon, John Wiley & Sons, New Yorl. 99(1979).
- Sprules F. J., Price D., Production of fatty ester. US Patent 2: (1950)346-494.
- Supez G. J., Dasari M., Doskoci E.J., Mankidy E. J., Goff M. J., Transesterification of

soybean oil with zeolite and metal catalyst. Appl. Catal. 257(2004)23-213.

- Weist P. B., Haag W. O., Rodeweld P. G., *Catalytic production of high grade fuels from biomass compound by shapedelective catalysis.* Science 206(1979)57-58.
- Xiangmei Meng, Guanyi Chen, Yonghong Wang. *Biodiesel production from waste* cooking oil via alkali catalyst and its engine test. Fuel Proc. Tech. 2008 89:851-857
- Yong Wang, Shiyi Ou, Pengzhan Liu, Zhisen Zhang. Preparation of biodiesel from waste cooking oil via two step catalyzed process. Energy Conv. And Manag. 48(2007) 184-188.
- Zanin G, Santana C. C., Bon E. P. S., Jordano R. C. L., Moraes F. F., Andrietta S. R., Carvalho Neto C. C., Macedo I. C., Lahr Filho D., Ramos L. P., Fontana J. *Brasilian bioethanol program* Biotechnology and Applied Biochemistry, 2000;84:1147-1161.
- Zhang Y., Dube M. A., McLean D. D., Kates M., Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis, Biosour. Technol. 90 (2003) 229

APPENDIX A

CALCULATION OF METHANOL NEEDS

A.1 Calculation for Volume of Methanol

Density of RBD palm oil,
$$\rho = 860 \text{ kg/m}^3$$

= (860 kg/ m³) x (1000g/ 1 kg) x (1m³/ 1 x 10⁶ cm³)
= 0.86g/ cm³
Density of WCO, $\rho = 920 \text{ kg/m}^3$
= (920 kg/ m³) x (1000g/ 1 kg) x (1m³/ 1 x 10⁶ cm³)
= 0.92g/ cm³

Density of methanol,
$$\rho = 791 \text{ kg/m}^3$$

= (791 kg/ m³) x (1000g/ 1 kg) x (1m³/ 1 x 10⁶ cm³)
= 0.791g/ cm³

In this experiment, the molar ratio methanol to oil is 6:1 and the required volume of methanol needs was summarized in Table A.1 and Table A.2.

Properties	Methanol	RBD Palm Oil
Molar Ratio	6	1
Density, p	0.791g/ cm^3	0.86g/ cm^3
Molecular Weight, M _A	39.049 g/mol	1000 g/mol
Mass Ratio	6 mol x 39.049 g/mol	1 mol x 1000 g/mol
	= 192.24 g	= 1000 g
Volume Ratio	$\frac{192.24 \text{ g}}{0.791 \text{g/ cm}^3}$ = 243.034 cm ³	$\frac{1000 \text{ g}}{0.86 \text{ g/ cm}^3}$ = 1162.791 cm ³
Required Volume, V	209.009 cm^3	1000 cm^3

 Table A.1: Required volume of methanol in RBD palm oil

Table A.2: Required volume of methanol in WCO

Properties	Methanol	WCO
Molar Ratio	6	1
Density, p	0.791g/ cm^3	$0.92g/cm^{3}$
Molecular Weight, M _A	39.049 g/mol	1000 g/mol
Mass Ratio	6 mol x 39.049 g/mol	1 mol x 1000 g/mol
	= 192.24 g	= 1000 g
Volume Ratio	$\frac{192.24 \text{ g}}{0.791 \text{g/ cm}^3}$ = 243.034 cm ³	$\frac{1000 \text{ g}}{0.92 \text{ g/ cm}^3}$ = 1086.96 cm ³
Required Volume, V	223.59 cm^3	1000 cm^3

APPENDIX B

EFFECT OF CATALYST CONCENTRATION AND REACTION TIME

B.1 Calculation for biodiesel yield (%)

The values of biodiesel yield for each sample from stage 1 through stage 3 were calculated using equation 3.1.

