Applied Mechanics and Materials Vols. 465-466 (2014) pp 316-321
© (2014) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMM.465-466.316

Effect of storage temperature and storage duration on Biodiesel properties and characteristics

Hanis Zakaria[1,a], Amir Khalid[1,b], Mohamad Farid Sies[1,c], Norrizal Mustaffa[1,d], B. Manshoor[1]

[1]UniversitiTun Hussein Onn Malaysia, Parit Raja, 86400 BatuPahat, Johor, Malaysia
[a]hanisz@uthm.edu.my,[b]amirk@uthm.edu.my

Keywords: Biodiesel, storage, Biodiesel properties, Crude Palm Oil, Viscosity

ABSTRACT

Biodiesel based on vegetable oils offer the advantage being a sustainable and environmentally attractive alternative to conventional petroleum based fuel. Biodiesel is produced from any fat or oil such as soybean oil, through a refinery process called transesterification. The key issue in using vegetable oil-based fuels is oxidation stability, stoichiometric point, bio-fuel composition, antioxidants on the degradation and much oxygen with comparing to diesel gas oil. Biodiesel can be used as a pure fuel or blended with petroleum in any percentage but the standard storage and handling procedures used for biodiesel are the main issue due to the biodiesel fuel specifications. In the quest for fulfill the industry specifications standard; the fuel should be stored in a clean, dry and dark environment. In this research, three different storage temperature were study which are; low (0 – 5 °C), ambient, and high (40 – 50 °C). The key parameters that are required to store biodiesel are discussed, and the recent research advances are noted. Five types of biodiesel after storage all the samples for 2016 hours were tested plus with two product of combustion. Images analysis for combustion process was used to image appearances analysis. Under 2016 hours of storage duration, the effect of degradation was happen although the effect is not significance because the changes are still in acceptable ranges.

Introduction

Biodiesel can be used as a pure fuel or blended with petroleum in any percentage but the standard storage and handling procedures used for biodiesel are the main issue due to the biodiesel fuel specifications. The fuel should be stored in a clean, dry, dark environment. Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751 or EN 14214) in order to insure proper performance. The key issue in using vegetable oil-based fuels is oxidation stability, stoichiometric point, bio-fuel composition, antioxidants on the degradation and much oxygen with comparing to diesel gas oil[1-3]. Some research was done by some researcher to study the effect of storage duration, storage temperature, storage material, and effect of antioxidant to biodiesel properties and biodiesel properties and characteristics.

Hydro-peroxide produced from the oxidative degradation undergo the complex secondary reactions further oxidize into acids, leading to an increase in acid value[1]. Increasing rate of acid value depends on storage duration [4-8]. Leung et al., acid value increases differently depending on storage temperature. High storage temperature will give higher result of acid value compared to low temperature[4]. Berrios et al. also found that acid value increases higher in high temperature of storage compared to low temperatue. Nonmetal storage may effect the increasing rate of acid value compared to metal storage [6]. Bouaid et al has done the research using different storage condition (expose and not expose to sunlight). Sunlight give higher increasing rate of acid value to biodiesel storage [5]. Shahabuddin et al. gets an increasingamount of acid value in his study. Diesel gives the lowest number of acid value. However, all studies show an increasing rate of acid with long duration of storage time [7]. The densities of biodiesels also increase with storage time. This increase was potentially due to the increase in molecular interaction of degraded biodiesels as peroxides were formed. C. Pattamaprom et al., density of biodiesel increase about 5g/m^3 after 6 months of low storage temperature. M. Shahabuddin et al. in a study has also found an increasing pattern of densities although it shows an increase in a small range [7]. 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. Many studies had found the kinematic viscosity will increase after certain storage duration. M. Berios et al. found that after 30 days, the viscosity of B100 sample higher than EN 14214 standards. Higher viscosity increase in low temperature storage compared to high temperature storage. Metal storage increases the rate of kinematic viscosity [6]. C. Pattamaprom et al. found that all sample remain unchanged in kinematic viscosity. This is due to storage condition with ambient temperature in dark area applied to all samples. A. Bouaid et al. found an increase in kinematic viscosity for all the samples except for a sample which showed an increase of water content [5]. A. Obadiah et al. found that biodiesel without antioxidant gave a significant increase in kinematic viscosity after 50 weeks. Thesample with antioxidant still maintain under control for kinematic viscosity. Antioxidant gives more stability to biodiesel to maintain its properties [1]. Water content in sample would make the kinematic maintain and decrease because the kinematic viscosity is measure of resistance of substance to flow.

