BIODIESEL FUEL FROM WASTE COOKING OIL & RBD PALM OIL VIA TRANSESTERIFICATION REACTION WITH THE AID OF SODIUM METHOXIDE, METHANOL, AND ULTRASONIC REACTOR

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Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in
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Faculty of Chemical and Natural Resources Engineering
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APRIL 2008

I declare that this thesis entitled “*Biodiesel Fuel from Waste Cooking Oil and RBD Palm Oil via Transesterification Reaction with the aid of Sodium Methoxide, Methanol, and Ultrasonic Reactor*” 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 degree.

Signature : …………………………
Name : MUGHIRAH BIN ABDULLAH
Date : 21 APRIL 2009

Special Dedication of This Grateful Feeling to My…

Beloved father and mother;
Mr. Abdullah bin Awang and Mrs. Fatimah binti Mahamad Akid

Loving brothers and sisters;
Aishah Zunairah, Anas Harithah, Nurul Insyirah, Muhammad Fitri and Muhammad Muhaimin

Supportive friends

For Their Love, Support and Best Wishes.

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ABSTRACT

Using petroleum diesel as well fuels from natural resources will contribute to air pollution due to high amount of air pollutants emitted. Also the aggressive action to use sources like petrochemical source, and natural gas resulted the depletion drastically in natural energy resources thereby making those energy resources becomes limited day by day thus making the global price increase. This situation makes the world becomes worst and some alternatives method should be implemented to reduce the burden of problems. One possible alternative to fossil fuel is biodiesel. Regarding to that the transesterification process was chosen compared other methods with the aid of controllable parameter such as type of catalyst, type of solvent, reactor system, condition of reaction temperature, concentration, molar ratio, mixing intensity and reaction time. In this research, two raw oils are used which is refined, bleaced, deodorized (RBD) and waste cooking oil (WCO). In order to find the optimized condition in producing biodiesel it was categorized into three stages. At first stages is to investigate the effect of catalyst concentration (0.25-1.5 wt%) to yield and purity of biodiesel. The results show the optimum value was achieved at concentration of 1 wt% for both raw oils. At second stages is to investigate the effect of reaction time (20-60 min) to yield and purity. The results show that the optimum reaction time for using both WCO and RBD were at 40 min and 30 min respectively. At third stage, the biodiesel fuel was prepared using optimum condition and analyzed in order to find the gas emission. It shows the decrease amount of carbon monoxide and carbon dioxide as compare to petroleum diesel with error 51% and 2% for RBD and 50% and 5.3% for WCO. As conclusion, the objective to reduce hazardous gas emission was achieved via biodiesel fuel which was produced using transesterification with the aid of sodium methoxide.

ABSTRAK

Menggunakan diesel sebagai bahan api akan menyumbang kepada pencemaran udara. Tindakan aggresif menggunakan sumber tenaga seperti petrokimikal, arang batu, gas asli dan tenaga nuklear menyebabkan pengurangan mendadak kepada sumber tenaga semulajadi dengan itu menyebabkan kesemua nya menjadi semakin terhad. Situasi ini menjadikan dunia semakin bahaya dan tindakan gantian penting untuk mengurangkan masalah. Satu kemungkinan penyelesaian ialah biodiesel. Oleh itu proses transestrifikasi telah dipilih berbanding kaedah lain dengan bantuan parameter kawalan seperti jenis mangkin kimia, jenis bahan pelarut, sistem reactor, kondisi suhu tindakbalas, kepekatan, nisbah molar, keamatan campuran dan tindakbalas masa. Minyak masak tulen dan minyak masak terpakai telah digunakan sebagai bahan mentah. Proses penghasilan biodiesel juga telah dibahagikan kepada tiga peringkat untuk mencari keadaan optima. Peringkat pertama ialah mengkaji kesan kepekatan mangkin kimia (0.25-1.5 wt%) terhadap penghasilan produk dan ketulenan. Keputusan menunjukkan nilai optima telah dicapai pada 1 wt% untuk kedua-dua jenis minyak. Pada peringkat kedua, ialah untuk mengkaji kesan tindakbalas masa (20-60 min) terhadap penghasilan produk dan ketulenan. Keputusan menunjukkan tindakbalas optima bagi minyak masak terpakai dan minyak tulen adalah pada 40 min dan 30 min. Pada peringkat ketiga, bahan api biodiesel dihasilkan menggunakan parameter optima terdahulu, dan kemudian di analisis. Keputusan menunjukkan pengurangan nilai CO and CO_2 jika dibanding dengan petroleum diesel dengan perbezaan 50% dan 2% untuk RBD dan 50% dan 5.3% untuk WCO. Kesimpulannya adalah objektif untuk mengurangkan pembebasan gas bahaya telah dicapai dengan menggunakan bahan api biodiesel yang dihasilkan menggunakan kaedah transesterifikasi bersama mangkin kimia Natrium Metoksida.

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LIST OF ABBREVIATIONS

WCO - Waste cooking oil

RBD - Refined, bleached and deoderized

CO - Carbon monoxide

CO_2 - Carbon dioxide

CH_3ONa - Sodium methoxide

CH_3OH - Methanol

O/W - Oil in water

W/O - Water in oil

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, alternative fuels are very important things due to environmental concerns and sources depletion (Scholl and Sonrenson, 1993; Zhang and Van Gerpen, 1996; Cardone *et al*., 2001, 2005). Long time ago, the majority of the world energy is fulfilled through petrochemical sources, coal, natural gas, hydroelectricity, and nuclear power. Thus, it will affect the reduction of natural resources currently thereby make the global now concerned about the source of petroleum. Regarding to limited fuel reserves, it affect the global high price over the world unless make the high inflation among the society. Therefore, the competition to create an alternatives fuel were begin as well as to reduce the cost, get high profitability, and less pollution to human and environment.

One of the alternatives fuel is making the biodiesel. It is one of the economical fuels that could replace the petroleum diesel with lower gas air emission and reduction the cost of raw materials. Importantly, the alternatives fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. Basically during the production of biodiesel fuel, the raw materials from vegetable oils or animal fat were used with the aid of alcohol and some type of catalyst. Therefore the lower price of feedstock was essentially needed to compete with petroleum diesel since the biodiesel price is highly dependent on the purchasing cost of raw material. In the senses, the use of waste cooking oil was the effective way to reduce the raw material cost because the price of waste cooking oil was expected half of the price for virgin oil. Otherwise the palm oil was the second choice of feedstock because of large production of palm plant mostly at Asean countries such as Malaysia, Indonesia and Thailand. Therefore this is an advantage for these countries in developing biodiesel fuel as an alternative fuel.

Other than that, there are several reasons why we are focus on biodiesel fuel. First, it could helps to reduce global warming gas emissions such as carbon dioxide as well as it is renewable in nature and safer to handle, has no aromatic compounds, practically no sulfur content, and an oxygen atoms in the molecule of fuel which may reduce the emissions of carbon monoxide, hydrocarbon and particulate matter (Lapuerta *et al*., 2005, 2002; Freedman *et al*., 1984; Ballesteros, 2002). However, biodiesel fuel also may cause several problems than petroleum diesel fuel such as worse low temperature properties (Dunn *et al*., 1996; Ballesteros, 2002), and higher production costs (Mittelbach *et al*., 1992).

Even though the biodiesel was substituted as an alternatives fuel, but it still have disadvantages. Making biodiesel could required high cost of production due to virgin vegetable oil such as pure soybean oil and rapeseed oil. Thus, the methods that permit to minimize the raw material are the special interest and need to be implemented. As a support, using the waste raw material such waste cooking oil and used frying oil is an effective's way to overcome this problem. These raw materials are cheaper than unused vegetable oil and animal fats and easy to get. Usually it could come from restaurants, hotels, and public waste. The most important thing is the utilization of waste oils diminishes the problems of contamination because the reusing of these waste oils can reduce the burden of the government in disposing of the waste, maintaining public sewers, and treating the oil wastewater. Because of the environment improvement of management, many countries pay much attention on it thus focusing very deeply in R&D of biodiesel. In Europe such as, almost than 2.7 million tons biodiesel was made in 2003, and 8-10 million tons is expected in 2010, accounting for 5.7% among the total diesel market and 20% among the diesel market in 2020 (Xiangmei Meng[a,b,*], Guanyi

Chen[a], Yonghong Wang[c], 2008). As supported of biodiesel demand, the government starts to publish some biodiesel plants in Malaysia that now already have at Kuantan, Negeri Sembilan and Kemaman in progress. Commodities Minister Peter Chin Fah Kui told an international palm oil congress in Kuala Lumpur, the palm biodiesel is set to become a viable alternative way to substituted petroleum diesel.

1.2 Problems Statement

Based to the previous research, several sources of making biodiesel have been studied such as animal fats and vegetable oils. However, the current problem is using a fresh vegetable oils or animal fats as raw materials will make government to pay high cost for the process greater than petroleum diesel. Thus, it still could not help to solve the problems. Because of that issues, with good characteristic and lower price of waste cooking oil, it can substituted the vegetables oil as a raw material. Moreover, it also can reduce the amount of schedule waste with recycle back the waste cooking oil into profitable oils. As well as, the burden of government to handle and manage those wastes is reduced as long as the effort of market the waste cooking is very aggressive. Using RBD palm oil also will help to support the process due to availability to find the sources with a large quantity and stable price. As well known, others raw material such as Jojoba wax oil, Soybean oil and Jatropha oil were also can substituted as a raw material. But, need to highlight here, in Malaysia, all that kinds of raw material were not available and difficult to find. Against, the palm oil was the advantages than others because of large amount of sources. Actually the palm oil is one of the largest plants produced in Asean country such as Thailand, Indonesia and Malaysia. With that situation, it is better to introduce palm oil as a commercial raw oils of biodiesel than using others raw oils due to close distance and large sources.

During handle the production of biodiesel, there are several methods that are probable to introduce such as microemulsion, pyrolysis, direct use and blending, and transesterification process. The regular method that always use was transesterification process. First method such as microemulsion and dilution method were unsuitable to use due to high viscosity of raw oils. Actually, these methods have such problems when use with the high viscosity oil. Using the biodiesel fuel from these methods will contribute to engines performance problem. Second method such as pyrolysis also is able to use. But it also has lack of problems which it will produce more biogasoline than biodiesel fuel. Thus, it wills lowers the product yield resulted low cost of sells. So, to overcome those problems using the transesterification process was found to be the most viable oil modification process. But it must depend on others factors too such as the type of catalyst use, amount of concentration, reaction time and type of process such as ultrasonic system.

Based to catalyst brand, the regular catalyst use are alkaline catalyst such as sodium methoxide, sodium hydroxide and potassium hydroxide. Regarding to prices, the sodium methodie was the highest price than potassium and sodium hydroxide. However, it also the highest purity than others catalyst means the amount of methyl ester content is greater for sodium methoxide. In business it is most profitable for long time period due to large sale of production.

