A Review of Palm Oil Biodiesel under Long-Term Storage Conditions

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***Abstract*—**Palm-oil biodiesel is widely used as alternative to diesel; the influences of long-term oxidative degradation on its burning characteristics are a matter of some concern. To further our understanding of this issue, this study investigated the heat release, carbon residue, flash point, and cetane index, oxidative stability, Density, Viscosity, Total acid no. of palm-oil biodiesel in a constant-temperature water bath after long-term storage.

Keywords- *Diesel,Palm Biodiesel,Oxidation degradation,Burning characteristics,Storage temperature,Total acid no., Flash point, Oxidative stability*

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I. INTRODUCTION

Ever since past few decades, biodiesel, as a renewable alternative fuel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [1,2]. Biodiesel having very close property to that of diesel fuel provides some technical advantages over traditional diesel. These include reduced exhaust emission, higher cetane number, higher flash point, better lubricity etc. [3-5]. However, compatibility of biodiesel with automotive materials is being considered as a growing concern [6-7]. Elastomers as one of the most important groups of materials, used in fuel system are of particular concern [9]. This is because the elastomers are weak attack by various chemicals and can undergo degradation of their physical properties and stability [10]. This paper study the results carried out to evaluate the oxidation and storage stabilities of various biodiesel fuels. Oxidation stability of the samples was measured by induction period (IP) using a Rancimat instrument. Other properties such as density, viscosity, flash point, total acid number (TAN), and total base number (TBN)were measured. Properties of biodiesel such as cetane number, viscosity, calorific value, cold flow, oxidative stability and lubricity are determined by the structure of their alkyl esters, in such a way that for a certain biodiesel composition some of these properties are satisfactory while others are not. For instance, palm biodiesel has good oxidative stability but very poor cold-flow properties, while soy biodiesel has good cold-flow properties but poor oxidative stability. Among the strategies that have been developed to solve the technical problems linked to the biodiesel composition are the mixing of biodiesel with traditional fossil diesel in different proportions to achieve an optimal blend, the use of additives to correct the negative properties of biodiesel, changing the chemical structure of esters that comprise biodiesel and the change in the composition of biodiesel.

II. MATERIALS AND METHODS

A. Burning characteristics of palm-oil biodiesel under long-term storage conditions

Chern – yuan- lin et al.[8]investigated that Palm-oil biodiesel is widely used as alternative to diesel, the influences of long-term oxidative degradation on its burning characteristics are a matter of some concern. To further our understanding of this issue, this study investigated the heat release, carbon residue, flash point, and cetane index of palm-oil biodiesel in a constant-temperature water bath after long-term storage. The results and their implications can be summarized as follows:

- A high storage temperature and the absence of an adequate antioxidant caused deterioration in the oxidative stability of the biodiesel. Water, impurities, and polymers were continuously produced from the unsaturated fatty acids in the palm-oil biodiesel with storage time through the per oxidation reaction mechanism. As a consequence, the sample that was stored at 60 °C and did not contain an antioxidant was observed to suffer the greatest oxidative degradation, and hence had the lowest heat release with storage time among the samples. The presence of the chain-breaker type antioxidant BHT retarded the oxidative degradation rate and thus decreased the reduction in heat release with storage time in the biodiesel.
- Diesel was found to have a higher carbon residue than the palm-oil biodiesel due to its higher aromatic content. Larger quantities of sediment composed of primary and secondary oxidative products with higher molecular weights were formed in the samples through the peroxidation chain mechanism under higher storage temperatures, longer storage times, and in the absence of an adequate antioxidant. This led to the production of a larger carbon residue after the burning process.
- The flash point of the palm-oil biodiesel was significantly higher than that of Diesel, which indicates that it is safer during transportation, storage, and operation. The unsaturated fatty acids in the biodiesel were continuously converted into primary and secondary oxidative products such as free fatty acids and water over time due to the effects of oxidative degradation. Hence, the sample that was stored at a lower temperature, for a shorter storage time, and contained the antioxidant BHT experienced less oxidative degradation and in turn less unsaturated fatty acid decomposition, thus retaining a high flash point.
- A higher cetane index indicates favorable combustion characteristics, including fewer occurrences of engine knocking and a shorter ignition delay and burning time. The biodiesel sample that was stored at a lower temperature and contained the antioxidant BHT was

observed to experience a slower decrease in cetane index with storage time because it underwent less oxidative degradation.

