Research Paper Ref. No 2518

Comparative Study of Biodiesel Production from Pure Palm Oil and Waste Palm Oil

دراسة مقارنة لإنتاج الديزل الحيوي من زيت النخيل النقي ومخلفات زيت النخيل بعد الاستخدام

A.B.M. Sharif Hosain and A. Nasrulhaq Boyce

أ.ب.م. شريف حسين و أ. نصرالحق بويس

Bioenergy Laboratory, Programme of Biotechnology, Institute of Biological Sciences,

Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

E-mail: sharif@um.edu.my, sharifhort@yahoo.com

Abstract: Comparison of the optimum conditions for biodiesel production from pure palm cooking oil (PPCO) and waste palm cooking oil (WPCO) through transesterification process using alkaline catalysts was studied. Some important variables such as volumetric ratio and types of reactants, catalytic activities were selected to obtain a high quality biodiesel fuel that comply with the specification of standard methods (ASTM D 6751 and EN 14214). The highest yield of approximately 99% was acquired under optimum conditions of 1:6 volumetric oil-to-methanol molar ratio, 1% KOH catalyst, 40°C reaction temperature, and 320 rpm stirring speed. Results showed that the production of biodiesel from PPCO and WPCO was exhibited no considerable differences. The research demonstrated that biodiesel obtained under optimum conditions from PPCO and WPCO was of good quality and could be used as a diesel fuel. Waste cooking palm oil after frying could be used as recycled material for waste management to produce renewable energy.

Keywords: *biodiesel, transesterification, palm oil, waste cooking oil.*

المستخلص: أجريت دراسة مقارنة للظروف المثلى لإنتاج الديزل الحيوي (البيوديزل) من زيت النخيل النقي (PPCO) ومخلفات زيت النخيل بعد الاستخدام (WPCO) وكمية الديزل المنتج من كل منهما بواسطة عملية الاسترة التبادلية باستخدام القلويات الحفزية (هيدروكسيد الصوديوم، هيدروكسيد البوتاسيوم). بناء على ذلك تم اختيار بعض المتغيرات الهامة للحصول على وقود ديزل حيوي عالي الجودة يتوافق مع المواصفات القياسية للجمعية الأمريكية لفحص المواد (EN 14214 و ASTM D 6751). أظهرت النتائج أن استخدام 1مل من الزيت مع 6 مل من الايثانول (6:1) مع استخدام 1% من هيدروكسيد الصوديوم كمحفز للتفاعل تحت درجة حرارة 40°م و320 دورة في الثانية تعتبر ظروف مثالية للحصول على الديزل الحيوي، حيث تم الحصول على أعلى محصول (حوالي 99%) من الديزل الحيوي تحت هذه الظروف. كما أظهرت النتائج أنه لا يوجد إختلاف بين كمية الديزل الحيوي المنتج من زيت النخيل النقي ومخلفات زيت النخيل في ظل هذه الظروف المثالية. كما أثبتت النتائج أيضا أن الديزل الحيوي المتحصل عليه تحت الظروف المثالية ذو نوعية جيدة ويمكن استخدامة كوقود. بالإضافة لذلك، يمكن استخدام المخلفات الزيتية بعد الطبخ كمواد معاد استخدامها في عملية إدارة المخلفات لإنتاج طاقة متجددة.

كلمات مدخلية: *الديزل الحيوي، الأسترة التبادلية، زيت النخيل، مخلفات زيت النخيل.*

INTRODUCTION

With the advent of industrialization and population increase the demand for energy is greater than ever before. The current energy sources are petroleum, natural gas, coal, hydro, and nuclear. Petroleum-based or fossil fuels still dominate worldwide, but the depleting oil reserves, and their atmospheric pollution, have necessitated the need for an alternative source of energy (Kulkarni and Dalai, 2006). Additionally, fuels from alternative sources or alternative fuels are required to be environmentally friendly, technically satisfactory, economically competitive and readily available (Oliveira and Rosa, 2006; Srivastava and Prasad, 2000). Biodiesel is one possible alternative to fossil fuels which have several benefits over the petroleum diesel fuel (Stamenkovic´, *et al*. 2007). According to the US Standard Specification for Biodiesel (ASTM 6751), biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (Vicente, *et al*. 2007). It is biodegradable, produced from renewable sources and contributes a minimal amount of net green house gases or sulfur to the atmosphere (Bouaida, *et al*. 2007).