Finally the conventional method that already use regularly was still in lack of technology. The reason is the time consuming in the process will affect high cost of production. So, to reduce the time consumed, the high technology that can shorten the time must be used such as ultrasonic technology. This concept of ultrasonication will increases the chemical reaction speed of the transesterification of RBD palm oil and waste cooking oil into biodiesel fuel. This allows the changing of production method from batch processing to continuous flow processing. The cavitational mixing in ultrasonification is an effective alternative means to achieve a better mixing in commercial processing. Ultrasonic cavitation provides the necessary activation energy for the industrial transesterification process. All those factors will reduce the operational costs and also can reduce the investment in production.

1.3 Objectives

To determines optimal condition in producing biodiesel with high purity of methyl ester and environment friendly biodiesel from Refined Bleach Deoderized (RBD) and Waste Cooking Oil (WCO) using ultrasonic reactor via transesterification process.

1.4 Scope of Study

In order to achieve the objective of this research, there are three scopes that could be followed which are:

1. Conduct the transesterification reaction in range 0.25-1.5 wt% catalyst concentration and 20-60 min reaction time.
2. Analyze methyl ester (ME) concentration using gas chromatography.
3. Compare the gas emit from biodiesel and standard diesel using gas analyzer.

The fix condition was controlled during the whole operation which is the fixed molar ratio methanol to oil of 6:1, the fix reaction temperature of 40°C and the mixing intensity of 1000 rpm with the aid of ultrasonic reactor, catalyst sodium methoxide and solvent methanol.

1.5 Rationale and Significance

The research of producing biodiesel fuel from waste cooking oil and RBD palm oil have been made in order to reduce the high cost of raw material used instead of using fresh vegetables oil and animals fat sources. Other than that, the biodiesel fuel energy will help to reduce the CO_2 emission to atmosphere help to reduce the emissions of carbon monoxide, hydrocarbon, and particulate matter with aid of oxygen content in molecule and it also contain no aromatics compounds such as sulfur content. All these factors were very important as well as will help to reduce the air pollution, can reduce health disease, renewable source, and environmentally product. The significance is to conduct the biodiesel research from waste cooking oil and RBD palm oil via transesterification process with the aid of ultrasonification process, catalyst sodium methoxide, and solvent methanol.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Biodiesel

Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in diesel engines with little or no modifications. Biodiesel is simple to use, nontoxic, biodegradable, and essentially free of sulfur and aromatics. Biodiesel can be used as a pure fuel or blended with petroleum in any percentage. As type of B20 which means a blend of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel has present significant environmental benefits with a minimum increase in cost for operations and other consumers.

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix. Fuel containing 20% biodiesel is labeled B20, while pure biodiesel is referred to as B100. It is common to see B99, since 1% petroleum diesel is sufficiently toxic to retard mold. B20 type can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form which B100 type, but may require certain engine modifications to avoid maintenance and performance problems. Blending B100 with petro diesel may be accomplished by mixing in tanks at manufacturing point prior to delivery to tanker truck, splash mixing in the tanker truck which mean adding specific percentages of biodiesel and petroleum diesel, in-line mixing, two components arrive at tanker truck simultaneously. Biodiesel can be used in pure form B100 or may be blended with petroleum diesel at any concentration in most modern diesel engines. Biodiesel has different solvent properties than petroleum diesel, and will degrade natural rubber gaskets and hoses in vehicles, mostly vehicles manufactured before 1992, although these tend to wear out naturally and most likely will have already been replaced with FKM, which is nonreactive to biodiesel. Biodiesel has been known to break down deposits of residue in the fuel lines where petroleum diesel has been used. (McCormick, R.L., 2006). As a result, fuel filters may become clogged with particulates if a quick transition to pure biodiesel is made. Therefore, it is recommended to change the fuel filters on engines and heaters shortly after first switching to a biodiesel blend. Figure 2.1 shows the schematic diagram of making biodiesel fuel.

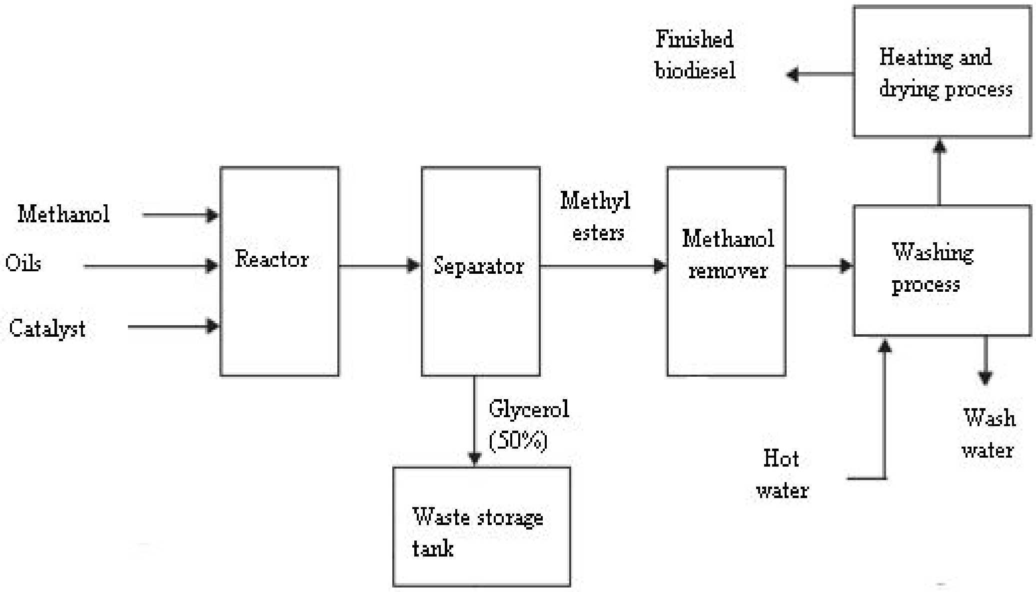


Figure 2.1: Process flow schematic for biodiesel production

2.2 Raw Materials

Raw material of biodiesel fuel mainly comes from animal fat and vegetable oils. The vegetable oils were categorized into four types which are edible oil, non-edible oil, virgin oil and waste cooking oil. Edible oil is oil which is used in food industry and they are like canola, soybean and corn. All have been used for biodiesel production and found to be good as a diesel substitute. But the non-edible is oil which is not use in food industry and normally comes from vegetable oil that growth wildly and retain survive in bad weather condition. For example are Algae, Madhuca Indica, Jatropha Curcas and Pongamia Pinnata. Virgin oil is a kind of pure vegetable oil such as palm oil, sunflower oil, soybean oil, and rapeseed oil. However waste cooking oil is also a type of vegetable oil which categorized as used frying oil collected from nearby restaurants, hotels, and public. All these raw materials usually use to synthesis biodiesel fuel.

2.2.1 Animal Fats

In late 2001, SARIA Bio-Industries GmbH, an enterprise of the Rethmann group, started their own biodiesel production in Malchin, Germany, to make use of the animal fat left as a by-product at their nearby rendering factory. The applied production process, developed and built by BDI Anlagenbau GmbH, enables SARIA to annually produce 12,000 tons of biodiesel from animal fats at the highest quality according to the European standard, EN 14214. Table 2.1 shows the qualitative and quantitative composition of the fatty acids methyl esters in beef tallow and in the produced biodiesel.

Table 2.1: Composition of fatty acids methyl esters in beef tallow and in the produced biodiesel

Designation	**Acid name**	**Composition (%)**	**mw_{acid}**	**mw_{ester}**
C14:0	Miristic	2.72	228	242
C15:0	Pentadecanoic	0.86	242	256
C16:1	Palmitoleic	2.02	254	268
C16:0	Palmitic	25.33	256	270
C17:0	Heptadecanoic	1.67	270	284
C18:2	Linoleic	0.75	280	294
C18:1(cis)	Oleic	29.87	282	296
C18:1(trans)	Elaidic	1.82	282	296
C18:0	Stearic	34.7	284	298
C20:0	Arachidic	0.28	312	326
Mass ratio of saturated and unsaturated		1.9		
Average molecular weight (amw)	273.5(a)	858.5(b)	287.6(c)	

(a) mw of acids in the beef tallow=Σ(%composition x mw_{acid})
(b) mw of beef tallow(g/mol)=3(amw_{acid})+$mw_{glycerol}$-3(mw_{water})
(c) mw of biodiesel(g/mol)=Σ(%composition x mw_{ester})

2.2.2 Vegetable Oil

Difference raw materials have difference properties and yet difference results at final product. Some chemical properties and fatty acid compositions of waste cooking oil and some pure vegetable oils were already investigated and it was summarized as Table 2.2 (Xiangmei Meng[a,b,*], Guanyi Chen[a], Yonghong Wang[c] , 2008).

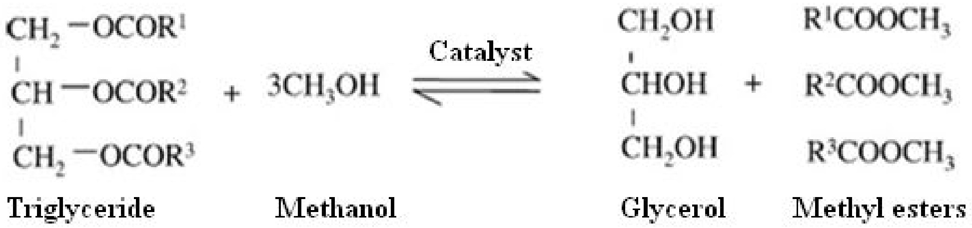
Table 2.2: Comparison of chemical properties and fatty acid composition raw material

Property	WCO	Cottonseed oil	Rapeseed oil	Soybean oil
Fatty acid composition (%)				
Palmitic acid C16:0	16	11.67	3.49	11.75
Stearic acid C18:0	5.21	0.89	0.85	3.15
Oleic acid C18:1	34.28	13.27	64.4	23.26
Linoleic acid C18:2	40.76	57.51	22.3	55.53
Linolenic acid C18:3	0	0	8.23	6.31
Specific gravity	0.925	0.912	0.914	0.92
Viscosity (mm^2/s) at 40°	66.6	50	39.5	65
Acid value (mg KOH/g)	7.25	0.11	1.14	0.2

2.3 Process of Synthesizing Biodiesel

2.3.1 Transesterification

Generally, biodiesel is produced by means of transesterification. Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol. It is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis (cleavage by an alcohol). The reaction as shown in equation 2.1 is reversible, and thus an excess of alcohol is usually used to force the equilibrium to the product side. The stoichiometry for the reaction is 3:1 alcohol to lipids. However, in practice this is usually increased to 6:1 to raise the product yield.



—(2.1)

Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol (Ma F., Hanna M. A., 1999, Meher L. C. *et al.*, 2006).

2.3.1.1 Reaction and Mechanism of Transesterification Process

Figure 2.2 summarize the mechanism of alkali catalyzed transesterification. The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (alkoside ion) to form a tetrahedral intermediate. In the second step, the intermediate reacts with an alcohol to regenerate the anion of the alcohol (alkoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. In the pre-step, when NaOH, $CaNOH_3$ or other similar catalysts are mixed with alcohol, the actual catalyst, alkoxide group is formed (Ma F., Hanna M. A., 1999, Meher L. C. *et al.*, 2006).

