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Property variation of palm biodiesel and its blends under long-term storage conditions - An experimental investigation

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***Abstract*— The influences of oxidative variables on the various property of palm biodiesel were investigated experimentally in this study. Biodiesel, which is composed of mono alkyl esters of long-chain fatty acids, generally has an inferior oxidative stability than petroleum diesel. Hence, the long term oxidative stability of palm biodiesel has received much industry attention because it is used widely as an alternative to pure diesel fuel. Palm biodiesel and its various blends were stored in an atmospheric condition continuously for 1344 h to observe the variation in its oxidative degradation of property. Such as calorific value, kinematic viscosity, density and Flash point. The experimental results reveal that the palm biodiesel suffered greater oxidative degradation and in the absence of an antioxidant, which resulted in a faster decrease in the amount calorific value as the storage time elapsed. The oxidative stability of the palm biodiesel was worst at a longer storage time, which caused the more extensive formation of sediments of oxidative products and hence a larger carbon residue after burning. The greater oxidative degradation also caused the more extensive decomposition of unsaturated fatty acids into oxidative products, which decreased the flash point, kinematic viscosity, density and cloud point the of the.**

***Index Terms*— Palm Biodiesel, Oxidation stability, Induction period, Flash point, Degradation, Diesel, kinematic viscosity, density, Calorific Value**

I. INTRODUCTION

Palm oil is one of major sources of raw vegetable oils for biodiesel production, primarily due to its high lipid content and relatively cheap price in relation to other oleaginous land plants. However, biodiesel is considered to have inferior oxidation stability in comparison petro-diesel [1]. Palm-oil biodiesel is widely used as an alternative fuel to petro-diesel in diesel engines, electric generators, and merchant vessels, but the degradation of its burning characteristics as a result of its oxidation instability is cause for concern. Viscous sediment, water, colloids, and other impurities may be formed in biodiesel after a period of storage or engine operation. Such impurities result in the formation of carbon residue on the tips of fuel injectors and fuel filter blockages in diesel engines [5], causing them to stall or even break down. Temperature is considered to be one of the significant factors in the decomposition of biodiesel. In addition, Bouaid et al. [10] indicated that both the presence of water in biodiesel and its long-term exposure in a humid environment disrupt its oxidative stability. The presence of water causes biodiesel to hydrolyze to form alcohols and acids, leading to deterioration in its fuel properties. The oxidative stability of the fatty acids in biodiesel under various storage conditions were evaluated by Leung et al.[7], who found that oxidative instability increases the kinematic viscosity, peroxide value, and acid value of biodiesel. However, no long-term evaluations of the influence of oxidative variables on the burning characteristics of biodiesel have been reported in the literature. The experimental longitudinal study reported here was thus initiated to fill this research gap by investigating the effect of oxidative degradation on the burning characteristics of palm-oil biodiesel. The amount of heat released, the flash point, and the carbon residue of palm-oil biodiesel samples in a constant-temperature water bath were observed unceasingly for 1344 h. The effects of storage temperature and the addition of an antioxidant were studied as a step toward improving the oxidation stability and burning characteristics of this fuel.

II. MATERIALS AND METHODS

BIODIESEL PRODUCTION

Paragraph Biodiesel was produced by transesterification of refined oils with methanol (methanol/oil molar ratio 6/1) and using KOH as catalyst (0.7% w/w based on oil). This reaction was carried out in round bottom flasks connected to a reflux condenser, heating at 65 °C under magnetic stirring for 1 hour. The final product was transferred to a funnel to separate biodiesel and glycerin. Excess methanol was removed from the ester phase using a roto-evaporador, then the biodiesel was washed with hot water until neutral pH. Ultimately, residual moisture was removed from biodiesel adding anhydrous sodium sulfate followed by a filtration step [10]. Biodiesels thus prepared were tested for acid value, peroxide and methyl ester content. The acid value and peroxide value were assessed by titration, which was conducted using a Titrino Plus 848 automatic titrator (Metrohm). Methyl esters content was determined by gas chromatography following the standard EN 14103 [16], using gas chromatograph (Agilent 7890A) with a capillary column (Agilent J & W HP-Innowax), flame ionization detector and tetradecanoic acid as internal standard. The viscosities of biodiesels were measured following the standard ASTM D 445 [3].

PHYSIO-CHEMICAL PROPERTIES

1. VISCOSITY

Fig .1. Redwood viscometer

Redwood viscometer apparatus are widely used in Petroleum Laboratories, Industries, Oil Refineries, Educational Institutions, Research Organisations for standardisation and determines the Viscosity of Petroleum products, which flows in a newtonian liquid except cut back Bitumens and road oils at the set temperature, They confirm to requirement of IP 70. Two adaption of Redwood Viscometers are available. Redwood Viscometers No. I for liquids having Redwood Flow 20 seconds to 2000 Seconds and Redwood Viscometers No. II exceeds 2000.The complete outfit comprises hemmer tone finish, copper/Stainless steel bath with drain plug, electrical heating arrangement, Suitable to operate at 220 Volts 50 Hz AC mains Or gas heating arrangement with silver plated oil cup with precision stainless steel jet, ball value, cover, thermometer clip, stirrer and suitable stand with levelling screws. The sample required to be tested, is to fill in to the required level as indicated by the gauge in a cup having a Stainless Steel jet fixed in the bottom. The temperature is maintained during the test by heating the liquid in a bath surrounding the cup, and the flow time for 50 ml of the sample is measured.

