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BIODIESEL PRODUCTION FROM WASTE COOKING PALM OIL AND ENVIRONMENTAL IMPACT ANALYSIS

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Abstract

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The inevitability of oil depletion, global warming and the greenhouse effects has put the world on an alarming condition. It needs more than ever before to search for alternative forms of energy and this includes biodiesel, which is an environmentally friendly form of alternative energy compared to petrodiesel. The present study was carried out to investigate biodiesel production via alkaline transesterification using waste palm cooking oil and its chemical characteristics compared to conventional biodiesel. The highest yield of biodiesel was produced using a temperature of 55°C with methanol to oil molar ratio of 6:1 and at a catalyst (KOH) concentration of 1.0%. The quality of the biodiesel produced was evaluated by the determinations of important properties, such as kinematics viscosity, total acid number (TAN), total base number (TBN) and ash content. The biodiesel produced was found to contain a low base number and undetected acid level but had a higher ash content and Ca, Mg and Na levels. Its kinematic viscosity and phosphorus level were found within the limits prescribed by the latest American Standards for Testing Material (ASTM). In the engine tests, the emissions of unburned hydrocarbons, oxides of nitrogen and carbon monoxide using biodiesel fuel were lower than that using conventional diesel fuel although the biodiesel fuel exhibited a higher specific fuel consumption compared to the diesel fuel. It can be concluded that biodiesel made from waste palm oil can be considered as a great potential source of commercial biodiesel. Emission tests showed that the level of unburned hydrocarbons, oxides of nitrogen and carbon monoxide were lower than conventional diesel fuel.

Key words: biodiesel; palm oil; alkaline transesterification, optimization, emission

Introduction

Fuel from fossil sources such as petroleum, coal and natural gases have been the main sources of energy throughout the world for a long time. However, these sources are limited and will be depleted in the not too distant future. The possibility of this happening, together with global warming and the greenhouse effect has put the world on an alarming footing where the need to search for an alternative energy has never been greater. These alternatives include energy from water, wind, solar, biomass, hydrogen, geothermal, and nuclear energy, which are natural and is readily available and sustainable (Demirbas, 2005). By utilizing these energy sources wisely, we can overcome or reduce the problem of air pollution, global warming, the greenhouse effect, which can be detrimental towards our health.

Fortunately, for environmental reasons, the high petrol and diesel fuel price today has made biodiesel a viable alternative fuel. Biodiesel has been chosen as one of the main alternative fuel because of its good, if not better, characteristics and advantages such as being a renewable source, highly biodegradable, high flash point, excellent lubricity, low in sulphur and nontoxic, with relatively low amount of polycyclic aromatic hydrocarbons, which are carcinogenic (Wyatt et al., 2010). Therefore, this environmental friendly biodiesel can be utilized in engines without any modification (Merve et al., 2005). The main feature of this fuel is the low production of soot after combustion due to the absence of sulphur (Salis et al., 2005). According to Gerpen (2005), a life cycle analysis of biodiesel showed that overall carbon dioxide emissions were reduced by 78% compared with petroleum-based diesel fuel.

Amongst all the renewable energy, biodiesel remains as one of the most promising energy sources. As has been well documented biodiesel is the mono-alkyl esters of fatty acids derived from animal fats and vegetable oils. It is produced

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when vegetable oil or animal fat is reacted chemically with an alcohol to produce fatty acid alkyl esters (transesterification) (Somporn and Shabbir, 2009; Hossain and Boyce, 2009a). A catalyst is normally added in but is not mandatory. The chemical equation below shows that glycerol and fatty acid methyl esters are produced as a by-product.

The reason that biodiesel is not utilized widely around the world is due to the high cost of raw materials. To overcome this, one can use lower quality oils, for example, waste cooking oils or animal fats that are produced in excess in food processing industries. Use of waste cooking oil can also help to alleviate the problem of waste oil disposal (Zhang et al., 2003).

A lot of research has been carried out on the production of biodiesel from fresh vegetable and animal oil sources but the use of waste cooking oil, such as palm oil, where Malaysia is a leading producer of palm oil, has not been well documented, although often mentioned (Abdullah et al., 2009; Cherng and Rong-Ji, 2009; Hossain and Boyce, 2009b). The main objectives of the present research are to optimize the conditions for biodiesel production from waste cooking palm oil, to identify the fatty acid methyl esters produced and to characterize it based on its viscosity, total acid number, elemental composition, emission rate and engine performance.