The current feedstocks for production of biodiesel are vegetable oil, animal fat, microalgal oil and greases. Vegetable oils are currently being used as a sustainable commercial feedstock. However, the relatively high cost of vegetable oil influences the production cost of biodiesel. In view of this, large amount of waste cooking oil is produced from restaurants, catering establishments and food industries every year, and the discarding of this waste cooking oil can be problematic because it can contaminate water resources (Kulkarni and Dalai, 2006). Thus, biodiesel production from this waste oil may alleviate this environmental pollution.

In Malaysia, one of the world's leading palm oil production country, total crude palm oil production in 2007 was 15.8 million tones which was the highest source for oil production in the country (DSM, 2008). Study on the use of biodiesel produced from solid palm oil as an alternative diesel fuel had been carried out at PORIM (Palm Oil Research Institute Malaysia), University of Technology, Malaysia, the University of Malaya, Proton (National Automobile Industry of Malaysia), and Castrol Malaysia Sdn. Bhd. (Kalam and Masjuki, 2002). However, literatures are not available on biodiesel production from waste palm edible oil in Malaysia.

Earlier, many researchers focused their experiment on virgin oil such as soybean oil, sunflower oil, cotton-seed oil, and rape oil as a source (Korus, *et al. 1992;* Wagner, *et al*. 1984). However, the high cost of using virgin oil becomes a barrier to commercialize biodiesel as alternative to diesel fuel. Therefore, the use of waste vegetable oil should greatly reduce the cost of biodiesel because of relatively low price of waste cooking oil.

To obtain biodiesel from feedstocks, transesterification of triglycerides with low molecular weight alcohols catalyzed by homogenous catalysts is the most researched (Aranda, *et al*. 2007). As a result of higher content of fatty acids and water in used cooking oil, application of base catalysts might cause problems due to the side saponification reaction which creates soap and consumes catalyst (Issariyakul, *et al*. 2008). Despite these disadvantages, transesterification process using base catalyst has some benefits, such as low production cost, faster reaction speed and mild reaction conditions (Aranda, *et al*. 2007). Recently, research has focused on heterogeneous catalysts for reduction of the processing costs associated with homogeneous catalysts and many alkaline catalysts such as sodium hydroxide, potassium hydroxide, calcium carbonate rock, and Endoscopic Sclerotherapy (EST-4) and (EST-10) catalysts, and $Na/NaOH/\gamma\text{-}Al_2O_3$ were studied (Trakarnpruk and Porntangjitlikit, 2008).

The present study aims at comparing the optimum conditions for fatty acid methyl ester (FAME) formation or biodiesel production from pure and waste palm cooking oil through the transesterification process using alkaline catalysts. The quality of biodiesel from both pure and waste edible palm oil was also analyzed and compared.

MATERIALS AND METHODS

Materials

Palm oil (PPCO) was purchased from a local grocery shop whilst waste palm cooking oil (WPCO) was obtained from restaurants next to the University of Malaya campus in August 2007. To remove impurities, the WPCOs were filtered under vacuum pressure (11 bar). Potassium hydroxide, sodium hydroxide, magnesium sulphate anhydrous, methanol and ethanol were purchased from SYSTERM / Classic Chemicals Sdn Bhd, Malaysia.

Transesterification Reaction

The transesterification reaction was performed at different volumetric ratios of oil to alcohol (methanol, ethanol), varying from 3:1 to 6:1 (4:1, 3:1, 1:3, 1:4 and 1:6) at 40°C and 350 rpm. The reaction time was kept constant at 2 - 3 hours for all experiments. Two types of catalysts were used, NaOH and KOH at a range of 0.5 – 2.0% wt. of oil. After transesterification, the biodiesel was separated from glycerol using a separating funnel and finally washed with 5% water followed by magnesium sulphate anhydrous to remove the water. Several basic variables, namely, catalyst type and concentration, alcohol to oil ratios, and reaction temperature were investigated as they have been reported to play a significant role in biodiesel production (Ma and Hanna, 1999).