B. Degradation of physical properties of different elastomers upon exposure to palm biodiesel

M.A.Fazal et al[11].investigated past few decades, biodiesel, as a renewable alternative fuel is receiving much attention to substitute diesel partially or completely. It is composed of fatty acid alkyl esters derived from vegetable oils or animal fats [11, 12]. Biodiesel having very close property to that of diesel fuel provides some technical advantages over traditional diesel. These include reduced exhaust emission, higher cetane number, higher flash point, better lubricity etc. However, compatibility of biodiesel with automotive materials is being considered as a rising concern. Elastomers as one of the most important groups of materials, used in fuel system are of particular concern. This is because the elastomers are vulnerable attack by various chemicals and can undergo degradation of their physical properties and stability.

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C. An experimental investigation into biodiesel stability by means of oxidation and property determination

H.H.Masjuki et al.[13]. investigated that there were six different types of fuel samples tested and analyzed in this study using different tests and experimental procedures.

TABLE I
INITIAL PROPERTIES OF THE FUEL SAMPLES

Properties	Unit	PME	PME 20	DIESEl	JME	JME 20	COME
Density	kg/m^3	843.963	839.15	864.02	847.32	844.42	816.18
Kinematic viscosity	Cst	4.92	4.61	4.81	4.49	3.67	3.63
Flash point	°c	259	195	238	206	241.5	75

D. Oxidative stability and cold flow behavior of palm, sacha-inchi, jatropha and castor oil biodiesel blends.

Pedro N. Benjumea et al.[14]. Blending of biodiesel from different oils is another technique that has been recently studied to improve the properties of this biofuel. Park et al. studied blends of biodiesel from palm, rapeseed and soybean, and determined their oxidative stability and CFPP[14] Moser evaluated some fuel properties of soy biodiesel (oxidative stability, CFPP, cloud point, kinematic viscosity, lubricity, acid value and iodine value) and its mixture with methyl esters of palm, canola and sunflower[15]. Sarin et al. examined blends of jatropha and palm biodiesel in order to study their physicochemical properties and to achieve an optimal blend in terms of cold flow properties and oxidative stability [16]. The African oil palm is the oilseed species with the highest oil production per hectare (4 ton/ha year), making it the main source of biodiesel in tropical countries. Biodiesel from this oil has very good oxidative stability due to the high content of saturated fatty acids and natural antioxidants. Unfortunately, this high content of saturated fatty acids causes poor cold flow properties. The use of palm oil for biodiesel production has been questioned in some countries because it can compete for food use. However, it has been argued that production volumes of this oil, present and future, can meet both requirements.

The oxidative stability and the CFPP of palm, castor, jatropha, sacha inchi biodiesels and their blends are properties that depend on the type of methyl-ester constituents. A higher content of polyunsaturated methyl esters decreases the oxidative stability. A higher content of saturated methyl esters increases the CFPP. Among the tested pure biodiesels, oxidation stability varies in the order castor>palm>jatropha>sacha inchi. As for the cold flow properties, the CFPP varies in the order sacha inchi<castor<jatropha<palm.