Materials and Methods

Preparation of potassium methoxide

KOH was utilized as the catalyst in the alkaline transesterification process. The amount of methanol needed to produce potassium methoxide depended on the alcohol to oil mixing ratio. Potassium hydroxide was added into the methanol in a conical flask covered with aluminium foil, as methanol is volatile and evaporates easily. The solution was then stirred using a shaker to make sure that all the catalyst was dissolved. The chemical reaction below shows the production potassium methoxide from catalysts and methanol.

$$KOH + CH_3OH \longleftrightarrow KOCH_3 + H_2O$$

Biodiesel production from waste palm cooking oil

Waste palm cooking oil was utilized in this study to produce biodiesel. Waste palm cooking oil was collected from restaurants in the University of Malaya and filtration was carried out using a filter funnel with filter paper. This oil was used for the subsequent alkaline transesterification experiments using different concentrations (0.5, 1.0, 1.5 and 2.0 %) of catalyst (KOH) and different molar ratios of oil:methanol (4:1, 3:1, 1:4 and 1:6). These parameters were studied to analyze their effects towards biodiesel yield in terms of quantity as well as quality (Hossain and Boyce, 2009a). When the transesterification process was completed, the solution will be separated into two distinct layers of crude biodiesel and glycerol due to the principle of gravity difference between both layers (Lin and Li, 2008). Separation is done by pouring the solution into a separating funnel and letting it settle down. Two distinct layers are formed, the upper being biodiesel and lower glycerine with excess water. The washing step is completed when the distilled water looks clear after washing the methyl esters for several times. The molar ratio of distilled water to methyl esters used was about 1:1. Small amounts of water will be eliminated when biodiesel is dried in the oven, whereas, larger amounts of water are removed by using sodium sulphate anhydrous. The use of anhydrous sodium sulphate results in the formation of hard crystals, which can be filtered off by pouring the solution through a filter paper. Purified biodiesel is then stored for analysis and engine tests.

Biodiesel analysis

The purified and dried biodiesel is then used for subsequent analysis such as biodiesel characterization (total acid number, total base number, viscosity and multi- element analysis) and engine test (CO, HC and NOx emissions and fuel consumption).

Gas Chromatography-Mass Spectrometer analysis

The prepared biodiesel was sent for GC-MS analysis. The main purpose of this analysis was to identify what type of methyl esters is present in the biodiesel produced and the GC-MS output is essential in determining the conversion rate of triglycerides of waste cooking palm oil to methyl esters (Wisniewski et al., 2010).

Biodiesel characterization

Biodiesel characterization was done in Tribology Laboratory of the Department of Mechanical Engineering in the Faculty of Engineering, University of Malaya. The determination of total acid number, total base number, multielement analysis and viscosity of biodiesel is carried out and then compared with ASTM value. The ASTM standards are as follows; for TAN: ≤ 0.5 mg of KOH/g; viscosity: 1.9 – 6.0 (centistokes or cSt.); for certain elements: ≤ 5 ppm for sodium, magnesium and calcium and ≤ 10 ppm for phosphorus.

Emission test

This test was carried out in the Tribology Laboratory of the Department of Mechanical Engineering in the Faculty of Engineering, University of Malaya as well. The model of the engine is YANMAR TF120-M. The produced biodiesel was used to run the diesel engine and its emissions were analyzed using a BOSCH gas analyzer, which was used to analyze the carbon monoxide and unburned hydrocarbon. A BACHARACH gas analyzer was used to analyze the NOx emission.

The engine specifications for the YANMAR Model TF120-M are as follows; Type: 1-cylinder, horizontal, water-cooled, four stroke diesel engine with a direct injection combustion system and natural aspiration. The cylinder bore × stroke: 92 mm × 99 mm with a displacement of 638cc and a continuous rated output of 10.5 Ps/7.7kw@2400 rpm and a 1-hr rated output of 12.0 Ps/8.8kw@2400 rpm. The cooling water capacity was 2.3 litres. The engine dry weight was 101.5 kg.

Results and Discussion

The effect of catalyst concentration on biodiesel yield

As can be seen in Figure 1, where biodiesel yield was plotted against catalyst concentration, optimum alkaline transesterification was observed when 1% KOH was used. It has been reported that as the catalyst concentration increases, the biodiesel yield increases as well until a maximum concentration of 1% was reached (Bhattia et al., 2008). When it exceeded 1%, a decrease was observed. When the catalyst concentration exceeded 1%, emulsion or soap, due to saponification reaction with unreacted sodium hydroxide, will be formed and hence will increase the viscosity of the whole solution and finally result in the formation of a gel. These results show that a catalyst concentration of 1% is optimum for transesterification of waste palm oil.