Biodiesel Analysis

The produced biodiesel was analyzed by specific methods to verify whether the products fulfill the specification of standard methods (ASTM D 6751 and EN 14214). An atomic emission (AE) spectroscopic multi-element oil analyzer (MOA) was used to determine the group I metals (Na, K), group II metals (Ca, Mg) and phosphorus content. Viscosity was measured in cSt at 40°C using houillon viscometer (France) with ISL software version 2.1. Total acid value was measured by titration method with KOH and phenolphthalein as an indicator.

RESULTS AND DISCUSSION

Properties of PPCO and WPCO

Two important properties of PPCO and WPCO were summarized in Table (1). The acid value unveiled the low amount of free fatty acids (FFA) in both types of oils. Both oils can be utilized as fuel in diesel engines, but the main obstacle is their high viscosity which creates problems in atomization of the fuel spray and operation of the fuel injectors.

Table 1. Acid value and viscosity of Pure Cooking Palm Oil (PPCO) and Waste Cooking palm Oil (WPCO).

Oil type	Acid value (mgKOH/g oil)	Viscosity (cSt at 40°C)
PPCO	0.22	4.42
WPCO	0.43	4.10

Effect of Molar Ratio

The effect of molar ratio of methanol and ethanol to oil was studied. Methanol, ethanol, propanol, butanol and amyl alcohol can be used in the transesterification reaction. Amongst these alcohols, methanol is applied more frequently as its cost is low and it is physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols (Demirbas, 2005). According to Demirbas (2007) in contrast, ethanol is also a preferred alcohol for use in the transesterification process compared to methanol, since it is derived from agricultural products and is renewable and biologically less offensive in the environment. However, results demonstrate that highest biodiesel yield was nearly 100% at 1:6 oil/methanol or ethanol with an exception yield (96%) in case of 1:6 PPCO/ ethanol (Figures 1, 2). In comparison, biodiesel yield from WPCO and PPCO showed no significant difference. From Figure (2), it can be observed that biodiesel yield continuously increased with the increase of ethanol ratio. Conversely, in Figure (1), methanol did not show the same trend. In this case, yield at 1:4 oil/methanol was lower than 1:3 oil/methanol most probably due to emulsification during washing process. Despite this exception, the overall results proved that the increase of both type of alcohol ratio improves the yield of biodiesel. As using methanol (oil:methanol = 1:6) achieved the highest yield percentage, further study such as effect of catalyst was performed applying the same alcohol.

Effect of Catalyst

A previous study (Knothe, 2000) indicated that production of biodiesel from waste frying vegetable oil, using KOH as catalyst with reaction carried out at ambient pressure and temperature, achieved conversion rates of 80-99%. From Figure (3), it could be seen that highest biodiesel yield

(90%) was achieved using KOH at 40°C. Because of the higher yield, KOH was used as a catalyst to study the effects of catalyst concentration on biodiesel yield. The biodiesel yield increased from about 78% to 94% when the KOH concentration increased from 0.5% wt to 2.0% wt. (Figure 4). Paradoxically, during separating and washing of biodiesel the emulsification phenomena had been observed. This usually happens due to soap formation by these base catalysts and free fatty acids in the oil in presence of water (Arzamendia, *et al*. 2007). This emulsification can be mitigated by reducing shaking intensity during washing and separation of biodiesel from glycerol.

Analysis of Produced Biodiesel

The biodiesel samples produced from the above experiments under optimum conditions of 1:6 volumetric oil-to-methanol ratio, 1% KOH catalyst and 40ºC reaction temperature were analyzed with regard to some important requirements for biodiesel use as fuel in diesel engines. These results are compiled in Table (2). Most of these properties fulfilled the limits in biodiesel standard in ASTM D 6751 and EN 14214. On the contrary, biodiesel obtained from WPCO had a slightly higher acid value (0.43 mgKOH/g) compared to biodiesel produced from PPCO. Both produced biodiesels showed nearly similar viscosity. Viscosity is an essential property of diesel fuel because of its influences on the wear rate of engine components (Knothe, 2006). Additionally, it can be observed from Table (2) that PPCO biodiesel had considerably higher phosphorus concentration than WPCO although it fulfills the requirement of the standards.