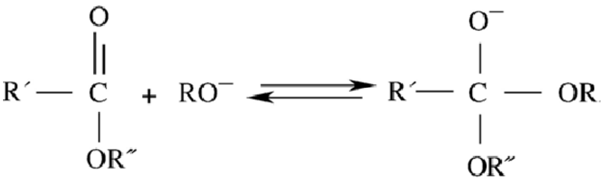
The detail mechanism of transesterification is described as Figure 2.2.

Pre-step

$$OH^{-} + ROH \rightleftarrows RO^{-} + H_2O$$

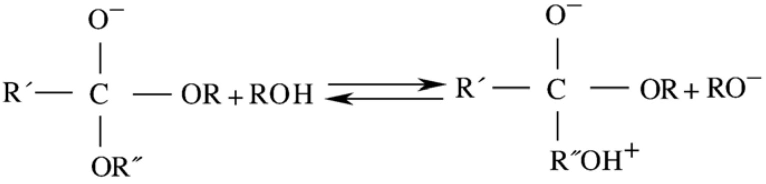
$$\text{or } NaOR \rightleftarrows RO^{-} + Na^{+}$$

Step 1



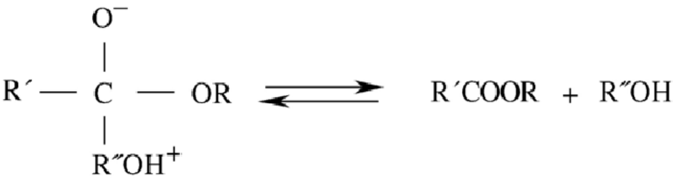
$$R'-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR''}{|}}{C}} + RO^{-} \rightleftarrows R'-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle OR''}{|}}{C}}-OR$$

Step 2



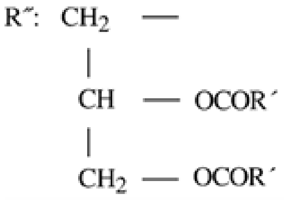
$$R'-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle OR''}{|}}{C}}-OR + ROH \rightleftarrows R'-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle R''OH^{+}}{|}}{C}}-OR + RO^{-}$$

Step 3



$$R'-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle R''OH^{+}}{|}}{C}}-OR \rightleftarrows R'COOR + R''OH$$

Where



$$R'': \begin{array}{l} CH_2 - \\ | \\ CH - OCOR' \\ | \\ CH_2 - OCOR' \end{array}$$

R’: Carbon chain of fatty acid

R : Alkyl group of alcohol

Figure 2.2: Summary of mechanism of alkali catalyzed transesterification

2.3.2 Micro-Emulsion

Microemulsions are thermodynamically stable systems composed of water, oil and surfactant, and, in some cases, an alcohol can be added as co-surfactant (Radomska A., Dobrucki R., 2000). Microemulsions are apparently homogeneous under visual observation, but in fact they are nanoheterogeneous, i.e., systems formed of particles with diameters in the order of 5–100 nm suspended in a continuous phase (Klier J. *et al.*, 2000). This technique allows the use of aqueous standards for calibration instead of expensive and instable organometallic standards. A system based on oil-in-water (O/W) microemulsion, mainly with a large amount of water, is very advantageous in order to reduce the costs and because it is similar to aqueous solutions, being much simpler to obtain optimized instrument parameters for analysis without drastic changes after aqueous solutions analysis. Calibration against aqueous standards could also be expected. Although emulsions have been used for determination of trace metals in vegetable oils and fats by techniques based on nebulization systems for sample introduction (Jim´enez M.S. *et al.*, 2004), emulsions are unstable and the separation between phases takes place after a short period of time, requiring agitation to maintain the stability of the system during the analysis. To avoid this inconveniency, in this work the use of water-in-oil (W/O) microemulsion was chosen, using a maximum of 8% (w/w) of water. The water phase was also used to introduce the inorganic standard in the microemulsions prepared for calibration. Nitric acid was also introduced into this phase as it is very important to improve the stability of the analyte in the microemulsified samples and standards. The use a relatively large amount of co-surfactant for the hydrophobic phase stabilization is related in the literature (T.P. Hoar, J.H. Schulman, 1943). The formation of microemulsion was achieved using either *n*-butanol or *n*-pentanol as co surfactant. The use of Triton X-100 was chosen because most of ionic surfactants frequently present alkali metal contaminations. The microemulsion formation was achieved for surfactant/co-surfactant ratios in the range of 1:1–1:8, considering the percentage of water not exceeding 8% in mass. Concerning the amount of biodiesel, it was possible to stabilize up to 90% (w/w) of sample. The use of a maximum amount of sample in the microemulsion is desirable to increase the analysis sensitivity, but it also increases the viscosity, reducing the nebulization efficiency. Therefore the amount of 20% (w/w) was adopted. In Figure 2.3 showed the obtained pseudo-ternary diagram for the microemulsion is shown. The mass proportion adopted for microemulsion preparation for biodiesel analysis was 57.6% of *n*-pentanol or *n*-butanol, 20% of biodiesel, 14.4% of Triton X-100 and 8% of water (NaCl or KCl aqueous standard in/or diluted nitric acid). This composition was also efficient for the microemulsion formation with vegetable oil or mineral oil (replacing the biodiesel).

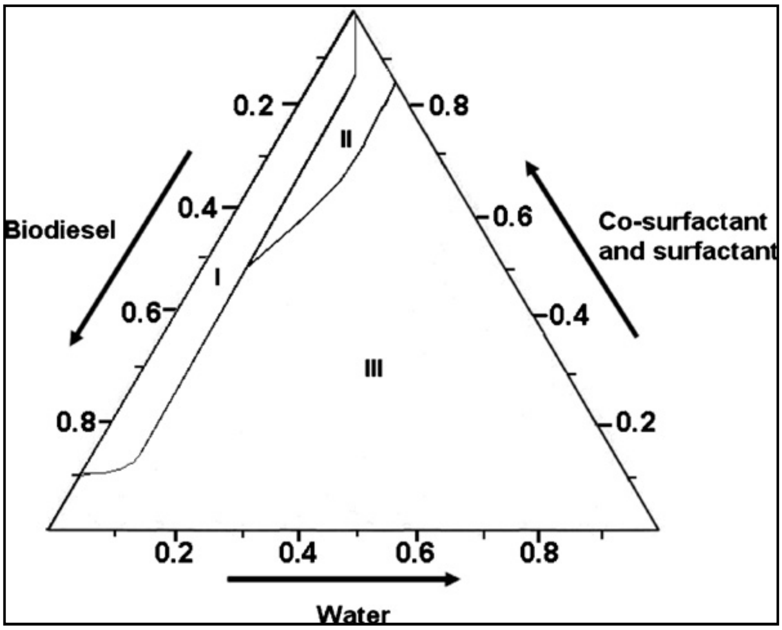


Figure 2.3: Phase diagram of biodiesel/water/Triton X-100 and *n*-pentanol mixtures at 25 °C. Region I: microemulsion with *n*-butanol or *n*-pentanol; region II: microemulsion with *n* buthanol; region III: emulsion.

2.3.3 Pyrolysis

Pyrolysis is the thermal degradation of vegetable oils by heat in the absence of oxygen, which results in the production of alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small amounts of gaseous products. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses which are conventional pyrolysis, fast pyrolysis and flash pyrolysis. The yields of pyrolysis of some vegetable oils are given in Table 4. The main components are alkanes and alkenes, which accounted for approximately 60% of the total feeder weight. Carboxylic acids accounted for another 9.6–16.1%. It is believed that as the reaction progresses, the residue becomes less reactive and forms stable chemical structures, and consequently, the activation energy increases as the decomposition level of the vegetable oil residue increases (Demirbas, 2002). Catalytic cracking of vegetable oils to produce liquid biofuels has been studied from previous research (Pioch *et al.* 1993). The most interesting temperature range for the selectivities of cracking products as a function of pyrolysis temperature is between 825 and 1125 K (Billaud F *et al.*, 1995). The chemical compositions of the heavy hydrocarbons were similar to those present in petroleum refinery products. The production of hydrogen by the catalytic steam reforming of sunflower oil (Marquevich M *et al*., 2000) has been studied. The study was performed in a fixed bed reactor with a commercial nickel based catalyst for steam reforming naphtha. Sunflower oil was completely converted to hydrogen, methane and carbon oxides, except for the runs performed at the lowest temperatures and an S/C ratio of 3. The hydrogen yield ranged from 72% to 87% of the stoichiometric potential, depending on the steam-to-carbon ratio and the catalyst temperature, which governed the equilibrium among the gas species.

Table 2.3: Yields of pyrolysis of vegetable oils (percent by weight)

	High oleic acid safflower		**Soybean**	
	N_2 sparge	**Air**	**N_2 sparge**	**Air**
Alkanes	37.5	40.9	31.1	29.9
Alkenes	22.2	22	28.3	24.9
Alkadienes	8.1	13	9.4	10.9
Carboxylic acids	11.5	16.1	12.2	9.6
Unresolved unsaturates	9.7	10.1	5.5	5.1
Aromatics	2.3	2.2	2.3	1.9
Unidentified	8.7	12.7	10.9	12.6

Source: Schwab *et al.,* 1988

2.4 Solvent

A solvent is a liquid or gas that dissolves a solid, liquid, or gaseous solute, resulting in a solution. The most common solvent in everyday life is water. Most other commonly-used solvents are organic chemicals that are called organic solvents. In biodiesel production via transesterification process, the almost solvent used is alcohol such as methanol, ethanol, propanol, buthanol, and amyl alcohol. In chemistry, an alcohol is any organic compound in which a hydroxyl group (-OH) is bound to a carbon atom of an alkyl or substituted alkyl group. The general formula for a simple acryclic $^{+1}$OH, alcohol is C_nH_{2n} . The methanol is more preferable than ethanol because of low price and chemical and physical advantages. Methanol also is the simplest alcohol, and is a light, volatile, colourless, flammable, poisonous liquid with a distinctive odor that is somewhat milder and sweeter than ethanol. Sometime each solvent can be mixed together in order to increase rate of transesterification process. But this mixed solvent will produced methyl ester and ethyl ester with 50% composition each other.

2.5 Catalyst

Catalysis is the process in which the rate of a chemical reaction is increased by means of a chemical substance known as a catalyst. A catalyst is a substance that speeds up the rate of reaction. It lowers the energy of activation, thus increasing the rate of the catalyzed reaction. The energy of the reactants and products is the same in both the uncatalyzed and catalyzed reactions, so the position of equilibrium is unaffected. It is dividing into homogenous and heterogenous catalyst, depending on whether a catalyst exists in the same phase as the substrate. The catalyst used has a determinant effect on the reaction, raising the rate notably. In transesterification process, the reaction can be catalysed by difference condition either in both acid-bases catalyst based homogenous or heterogenous type and also can conducted under neutral conditions. But the results will be difference with different manipulated catalyst type conditions. Some aspect only need changeable various reaction variables of catalyst in order to know the effects of oil conversion. It is known that basic catalysts require short times (30 min) to complete the reaction even at room temperature, while acid catalysts, such as sulfuric acid, require higher temperatures 100 °C and longer reaction times 3–4 hour (Schwad A.W. *et al.,* 2006; Van Gerpen J., 2005). Table 2.4 below showed the prices of some catalyst based year 2005.