Water can be present in two forms, either as dissolved water or as suspended water droplets. While biodiesel is generally considered to be insoluble in water, it actually takes up considerably more water than diesel fuel [9]. Leung, D Y C et al. has found that water content will only increase if the sample is stored in air exposure condition with high temperature. In this condition, water content increases about 30% within week 10 to week 50 of storage. In low temperature storage the result showed water contents almost unchanged in acid value even in air exposure condition. For sealed storage bottle, also showed that there is no increasing in water content [10]. A. Bouaid et al. found an increase of insoluble impurities in all sample. However, effect of light did not show any difference to the impurities of biodiesel [5]. Water content will increase more if the sample is exposing to the air. The flash point indicates the difference between a highly flammable, volatile and a relatively non-flammable non-volatile material[11]. 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 combustion chamber. Cherng-Yuan Lin and Chu-Chiang Chiu [12] has found that the flash point of storage biodiesel is higher for biodiesel storage which has antioxidant. The biodiesel with this storage condition showed a flash point of 187.1°C. This is higher than EN14214 standard which is 101°C. Meanwhile, biolipids contains more free fatty acids or higher water content [13] have lower flash points. However, other storage condition samples had shown a number of reductions in flash point depending on storage time. M. Shahabuddin et al. studies, showed that the flash point reduces depending on storage duration.

In this study, six ratio of biodiesel blended from crude palm oil (CPO) based were using for this research, B5, B10, B15, B25, B35 and B45. All of the sample were stored in a liter transparences glass bottles in three condition; low temperature 0°C–5°C, ambient temperature 26°C-32°C and high temperature 40°C-50°C. Sample were stored for 2016 hours and tested every week. Five types of properties testing were tested for this study; water content, density, kinematic viscosity, flash point and acid value. For these testing, European standard testing procedures were used.

Results and Discussions

Water Content

A storage container condition, which is glass bottle with transparent glass bottle give the maximum exposure of the entire sample to light or sunlight. Light will give the increasing rate of water content in biodiesel.Figure 1 illustrates that the highest rate of increasing number of water content is appear in high temperature of storage condition. Sample with high ratio of biodiesel also give the highest rate of increasing water content compared to highest rate of diesel content in the sample.High storage temperature show the significance of increasing of water content value compared to ambient and low temperature.The different for each B45 sample for each storage temperature in percentage of increasing were about 56 percent for low temperature, 89 percent for

ambient temperature and 139 percent for high storage temperature. It also shown that, sample with higher biodiesel ratio was more unstable compared to sample with lower ratio of biodiesel. Figure shows the highest rate of changes is B45 samples. The results suggest that biodiesel stored in high temperature is the main factors affecting the degradation rate in increasing the percentage of biodiesel.