Figure 2 shows the maximum biodiesel yield is achieved using a molar ratio of 1:6 for oil: methanol. Theoretically, an oil/methanol ratio of 1:3 is sufficient to form methyl esters from the reaction of methanol with triglycerides. However, the reverse reaction is possible at equilibrium and a backward reaction can occur. The yield of methyl esters will increase as the methanol: oil ratio increases, however, their relationships are not directly proportional but rather hyperbolical. According to many studies, a ratio of 1:6 is sufficient for a high yield, almost complete, of methyl esters (Guan et al., 2008). With higher oil: alcohol ratio only a slight improvement in methyl esters yield can be obtained. In order to make the biodiesel production more economically viable, a maximum oil:methanol ratio of 1:6 was used and it contributed to maximum conversion rate in this experiment.

GC-MS analysis of biodiesel

From the GCMS analysis, five main peaks were detected in the chromatogram shown in Figure 3. The percentage area of every peak indicated the relative quantities of the compounds in the biodiesel. As shown in Table 1 the first peak had a total area of 2.14%, the second peak, 36.85%, the third

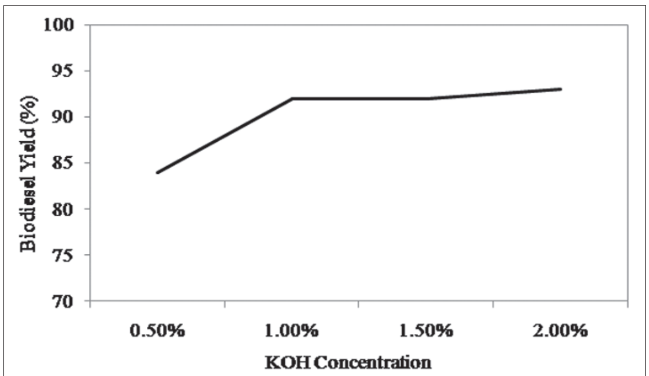

Fig. 1. Optimization of alkaline transesterification of waste palm oil

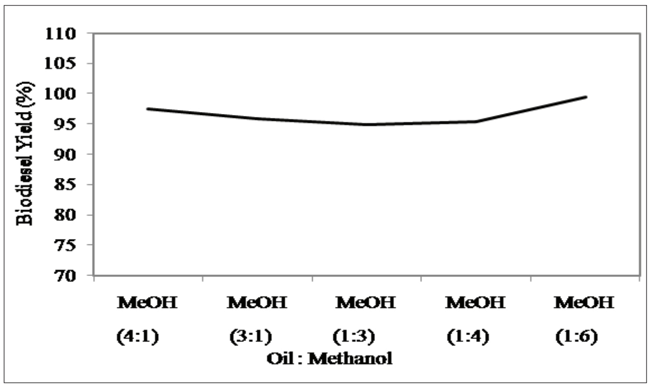

Fig. 2. The effect of different oil:methanol molar ratios on biodiesel yield

Table 1
Peak serial and chemical composition of palm biodiesel

Total peak number	Peak serial	RT, min	Methyl ester of	% Relative
5 peak for palm	1	20.170	$C_{16}H_{29}O_2CH_3$	2.14
	2	20.595	$C_{16}H_{31}O_2CH_3$	36.85
	3	23.767	$C_{18}H_{31}O_2CH_3$	11.11
	4	23.898	$C_{18}H_{33}O_2CH_3$	44.66
	5	24.330	$C_{18}H_{35}O_2CH_3$	5.24

peak, 11.11%, the fourth peak 44.66% and the final peak 5.24%. The identification of these peaks are shown in Figure 4 and Table 1, where from the library search report, the identities of methyl esters as methyl cis-7-hexadecenoate in the