Table 2.4: Unit price of catalyst as of 2005

	NaOH (purity: 99%)	**KOH (purity: 92%)**	**CH_3ONa (purity: 99%)**
Price[a] (US$/ton)	400	770	2300

[a] Prices are quoted from companies in China

2.5.1 Homogenous Catalyst

Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles invoked in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates. Basically, there two types of catalyst that is acid catalyst and alkaline catalyst. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in transesterification. However, a large amount of water is required to transfer the catalysts from the organic phase to a water phase (Du W. *et al.,* 2004, Ebiura T. *et al.,* 2005, Ma F. and Hanna M.A., 1999). Therefore, it is considerably costly to separate homogeneous catalysts (Kim H.J. *et al.,* 2004). Table 2.5 is the simply brief of difference between acid catalyst and alkaline catalyst.

Table 2.5: Differences between acid and alkaline catalysts

Acid catalyst	Alkaline catalyst
1) Example; sulphuric acid, phosphoric acid, hydrochloric acid, organic sulfonic acid. 2) The catalyst reaction in transesterification process is much lower than alkaline catalyst (Freedman *et al.*,1984). 3) The catalyst requires higher temperature while in process operation. 4) Its more preferable during reaction with raw material that contain higher free fatty acid and water (Sprules and Price, 1950; Freedman *et al.*, 1984).	1) Example; sodium methoxide, sodium hydroxide, potassium hydroxide, potassium methoxide, sodium hydride, sodium amide, potassium amide, potassium hydride (Sprules and Price, 1950). 2) Sodium methoxide is widely used due to cheaper price. 3) The performance of alkaline catalyst in transesterification process is much faster than acid catalyst and give high yield (Krisnamgkura K. *et al.*, 1992) 4) This alkaline catalyst is preferable used to raw material that contains low free fatty acid and water.

2.5.2 Heterogenous Catalyst

Heterogeneous catalysts are present in different phases from the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Helmut Knözinger, Karl Kochloefl, 2003). For example, in the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto "active sites" on the iron particles. Once adsorbed, the bonds within the reacting molecules are weakened, and new bonds between the resulting fragments form in part due to their close proximity. In this way the particularly strong triple bond in nitrogen is weakened and the hydrogen and nitrogen atoms combine faster than would be the case in the gas phase, so the rate of reaction increases. Heterogeneous catalysts are typically “supported,” which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Sometimes the support is merely a surface upon which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction.

2.5.3 Enzymes Catalyst

Enzymes are biochemical catalyst composed of amino acids held together in a very specific three dimensional shape. The catalyst that synthesize and break down biomolecules in living organism are governed by the same principles as the acids and metals in organic reactions. The catalyst in living organisms, however are usually protein molecules called enzymes. An enzyme contains a region called its active site, which binds an organic reactant, called a substrate. When bound, this unit is called the enzyme-substrate complex. Understanding the nature of the active sites of enzymes is often important in designing drugs to treat diseases. Once bound, the organic substrate undergoes a very specific reaction at an enhanced rate. An enzyme speeds up a biological reaction in a variety of ways. It may hold reactants close in the proper conformation to facilitate reaction, or it may provide an acidic site needed for a particular transformation. Once the reaction is completed, the enzyme releases the substrate and it is then able to catalyze another reaction (Janice Gorzynski Smith, 2006).

2.6 Ultrasonic

The oils and methanol are not completely miscible, the mixing efficiency was stated as one of the most important factors affecting the yield of the transesterification (Kusdiana D., Saka S., 2001). Low frequency ultrasonic irradiation is widely used in industry for emulsification of immiscible liquids. Our previous work showed that by using ultrasounds the efficient mixing problems could be overcome (Mason T.J., 1999). During the collapse of cavitational bubbles of methanol supersonic jets are created generating nano-sized drops that are extremely efficiently mixed thus abundantly enhancing the reaction surface.

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 Introduction

Every experiment that was conducted, it must have a procedure to achieve the target. In biodiesel production, there are several methods that need to be fulfilled. Basically, the experiment needs to undergo the transesterification process which is conducted based the parameter controlled that already mentioned earlier such as reaction concentration, reaction time, reaction temperature, molaratio and degree of mixing via ultrasonic reactor. Thus, the catalyst sodium methoxide was used in order to shorter the reaction times during transesterification reaction without modify any net free energy change of reaction. The experimental diagram is structured as Figure 3.7 and the list and explanation of few steps are stated as below.

- i) Raw material preparation
- ii) Equipment selection
- iii) Experimental methodology
    - a. Initial pre-treatment process
    - b. Transesterification process
    - c. Settling and separation process
    - d. Washing and methanol recovery
- iv) Sample analysis

All those steps above are very important in order to make the biodiesel. As for raw material, it is the first thing essentially to reconsider which is in this experiment we already used the waste cooking oil and RBD palm oil as raw materials. Difference materials have difference properties as well as difference method to fulfill the process. Choosing the equipment is also the most important and during the whole operation conducted, we are required to use the ultrasonic reactor instead of batch system, the stirrer, hotplate stirrer, rotary evaporator, gas chromatography, and gas combustion test. The experiment was supported by catalyst sodium methoxide and solvent methanol.

Referred to methodology, the initial pre-treatment is only conducted for waste cooking oil because of it properties which already contained large amount of sludge and need to remove first before going to further process. All the process compulsory to conduct under safety condition especially in handling methanol because of it’s volatility and flammability. Every detail steps were discussed in next subchapter.

3.2 Materials

3.2.1 Raw Material Preparation

In this experiment, the raw materials used are waste cooking oil (WCO) and refined bleach deionized (RBD) palm oil. This waste cooking oil was collected nearby restaurants, hotels, canteens, and home. RBD palm oil was bought from nearby market with a cheap price. However, both raw materials have different properties which waste cooking oil has much solid residue than RBD palm oil. As pre-caution method, waste cooking oil need to undergo pre-filter and pre-heat process at begin as well as to make the oil clear before going to the next process. The temperature used is around 90 ℃ to 100 ℃ for 15 min in order to remove water content. After that, it was cooled to 40˚C using ultrasonic reactor until achieve equilibrium state.

3.2.2 Catalyst Preparation

Catalyst is very important during transesterification reaction. Difference catalyst gives difference effect of product yield but the most important is it will enhance the speeds of rate reaction, lowers the energy of activation without change any net free energy in the system. As example of alkaline catalyst used are sodium methoxide, sodium hydroxide and potassium hydroxide. In this experiment, the catalyst was prepared using sodium methoxide mixed with alcohol. It was brand by Fluka Analytical with series number 71750. The catalyst was bottled in a white powder form with an amount of 500g. During handling the catalyst, it is important to remember that it needs to be stored in a dry place, wearing mask while weighing the catalyst, bulk storage of sodium methoxide solution should conform to the general requirements for methanol and avoid every sources of ignition like sparks, flames, heat and electrical discharges. The catalyst could do not expose to atmosphere for long time in order to prevent volatility.

3.2.3 Solvent Preparation

Other than catalyst, the solvent is one of the requirements to complete the process. In this experiment, the solvent alcohol was used mixed with catalyst sodium methoxide. The methanol was mixed with sodium methoxide to form catalyst solution. During handling methanol, the most important is do not expose openly to atmosphere due to its volatility. Furthermore please wash thoroughly after handling it, ground and bond containers when transferring material, empty containers retain product residue, keep container tightly closed, avoid contact with heat, sparks and flame, and use only in a chemical fume hood. After mixing the solvent and catalyst, it was stirred continuously using magnetic stirrer placed on the hotplate stirrer until well mixed. The time mixing that was proposed to conduct is around 10 min depending on the amount of catalyst.

3.2.4 Equipment Selection

The experiment is conducted in small scale production for one liter production of oil. There are several equipments that being used in producing biodiesel fuel. The types, brand and uses of equipment is mentioned in Table 3.1:

Table 3.1: Summary of equipments

Equipments	Brand/model	Purpose of use
Ultrasonic reactor	CREST Ultrasonic	Transesterification process
Gas chromatography	Agilent Technologies 6890 series GC System	Methyl ester analysis
Gas combustion	NU-WAY and P.A.Hilton td.	Gas emission analysis
Rotary evaporator	BÜCHI Rotavapor R-200 and BÜCHI Heating Bath B-490	Methanol recovery process
Filter press	Not available	Intial pre-treatment process for WCO
Hotplate stirrer	EMS-HR 1000 and ERLA®	Mixing process during catalyst preparation
Digital overhead stirrer	EUROSTAR digital IKA® - WERKE	Mixing process during transesterification reaction

Figure 3.1 to Figure 3.6 shows all the equipment used in order to complete the experiment until end process.

Figure 3.1: Filter press

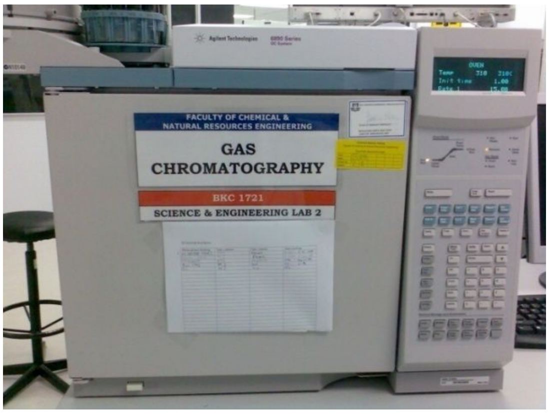


Figure 3.2: Gas Chromatographic Analyzer

Figure 3.3: Ultrasonic Reactor

Figure 3.4: Hot Plate Stirrer

Figure 3.5: Rotary evaporator

Figure 3.6: Digital Overhead Stirrer

3.3 Experimental Procedure

In the experiment, the procedures were running step by step starting from raw material preparation until get the sample biodiesel fuel. It consist 10 steps which included initial pre-treatment process, heating process, catalyst preparation, transesterification process, settling process, separation process, methanol recovery, washing process and sample biodiesel analysis. The parameter variables controlled during transesterification reaction which are divided into three stages of operation. At first stage, the reaction temperature of 40 ℃, reaction time of 40 min, molar ratio of 6:1, and mixing degree of 1000 rpm were fixed with varied catalyst concentration from 0.25 to 1.5 wt%. The objective is to find the optimum concentration of biodiesel. The experiment was conducted under ultrasonic reactor. The final biodiesel product is then analyzed using gas chromatography brand Agilent Technologies. At second stage, the optimum concentration from previous experiment was used. The transesterification reaction was conducted under reaction temperature of 40 ℃, molar ratio of 6:1, mixing degree of 1000 rpm and varied reaction time of 20-60 min. The sample is then analyzed again using gas chromatography. At third stage, the optimum results of concentration and reaction time are used. The operation was conducted under reaction temperature of 40 ℃, molar ratio of 6:1, and mixing degree for 1000 rpm. But the volume of oil is enlarging to 5 liter production and conducted step by step by small scale of 1 liter oil. This is because amount of sample needed for gas combustion analysis is at least 5 liter instead of 1 liter. At this final stage, the percentage of gas emission from biodiesel fuel was identified and was compared with petroleum diesel. All the result is tabulated and recorded as a final result. Figure 3.7 shows the summary of the method for making biodiesel.