- a) For RBD palm oil as raw material, Sample of 0.5 wt% catalyst (NaOCH₃) concentration. Mass of sample = 776.06 g Mass of RBD palm oil = 860 g Product yield = $\frac{\text{Weight of product}}{\text{Weight of raw material}} \times 100\%$ = $\frac{776.06 \text{ g}}{860 \text{ g}} \times 100\%$ = 90.24 %
- b) For WCO as raw material, Sample of 1.0 wt% catalyst (NaOCH₃) concentration. Mass of sample = 780.16 g Mass of RBD palm oil = 920 g $Product yield = \frac{Weight of product}{Weight of raw material} \times 100\%$ $= \frac{780.15 \text{ g}}{920 \text{ g}} \times 100\%$ = 75.43 %

B.2 Calculation for biodiesel purity, (%)

The values of methyl ester purity for each sample from stage 1 through stage 3 were calculated using equation 3.2.

a) For RBD palm oil as raw material,

Sample of 0.5 wt% catalyst (NaOCH₃) concentration

$$\begin{aligned} Product \, purity &= \frac{[\Sigma A] - A \, BI}{A \, ei} x \, \frac{C \, ei \, x \, V \, el}{m} x \, 100\% \\ &= \frac{[1.49574 E6] - [2.04761 E4 + 1.4351 E6]}{2.04761 E4} x \, \frac{10 \, x \, 5}{101.3} x \, 100 \\ &= \, 96.82 \, \% \end{aligned}$$

b) For WCO as raw material,

Sample of 1.0 wt% catalyst (NaOCH₃) concentration.

$$\begin{aligned} Product \, purity &= \frac{[\Sigma A] - A \, \text{EI}}{A \, \text{el}} x \, \frac{C \, \text{el} \, x \, V \, \text{el}}{m} x \, 100\% \\ &= \frac{[6.24972 \text{E6}] - [2.30804 \text{E4} + 1.71327 \text{E6}]}{2.30804 \text{E4}} x \, \frac{10 \, x \, 5}{103.4} x \, 100 \\ &= 94.56 \, \% \end{aligned}$$

The calculation of biodiesel yield and methyl ester purity for all sample in the experiment are same as in examples and the results were summarized in Table B.1, Table B.2, Table B.3 and Table B.4.

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(wt %)	(g)	Biodiesel (g)	(%)	
0.25	860	761.62	88.56	86.84
0.5	860	776.06	90.24	96.82
0.75	860	745.96	86.74	83.10
1.0	860	686.80	79.86	80.82
1.5	860	668.05	77.68	78.33

 Table B.1: Effect of NaOCH3 concentration for RBD palm oil

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(wt %)	(g)	Biodiesel (g)	(%)	
0.5	920	644.37	70.04	76.84
0.75	920	693.96	75.43	80.04
1.0	920	780.16	84.80	94.56
1.5	920	739.68	80.40	93.42

 Table B.2: Effect of NaOCH₃ concentration for WCO

Table B.3: Effect of reaction time for RBD palm oil

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(min)	(g)	Biodiesel (g)	(%)	
20	860	775.72	90.2	83.4
30	860	800.66	93.1	94.7
40	860	844.52	98.2	97.5
50	860	807.54	93.9	93.2

 Table B.4: Effect of reaction time for WCO

Sample	Mass of Sample	Mass of	Biodiesel Yield	Purity (%)
(min)	(g)	Biodiesel (g)	(%)	
20	920	699.20	76.0	90.2
30	920	728.64	79.2	93.1
40	920	830.56	96.8	94.7
50	920	798.56	86.8	93.9

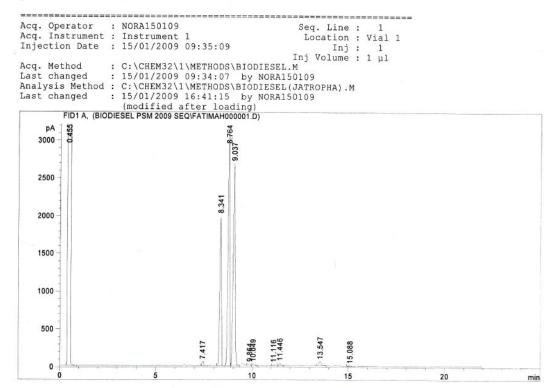
APPENDIX C

RESULT OF ANALYSIS FROM GAS CHROMATOGRAPHY

C.1 Effect of Catalyst Concentration

.