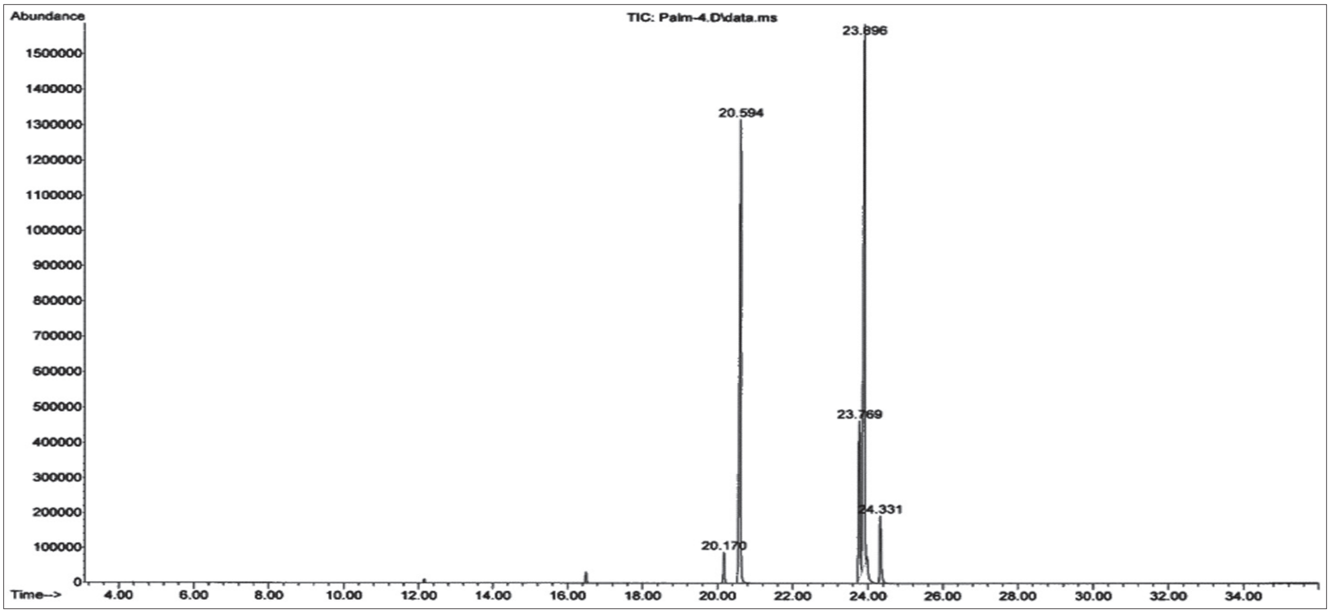

Fig. 3. The chromatogram from gas chromatography

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                         Library Search Report

    Data Path : D:\Data\Prof. Amru\
    Data File : Palm-4.D
    Acq On    : 11 Mar 2009  12:17
    Operator  : Guan Serm
    Sample    : Palm
    Misc      : 100-5-280
    ALS Vial  : 2   Sample Multiplier: 1

    Search Libraries:   C:\Database\NIST05.L            Minimum Quality:  90

    Unknown Spectrum:   Apex
    Integration Events: Chemstation Integrator - autoint1.e

  Pk#     RT   Area%          Library/ID                    Ref#     CAS#    Qual
  ______________________________________________________________________________
    1  20.170   2.14 C:\Database\NIST05.L
                      7-Hexadecenoic acid, methyl ester, 104151 056875-67-3 90
                       (Z)-
                      9-Hexadecenoic acid, methyl ester, 104156 001120-25-8 59
                       (Z)-
                      Chloromethyl 7-chlorododecanoate   112922 080419-03-0 41

    2  20.595  36.85 C:\Database\NIST05.L
                      Hexadecanoic acid, methyl ester    105639 000112-39-0 98
                      Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 98
                      thyl ester
                      Hexadecanoic acid, methyl ester    105644 000112-39-0 96

    3  23.767  11.11 C:\Database\NIST05.L
                      9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
                      ester, (E,E)-
                      9,12-Octadecadienoic acid, methyl  121093 002462-85-3 99
                      ester
                      10,13-Octadecadienoic acid, methyl 121100 056554-62-2 99
                       ester

    4  23.898  44.66 C:\Database\NIST05.L
                      9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                      ster
                      9-Octadecenoic acid (Z)-, methyl e 122323 000112-62-9 99
                      ster
                      9-Octadecenoic acid, methyl ester  122299 002462-84-2 99

    5  24.330   5.24 C:\Database\NIST05.L
                      Octadecanoic acid, methyl ester    123709 000112-61-8 98
                      Octadecanoic acid, methyl ester    123708 000112-61-8 97
                      Heptadecanoic acid, 16-methyl-, me 123732 005129-61-3 96
                      thyl ester

  ESSENTIALOIL.M Fri Mar 13 15:10:39 2009 MSD
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Fig. 4. Library search report of produced biodiesel

first peak, methyl hexadecanoate and methyl 14-methyl pentadecanoate in the second peak. Methyl cis, cis-9,12- octadecadienoate and methyl cis,cis-10,13-octadecadienoate are the possible identities of the third peak of the chromatogram whereas the fourth peak was methyl cis-9-octadecenoate. The fifth peak was identified as methyl octadecanoate and methyl 16-methyl-heptadecanoate.