III. CONCLUSIONS

A. Amount of heat released

The amount of heat released in burning the palm-oil biodiesel samples is shown in Figure 1. A greater heat release from a hydrocarbon fuel means that a smaller fuel mass can be

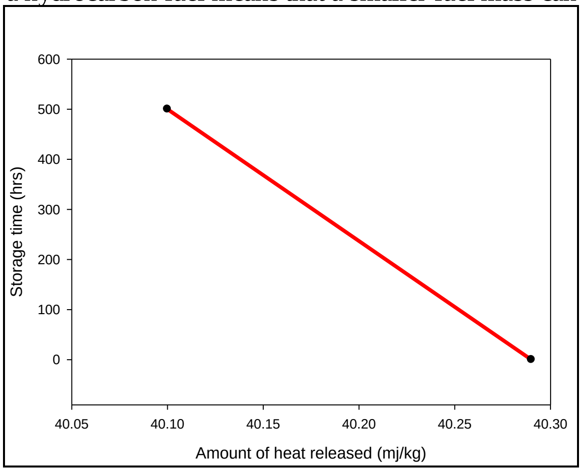

Figure 1: Comparison of the heat release of palm-oil biodiesel at various storage temperatures and times

Used to attain the same engine power output, and is thus more favorable. The amount of heat released from burning the neat palm-oil biodiesel was 40.29 MJ/kg, which is lower than the 46.13 MJ/kg released by diesel. This is primarily due to the lower elemental carbon content and higher oxygen content of the biodiesel compared with diesel.

B. Carbon residue

Insoluble impurities begin to form in biodiesel after it is stored for an extended period. These insoluble impurities may plug fuel filters, fuel pumps, and nozzles in the fuel feeding system, and are converted to carbon residue after the fuel is burned. Diesel appears to form a larger carbon residue than palm oil biodiesel by 33.3 wt.%. This is primarily attributed to the larger content of aromatics in the former [17].Which causes more serious carbon deposition inside the combustion chamber of diesel engines.

ISSN: 2321-8169
313 – 317

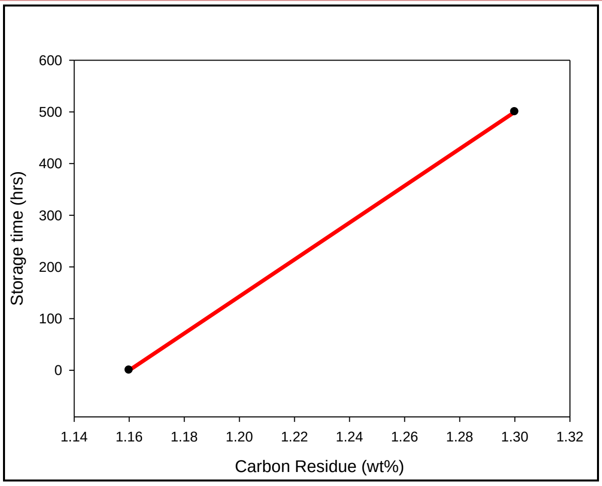

Figure 2: Comparison of the carbon residue of palm-oil biodiesel at various Storage temperatures and times

C. *Flash point*

The components of liquid fuel with a low boiling point are gradually vaporized with increasing temperature. The lowest temperature at which the vaporized gas from a liquid fuel produces a temporary flash but discontinuous burning is defined as its flash point. A liquid fuel with a higher flash point is less likely to auto ignite and is thus less of a fire hazard, making it safer to transport, use, and store. The flash point of the palm-oil biodiesel was found to be 187.1 °C, which is significantly higher than the 75.6 °C of diesel. The weight of the unsaturated fatty acids in the samples decreased with storage time. For example, the unsaturated fatty acid weight of sample 2 decreased from 51.55 wt.% to 50.37 wt.% and then 48.64 wt.% after 1500 h and 3000 h of storage time, respectively. This occurred because, over time, oxidative degradation converts unsaturated fatty acids to primary and secondary oxidation products such as free fatty acids, hydro peroxides, polymers with a high molecular weight, and water [7].