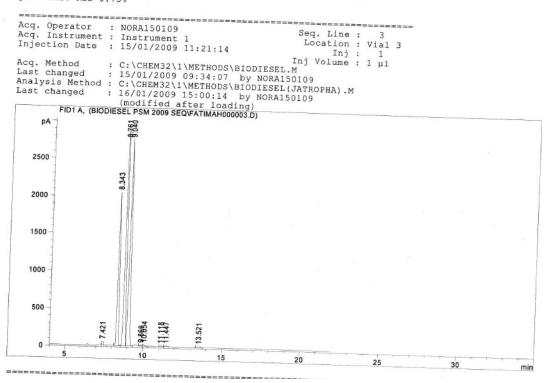
Data File C:\CHEM32\1\DATA\BIODIESEL PSM 2009 SEQ\FATIMAH000001.D Sample Name: RBD 0.25%



Sample Name: RBD 0.5%

0	57.425 9.490 9.490	5 11.445	-		
500 -	0 .				
	- # 111				
1000	111				
1500	A U				
2000	1.81				
2500	8.344				
	4				
3000					
pA j		09 SEQ/FATIMAH000002.))		
onungeu	(modifie	d after ladiu	NORA150109		
nalysis Meth ast changed	nod : C:\CHEM3	009 09:34:07 by 32\1\METHODS\BIO	DIESEL / TAMPODUA	.).M	
cq. Method ast changed		32\1\METHODS\BIO	DIESEL M	ume : 1 µl	
njection Da	te : 15/01/20	009 10:04:27	1	lon : Vial 2 Inj : 1	
cq. Operato	r : NORA150: ent : Instrume	109	Seq. Li	ine : 2	

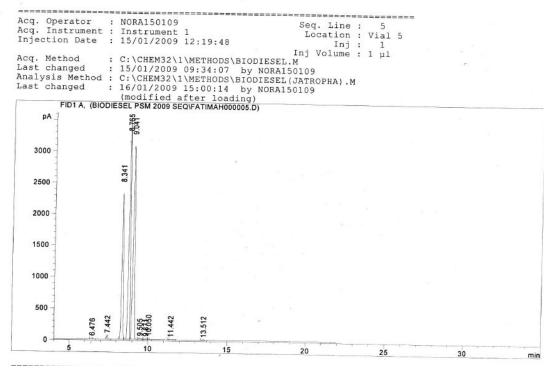
Sample Name: RBD 0.75%



Data File C:\CHEM32\1\DATA\BIODIESEL PSM 2009 SEQ\FATIMAH000004.D Sample Name: RBD 1.0%

500	6.472	7.438	9.501	11.124	13.517						
1000											
1500											
2000 -											
2500		8.335									
3000		8.762	9.033								
pA –				JO OLQU							
last chan	ged :	: 16/ (mo	01/20 difie	09 15 d aft	:00:14 er loa	l by NOR (ding)	A150109	1).M		 	
Acq. Meth Last chan	ged	: 15/	01/20	09 09	:34:07	S\BIODIES	EL.M		μт		
cq. Inst					:50:30)		on : V: nj : me : 1	1		
			A1501				Seq. Li		4		

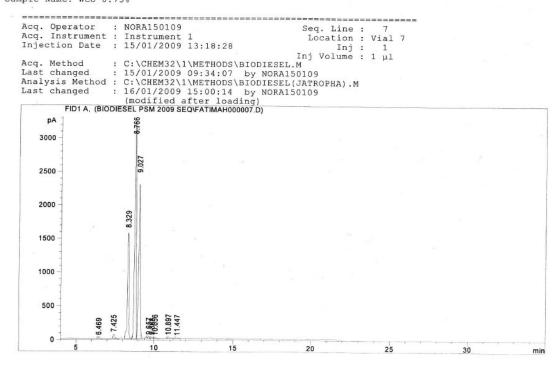
Data File C:\CHEM32\1\DATA\BIODIESEL PSM 2009 SEQ\FATIMAH000005.D Sample Name: RBD 1.5%