2. CALORIFIC VALUE

Fig. 2. Bomb Calorimeter

It is used for determination of heat of combustion, calorific value and sulphur contents of solid and liquid fuels. The Bomb body and lid are machined from corrosion resisting stainless steel rod. Its capacity is approx .300ml .It is provided with high pressure valve and electrodes. The calorimeter vassel and electrodes. The calorimeter vassel /stirrer FHP motor are provided and water jacket as per IP. The Bomb calorimeter is supplied with firing unit, Digital /Glass Beckman Thermometer, Pallet press, ignition Nichrome wire and pressure gauge with copper pipe fitting.

3. FLASH AND FIRE POINT

Fig .3. Redwood viscometer

The apparatus is used for determination of Flash Point & Fire Point of Petroleum products except fuel oil with open flash 800C as per specification IP 36/57, IS 1448(P:69) 1969 and ASTM-D-92-67 The apparatus consists of a cup heating plate to specific dimensions thermometer clip and test flame attachment with swivel joint for passing over liquid surface in the prescribed manner, heater is controlled by means of different types of regulators fitted to the apparatus suitable for operation on 220 Volts AC mains.

III. RESULT

1. CALORIFIC VALUE

The amount of heat released in burning the palm-oil biodiesel samples is shown in fig.1. A greater heat release from a hydrocarbon fuel means that a smaller fuel mass can be used to attain the same engine power output, and is thus more favourable. The amount of heat released from burning the neat palm-oil biodiesel was 8750 Kcal/kg, which is lower than the 9978 Kcal/kg released by diesel. This is primarily due to the lower elemental carbon content and higher oxygen content of the biodiesel compared with diesel. Water forms in biodiesel through the per-oxidation chain mechanism following the occurrence of oxidative instability, and hence the amount of water in the samples increased with the extent of oxidative instability [13] The amount of heat released thus also decreased with storage time in the samples of all blends because of the production of water during the per-oxidation chain reaction.

In B20 Calorific value is decrease by 2% and in other blends B50,B75 Calorific value is decrease by 1.4% and 2.1% respectively.

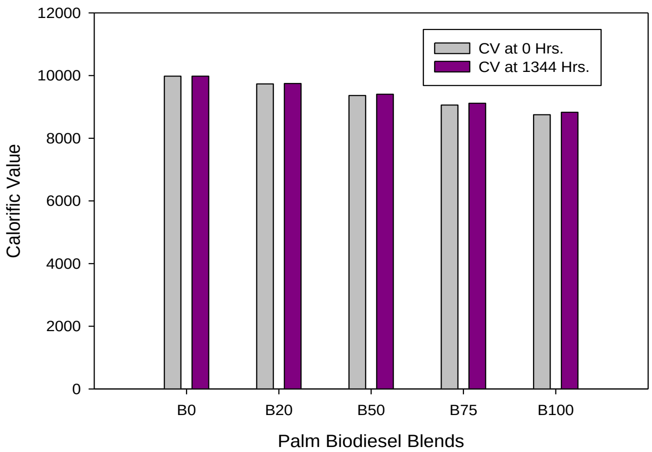

Fig. 1. Comparison of the Calorific Value of palm biodiesel and its various blends at 1344h storage times

2 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. 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 [16] It is expected that a good fuel should have a low auto-ignition temperature, especially in a diesel engine,

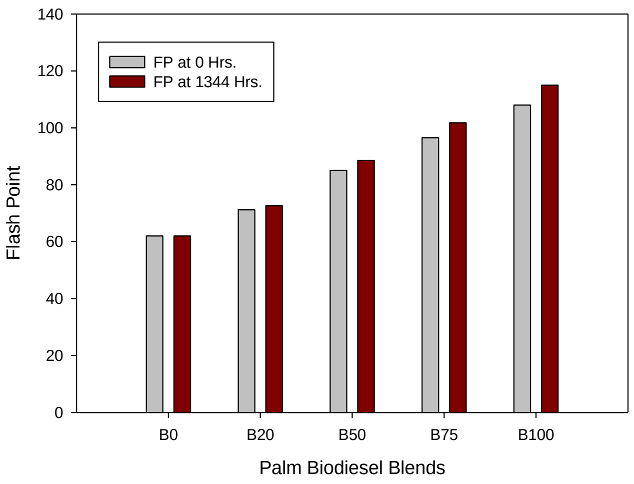

Fig. 2. Comparison of the flash point of palm biodiesel and its various blends at 1344h storage times

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 62°C can be considered to be safer fuels; therefore, biodiesel is a safer fuel for handling and storage [3]. From the experimental data shown in Fig.2, it is obvious that after 1344 h of storage, the flash points of all biodiesel samples were adequate and above the limiting value for safer fuels. Among these fuel samples, the increased flash point over the entire storage period for palm biodiesel was found to be 115°C, which is significantly higher than the 62 °C of diesel. This occurred because, over time, oxidative degradation converts unsaturated fatty acids to primary and secondary oxidation products such as free fatty acids, hydroperoxides, polymers with a high molecular weight, and water. Biolipids that contain more free fatty acids or higher water content have lower flash points.