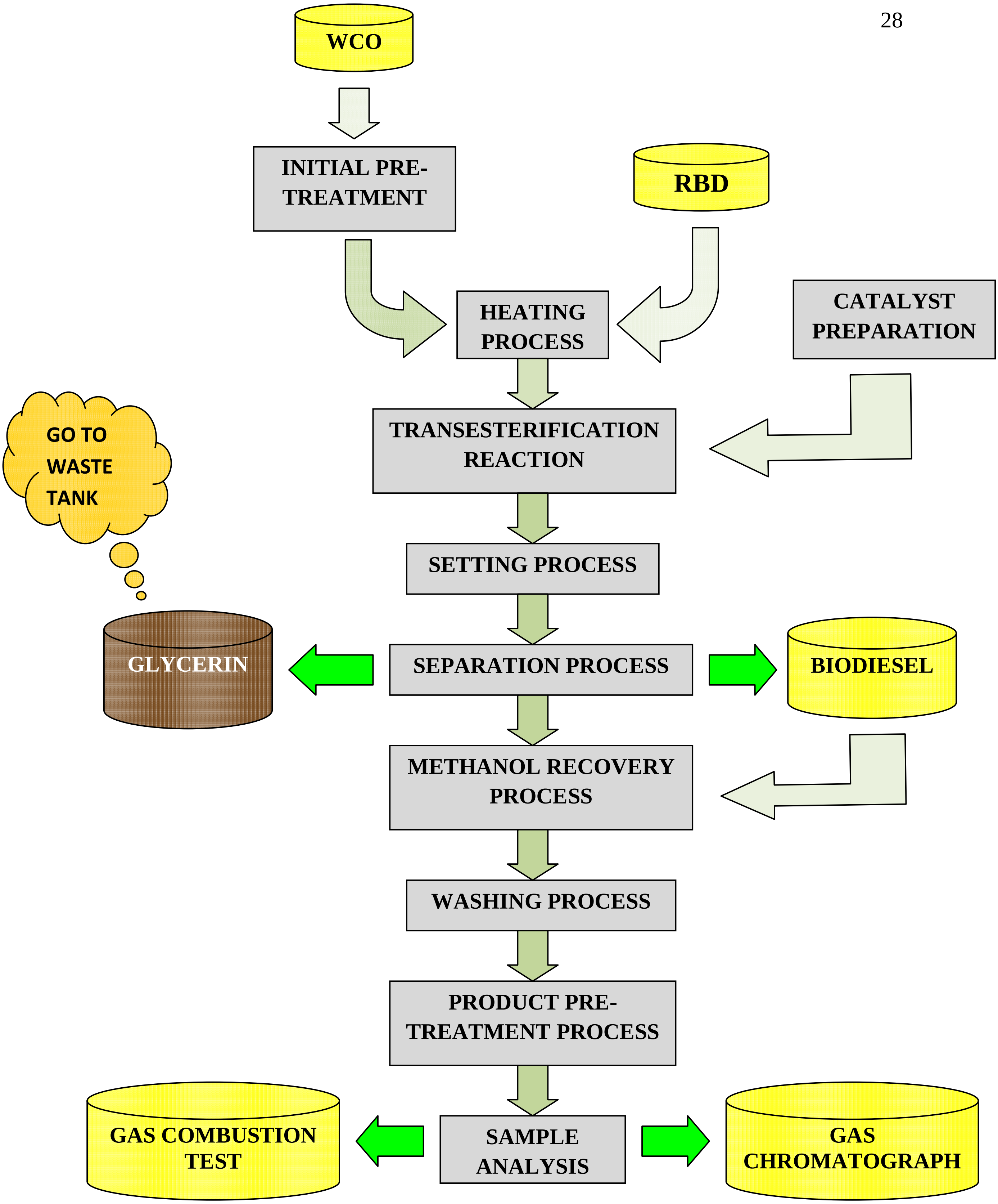


Figure 3.7: Experimental Method

3.3.1 Initial Pre-Treatment Process

After collecting raw material nearby restaurant, hotel and canteen, they were stored in 80 liter tank. The solid compounds contained in waste cooking oil are separated using filter press in order to reclear the waste oil before go to the next process. The filtrated waste cooking oil is then pre-heat to 90-100 ℃ in order to remove excess water. After heating process, it was left for 15 min to cool down the sample before continuing to next step. The temperature proposed for cooling process is 40 C. For the RBD palm oil, the procedure is same as waste cooking oil except filtration process due to no solid compound in oil. Figure 3.8 shows the process of filtration of sludge particle and heating process.

Figure 3.8: Pre-treatment process

3.3.2 Transesterification Reaction

Transesterification of waste cooking oil and RBD palm oil was carried out in one liter amount of beaker take places in ultrasonic reactor. The beaker is warming to 40 ℃. Meanwhile, do the preparation of catalyst solution. Firstly, prepare an amount of solvent methanol. Second, weight an amount of catalyst sodium methoxide. After a while, both catalyst and solvent were mixed, and then stirred using magnetic stirrer until the mixture well mixed. After oil reached to desirable temperature, the catalyst that already prepared is then mix together with the oil using agitator at 1000 rpm. All the reaction was conducted under ultrasonic reactor. The condition was fixed at reaction temperature of

40 ℃, molar ratio 6:1, mixing degree of 1000 rpm, varied concentration of 0.25-1.5 wt% and reaction time of 20-60 min. The reaction was left until it was completely reacted. The sample is then settled down for 12 hour until two or three layer form. The whole process conducted was same for both waste cooking oil and RBD palm oil. During the transesterification process, the valuable ratio of oil to methanol suggested is 6:1 to raise the product yield. All the experiment is conducted under three stage conditions as mentioned in section 3.2. The Figure 3.9 shows the process of transesterification reaction.

Figure 3.9: Transesterification

3.3.3 Settling and Separation Process

After finish the reaction in ultrasonic reactor, the mixture was transferred into suitable placed and left around 12 hour for settling process. It was completed until the intermediate sample show the formation of two or three layers. Theoretically, the density of glycerin is heavier than density of crude biodiesel and it was separated exactly due to gravity force. Generally, if there were two layer forms, the upper layer should be the crude biodiesel with light colour performance and the second layer should be the glycerin with black and solid performance. However, if three layer forms, the middle of two layers will be an emulsion which it is in liquid phase and white colour performance. Experimentally, the upper crude biodiesel layer will transferred out onto another beaker for further treatment. In the settling process, the available temperature considered is between 25-30 ℃ instead of below 20 ℃ to prevent transformation into jelly form. The rest waste product is store out into waste storage.

Figure 3.10: Settling and separation process

3.3.4 Methanol Recovery and Washing Process

After crude oil was transferred out in settling process, it then continues into process recovering methanol. The crude oil is filling into rotary evaporator under vacuum condition at 70 ℃. The vacuum is functioned to lower the boiling point of the methanol and make it easier to recover excess methanol. Then the crude biodiesel oil was washed with hot water by slowly pouring it into the solution. After that, the water is drain and this washing and draining process was repeated for average three times to make sure the intermediate sample is clear. Finally, the biodiesel was filtrated using filter paper in order to remove remaining solid and heat up to 100 ℃ by stirring hotplate equipment to dry up remaining residual water in intermediate sample biodiesel product.

3.4 Sample Analysis

In both experiment, three parameters were considered as data analyses which are biodiesel yield, methyl ester content, and gas emission amount. The optimum condition was verified from analyzed data after the experiment had done. The Figure 3.11 shows the equipments used during conducted the analyses.

Figure 3.11: Gas chromatography and Gas combustion

3.4.1 Biodiesel Yield

Product yield is defined as percentages of weight of the final biodiesel product over to weight of the waste cooking oil at first experiment. The formula related is as equation 3.1:

$$Product\ yield = \left(\frac{Weight\ of\ product}{Weight\ of\ raw\ oil}\right) X\, 100\% \quad \text{——(3.1)}$$

3.4.2 Methyl Ester Content

In this study, the purity of biodiesel product, denoted by its ester content, is defined as the weight percentage of methyl esters in the final product after the purification and the removal of glycerol, excess methanol, alkaline catalyst and soap in the product mixture. In this experiment, the methyl ester content was analyzed using Gas Chromatography type 6890 series; GC system by Agilent Technologies. It was employing column HT-S/DB wax, oven ramping; 50°C of 1 min, 75°C of 3 min, 200°C of 3 min, 230°C of 18 min, injection 1 micro lid and detector of 280°C. Usually the objective of gas chromatography is to separate the various molecular entities of a sample, and this is often accomplished readily with capillary GC. Derivatization, a separate sample treatment which makes substances essentially non-volatile, more volatile, makes possible the determination of many of the impurities by gas chromatography. Glycerol, sterols, free fatty acids, residual alcohols, mono and diglycerides are all readily derivatized with the silylating agent BSTFA (C. F. Poole, 1979), and this forms the basis of current GC methods for impurity determinations. (Richard W. Heiden, 1996). The formula related as equation 3.2:

$$Ester\ content = \left(\frac{Weight\ of\ ester}{Weight\ of\ product}\right)100\% \quad \text{——(3.2)}$$

3.4.3 Gas Combustion Test

After finalized the optimum product from optimum condition, the sample biodiesel product was then analyzed using gas combustion equipment with gas analyzer. This equipment was detected the percentages of gas emit in biodiesel fuel and the result was compared with a regular petroleum diesel.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Catalyst Concentration

Catalyst concentration is one of the factors that will affect the methyl ester formation and the product yield. In previous research, the catalyst amount shows the significant effect on the ester formation and product yield compared to reaction temperature and reaction time in the reaction stage. In this first section of experiment, the first objective is to find the optimal amount of concentration ranging from 0.25 to 1.5 wt%. The operation conditions during the whole reaction were fixed at reaction temperature of 40°C, reaction time of 40 and molar ratio of methanol to oil at 6:1. The reaction was conducted in ultrasonic reactor with the aid of sodium methoxide and methanol as a catalyst and solvent. The raw oil of waste cooking oil and RBD palm oil were used in this experiment and the effect of difference properties were observed due to product yield and ester content.

