Experiment on the Effects of Storage Duration of Biodiesel produced from Crude Palm Oil, Waste Cooking oil and Jatropha

Nadiarulah Nanihar1,a, Amir Khalid1,2,b, Norrizal Mustaffa1, Norrizam Jaat2, Azwan Sapiti2, Azahari Razali2, Norshuhaila Mohamed Sunar3

1Automotive and Combustion Synergies Technology Group, Advanced Technology Centre (ATC), Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat 86400 Johor, Malaysia.
2Centre for Energy and Industrial Environment Studies (CEIES), Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, 86400 Johor, Malaysia.
3Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia.

*Corresponding E-mail: nmucuhammadnadiarulah@gmail.coma, amirk@uthm.edu.comb

Abstract. Biodiesel based on vegetable oil is an alternative that had various advantage in term of sustainability and environmental attractive compare to others conventional diesel. Biodiesel is product of any fat or oil that derived from any organic sources through a refinery process called transesterification process. This research investigates the effects of storage duration and variant ambient condition on the biodiesel properties and characteristics. In this study, there are three types of blending which is 5vol% blends (5vol% plant oil 95vol% diesel), 10vol% blending (10vol% plant oil and 90vol% diesel) and 15vol% blending (15vol% plant oil and 85vol% diesel) each called CPO5 (crude palm oil 5vol%), CPO10 (crude palm oil 10vol%), CPO15 (crude palm oil 15vol%), JO5 (jatropha oil 5vol%), JO10 (jatropha oil 10vol%), and JO15 (jatropha oil 15vol%) respectively. Biodiesel samples were stored at indoor condition and outdoor condition for a 3 months period. The fuel properties such as acid value, viscosity, density, water content and flash point are observed with the laboratory instrument. Flash point value and water content increased under both of indoor and outdoor condition and a steady data for viscosity and density. However, acid value at indoor condition nearly constant but increased dramatically for outdoor condition over the time.

1. Introduction
Alternative fuels, energy efficiency, energy conservation, environmental protection and management have become important due to depletion of fossil fuel and environmental degradation for last two decade. The alternative fuels or so called biodiesels, can be better used for diesel engine as compared to petrol engines because of the construction of the diesel engine is very robust and can work under high compression ratio along with a significant amount of excess air [1-5]. It 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 specification for this type of file must strictly refer to (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 [2-6]. 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. Oxidative degradation undergo the complex secondary reactions further oxidize into acids, leading to an increase in acid value cause by the formation of hydrogen peroxide [2]. Increasing rate of acid value depends on storage duration [3–6]. High temperature of storage can cause the increasing value for the result [5]. 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 [2,7-8]. M. Shahabuddin et al stated that acid value, density and viscosity is increasing throughout the time [3]. A. Obadiah et al. found that biodiesel without antioxidant gave a significant increase in kinematic viscosity after 50 weeks. The sample with antioxidant still maintain under control for kinematic viscosity. Antioxidant gives more stability to biodiesel to maintain its properties [9-10]. Water content in sample would make the kinematic maintain and decrease because the kinematic viscosity is measure of resistance of substance to flow. The comparison of diesel and biodiesel is described as Table 1.

Table 1: The Comparison of Standards For Diesel And Biodiesel Based On American Society For Testing And Material (ASTM) [11].

| Fuel Property                | Diesel ASTM D975 | Biodiesel ASTM D6751 |
|------------------------------|------------------|----------------------|
| Lower Heating value, BTU/gal | 129,050          | 118,170              |
| Kinematic viscosity @ 40°C, cSt | 1.3-1.4          | 4.0-6.0              |
| Specific gravity @ 60°C, g/cm³ | 0.85             | .88                  |
| Carbon, wt%                  | 87               | 77                   |
| Hydrogen, wt%                | 13               | 12                   |
| Oxygen, by dif. wt%          | 0                | 11                   |
| Sulfur, ppm                  | 500              | 0                    |
| Boiling Point, °C            | 180 to 340       | 315 to 350           |
| Flash point, °C              | 60 to 80         | 100 to 170           |
| Cloud point, °C              | ~15 to 5         | ~3 to 12             |
| Pour point, °C               | ~35 to ~15       | ~15 to 10            |
| Cetane number                | 40-55            | 48-65                |
| Lubricity (HFRR), µm         | 300-600          | <300                 |

In this study, six ratio of biodiesel blended from crude palm oil (CPO) based were using for this research, CPO5 (crude palm oil 5vol%), CPO10 (crude palm oil 10vol%), CPO15 (crude palm oil 15vol%), JO5 (jatropha oil 5vol%), JO10 (jatropha oil 10vol%), and JO15 (jatropha oil 15vol%) respectively. All of the samples of one liter were stored in transparence glass bottles under two condition; indoor condition (22-24°C) and outdoor condition (28-30°C). Sample were stored for 1960 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.