Data File C:\CHEM32\1\DATA\BIODIESEL PSM 2009 SEQ\FATIMAH000006.D Sample Name: WCO 0.50%

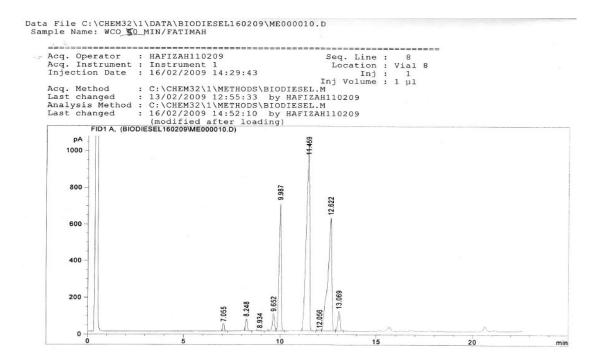
500 -	6.474	× 7.422	8.656 10:055	11.449			~					
1000						6						
1000												
1500 -												
2000			8									
1 1			8.343								6 11	
2500												
3000			6									
-			9.043 ^{8.77} 0									
pA	FIDTA, (BIO	DIE		SEQIFATI	MANUUUUU	JO.D)						
ast cha			16/01/20 (modified SEL PSM 200	d after	loadir	ng)	120103			 	 20010-200	
nalysis	Method	:	C:\CHEM3:	2\1\MET	HODS\BJ	ODIESE	L (JATRO	PHA).M				
			C:\CHEM3: 15/01/20									
njectio			15/01/20					Inj : olume :				
			Instrume				Loc	ation :				
Aca. Ope	erator	:	NORA1501	19			Seq.	Line :	6			

Data File C:\CHEM32\1\DATA\BIODIESEL PSM 2009 SEQ\FATIMAH000007.D Sample Name: WCO 0.75%

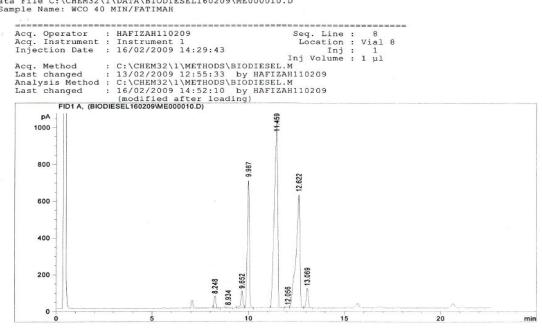


	5	10		15		20	25		30	
500	56.478 5.743	8888	11.456	7 13.555						
1000										
1500										
2000 -		8.340								
2500		6								
3000										
		9.037								
pA 3500 -		8.768								
	FID1 A, (BIOD	IESEL PSM 2	009 SEC	FATIMAH000	008.D)					
Last cha		(modif:	ied af	ter load:	by NORA15	50109				
Analysi	s Method :	C:\CHEI	132\1\	METHODS	by NORA15 BIODIESEL	(JATROPHA) . N	1			
Acq. Me	thod : anged :					. M	. т µт			
Injecti	on Date :	15/01/	2009 1	3:47:56			: 1			
	strument :		nent 1			Seq. Line Location		8		
Acc. Op	erator .	NORA15	0109			Sog Line	. 0			