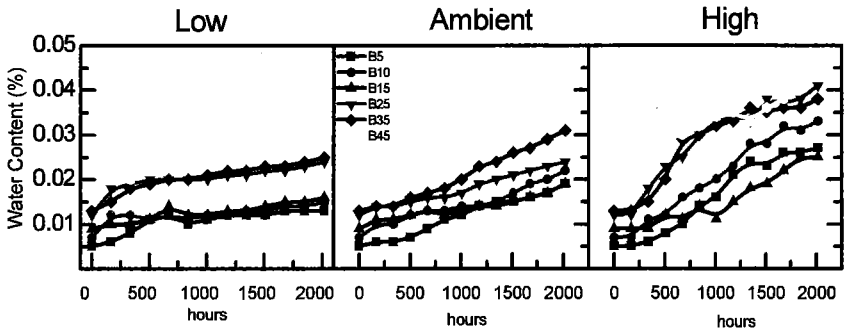

Figure 1: Water content of biodiesel

Density

Density is the measure of the mass per unit volume. Fuel density generally increases with increasing molecular weight of the fuel molecules.Trend of the changes of biodiesel fuel density for all blending ratio with different time duration are clearly shown in figure 2.As seen in figure, the increasing in density of B45 sample 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 crystalized 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. Comparing to all condition, high temperature storage condition give very high changes of values of density compared to others. However the increasing of value for density of biodiesel is not significance in short time of storage. The maximum change is about 0.025 kg/m^3.Increases in density of biodiesel which is important property as it affect the fuel injection equipment; especially at low temperature the fuel atomization characteristics become very poor due to the higher viscosity.

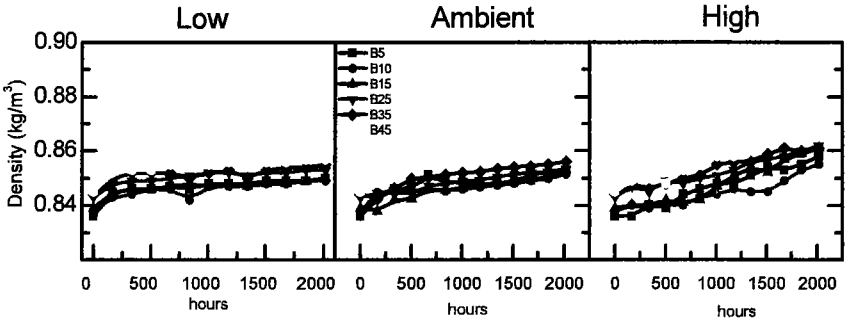

Figure 2: Density of biodiesel

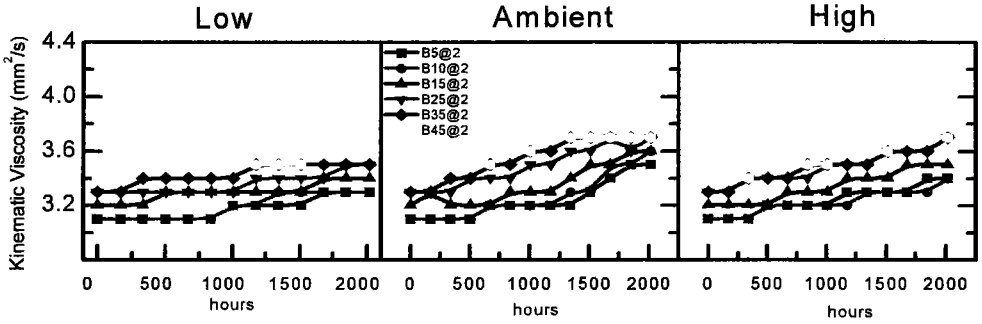

Figure 3: Kinematic viscosity of biodiesel

Kinematic Viscosity

Kinematic viscosity is the measure of resistance to flow. It is important due to the effect on the fuel injection system at low temperatures. As seen in figure 3, comparing the three condition of storage, low temperature storage gives more stability to kinematic viscosity of biodiesel.The graph for high storage temperature show slightly the increasing number of kinematic compared to others. Higher viscosity leads to lower atomization characteristics in the fuel injector, which leads to several severe effects on engine performance.Oxidation of methyl ester begins with build-up of peroxides; viscosity starts to increase only after the peroxides have reached a certain level.During storage, the viscosity of the methyl esters increases by the formation of more polar, oxygen containing molecules and also by the formation of oxidized polymeric compounds that can lead to the formation of gums and sediments that clog filters. Oxidation process leads to the formation of free fatty acids, double bond isomerization, saturation and the production of higher molecular weight molecules, and that viscosity increases with increasing oxidation with storage period.