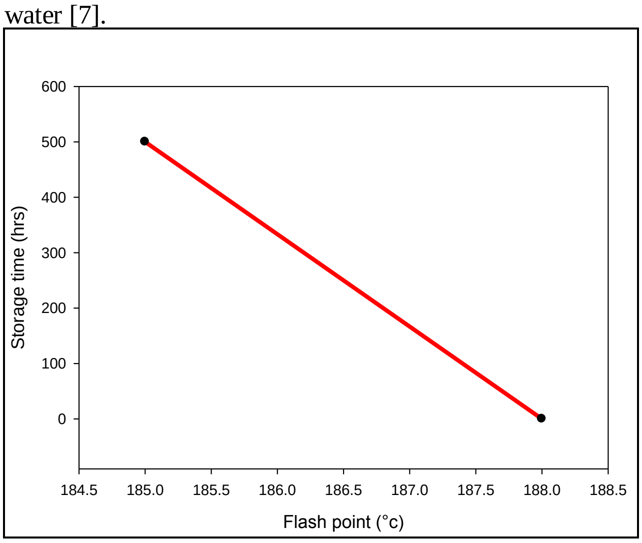

Figure 3: Comparison of the flash point of palm-oil biodiesel at various storage temperatures and times

D. *Cetane index*

The cetane index is an important index of the combustion characteristics of fuels, particularly diesel. Liquid fuels with a higher cetane index have a shorter ignition delay, which leads to a shorter burning time, fewer occurrences of engine knocking, and less nitrogen oxide formation [1]. The cetane indices of the samples decreased with increasing storage time, as shown in Figure 4.

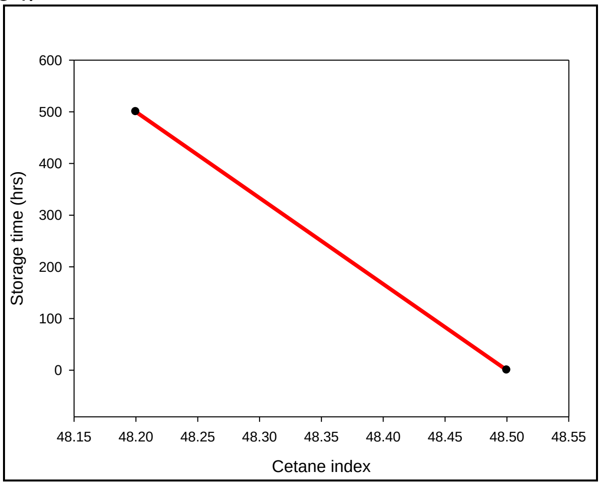

Figure 4: Comparison of the cetane index of palm-oil biodiesel at various Storage temperatures and times

E. *Oxidation stability*

Oxidation stability is the most important factor to assess biodiesel fuel quality, which is initiated by the chemical reaction between a free-radical and free unsaturated fatty acids. Table I shows the fatty acid content of the tested biodiesels parent oil.

F. *Density*

Density is the measure of the mass per unit volume, which is expressed in kilogram per cubic meter (kg/m3). Fuel density generally increases with increasing molecular weight of the fuel molecules. From Figure 5, a trend can be seen in the density for all the fuel samples, which increases with storage time. The increasing trend of COME was most noticeable with a slope equal to 0.0059. This was followed by diesel with a slope of 0.002 and PME 20 with a slope of 0.0017. The JME showed the least increment in density with a slope of 0.0009. The increase in density was caused by the formation of oxidation products, including insoluble sediments.

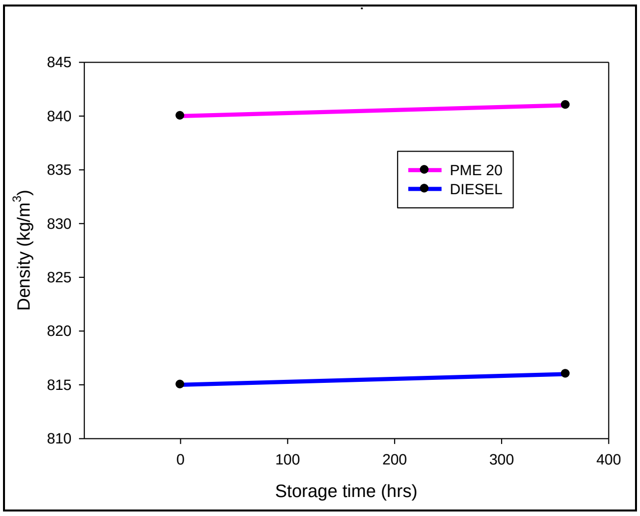

Figure 5: Density vs. storage time.