4.1.1 Effect of Catalyst Concentration to Product Yield

Figure 4.1 shows the effect of catalyst concentration on product yield from RBD and WCO. It shows the RBD product yield is greater than WCO for the whole concentration. For RBD, product yield was increased relatively from concentration of

0.25 to 1 wt% and decreased from concentration of 1 to 1.5 wt%. The optimum product yield of 89.01 % was exhibited at concentration of 1 wt%. For WCO, product yield was increased significantly with catalyst concentration from 0.5 to 1 wt%. But no product yield achieved at concentration 0.25 and 1.5 wt%. The maximum product yield of 86.33% was achieved at concentration of 1 wt%. During experiment conducted at concentration 0.25 wt%, the observation of final product was recorded. It showed no separation layer occurred after settling process and only a large amount of fatty acid was exhibited without any biodiesel oil exist on upper layer. According to formation of soap, the alkaline catalyzed system is very sensitive to both water and free fatty acid (FFA). The presence of water under alkaline conditions causes ester saponification produced soap form which causes formation of emulsions. The reason probably due to range of reaction time with the lower concentration will cause hydrolysis of ester, resulted in a loss of esters as well as causing more fatty acids to form soap (Zhang Y. *et al.*, 2003). At 1.5 wt% of concentration, the blank result probably because of excess catalyst amount. This is because excess amount of catalyst caused more triglyceride participating in the saponification reaction with CH_3ONa producing more soap, thereby reducing the ester yield.

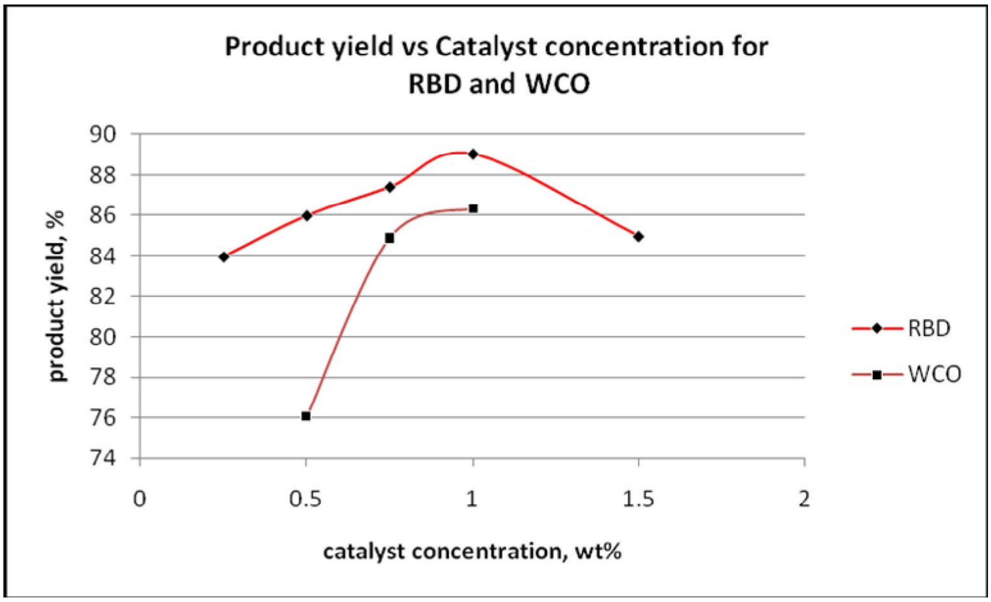


Figure 4.1: Effect of catalyst concentration on product yield

4.1.2 Effect of Catalyst Concentration to Methyl Esters Content

As showed in Figure 4.2 for RBD, the methyl ester was relatively increased from concentration 0.25 to 1 wt% then decreased from concentration 1 to 1.5 wt%. The maximum methyl ester content of 89.28 % was achieved at concentration 1 wt%. But, for WCO the result showed the methyl ester content was slightly increase with the increase of concentration from 0.5 to 1.0 wt%. The highest ester content of 76.07 % was achieved at 1 wt% concentration. However, the experimental results also showed there is no result at concentration 0.25 and 1.5 wt%. This is because of large amount of free fatty acid and some impurities contained in waste cooking oil (Leung D.Y.C., Guo. Y., 2006). Free fatty acids in the raw oil predominantly react with the alkaline catalyst to form sodium based soap and water. Accordingly, the free fatty acids in the raw oil were not converted into ester but to side product soap. Also some impurities in the oil could not be converted to esters and remained in the final product, resulted the lower biodiesel yield and product purity.

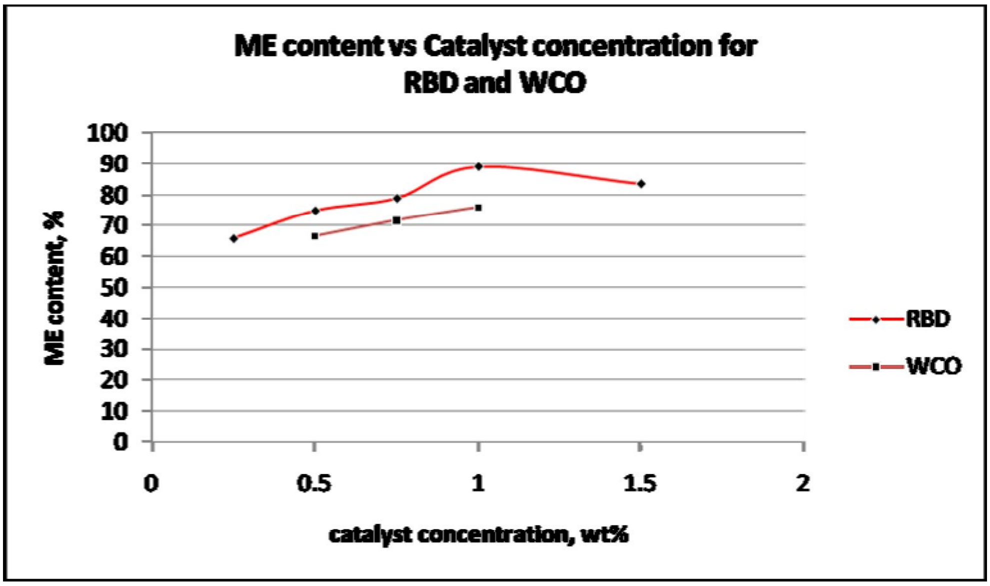


Figure 4.2: Effect of catalyst concentration on methyl ester content

4.2 Effect of Reaction Time

Even though the effect of reaction time on ester formation is not a great influence, but it mostly support the transesterification process. Increase reaction time will increase amount of yield and ester content. However, extent of reaction time will give negative impact to biodiesel product. Actually, the factor of reaction time varied significantly with reaction temperature. In this second stage of experiment, the optimum catalyst concentration of 1 w% from previous experiment was used. It will supported by reaction condition of reaction temperature of 40°C, molar ratio methanol to oil of 6:1, and highest mixing degree of 1000 rpm. The results during the whole experiment was investigated and recorded. The experiment conducted for both raw oils of waste cooking oil and RBD palm oil.

4.2.1 Effect of Reaction Time to Product Yield

Figure 4.3 shows the effect of reaction time on product yield for both the raw oils. For RBD, the result showed that reaction process was achieved the optimum product yield of 91.03 % at reaction time 30 min. But, for WCO it achieved optimum reaction time at 40 min. It showed the waste cooking oil needs higher reaction time than RBD palm oil in order to complete the conversion of triglyceride reaction. High reaction time was important to complete the transesterification reaction and it mostly depends on reaction temperature conducted. Thus the fixed temperature of 40°C conducted requires high reaction time for WCO in order to achieve complete conversion of triglyceride due to higher free fatty acid, viscosity and some impurities. The result indicated that the advantages of using ultrasonic reactor in this process where ultrasonic allow a short reaction time and high product yield because of emulsification and cavitations of the liquid-liquid immiscible system. From literature without using ultrasonic reactor, it shows the reaction time taken in order to achieve the equilibrium state is within range 30 to 120 min for used frying oil (Encinar J.M. *et al.*, 2007).

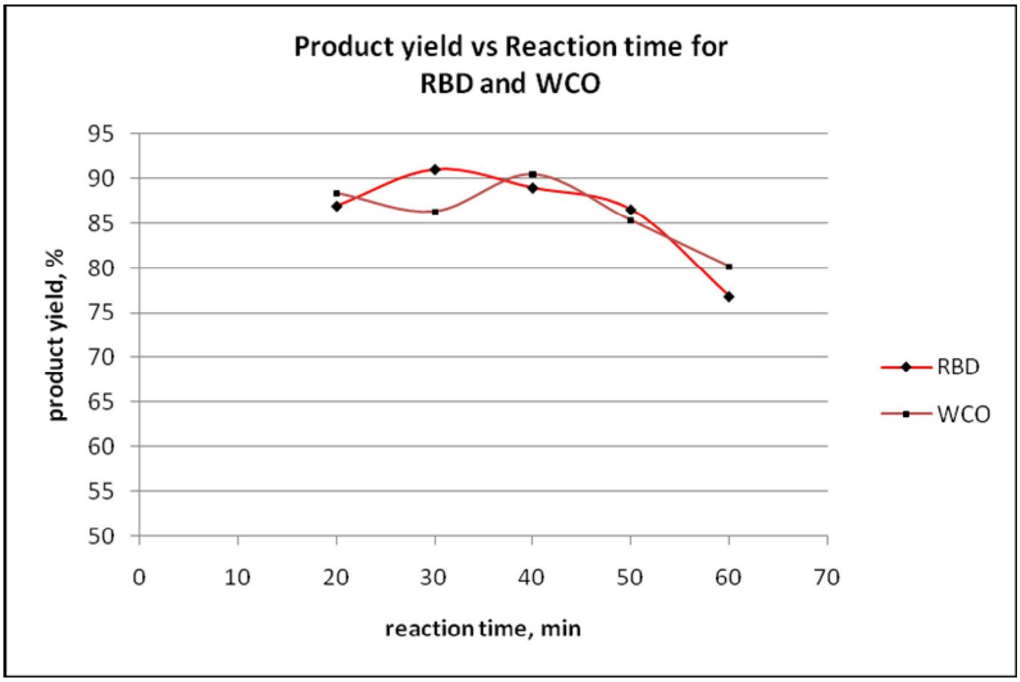


Figure 4.3: Effect of reaction time on product yield

4.2.2 Effect of Reaction Time to Methyl Esters Content

The effect of reaction time on methyl ester content was shown in Figure 4.4. For RBD, the ester content was increased from reaction time of 20 to 30 min and decreased from reaction time of 30 to 60 min. It was achieved the maximum ester content of 94.02% at time of 30 min. The experimental result showed that the reaction was very fast at first 5 min and then it was started to slow down and entered a slow rate stage till the reaction achieved an equilibrium phase. At this stage, the observation of clear phase was being formed which sample colour turn from cloudy to clear light colour. For WCO the ester content was relatively constant at reaction time between 20 to 40 min and slightly decreased at reaction time 40 to 60 min. The result indicated that the optimal methyl ester content achieved at 93.1% at reaction time of 40 min. The extent reaction time will cause the reduction in ester content due to further reaction of hydrolysis of ester thereby cause more fatty acid form. The free fatty acid in raw oil for both waste cooking oil and RBD palm oil will react with the catalyst in reaction process resulted more sodium soap formed instead of ester content. The increase of free fatty acid in the final biodiesel product and it may cost extra financial in order to separate the biodiesel oil and soap.

