

UP-SCALE STUDY ON ULTRASONICALLY ASSISTED OF BIODIESEL
PRODUCTION FROM WASTE COOKING OIL (WCO)

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ABSTRACT

Up-scale for the production of biodiesel from waste cooking oil (WCO) and Refined-Bleached-Deodorized (RBD) under ultrasonic condition was studied. The effects of sodium hydroxide as a catalyst and time on the biodiesel conversion were investigated. Experiments have been performed to determine the optimum condition for this alkali-catalyzed transesterification process where the temperature is fixing at 40°C and the stirring rpm are 1000 rpm. The results showed that transesterification process under ultrasonic condition was proved to be time and energy saving. Gas Chromatography (GC) is used to study the formation of methyl ester of waste cooking oil and combustion test to study the combustion characteristic of biodiesel. The optimum experimental condition for catalyst concentration is 1 wt% sodium hydroxide (NaOH) and the reaction time is 40 minutes for WCO while 0.75 wt % sodium hydroxide (NaOH) and the reaction time is 30 minutes for RBD. The level of carbon dioxide (CO₂) and carbon monoxide (CO) in biodiesel from WCO are low compare to the RBD and diesel fuel.

ABSTRAK

Penghasilan biodiesel daripada sisa minyak masak dan minyak masak mentah dengan bantuan ultrasonik di kaji. Kesan tindakbalas kepekatan pemangkin (natrium hidroksida) dan masa tindakbalas di kaji. Kajian telah dijalankan untuk menentukan keadaan terbaik untuk proses transesterification ini dimana suhu ditetapkan pada 40°C dan pemutar pada 1000 rpm . Kajian menunjukkan bahawa proses transesterification dengan bantuan ultrasonik menjimatkan masa dan tenaga. Gas chromatography (GC) digunakan untuk mengkaji pembentukan metil ester dan ujian pembakaran untuk mengkaji ciri pembakaran biodiesel. Keadaan yang terbaik untuk mencapai hasil produk biodiesel yang terbaik adalah menggunakan 1.0 peratus berat mangkin (natrium hidroksida) pada suhu tindakbalas 40°C dan masa tindak balas selama 40 minit untuk penghasilan biodiesel daripada sisa minyak masak manakala 0.75 peratus berat mangkin (natrium hidrosida) pada suhu tindakbalas 40°C dan masa tindakbalas selama 30 minit untuk penghasilan biodiesel daripada minyak masak mentah. Kandungan carbon dioksida (CO₂) dan carbon monoksida (CO) di dalam biodiesel daripada sisa minyak masak adalah lebih rendah dibandingkan dengan biodiesel daripada minyak masak mentah dan diesel.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Petroleum based fuel are experiencing instability prices due to uncertain demand in the industries all around the world. Prices shot up from \$12/barrel in 1999 to close to \$80/barrel in August 2006 and then continued to break all records by approaching \$100/barrel in November 2007 (Miltos *et al.*, 2008). Because of this, there is increasing interest in finding alternative fuels.

According to M.K. Hubbert, who proposed the “peak oil theory” in the 1950s, production of crude oil curve is “bell shaped” based on the discovery and production of oil. This is based on the observation that oil discoveries grow exponentially at first peak followed by proceeded to decline. This is because at first oil was very easy to find, thus discoveries rise rapidly. However, as more of these easy to find reservoirs are discovered, further reservoirs become harder to find and the rate of discovery slows.

The production also follow bell shaped curve, which is after first oil discovered, production increased steadily because oil is easy and cheap to reach. However, as more of the oil in a reservoir is extracted, it becomes harder, more time consuming and expensive to extract. Thus, production increases at first then

reaches a peak where the point at which the maximum amount of oil is being produced and then it will declines (UgoBardi, 2008).

The followers of King Hubert may or may not be correct in their quantitative prediction of when the exactly peak will occur. Regardless of whether peak oil theorist are correct, we know that oil will not last forever, thus it seems prudent to start preparing now by putting more attention on alternative energy sources. One of those alternative is “biodiesel” a clean burning, lower emission fuel which is derived from mono-alkyl esters, a derivative of certain vegetable oils or animal fats. The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emission, its biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect (Barnwal and Sharma, 2005).