Acid Value

The acid value is a measure of the amount of acidic substances in fuel. From the figure 4, it shown that generally higher temperature will give higher effect in acid value changes. The hydro-peroxide produced from the oxidative degradation can undergo the complex secondary reactions including a split into more reactive aldehydes, which further oxidize into acids, leading to an increase in acid value.Lowerstorage temperature will give the stability to the sample. The rate of changes for acid value in low storage condition is slower compared to high temperature. From all the conditions, high ratio of biodiesel in sample will lead to higher rate of increasing of acid value in the sample. Higher ratio of diesel gives stability to the sample. Diesel is more stable without oxidation process compared to biodiesel because of oxygen content in biodiesel. One of the causes in increasing of acid value is storage container material. Glass is transparent and directly expose to light or sunlight. Light or sunlight will give higher rate of increasing in acid value.Another reason for the increase in acid value is the hydrolysis of methyl ester by the reaction of moisture in the ambient air with methyl ester.

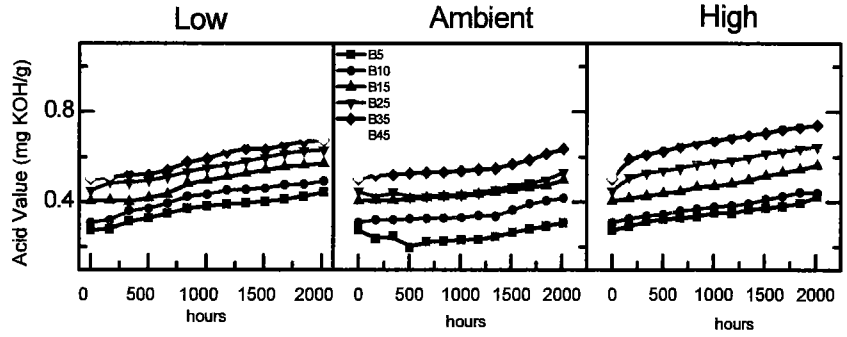

Figure 4: Acid value of biodiesel

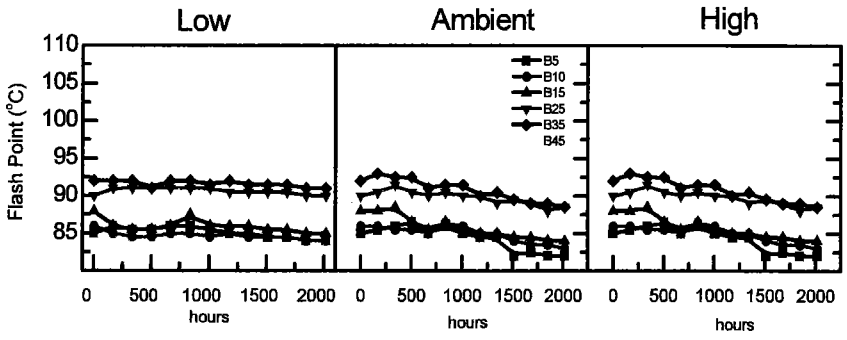

Figure 5: Flash point of biodiesel

Flash Point

The flash point is often used as a descriptive characteristic of liquidfuel, and it is also used to help characterize the fire hazards of liquids. It refers to bothflammable liquidsand combustible liquids. Flash point is important properties to fuel especially in term of handling. Figure 5 shown that low storage condition give the stability to biodiesel in term of flash point value especially for low ratio content of biodiesel. For B45 the value of flash point was decrease but is not very significance. Comparing to ambient and high storage temperature value of flash point show clearly that was decreasing for flash point especially for high storage temperature. Ambient and high storage temperature gives almost similar in decreasing of value for flash point. Under all conditions of storage show the decreasing of flash point value for each sample. Although, the value were still is safer fuel category.