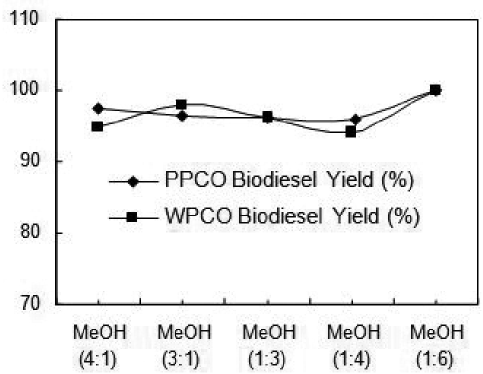

Fig. 1. Effect of volumetic ratio of oil to methanol (MeOH) on biodiesel yield (Reaction conditions: temperature = 40°C, catalyst KOH = 1 wt. %, RPM = 350, reaction time = 180 minutes).

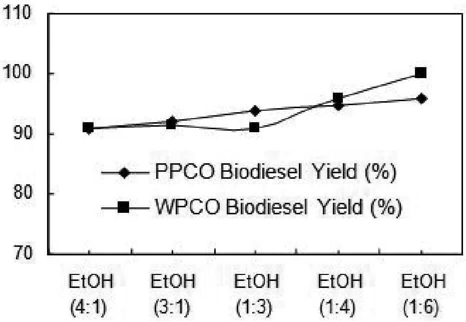

Fig. 2. Effect of volumetric ratio of oil to ethanol (EtOH) on biodiesel yield (Reaction conditions: temperature = 40°C, catalyst KOH = 1 wt. %, RPM = 350, reaction time = 180 minutes).

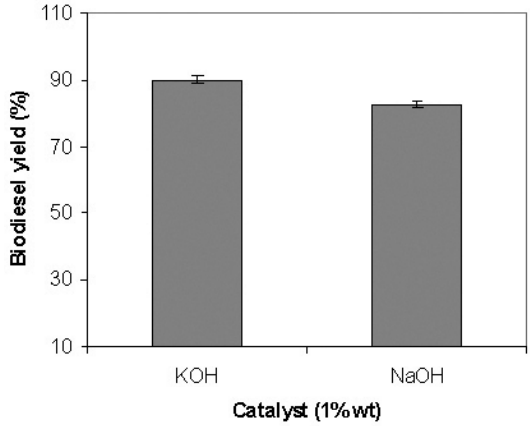

Fig. 3. Effect of different catalysts on ester yield (Reaction conditions: temperature = 40°C, oil: methanol = 1:6, catalyst = KOH, RPM = 350, reaction time = 120 minutes). Vertical bars indicate SE (n = 3).

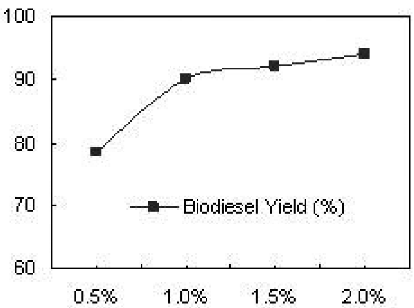

Fig. 4. Effect of catalyst concentration (Reaction conditions: temperature = 40°C, oil: methanol = 1:6, catalyst = KOH, RPM = 350, reaction time = 120 minutes). Different letters (a, b) showed difference at 5% level of significant by Duncan Multiple Range Test (DMRT).

Table 2. Characteristics of biodiesel produced under optimum condition in contrast with standard value (Wagner *et al*.1984).

Property	Unit	Standard Method	Value according to standard method	Biodiesel (PPCO)	Biodiese (WPCO)
Viscosity	cSt at 40°C	ASTM D 6751	1.9 - 6.0	4.42	4.10
Acid number	mgKOH/g oil	ASTM D 6751	0.50 max	0.22	0.43
Group I metals (Na + K)	mg/kg	EN 14214	5.0 max	2.70	2.70
Group II metals (Ca+ Mg)	mg/kg	EN 14214	5.0 max	3.00	2.70
Phosphorus content	mg/kg	EN 14214	10.0 max	4.70	2.10

CONCLUSION

This study has shown that waste cooking palm oil (WPCO) may be utilized as a source to produce biodiesel as fuel in diesel engines. The optimum conditions for the production of biodiesel from pure and waste palm cooking oil has been obtained. The produced biodiesel is of good quality within the range of standard method specifications and the production yield is suitable, up to approximately 99% under optimum conditions. Additionally, this research reveals that the production of biodiesel from waste palm cooking oil (WPCO) and pure palm cooking oil (PPCO) showed little significant difference. Thus after frying, waste palm oil can be used as recycled material and renewable energy source produced from biomass which contributes to better waste management.