Biodiesel was introduced for the first time in Augsburg, Germany on August 10, 1893 by Rudolf Diesel. He demonstrated his compression ignition engine by using peanut oil the first biodiesel as a prototype engine on his prime model, a single 10 ft (3 m) iron cylinder with a flywheel as a base. On 1900 Rudolf Diesel again demonstrated his engine at the World Fair in Paris and received a “Grand Prix” and from that time vegetable oil used as a fuel until 1920’s (Stavarache *et al.*, 2005) During 1920’s modification was made to the engine to enabling it to use with petroleum diesel. After the modification was made petroleum diesel accepted quickly by worldwide because of better price, availability and government subsidies.

Raw material from vegetable oils has been extensively studied in recent literature review; however the costs and limited availability of vegetable oil feedstock are always critical issues for the biodiesel production. The high cost of vegetable oils sometimes can be up to 75% of the total manufacturing cost, has led the production costs of biodiesel becoming 1.5 times higher than diesel.

While, the price of waste cooking oils (WCO) is 2-3 times cheaper than virgin vegetable oils, which mean the total manufacturing costs of biodiesel can be significantly reduced (Zhang *et al.*, 2003). In addition, a similarity in the quality of biodiesel derived from WCO and from vegetable oils could be achieved at an optimum operating condition (Cetinkaya and Karaosmanoglu, 2004) .

The transesterification process is affected by alcohol type, molar ratio of alcohol to oil, type and amount of catalyst, temperature and purity of the reactants (Ma *et al.*, 1999). The transesterification of triglycerides with methanol is a heterogeneous reaction and blending together the reagents was a crucial. Because of that, one of the most important parameters affecting the transesterification reaction is the mixing efficiency (Meher *et al.*, 2004). According to Maeda *et al.* (2004) continuous transesterification of vegetable oils under ultrasonic irradiation proved that ultrasounds could successfully replace the classical mixing-heating conditions where the reaction time are much shorter, thus substantially reducing the production costs.

1.2 Problem Statement

The problem was to determine the extent to which the catalyst of sodium hydroxide (NaOH) and the effect of ultrasonic on various parameters where Refined-Bleached-Deodorized (RBD) and waste cooking oil (WCO) are used as a raw material in production of biodiesel.

1.3 Objective of The Project

Aim of this project is to study the effect of catalyst concentration and reaction time; between RBD palm oil and WCO in biodiesel production with the

aid of homogeneous catalyst sodium hydroxide (NaOH) using ultrasonic transesterification process.

1.4 Scope of Research Work

To achieve the objective of this research there are two scopes that have been identified:

1. To study the effect of catalyst concentration and time on yield and purity of biodiesel between RBD and WCO by using ultrasonic on transesterification process.
2. To study the combustion characteristic of biodiesel from ultrasonic transesterification process between RBD and WCO and analyze the both product by gas chromatographic.

In the research, temperature is set at 40°C while the catalyst concentration range used between 0.25 wt % to 1.5 wt % with time is between 20 to 60 minutes.

1.5 Rationale and Significance

The rationale of this proposed research project is to provide empirical evidence to prove that WCO and RBD are feasible to up scale, where ultrasonic transesterification process was carried to enhance the production of biodiesel in Malaysia.

The result of this research could signify the dawn of using WCO and RBD on an industrial scale in order to counter the current global shortage of fuel, due to high demand. This is especially to provide a better alternative feedstock. This in

turn would make it a rational choice for consumers especially in light of the recent global hikes in fossil fuel prices and the reduction in fuel subsidies by the Malaysian government.

In addition, with ultrasonic transesterification, the biodiesel production industry in Malaysia would be able to cater to the needs of Malaysians at a faster rate, thereby eliminating the need for any dependence on foreign alternative fuel that may arise in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Increasing concerns about the potential of global climate change, declining air and water quality, and serious human health concerns are inspiring the development of biodiesel, as a renewable, cleaner burning diesel alternative. The alternatives to diesel fuel must be technically feasible, economically competitive, environmental acceptable and readily available (Srivastava and Prasad, 2000). Many of these requisites are satisfied by vegetable oils or in general by triglyceride. Indeed, vegetable oils are widely available from a variety of sources and they are renewable (Encinar *et al.*, 2007). Vegetable oil based biodiesel fuel, as methyl or ethyl ester, have the following advantages over diesel fuel: as a neat fuel or in blends with diesel fuel they produce less smoke and particulates, have higher cetane numbers, produce lower carbon monoxide and hydrocarbon emissions, are biodegradable and non-toxic, and provide engine lubricity to low sulfur diesel fuels (Boehman and Foreword, 2005).