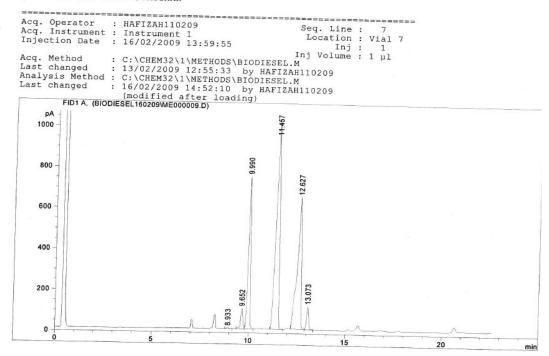
C.2 Effect of Reaction Time



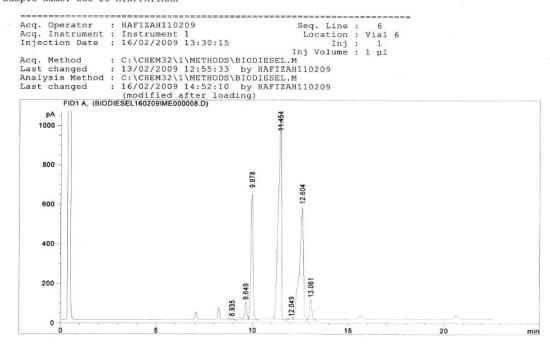
Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000010.D Sample Name: WCO 40 MIN/FATIMAH



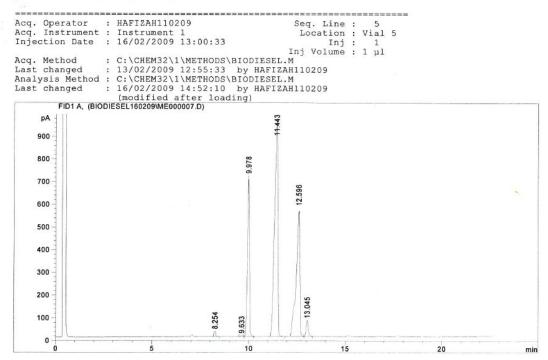
Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000009.D Sample Name: WCO 30 MIN/FATIMAH



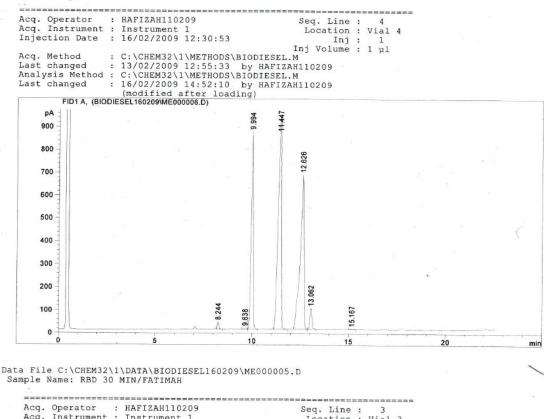
Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000008.D Sample Name: WCO 20 MIN/FATIMAH



Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000007.D Sample Name: RBD 50 MIN/FATIMAH



Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000006.D Sample Name: RBD 40 MIN/FATIMAH



neg. operator		HAFIZAHII0209		See	q. Line	:			
Acq. Instrument	:	Instrument 1			ocation			3	
		16/02/2009 12:01:12						5	
injection bacc		10/02/2009 12.01.12		T	Inj				
N				inj	Volume	:	1 µ1		
Acq. Method	:	C:\CHEM32\1\METHODS\	BIODIESEL.	M					
Last changed	:	13/02/2009 12:55:33	by HAFIZA	H110	0209				
Analysis Method	:	C:\CHEM32\1\METHODS\	BIODIESEL.	M					
Last changed		16/02/2009 14:52:10			0000				
		(modified after load:			0209				
FID1 A (BIO		ESEL160209\ME000005.D)	ing)						
		L3LL100209101E000003.D)							
pA			38						
			Ť						
900 -			4 32						
1			9.995						
800			o						
000			1 1	6					
			1 1	62					
700				12.626					
100									
				1					
600 -				1					
			1 11						
1				1					
500 -			8 H						
				1					
			1						

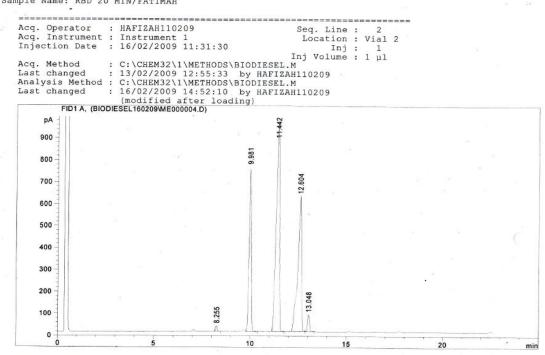
13.059

min

Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000003.D Sample Name: STANDARD ME