In this study, biodiesel is be produced by using jatropha oil, was involve a number of processes including titration process, transesterification, and investigate the physical properties of biodiesel. First, the titration was run to determine the content of FFA in the JO. If the value is higher FFA content, JO then must go through to reduce the amount of FFA esterification under 2%. If the FFA content of less than 2%, it will involve this transesterification process.
Biodiesel is fuels that can be compose from mono-alkyl esters of long chain fatty acids originates from plant or animals that will need to fulfil requirement of ASTM D6751 fuel specification. The advantages of using extraction biodiesel is it can use either co-products or by-products [8]. Biodiesel is very environmental friendly and non-toxic. If compare with petroleum based diesel, biodiesel is the best in term of combustion emissions. It capable to reduce the emissions of carbon monoxide, particulate matter and unburned hydrocarbons [9]. Carbon dioxide produced form biodiesel can recycled by photosynthesis and will minimize the effects of greenhouse effects [10]. Table 2 shows the fuel properties of jatropha oil, jatropha biodiesel, and diesel. Jatropha (Jatropha carcass) is one of such non-edible oils, which has an estimated annual production potential of 200 thousand metric tons in India and it can be grown in waste land [12]. The oil content for jatropha kernel is 63.16% [13] and higher linseed, soybean, and palm kernel which is 33.33%, 18.35% and 44.6%, respectively [14]. Hence jatropha will be the perfect biodiesel because it more economical in term of oil contains. Table below will show the fuel properties of jatropha oil, jatropha biodiesel, and diesel; Table below will show the fuel properties of jatropha oil, jatropha biodiesel, and diesel [15-16].

### Table 2: The fuel properties of jatropha oil, jatropha biodiesel, and diesel [12].

| No | Fuel Blended | Density (Kg/m³) | CV (kJ/kg) | Viscosity @ 40 °C (cSt) | Flash Point (°C) |
|----|--------------|----------------|-----------|------------------------|-----------------|
| 1  | Diesel       | 850            | 44000     | 2.87                   | 76              |
| 2  | JO20         | 852            | 43759.5   | 3.02                   | 88              |
| 3  | JO50         | 857            | 42673     | 3.59                   | 113             |
| 4  | JO100        | 873            | 43690     | 4.23                   | 148             |
|    | Testing Procedure | ASTM D4052 | ASTM D240 | ASTM D445 | ASTM D93 |

#### 2. Storage Method and Parameter

Biodiesel samples were stored in glass containers under room temperature condition, and ambient temperature condition for 10 weeks in total. These samples were monitored on a weekly basis through the test properties. The tested parameter is acid value, viscosity, density, water content and flash point. This process was be done at a certain temperature and mixing them to produce biodiesel in the presence of methanol and base catalyst. Physical characteristics have been considered including acid value, viscosity, density, water content, and flash point. In this study there are 4 samples are taken which is 5% blends of jatropha oil (JO 5), 10% blends of jatropha oil (JO 10), 15% blends of jatropha (JO 15). A block diagram of blending process and schematic diagram were shown in Figure 1. The purified jatropha oil methyl ester was blended with commercial diesel. The mixer was scale at 60°C and the mixture was stirred at 70°C for 1 hour. The blade speed was maintained at 270 rpm.

![Figure 1: The Schematic Diagram of Blending Process](image-url)
According to this study, the objectives were to determine the density, viscosity, acid value, water content and flash point of biodiesel blend stored at different storage container material and period. Figure 2 shows the flowchart of the process involved in this study.

3. Procedure of Properties Test
All of the samples is kept on two different conditions, first is inside a cupboard, and another is on a field. Then the sample is undergo five monthly properties test, which is density, viscosity, water content, acid value and lastly flash point test. Density is an important property which influences the overall standard of a biodiesel. The density of biodiesel blend was measured according to, EN ISO 3675 European Standard. By taking approximately 30 ml of sample it was poured into a beaker and left to cool down to 15°C inside a refrigerator. The measured weight of an empty 10.104 ml pycnometer by using a weighing machine and level the weight indicator. The cooled sample was poured into the pycnometer until it was completely filled it. The pycnometer was measured again on a weighing machine and the weight shown this time would be the weight of the sample inside the pycnometer. Viscosity is an important property which indicates the ability of a material to flow. For the viscosity test, EN ISO 3104 European Standard was followed. The sample needed to be heated up to the temperature of 40°C. Heated sample was then poured into a graduated cylinder. A solid stainless steel sensor of the viscometer (Viscolite 700) was then immersed into the sample. The sample level had to be higher than the line on the sensor and the side of the viscometer sensor must not be touching with the graduated cylinder. The reading of the viscometer result was in centipoises (cPs). The left-over of sample on the solid stainless steel sensor was
wiped cleanly after used. The acid value analysis was based on the titration process of the sample through the use of sodium hydroxide, phenolphthalein and biodiesel sample. In the process of preparing the alkaline reagent, sodium hydroxide (NaOH) 0.1M, 2 g of sodium hydroxide (NaOH) in powder or pellets form were mixed with 500 ml of distilled water inside a volumetric flask.