Biodiesel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and must be meeting with the requirements of American Society of Testing and Materials (ASTM). The purpose of this standard is to have biodiesel meet the performance requirements of engines without specifying the actual composition of the fuel. System "B" factor is use to state the

amount of biodiesel in any fuel mix. For example, fuel containing 20% biodiesel is labeled B20 while pure biodiesel is referred to as B100.

2.1.1 Properties and Specification of Biodiesel

Since biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. Austria was the first country in the world to define and approve the standards for rapeseed oil methyl esters as diesel fuel. As standardization is a prerequisite for successful market introduction and penetration of biodiesel, standards or guidelines for the quality of biodiesel have also been defined in other countries like Germany, Italy, France, the Czech Republic and in the United states. The parameters, which define the quality of biodiesel, can be divided into two groups. One group contains general parameters, which are also used for mineral oil based fuel, and the other group especially describes the chemical composition and purity of fatty acid alkyl esters (Mittelbach, 1996). Table 2.1 contains the general and Table 2.2 the vegetable oil specification parameters and the corresponding value of fatty acid methyl esters according to standards of above countries.

Table 2.1: General parameters of the quality of biodiesel (Meher *et.al.*, 2004)

Parameters	Austria (ON)	Czech republic (CSN)	France (journal official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Density at 15 °C g/cm ³	0.85–0.89	0.87-0.89	0.87 – 0.89	0.875 – 0.89	0.86 – 0.90	-
Viscosity at 40 mm ² /s	3.5–5.0	3.5-5.0	3.5 – 5.0	3.5 – 5.0	3.5 – 5.0	1.9 – 6.0
Flash point (°C)	100	110	110	110	100	130
CFPP (°C)	0/-5	- 5	0 -1 /- 20	0 – 10/ -20	-	-
Pour point (°C)	-	-	-	-	0/- 5	-
Cetane number	≥49	≥48	≥49	≥49	-	≥47
Neutralization number (mgKOH/g)	≤0.8	≤0.5	≤0.5	≤0.5	≤0.5	≤0.8
Conradson carbon residue (%)	0.05	0.05	-	0.05	-	0.05

Table 2.2: Vegetable oil specific parameters for the quality of biodiesel (Meher *et.al.*, 2004)

Parameters	Austria (ON)	Czech republic (CSN)	France (journal official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Methanol/ ethanol (% mass)	≤ 0.2	-	≤ 0.3	≤ 0.3	≤ 0.2	-
Ester content (% mass)	-	-	-	-	≥ 98	-
Monoglyceride (% mass)	-	-	≤ 0.8	≤ 0.8	≤ 0.8	-
Diglyceride (% mass)	-	-	≤ 0.4	≤ 0.4	≥ 0.2	-
Triglyceride (% mass)	-	-	≤ 0.4	≤ 0.4	≥ 0.1	-
Free glycerol (% mass)	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≥ 0.05	≤ 0.02
Total glycerol (% mass)	≤ 0.24	≤ 0.24	≤ 0.25	≤ 0.25	-	≤ 0.24
Iodine number	≤ 120	-	≤ 115	≤ 115	-	-

Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters can go very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specifications proposed are nearly same as that of the diesel fuel. Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose.

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petrodiesel. Normally either pour point or CFPP are specified. Pour point is the lowest temperature at which the oil specimen can still be moved. French and Italian biodiesel specifications specify pour point where as others specify CFPP.

Cetane number is indicative of its ignition characteristics. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher the cetane number better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and HC. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency.

Neutralization number is specified to ensure proper ageing properties of the fuel and or a good manufacturing process. It reflects the presence of free fatty acids or acids used in manufacture of biodiesel and also the degradation of biodiesel due to thermal effects.

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Conradsons Carbon Residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities.

The presence of high level of alcohol in biodiesel cause accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content is required. Biodiesel fuel is mainly consists of fatty acid alkyl esters and its quantities are specified according to the specifications of various countries. The presence of mono- di- and triglycerides cause engine problems like fuel filter plugging affecting the fuel properties and are specified in most of the biodiesel standards.

2.2 Raw Materials

The raw materials for biodiesel production now mainly include biological sources such as vegetable seed oil, soybean oil and some recovered animal fats (Ana and Enoch, 2003). The types of feedstock use are varies from country to country and is dependent on an availability of the feedstock, price, its suitability with the local climate and the adherence of the final product towards national and international specifications. For example, in US commonly use rapeseed and soybean oil and in Malaysia use palm oil.