G. Viscosity

Viscosity is the measure of resistance to flow. Particularly, it is important due to the effect on the fuel injection system at low temperatures. Higher viscosity leads to lower atomization characteristics in the fuel injector, which leads to several severe effects on engine performance. Sarin et al.[48].stated that blending of biodiesel over two is a simple but effective method to improve the flow properties at low temperatures. Additionally, a highly viscous fuel would also take longer time to mix with air since the quality of the vaporization and atomization of the fuel is reduced. Kinematic viscosity is increased with the carbon chain length in biodiesel containing free fatty acids and hydrocarbons. However, the viscosity of diesel is lower, and the increasing trend in viscosity over time is lower as diesel is less oxygenated than biodiesel [19]. Figure

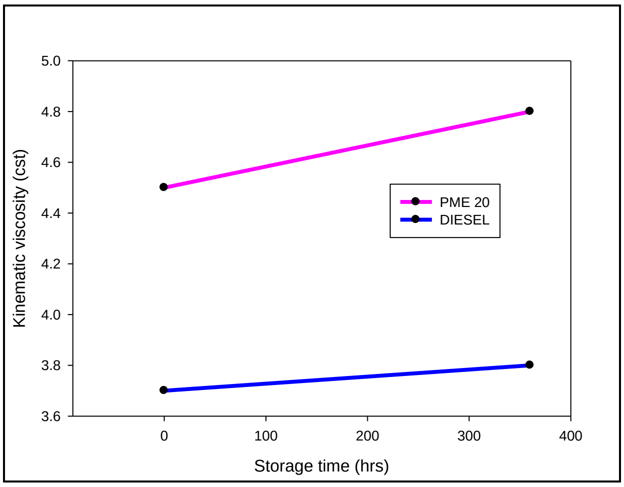

Figure 6: Viscosity vs. storage time at 40 °C.

6. shows the changes in viscosity with storage time at 40 °C, It can be seen that the viscosity of PME increases from 5.971 to 4.92 cSt after a storage time of 2160 h (3 months). The viscosity of other samples also increases; the only difference was the rate of the increase. The increasing trend in viscosity was due to the effect of oxidation. The JME came next with an increase of 0.94 cSt (initial: 4.81 cSt; final: 5.75 cSt). Diesel fuel showed good characteristics in terms of viscosity as oxidation did not affect its viscosity very much, with an increase of 0.49 cSt (initial: 3.20 cSt; final: 3.69 cSt).

H. Flash point

The flash point temperature is an important property for a fuel, especially in terms of handling, storage and forming of a combustible mixture. The flash point indicates the difference between a highly flammable, volatile and a relatively non-flammable non-volatile material [20]. It is expected that a good fuel should have a low auto-ignition temperature, especially in a diesel engine, since it has no extra mechanism to ignite the fuel in the combustion chamber.

The auto-ignition temperature of a fuel is the lowest temperature at which the fuel could spontaneously ignite without an external source of ignition. Fuels with a flash point above 66 °C can be considered to be safer fuels; therefore, biodiesel is a safer fuel for handling and storage [21].From the experimental data shown in Figure 7, it is obvious that after 2160 h (3 months) of storage, the flash points of all biodiesel samples were adequate and above the limiting value for safer fuels.

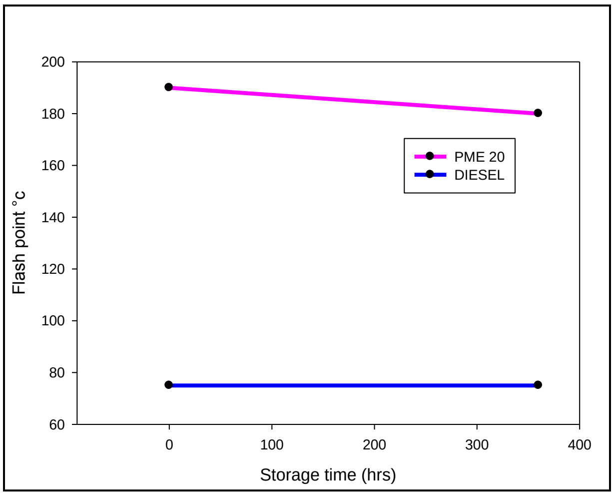

Figure 7: Flash point vs. storage time.