Conclusion

From the study, oxidation process was happen to all sample of biodiesel. Although only five properties were tested in this study it represent the oxidation process to the biodiesel sample. The oxidation process for all samples is not significant and still only in the acceptable range when the storage duration is short. Low storage condition is the best storage condition for this study. It may cause of the storage condition for this temperature is in the refrigerator, that's mean the sample is not expose directly to light or sunlight to help to decrease of biodiesel degradation.

Acknowledgement

The authors would like to thank the Universiti Tun Hussein Onn Malaysia for supporting this research under short term grant (STG) vot 1000.

References

[1] A. Obadiah, R. Kannan, A. Ramasubbu, and S. V. Kumar, "Studies on The Effect of Antioxidants on the Long-Term Storage and Oxidation Stability of Pongamia Pinnata (L.) Pierre Biodiesel," Fuel Processing Technology, vol. 99, pp. 56–63, Jul. 2012.

[2] Amir Khalid, " Effect of Ambient Temperature and Oxygen Concentration on Ignition and Combustion Process of Diesel Spray". Asian Journal of Scientific Research, 2013. pp.1-11.

[3] Amir Khalid, Tomoaki Yatsufusa, Takayuki Miyamoto, Jun Kawakami, Yoshiyuki Kidoguchi, "Analysis of Relation between Mixture Formation during Ignition Delay Period and Burning Process in Diesel Combustion", Small Engine Technology Conference (SETC2009), SAE Technical Papers No. 2009-32-0018, 2009

[4] C. Pattamaprom, W. Pakdee, and S. Ngamjaroen, "Storage Degradation of Palm-Derived Biodiesels: Its Effects on Chemical Properties and Engine Performance," Renewable Energy, vol. 37, no. 1, pp. 412–418, Jan. 2012.

[5] A. Bouaid, M. Martinez, and J. Aracil, "Long Storage Stability of Biodiesel from Vegetable and Used Frying Oils," Fuel, vol. 86, no. 16, pp. 2596–2602, Nov. 2007.

[6] M. Berrios, M. a. Martín, A. F. Chica, and A. Martín, "Storage Effect in The Quality of Different Methyl Esters and Blends with Diesel," Fuel, vol. 91, no. 1, pp. 119–125, 2012.

[7] M. Shahabuddin, M. A. Kalam, H. H. Masjuki, M. M. K. Bhuiya, and M. Mofijur, "An Experimental Investigation into Biodiesel stability by Means of Oxidation and Property Determination," Energy, vol. 44, no. 1, pp. 616–622, Aug. 2012.

[8] Amir Khalid, Keisuke Hayashi, Yoshiyuki Kidoguchi, Tomoaki Yatsufusa, "Effect of Air Entrainment and Oxygen Concentration on Endothermic and Heat Recovery Process of Diesel Ignition", SAE Technical Papers. 2011-01-1834, 2011

[9] J. Van Gerpen, B. Shanks, R. Pruszko, and D. Clements, "Biodiesel Production Technology," 2004.

[10] D. Y. C. Leung, B. C. P. Koo, and Y. Guo, "Degradation of Biodiesel under Different Storage Conditions.," Bioresource technology, vol. 97, no. 2, pp. 250–6, Jan. 2005.

[11] P. Kumaran, N. Mazlini, I. Hussein, M. Nazrain, and M. Khairul, "Technical Feasibility Studies for Langkawi WCO (waste cooking oil) Derived-Biodiesel," Energy, vol. 36, no. 3, pp. 1386–1393, Mar. 2011.

[12] C.-Y. Lin and C. C. Chiu, "Burning Characteristics of Palm-Oil Biodiesel under Long-Term Storage Conditions," Energy Conversion and Management, vol. 51, no. 7, pp. 1464–1467, Jul. 2010.

[13] D. Özçimen and F. Karaosmanoğlu, "Production and Characterization of Bio-oil and Biochar from Rapeseed Cake," Renewable Energy, vol. 29, no. 5, pp. 779–787, Apr. 2004.