2.2.1 Vegetable Oil

The use of vegetable oils as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in

his compression ignition engine. The use of vegetable oils for engine fuels may seem insignificant today. But such oils may in course of time be as important as petroleum and the coal tar products of the present time (Shay, 2003).

Vegetable oil can be categorized into two types, which are virgin vegetable oil and waste cooking oil (WCO). Examples of virgin vegetable oil are rapeseed, soybean oils, mustard, flax, sunflower, canola, palm oil, hemp, jatropha, algae, etc. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979). Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds).

Vegetable oils occupy a prominent position in the development of alternative fuel although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). These include; coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices, carbon deposits, oil ring sticking, thickening or gelling of the lubricating oil as a result of contamination by vegetable oils, and lubricating problems.

Other disadvantages to the use of vegetable is the high viscosity (about 11–17 times higher than diesel fuel), lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics. These problems are associated with large triglyceride molecule and its higher molecular mass and avoided by modifying the engine less or more according to the conditions of use and the oil involved. The modified engines built by Elsbett in Germany and Malaysia and Diesel Morten und Geraetebau GmbH (DMS) in Germany and in USA show a good performance when fuelled with vegetable oils of different composition and grades (Srivastava, 2000).

2.2.2 Waste Cooking Oil

The use of cheap low quality feed stocks such as waste cooking oil (WCO) instead of refined vegetable oil will help in improving the economical feasibility of biodiesel. The amount of WCO generated in each country is huge and varies depending on the use of vegetable oil. An estimate of the potential amount of WCO from the collection in European Union (EU) is approximately 0.7–1.0 Mt per year. The United States and Canada produce, on average, 9 and 8 pounds of yellow grease, respectively, per person (Holbein *et al.*, 2004). Currently, the inexpensive and large quantity of WCO from households and restaurants are collected and used as either animal feed or disposed causing environmental pollution. Thus, WCO offers significant potential as an alternative low cost biodiesel feedstock which could partly decrease the dependency on petroleum-based fuel.

The production of biodiesel from WCO is challenging due to the presence of undesirable components such as free fatty acids (FFAs) and water. Usage of homogeneous alkali catalyst for transesterification of such feedstock suffers from serious limitation of formation of undesirable side reaction such as saponification which creates the serious problem of product separation and ultimately lowers the ester yield substantially (Freedman *et al.*, 1984). Homogeneous acid catalysts have the potential to replace alkali catalysts since they do not show measurable susceptibility to FFAs and can catalyze esterification and transesterification simultaneously. However, slow reaction rate, requirement of high temperature, high molar ratio of oil and alcohol, separation of the catalyst, serious environmental and corrosion related problems make their use non practical for biodiesel production (Lotero *et al.*, 2005). Currently a dual step process has been used for biodiesel preparation from high FFA containing WCO (Zafiropoulos *et al.*, 2007). The first step of the process is to reduce FFA content in the oil by esterification with methanol to methyl ester catalyzed by an acid (generally sulfuric acid) followed by transesterification process, in which triglyceride (TG)

portion of the oil reacts with methanol and base catalyst (usually sodium or potassium hydroxide) to form ester and glycerol. The current process increases the production cost of biodiesel as it involves a number of steps including washing of the esters to remove acid/alkali catalysts in addition to creating contaminated water disposal issues.

2.2.3 Animal Fats

Animal fats are one of the raw materials for biodiesel production (Ana and Enoch, 2003). Animal fats include tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil. Omega-3 fatty acids are a family of unsaturated fatty acids that have in common a carbon-carbon double bond in the third bond from the methyl end of the fatty acid.

The main sources of animal fats are primarily meat animal processing facilities. Another source of animal fats is the collection and processing of animal mortalities by rendering companies. For example in beef, tallow the saturated fatty acid component accounts for almost 50% of the total fatty acids. Preliminary laboratory tests at Oak Park suggest that a good quality biodiesel could be produced from tallow, but that much more work was needed to establish process requirements and methyl ester properties. The higher stearic and palmitic acid contents give beef tallow the unique properties of high melting point and high viscosity (Fangrui, 1999).

The disadvantages to the use of animal fats same with vegetable oil that are the high viscosity (about 11–17 times higher than diesel fuel), lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics. These problems are associated with large triglyceride molecule and its higher molecular mass (Meher and Sagar, 2004).