3 DENSITY

Density is the measure of the mass per unit volume, which is expressed in gram per cubic centimeter (g/cc). Fuel density generally increases with increasing molecular weight of the fuel molecules. Fig 3 shows density of diesel, Palm oil biodiesel and different blends. Density of Palm biodiesel is 0.804 g/cc where as diesel has specific density of 0.814 g/cc. Due to higher density of Palm oil biodiesel, specific fuel consumption will be less than diesel but due to lower calorific value net effect is increase in specific fuel consumption. The increase in density was caused by the formation of oxidation products, including insoluble sediments. The increase in density of palm biodiesel was more which can be explained as the presence of saturated fatty acid percentages in the fuel. Since the fuels containing shorter chain hydrocarbon and more saturated fatty acid have more prone to be crystallized. thus, cause of reduction of its volume and consequently increased the density. Simultaneously the mass of the fuel is increased as the consequence of oxidation products as well. Increases in density of palm biodiesel and its blends by 2.3% in B20, 2.7% in B50 and 2.9% in B75.

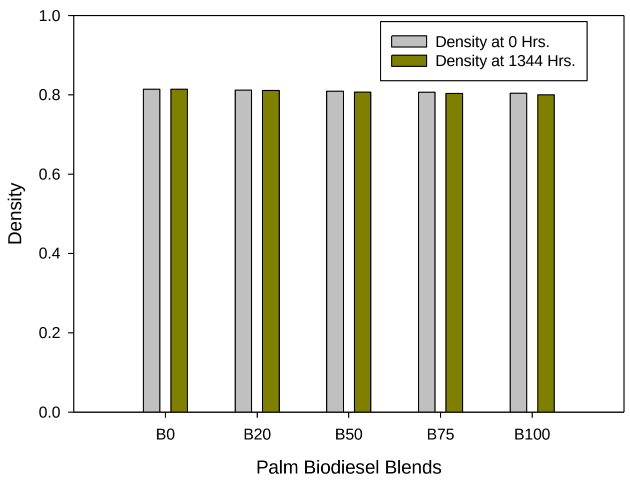

Fig. 3. Comparison of the Density of palm biodiesel and its various blends at 1344h storage times

4 Kinematic 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. 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

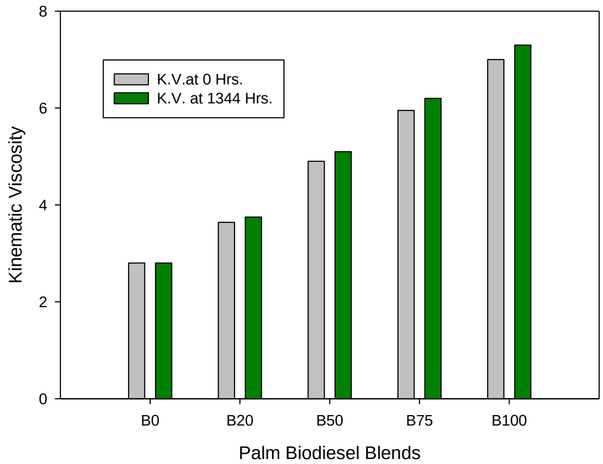

Fig. 4. Comparison of the Kinematic Viscosity of palm biodiesel and its various blends at 1344h storage times

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.[5] fig.4. shows the changes in viscosity with storage time, It can be seen that the viscosity of Palm biodiesel and its blends increases from 7 cst to 7.2 cst after a storage time of 1344 h. The viscosity of other samples of palm biodiesel and its blends also increases; the only difference was the rate of the increase. in B20 rate is 1.2% in B50,B75 rate of the increase is 2.3% 2.6% respectively. The increasing trend in viscosity was due to the effect of oxidation. 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). Approximately similar results have been previously observed by other researchers as it has been noted that the oxidation process leads to the formation of free fatty acids, saturation and the production of higher molecular weight molecules, and that viscosity increases with increasing oxidation with a longer storage period.

IV. Conclusions

Paragraph The following conclusions can be drawn from the present study. 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.

During the storage period of 1344h, 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.

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 palm biodiesel was noticeable.

From these results, it can also be concluded that palm biodiesel and its blends had the highest potential to prevent oxidation by retaining the properties of the fuel during storage period, 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.

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