The five components separated by GC are probably methyl palmitoleate, methyl palmitate, methyl linoleate, methyl oleate and methyl stearate (Table 1). This means that the major fatty acids present in the waste palm oil are palmitoleic acid, palmitic acid, linoleic acid, oleic acid and stearic acid. This is most probably the case as they are the components present in the palm oil as documented and explained by Ang et al. (1999).

Total acid number and Kinematic viscosity

The TAN is a direct determination of the free fatty acids in the biodiesel sample. Large acid number can lead to corrosion and may be a symptom of water in the fuel (Antolin et al., 2002). A TAN value of lower than 0.5 mg KOH/g is ideal as fuel for vehicles. However, in this study, the TAN value of palm biodiesel was well within the range of ASTM. This means it has a low content of free fatty acid, which makes it suitable for engine use as corrosion can be avoided. If the biodiesel sample had a lot of excessive free fatty acids, corrosion will be a problem. However, the biodiesel from waste palm oil exhibited a higher acid value (0.43) than that of biodiesel from pure palm oil (0.1) (Hossain and Boyce, 2009a.). This is probably due to waste palm oil having excessive free fatty acid because possibly triglycerides are broken down into free fatty acids during cooking. In addition, free fatty acids could come from the meat, if the oils were used to fry meat.

Viscosity is another important parameter in measuring the quality of biodiesel since it will affect the operation of fuel injection in biodiesel engines. According to ASTM D6751 standard, the standard range of viscosity for biodiesel is 1.9-6.0 cSt. at 40°C. The viscosity of the biodiesel sample with the maximum conversion conditions was 4.10 cSt. at 40°C, which falls well within the standard range of ASTM limits (Table 2). Excess viscosity will lead to poor atomization of fuel and low viscosity will cause power loss due to injection pump and injector leakage. Thus, the biodiesel produced meets the international standards and can be used as fuel.

Elemental analysis

Multi element analysis of waste cooking palm biodiesel showed that the level of magnesium, calcium and sodium contents were higher than the ASTM standard whilst the phosphorus level was within the standard according to ASTM D6751 (Figure 5). Phosphorus is a poison for the catalytic converters in the exhaust system of diesel engines and it increases the emission of CO, CO_2, SO_2 and HC (Korn et al., 2007). Phosphorus can cause severe damage to catalytic converters used in emissions control systems by scaling on combustion chambers or by plugging of filters and its level must be kept low to maintain low emissions. Thus, the presence in excess of certain elements can lead to operational problems. Since the phosphorus level is within the range of this present research, hence it will not cause any problem to the catalytic converters of diesel engines.

The concentration of calcium (Ca) in the biodiesel sample was 7.00 ppm, magnesium (Mg), 11.00 ppm and sodium (Na), 6.00 ppm and they were all slightly higher than the ASTM D6751 standard. Metal elements contained in the fuel can lead to the formation of ash after the combustion. Deposition of ash in the engine makes the engine become dirty and reduces the engine performance. Na and K are associated with the formation of ash within the engine, calcium soaps are responsible for injection pump sticking. Sodium and potassium hydroxides are utilized as catalysts, and magnesium and calcium are used as absorbents in the production of biodiesel and should be removed through the biodiesel production process. These residual metals can form deposits in fuel