I. Total acid number (TAN)

The acid number is the amount of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared non-aqueous basic buffer solution[22]. Figure 8 shows the changes in TAN over the storage period of 2160 h (3 months).

The TAN value increases with increasing storage time for all the biodiesels. The acid number increases as a result of increased hydro peroxides, which may be further oxidized into acids.

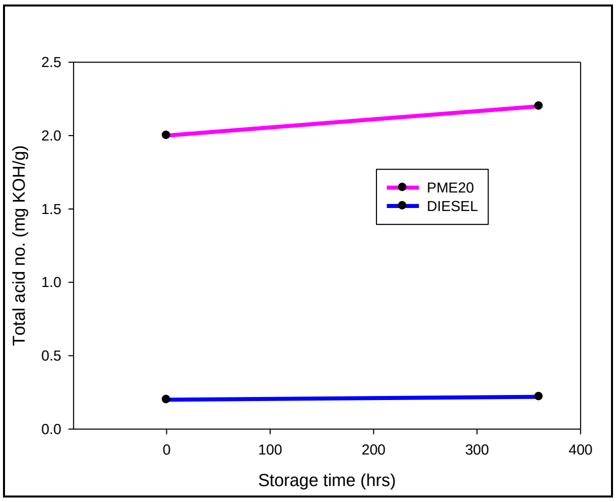

Figure 8: Total acid number vs. storage time.

The esters first oxidize to form peroxides, which then turn into complex reactions, including a split into more reactive aldehydes, which further oxidize into acids. Acids can also be formed when traces of water cause hydrolysis of the esters into alcohols and acids[23] Figure 8 indicates that PME experiences the highest rate of oxidation, while diesel is the lowest (2.54-2.89 mg KOH/g and 0.25-0.59 mg KOH/g, respectively), in terms of the TAN value over the entire storage period.
1. The unsaturated fatty acid percentages and the longer chain double bonded hydrocarbon in the biodiesel have the great influence on the stability of the biodiesel, as these are higher, the

quality of the fuel would be poor as well as the properties would be degraded faster with increasing storage time.

2. The induction period of all biodiesels showed promising results in terms of oxidation stability, and all fuels met the standard specification ASTMD6751 (3 h), except for JME and its biodiesel blend which did not meet the standard specification.

3. During the storage period of 2160 h (3 months), adverse effects of oxidation were observed in terms of density and kinematic viscosity, but the values did not exceed the limiting value of the standard specification.

4. With respect to property determinations, the flash point of biodiesel showed the best performance among other the properties analyzed in this study. However, a decreasing trend in the flash point of COME was noticeable.

5. The total acid number (TAN) was the most concerning for all the biodiesel samples since none of them met the standard specified value. From these results, it can also be concluded that COME had the highest potential to prevent oxidation by retaining the properties of the fuel during storage period, while JME and PME showed almost similar performance in terms of its properties. It can also be predicted from the trends of the figures that fuel quality would be deteriorated with increasing storage time. Since the oxidation of fuels are largely dependent on the storage conditions. Further study is required to investigate the stabilities of the biodiesel applying various conditions which would help to improve fuel quality by improving the oxidation, thermal and storage stabilities.

REFERENCES

[1] KT Tan, KT Lee , AR Mohamed, " Potential of waste palm cooking oil for catalystfree biodiesel production. Energy", in press. doi:10.1016/j.energy.2010.05.003.

[2] Chen Kang-Shin, Lin Yuan-Chung, Hsieh Lien-Te, Lin Long-Full, Wu Chia-Chieh, "Saving energy and reducing pollution by use of emulsified palmbiodiesel blends with bio-solution additive." Energy 2010;35:2043-8.