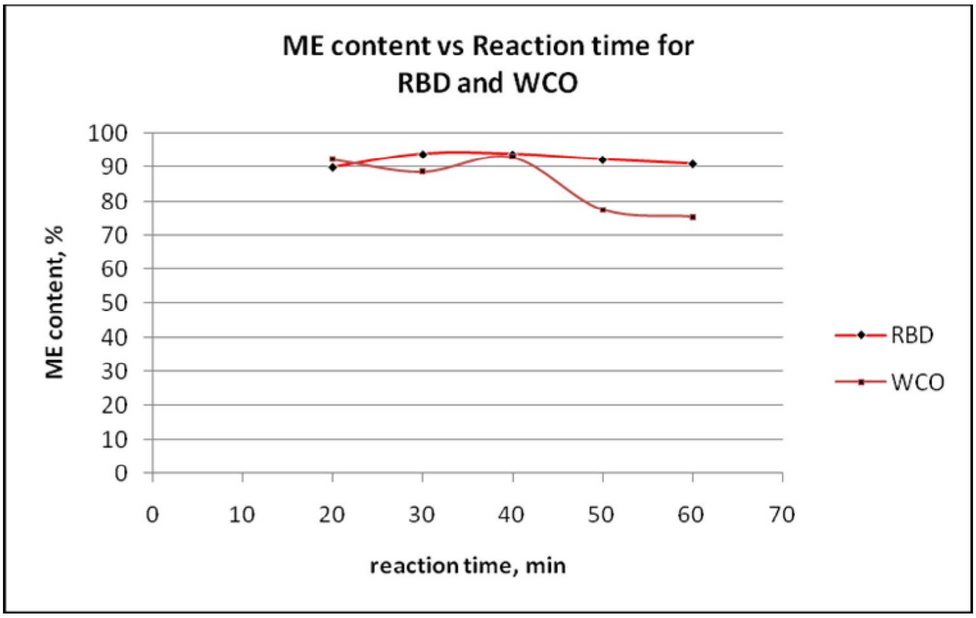


Figure 4.4: Effect of reaction time on methyl ester

4.3 Combustion Analysis

The combustion test analysis was investigated for the final sample product running at the optimized operation condition from previous two experiments. At the optimum concentration of 1 wt%, optimum reaction time of 30 min, fixed reaction temperature of 40°C, molar ratio methanol to oil of 6:1 and highest mixing degree of 1000 rpm the experiment was conducted for RBD palm oil. It was the same for waste cooking oil that used previous optimum concentration of 1 wt% and reaction time of 40 min. From literature, biodiesel fuel can reduce carbon monoxide, total hydrocarbons, and particulate matter emissions and smoke, along with increases in oxides of nitrogen, NO_x (Encinar J.M. *et al.*, 2007). Table 4.1 shows the comparison of gas emission for biodiesel and diesel.

Table 4.1: The comparison of amount of gas emission for biodiesel and diesel

Type of emission	**Biodiesel, %**		**Diesel, %**
	RBD palm oil	**WCO**	
O_2	8.6	9.0	8.3
CO	186	185	376
CO_2	9.3	9.0	9.5
X_{air}	70	69	66

The results shows the amount of gas carbon monoxide for RBD and WCO were decreased as compared to petroleum diesel with error 51% and 50% as well as the amount of gas carbon dioxide emitted with error 2.11% and 53% for RBD and WCO. Regarding to the results, using biodiesel fuel can support the reduction of gas hazardous emission such as gas carbon monoxide and carbon dioxide and it achieved the objectives target in this experiment.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study on the transesterification reaction of two feedstock oil that are waste cooking oil and RBD palm oil in producing biodiesel was investigated and the factors of catalyst concentration and reaction time was introduced in order to know the effect on product yield and ester content in biodiesel fuel. The percentages of gas emission in combustion analysis also studied by compare with petroleum diesel. The conclusion of the parameter investigated was presented as table 5.1 and table 5.2.

Table 5.1: The optimized results of the effect of catalyst concentration in producing biodiesel using RBD and WCO.

Type of parameter	**Biodiesel, %**	
	RBD palm oil	**WCO**
Concentration	1 wt%	1 wt%
Time	40 min	40 min
Temperature	40°C	40°C
Molar ratio	6:1	6:1
RPM	1300	1300
Product yield	89.01%	86.33%
ME content	89.28%	76.07%

Table 5.2: The optimized results of the effect of reaction time in producing biodiesel using RBD and WCO.

Type of parameter	**Biodiesel, %**	
	RBD palm oil	**WCO**
Concentration	1 wt%	1 wt%
Time	30 min	40 min
Temperature	40°C	40°C
Molar ratio	6:1	6:1
RPM	1300	1300
Product yield	91.03%	90.4%
ME content	94.02%	93.1%

5.2 Recommendation

Waste cooking oil and RBD palm oil were introduced as raw oil materials, resulted the differences effect for each yield product, ester content and gas emission. According to high amount of free fatty acid in raw oils especially for waste cooking oil, some alternatives method need to be implemented in the way of reduction of soap saponification reaction during the whole operation. Thus, the process of neutralization of free fatty acids in waste cooking oil could be implemented by titration of CH_3ONa into waste cooking oil and the amount of the catalyst needed can be determined for every liter of waste cooking oil.

Using ultrasonic reactor exactly can shorten the reaction time in transesterification process. But, ultrasound frequency in the ultrasonic reactor may affect the reaction temperature during the operation. It caused the instability of controlling the temperature resulted as a disturbance in transesterification reaction. To overcome the problem, water is used as a medium in ultrasonic reactor by adding the cold water into the reactor in order to balance the temperature.

As the final recommendation, the final biodiesel product could be stored in a room temperature instead of lower temperature in order to prevent precipitate form that may result the disturbance in engines. The justification is if the biodiesel product was exposed to the lower temperature, some impurities that already have in sample will solidified at cold temperature. So, it may give the negative effect to user if they use as fuel.

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APPENDICES

A.1 Experimental work data

From Malaysia Palm oil Board (MPOB) journal, the density appropriate to used for waste cooking oil (WCO) and RBD palm oil were shown in table A.1.

Table A.1-1: Density of oils

ρ_{WCO} (kg/m^3)	ρ_{RBD} (kg/m^3)
880	925

In order to find the mass of sodium methoxide and the volume of methanol, the following calculations have been done and showed as below.

***1st step:** Find the weight of raw oils*

Let assume volume of WCO and RBD used during conducting the experiment

$V_{oils} = 5000ml = 0.005\ m^3$

Find weight of raw oils,

$W_{oils} = \rho_{oils} \times V\ oils$

Thus,

$W_{RBD} = 0.435\ kg,\ W_{WCO} = 0.45\ kg$

***2^{nd} step:** Find weight of catalyst at each concentration for WCO and RBD*

The data were summarized in table A.2 below.

Table A.1-2: Amount of catalyst required

Concentration wt%	WCO (g)	RBD (g)
0.25	1.125	1.088
0.5	2.25	2.175
0.75	3.375	3.263
1.0	4.5	4.35
1.5	6.75	6.525

***3^{rd} step:** Find volume of methanol required for WCO and RBD*

The molar ratio of methanol to oil is 6:1 and it was used in calculation to find the amount of methanol. The data were summarized in table A.3 below.

Table A 1-3: Amount of methanol needed

Properties	Methanol	WCO	RBD
Density, ρ	0.791 g/cm3	0.900 g/cm3	0.870 g/cm3
Molecular weight, MW	32.049 g/mol	856 g/mol	847.3 g/mol

Molar ratio	6X32.049 g/mol = 192.294 g/mol	1X856 g/mol = 847.3 g/mol	1X847.3 g/mol = 856 g/mol
Scale down, X		1.948 g/mol	1.902 g/mol
Volume	V of methanol for WCO: = 1.28 L V of methanol for RBD: = 1.25 L		

A.2 Analysis data

A.2.1 Waste Cooking Oil

Table A.2-1: 1st stage experiment

Sample	Temp (^{0} c)	Time (min)	Catalyst conc, (wt %)	Product yield, %
1	40	40	0.25	NA
2	40	40	0.50	76.06
3	40	40	0.75	84.894
4	40	40	1.00	86.333
5	40	40	1.50	NA

Table A.2-2: 1st stage experiment

Sample	Temp (^{0} c)	Time (min)	Catalyst conc, (wt %)	Me content, %
1	40	40	0.25	NA
2	40	40	0.50	66.88
3	40	40	0.75	71.92
4	40	40	1.00	76.07
5	40	40	1.50	NA

Table A.2-3: 2nd stage experiment

Sample	Concentration, (wt %)	Temp (^{0} c)	Reaction time (min)	Product yield, %
1	1.00	40	20	88.389
2	1.00	40	30	86.333
3	1.00	40	40	90.444
4	1.00	40	50	85.306
5	1.00	40	60	80.167

Table A.2-4: 2nd stage experiment

Sample	Concentration, (wt %)	Temp (^{0} c)	Reaction time (min)	Me content, %
1	1.00	40	20	92.46
2	1.00	40	30	88.71
3	1.00	40	40	93.1
4	1.00	40	50	77.53
5	1.00	40	60	75.36

Parameter controlled for 3rd stage experiment:

1. At concentration: 1 wt%
2. At reaction time: 40 min
3. Molar ratio: 6:1
4. Mixing degree: 1000 rpm

Table A.2-5: 3rd stage experiment

Type of emission	**Biodiesel percentage, %**	**Diesel percentage, %**
CO	185	376
CO_2	9	9.5
X_{air}	69	66

A.2.2 Rbd Palm Oil

Table A.2-6: 1st stage experiment

Sample	Temp (^{0} c)	Time (min)	Catalyst conc, (wt %)	Product yield, %
1	40	40	0.25	83.954
2	40	40	0.50	85.977
3	40	40	0.75	87.393
4	40	40	1.00	89.012
5	40	40	1.50	84.966

Table A.2-7: 1st stage experiment

Sample	Temp (^{0} c)	Time (min)	Catalyst conc, (wt %)	Me content, %
1	40	40	0.25	65.99
2	40	40	0.50	74.97
3	40	40	0.75	79.01
4	40	40	1.00	89.28
5	40	40	1.50	83.68

Table A.2-8: 2^{nd} stage experiment

Sample	Concentration, (wt %)	Temp (^{0} c)	Reaction time (min)	Product yield, %
1	1.00	40	20	86.989
2	1.00	40	30	91.034
3	1.00	40	40	89.011
4	1.00	40	50	86.584
5	1.00	40	60	76.874

Table A.2-9: 2^{nd} stage experiment

Sample	Concentration, (wt %)	Temp (^{0} c)	Reaction time (min)	Me content, %
1	1.00	40	20	90.09
2	1.00	40	30	94.02
3	1.00	40	40	93.95
4	1.00	40	50	92.38
5	1.00	40	60	91.10

Parameter controlled for 3rd stage experiment:

1. At concentration: 1 wt%
2. At reaction time: 30 min
3. Molar ratio: 6:1
4. Mixing degree: 1000 rpm

Table A.2-10: 3rd stage experiment

Type of emission	Biodiesel percentage, %	Diesel percentage, %
CO	186	376
CO_2	9.3	9.5
X_{air}	70	66

A.3 Example of Calculation on Product Yield

Data for 1st experiment, sample 2 of WCO

Sample 2 at concentration 0.5 wt%

Mass of sample = 342.25 g

Mass of raw material = 450 g

Thus,

$$\%\text{biodiesel yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw material}}$$

$$= 76.06\%$$

*Note: The same method of calculations was implemented for every result in experiment.