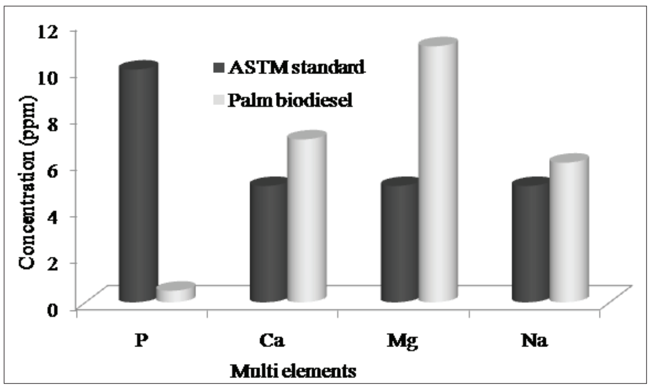

Fig. 5. Multielement analysis of biodiesel produced

Table 2
Total acid number (TAN) and kinematic viscosity of palm biodiesel

Property	ASTM value	Palm biodiesel	Unit
Acid value	0.50 max	0.43	mg KHO/g oil
Viscosity	1.9-6.0	4.10	mm^2/s at 40^0C

Table 3
Fuel consumption and greenhouse gas emission analysis

Sample	Load, Nm	Speed, rpm	Fuel consumption, ml/sec	HC, ppm	CO, vol. %	NOx, Ppm
Biodiesel	15	2000	0.613	22.40	0.020	503.00
Diesel	15	2000	0.588	25.33	0.028	515.40

injection system components and poison emission control after-treatment systems. Sodium and potassium, as well as calcium and magnesium, may also be present as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston and ring wear, and to engine deposits (Mittelbach and Enzelsberger, 1999). Since the level of magnesium, calcium and sodium contents are higher than the ASTM D- 6751 standard; hence, it can have deleterious effects on engine parts as stated above.

Fuel consumption and emission tests

The results of these emission tests and the fuel consumption are shown in Table 3. All tests were carried out at 2000 rpm and compared with conventional diesel, which acts as the standard. Specific fuel consumption (SFC) is an engineering term that is used to describe the fuel efficiency of an engine design with respect to thrust output (Durkovic and Damjanovic, 2006). It can be seen that the diesel shows a lower SFC (0.588 ml/sec) than palm-based biodiesel (0.613 ml/sec). This may be due to the lower TAN and viscosity value of palm-based biodiesel compared to the petrodiesel, thus contributing to higher specific fuel consumption.

Unburned hydrocarbon emission is known as partially oxidized hydrocarbon emission. Its emission can be caused by two main factors. It could increase due to (a) the fuel injection that is occurring too early, causing an increased in delay time and hence more fuel can contact with the relatively cool cylinder wall, or (b) the combustion process in the engine occurring too late, causing an insufficient time for complete combustion. Biodiesel fuelled engine shows a lower production of unburned hydrocarbon compared to conventional diesel (Table 3), probably because biodiesel has higher cetane number leading to faster evaporization and autoignition (Tiegang et al., 2009). All these factors enhance the complete combustion of biodiesel and hence reduce the production of unburned hydrocarbon (Lei et al., 2010).

Table 3 also shows that the concentration of CO produced from palm-based biodiesel is much lower than that of petrodiesel. The reduction in carbon monoxide emissions is probably due to the higher oxygen content of the biodiesel fuel. More oxygen means the fuel is burned more completely which also helps reduce CO emissions. Incomplete combustion will generate more CO.

NOx emission formation is highly temperature dependent. As the exhaust gas temperature increases, NOx emission also increases (Rajan and Senthilkumar, 2009). The palm-based biodiesel showed a slightly lower NOx emission when compared to petrodiesel, presumably because of the lower combustion flame temperature of palm-based biodiesel (Rhamadhas et al., 2005). Hence, biodiesel tend to generate less smoke because of the presence of oxygen in the biodiesel and greenhouse gas emissions can be reduced using more biodiesel.

Conclusions

From this study, the following conclusions can be summarized. The optimum conditions for maximum conversion rate of triglycerides of waste cooking palm oil to methyl esters was identified as using a molar ratio of 6:1 for methanol: oil and 1.0% KOH as catalyst. Five methyl esters, namely, methyl palmitoleate, methyl palmitate, methyl linoleate, methyl oleate and methyl stearate were present in palm biodiesel samples produced. Biodiesel characterization showed that the level of calcium, magnesium and sodium were slightly above the range of ASTM standards whilst it's TAN, kinematic viscosity and phosphorus level are in the range. However, the biodiesel exhibited higher fuel consumption compared to conventional diesel fuel. Emission tests by palm biodiesel showed that the level of unburned hydrocarbons, oxides of nitrogen and carbon monoxide were lower than that found with conventional diesel fuel. It can be concluded that biodiesel made from waste cooking palm oil can be considered as a great potential source of commercial biodiesel.

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