ACKNOWLEDGEMENT

The authors acknowledge the Ministry of Science, Technology and Innovation (MOSTI), Malaysia for financial assistance for the research project.

REFERENCES

Aranda, DAG, Santos, RTP, Tapanes, NCO, Ramos, ALD, and **Antunes, OAC** (2007) Acid-Catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acid. *Catalysis Letters*. **122**: 20-25.

Arzamendia, G, Campoa, I, Arguiñarenaa, E, Sánchezb, M, Montesb M, and **Gandía, LM.** (2007) Synthesis of biodiesel with heterogeneous. NaOH/alumina catalysts: comparison with homogeneous NaOH. *Chem. Eng. J*. **134**: 123–130.

Bouaida, A, Martineza, M, and **Aracil, J** (2007) Long storage stability of biodiesel from vegetable and used frying oils. *Fuel* 86: 2596-2602.

Demirbas, A (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification method. *Progress Energy Combus Sci*. **31:** 466–487.

Demirbas, A (2007) Biodiesel from sunflower oil in supercritical methanol with calcium oxide. *Energy. Conv. Manag*. **48**: 937-941.

DSM (2008). Department of Statistics Malaysia. www.statistics.gov.my

Issariyakul, T, Kulkarni, MG, Meher, LC, Dalai, AK, and **Bakhshi, NN** (2008) Biodiesel production from mixtures of canola oil and used cooking oil. *Chem. Eng. J*. **140**: 77-85.

Kalam, MA, and **Masjuki, HH** (2002) Biodiesel from palm oil – an analysis of its properties and potential. *Biomass and Bioenergy*. **23**: 471-479.

Knothe, G, Dunn, RO, and **Bagby, MO** (2000) Biodiesel: The use of vegetable oils and their derivatives as alternative diesel fuel. *J. Am. Oil Chem. Soc*. **77**: 5.

Knothe, G (2006) Analyzing biodiesel: standards and other methods. *J. Am. Oil Chemi. Soc*. **83**: *823- 833*.

Korus, R, Hoffman, D, Bam, N, Peterson C, and **Drown, D** (1992) Transesterification process to manufacture ethyl ester of rape oil. *In: Proceedings of 1st Biomass Conference of the Americas*. pp. 815–826.

Kulkarni, MG and **Dalai, AK** (2006) Waste cooking oil – An economical source for biodiesel: a review. *Ind. Eng. Chem. Res.* **45**: 2901-2913.

Ma, F and **Hanna, MA** (1998) Biodiesel production: a review. *Bioresour. Technol.* **70**: 1–15.

Oliveira, AC, and **Rosa, MF** (2006) Enzymatic transesterification of sunflower oil in an aqueous-oil biphasic system. *J. Am. Oil Chem. Soc.* **83**: 21–25.

Srivastava, A and **Prasad, R.** (2000) Triglycerides-based diesel fuels. *Renew. Sustain. Energy Rev.* **4:** 111–133.

Stamenkovic´, OS, Todorovic´, ZB, Lazic´, ML, Veljkovic´, VB, and **Skala, DU** (2008). Kinetics of sunflower oil methanolysis at low temperatures. *Bioresource Technology (in press)*.

Trakarnpruk W and **Porntangjitlikit, S** (2008) Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. *Renewable Energy* **33**:1558-1563.

Vicente, G, Martinez, M and **Aracil, J** (2007) Optimization of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. *Biores. Technol.* **98**: 1724–1733.

Wagner, L, Clark, S and **Schrock, M** (1984) Effects of soybean oil esters on the performance, lubricating oil, and wear of diesel engines. SAE Paper No. 841385.

Ref. No. (2518)
Rec.27/03/2009
In-revised form: 19/5/2009