A.4 Example of Calculation on Methyl Esters

In order to find amount of methyl esters (ME), the results got from gas chromatography analysis was used and shown as below

$$\%\text{conc of ME} = \frac{[\Sigma A] - AE1}{AE1} \text{ X } \frac{CE1 \text{ X } VEi}{M} \text{ X } 100\%$$

Where

ΣA: Total peak area for methyl ester in C14 to C24

A_{E1}: Peak area corresponding to methyl ester

C_{E1}: Concentration mg/ml of methyl ester stock solution

V_{E1}: Volume in ml of methyl ester solution being used

M: Mass of sample

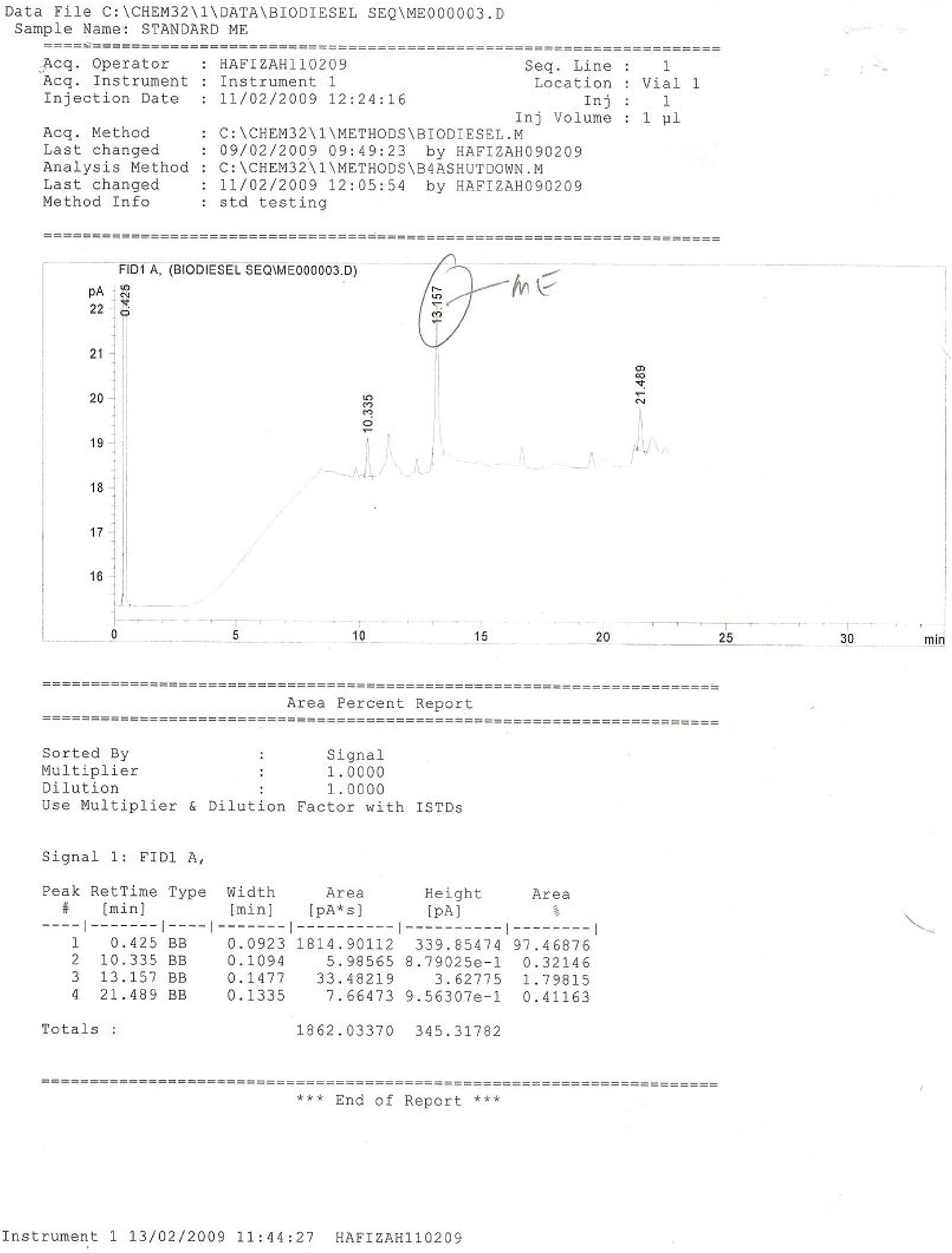
Let use sample 2 at concentration of 0.5 wt% for WCO

$$\%\text{conc of ME} = \frac{(1661150 - 1611200) - 20646.6}{20646.6} \text{ X } \frac{10 \text{ X } 5}{106.1} \text{ X } 100\%$$

$$= 66.88\%$$

*Note: The same method of calculations was implemented for every result in experiment.

A.5 Example of Result Analysis on Methyl Esters from Gas Chromatography



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    Injection Date   : 11/02/2009 12:24:16                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method      : C:\CHEM32\1\METHODS\BIODIESEL.M
    Last changed     : 09/02/2009 09:49:23  by HAFIZAH090209
    Analysis Method  : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed     : 11/02/2009 12:05:54  by HAFIZAH090209
    Method Info      : std testing

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

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


    Signal 1: FID1 A,

    Peak RetTime Type  Width      Area       Height      Area
      #   [min]        [min]    [pA*s]       [pA]         %
    ----|-------|----|-------|----------|----------|--------|
       1   0.425 BB    0.0923 1814.90112  339.85474 97.46876
       2  10.335 BB    0.1094    5.98565 8.79025e-1  0.32146
       3  13.157 BB    0.1477   33.48219    3.62775  1.79815
       4  21.489 BB    0.1335    7.66473 9.56307e-1  0.41163

    Totals :                  1862.03370  345.31782

    =====================================================================
                            *** End of Report ***



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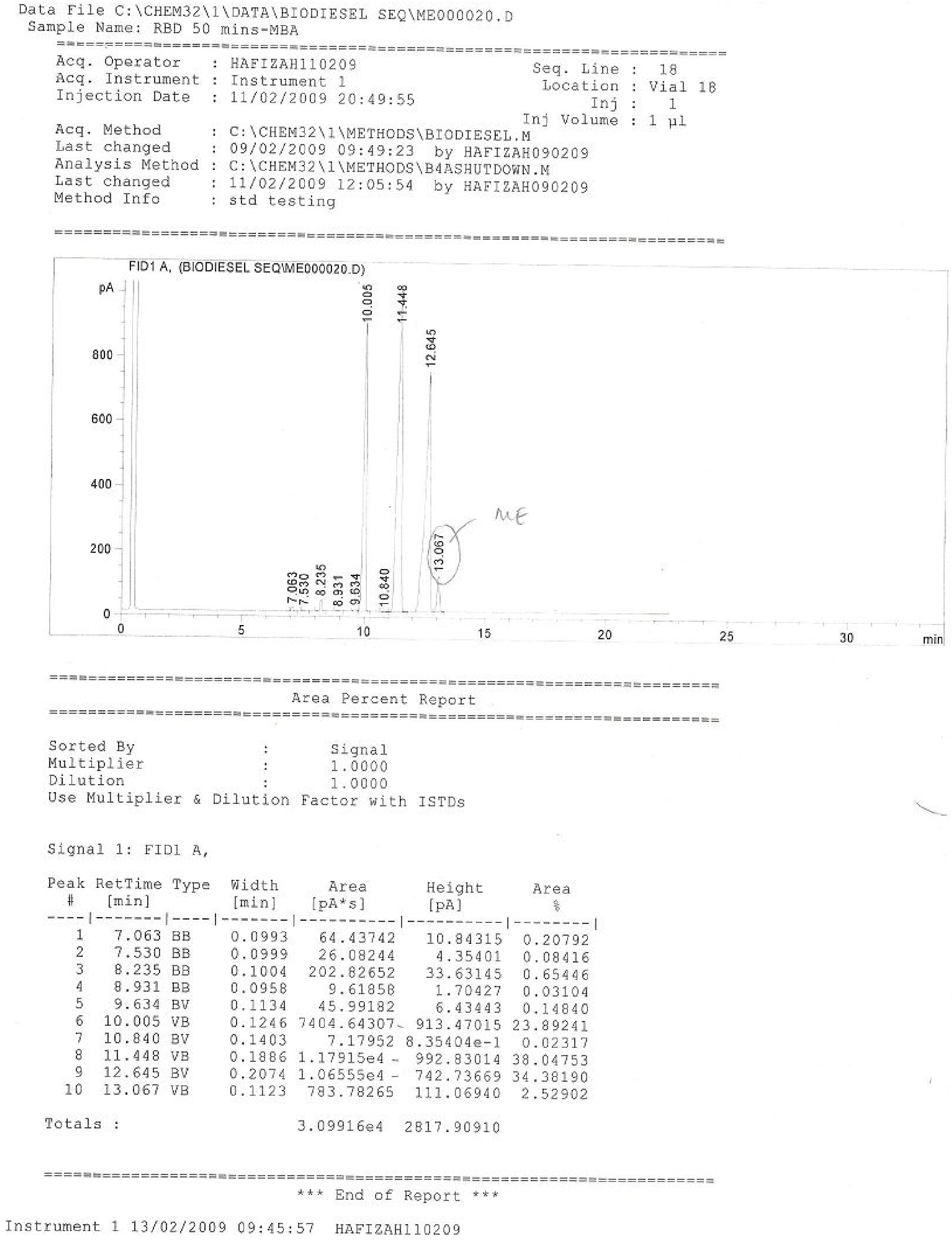

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    Acq. Instrument : Instrument 1                     Location : Vial 18
    Injection Date  : 11/02/2009 20:49:55                   Inj :   1
                                                     Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\BIODIESEL.M
    Last changed    : 09/02/2009 09:49:23  by HAFIZAH090209
    Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed    : 11/02/2009 12:05:54  by HAFIZAH090209
    Method Info     : std testing

    =================================================================
```

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

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


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area       Height      Area
      #   [min]        [min]   [pA*s]       [pA]         %
    ----|-------|----|-------|----------|----------|--------|
       1   7.063 BB    0.0993   64.43742   10.84315  0.20792
       2   7.530 BB    0.0999   26.08244    4.35401  0.08416
       3   8.235 BB    0.1004  202.82652   33.63145  0.65446
       4   8.931 BB    0.0958    9.61858    1.70427  0.03104
       5   9.634 BV    0.1134   45.99182    6.43443  0.14840
       6  10.005 VB    0.1246 7404.64307  913.47015 23.89241
       7  10.840 BV    0.1403    7.17952 8.35404e-1  0.02317
       8  11.448 VB    0.1886 1.17915e4   992.83014 38.04753
       9  12.645 BV    0.2074 1.06555e4   742.73669 34.38190
      10  13.067 VB    0.1123  783.78265  111.06940  2.52902

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