.cq. Opera		AFIZAH1102			Seq. L			
		nstrument : 6/02/2009				ion : Vi Inj :		
njection	Date : I	6/02/2009	11:01:50		Inj Vol			
.cq. Metho		:\CHEM32\1			L.M			
ast chan		3/02/2009 :\CHEM32\1						
ast chan		6/02/2009						
	J (1	modified a:	fter load					
	D1 A, (BIODIESE	EL160209\ME000	003.D)					
pA _				376	C.L.C.			
				1	Ê			
1								
600 -								
1								
500								
500					· · · ·			
1								
400 -								
1								
1								
300								
200								
200								
-		- 1 - L						
100 -				-	22	~		
-				9.899	2.387	5.147		
				5				

Data File C:\CHEM32\1\DATA\BIODIESEL160209\ME000004.D Sample Name: RBD 20 MIN/FATIMAH



• (=

APPENDIX D

RESULT FROM COMBUSTION TEST

D.1 RBD Palm Oil

КЕН: X05 ··· 2.6 КЕН: X05 ··· 2.6 КЕК: X05 ··· 2.6 ИОХ БЬЬ ··· 6 ИОХ БЬЬ ··· 6 ИОХ БЬЬ ··· 6 ИОХ БЬЬ ··· 6 ИОХ БСС X ··· 20 СОС X ··· 68 6.8 ··· 20 СОС X ··· 68	КВЕ XO XO XO HSC ББW XO B HSC БCC S XO B HSC CO FFW 200 CO FFW XO 200 CO FFW XO 200 CO FFW CO CO FFW CO CO FFW CO FFW CO CO FFW CO CO FFW CO FFW CO F	0.2 202 202 202 203 0.44 0 0.44 0 0.44 0 0.44 0 0.44 0 0.45 0.102 % 500 0.02 % 500 0.01 W3 0.02 % 500 0.01 W3 0.01
CO 54 01 01 01 01 01 01 00 00 00 00 00 00 00		MELL C 621 819CK C 633 9481EAL C 58
HELL C 625 BLUCK C 201 WHBIENI C 53 HEMAL OIC	HEWAX OIF LIWE 10:45:20 DVLE 11-02-03	HEWAA OIF 11WE 10:23:28 DWLE 17-02-03
	1EWPEST 100 UJ.3	1EMBER 100 U3.5

D.2 Waste Cooking Oil

*** TELEGAN ***	*** TELEGAN ***	*** TELEGAN ***
TEMPEST 100 V3.3	TEMPEST 100 V3.3	TEMPEST 100 U3.3
DATE 11-03-09	DATE 11-03-09	DATE 11-03-09
TIME 10:48:18	TIME 10:50:04	TIME 10:52:31
HEAVY OIL	HEAVY OIL	HEAVY OIL
AMBIENT C 29	AMBIENT C 29	AMBIENT C 30
STACK C 697	STACK C 702	STACK C 702
NETT C 667	NETT C 672	NETT C 672
02 % 9.1	02 % 9.0	02 % 8.9
RATIO 0.0007	RATIO 0.0004	RATIO 0.0003
CO PPM 65	CO PPM 36	CO PPM 32
CO2 % 8.9	CO2 % 9.0	CO2 % 9.0
XAIR % 77	XAIR % 75	XAIR % 75
EFF % (N) 59.5	EFF % (N) 59.6	EFF % (N) 59.7
DRY LOSS % 40.5	DRY LOSS % 40.4	DRY LOSS % 40.3
WET LOSS % 0.0	WET LOSS % 0.0	WET LOSS % 0.0
UCO LOSS % 0.0	WET LOSS % 0.0	UCO LOSS % 0.0
Prs. inWG 0.05	Prs. inWG 0.04	Prs. inWG 0.03
NO PPM 0	NO PPM 0	NO PPM 0
NOx PPM 0	NOx PPM 0	NOX PPM 0
H2S PPM 0	H2S PPM 0	H2S PPM 0
REF, %02 3.0	REF. %02 3.0	REF, %02 3.0