[3] Haseeb ASMA, SY Sia, MA Fazal, HH Masjuki, "Effect of temperature on tribological properties of palm biodiesel",Energy 2010;35:1460-4.

[4] MA Fazal, ASMA Haseeb, HH Masjuki, "Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials", Fuel Processing Technology 2010;91:1308-15.

[5] MA Fazal, ASMA Haseeb, HH Masjuki, " Biodiesel feasibility study: an evaluation of material compatibility, performance, emission and engine durability" Renewable and Sustainable Energy Reviews, in press. doi:10.1016/j.rser.2010.10.004.

[6] EW Thomas, RE Fuller, K Terauchi, "Fluoroelastomer compatibility with biodiesel fuels",SAE Technical paper No. 2007-01-40061.

[7] S Mitra, A Ghanbari-Siahkali, P Kingshott, HK Rehmeier, H Abildgaard, K Almdal, "Chemical degradation of crosslinked ethylene-propylene-diene rubber in an acidic environment", part I: effect on accelerated sulphur crosslinks.Polymer Degradation and Stability 2006;91(1):69-80.

[8] CY Lin, RJ Li. " Fuel properties of biodiesel produced from the crude fish oil from the soapstock of marine fish". Fuel Process Technol 2009;90:130–6.

[9] C Carraretto, A Macor, S Mirandola, A Stoppato, S Tonon. "Biodiesel as alternative fuel: experimental analysis and energetic evaluations". Energy 2004;29:2195–211.

[10] SL Dmytryshyn, AK Dalai, ST Chaudhari, HK Mishra, MJ Reaney. "Synthesis and characterization of vegetable oil derived esters evaluation for their diesel additive properties". Biores Technol 2004;92: 55–64.

[11] Nogueira LAH. "Does biodiesel make sense. Energy", in press. doi:10.1016/j. energy.

[12] A.Demirbas "Biodiesel production via non-catalytic SCFmethod and biodiesel fuel characteristics".Energy Conversion and Management 2006;47(15):2271-82.

[13] G.Knothe, KR Steidley."Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components". Fuel 2005;84(9):1059-65

[14] J.-Y. Park, D.-K. Kim, J.-P. Lee, S.-C. Park, Y.-J. Kim, J.-S. Lee, "Blending effects of biodiesels on oxidation stability and low temperature flow properties", Bio resource Technology 99 (2008) 1196–1203.

[15] B.R. Moser, "Influence of blending canola, palm, soybean, and sunflower oil methyl esters on fuel properties of biodiesel", Energy & Fuels 22 (2008) 4301–4306.

[16] R. Sarin, M. Sharma, S. Sinharay, R.K. Malhotra, Jatropha–palm biodiesel blends: an optimum mix for Asia, Fuel 86 (2007) 1365–1371.

[17] Dr. Tiwari, "Report of Committee on Development of Biofuel Planning commission of India", April 2003

[18] R. Sarin, M. Sharma, S. Sinharay, R.K. Malhotra, Jatropha–palm biodiesel blends: an optimum mix for Asia, Fuel 86 (2007) 1365–1371.

[19] P. Kumaran ,N. Mazlini , I.Hussein,M. Nazrain ,M. Khairul. " Technical feasibility studies for Langkawi WCO (waste cooking oil) derived-biodiesel". Energy 2011;36(3):1386-93.

[20] AK Agarwal, L Das. "Biodiesel development and characterization for use as a fuel in compression ignition engines". Journal of Engineering for Gas Turbines and Power; 2001:123440.

[21] Acid number by potentiometric titration: d664, guide to astm test methods for the analysis of petroleum products and lubricants. Available at: http://aegbiofuels. com/Pubs/D664_acid_number.pdf; [accessed 09,01,12].

[22] A. Ghorbani, B. Bazooyar, A. Shariati, S.M. Jokar, H. Ajami and A. Naderi: Applied Energy Vol 88, (2011), pp. 4725-4732.