The alkaline mixture was mixed well by shaking the flask thoroughly. The mixture was poured into a burette until it was fully filled. In order to ensure no bubble was trapped inside the burette, few drop of solution was titrated out until the bubble was gone. For the acid value test, EN 14104 European Standard was followed. The sample was heated up to around 60 – 70 °C. By taking 4 g of the heated sample was mixed with 50 ml of 2-propanol inside a conical flask. The mixture was heated up again to 40°C and then 5-7 drops of phenolphthalein is added in. It was titrated with the sodium hydroxide mixture until the first pink colour appeared and lasted for around 30 seconds. Water content test, EN ISO 12937: 2000 European Standard was followed. Coulometric Karl Fischer Titrators. It was suitable for small water volumes such as biodiesel blend in ppm unit. A syringe was used to draw approximately 5 ml of biodiesel sample and was weighted by using a weighing machine. The weighing machine was then levelled. The start button on the machine was pressed. The sample was injected into the machine solution through the inlet until a keypad screen appeared at the monitor. It was important that the sample is injected slowly so that no excess sample was injected. Then, the remaining sample in the syringe was weighted again. The weight appeared was the amount of sample injected and was inserted into the machine through the keypad appeared. The result of total water content in the sample was shown in a few seconds. Flash point is a parameter of practical importance because as the flash point increases, the higher is the safety level during handling, transportation and storage. For flash point test, EN ISO 2719: 2002 European Standard was followed. By taking approximately 60 ml of sample was poured into the brass cup until the inner line had reached. Every a part of the flash point tester was assembled back carefully and the estimation of boiling point of the sample was inserted into the machine which is around 80°C. The machine was switched on and the sample was heated up. The overall process was comprised of heating and cooling down of the sample. The duration of the overall process was done in 20 minutes.

4. Results and Discussions

Effect of the storage duration of biodiesel blending ratio from jatropha oil (JO) under room temperature was investigated at the base STD for biodiesel JO 5, JO 10 and JO 15 respectively. In this study, there are three types of blending which is 5vol% blends ( 5vol% plant oil 95vol% diesel), 10vol% blending (10vol% plant oil and 90vol% diesel) and 15vol% blending (15vol% plant oil and 85vol% diesel) each called CPO5 (crude palm oil 5vol%), CPO10 (crude palm oil 10vol%), CPO15 (crude palm oil 15vol%), JO5 (jatropha oil 5vol%), JO10 (jatropha oil 10vol%), and JO15 (jatropha oil 15vol%) respectively. The average storage temperature for room temperature and outdoor temperature are 24°C and 33°C, respectively.

Figure 3 and Figure 4 illustrates us the changes of physical properties such acid value, viscosity, density and water content for jatropha oil and crude palm oil on different storage condition under room condition and outdoor condition. Overall the graph for JO trends gives the highest result then followed by CPO and standard diesel. For flash point the Crude Palm Oil Biodiesel (CPO) and Standard Diesel showing a steady trend but increasing trend for all of JO 5, JO 10 and JO 15. The highest peak for JO which is store under indoor condition is almost 150°C but for the outdoor condition the value is below 140°C and also the water content increases higher than indoor condition. The peak of the data is at 2190 hours for JO 15 which is 4.4 cTs if we ignore the first data and the lowest is for CPO 10 at 3.0 cTs
Figure 3: Effect of flash point, water content for storage Duration (a) Storage Duration under Indoor Condition. (b) Storage Duration on Outdoor Condition.

Figure 4: Effect of acid value, viscosity and density for storage Duration (a) Indoor Condition. (b) Outdoor Condition.

The result for density is almost same over the time. The higher of the blending ratio biodiesel influences the higher the density. The maximum value is at 880g/cm³ for JO 15 and the lowest is for CPO 10 along 840g/cm³. For the viscosity graph outdoor condition give a surprising result. The JO viscosity decrease
throughout the time. The sample JO 10 and JO 15 might stabilize throughout the time. For acid value
testing, outdoor condition give us a significant increase for the entire sample. The highest value given
by the JO 15 at 0.7 mgKOH/g and the lowest is JO5, 0.2 mgKOH/g. The increasing of acid value was
cause by hydrolysis process of methyl ester that induces by the sunlight.

Conclusions
In this research, there are three types of blending which is 5vol% blends (5vol% plant oil 95vol% diesel),
10vol% blending (10vol% plant oil and 90vol% diesel) and 15vol% blending (15vol% plant oil and
85vol% diesel) each called CPO5 (crude palm oil 5vol%), CPO10 (crude palm oil 10vol%),CPO15
(crude palm oil 15vol%), JO5 (jatropha oil 5vol%), JO10 (jatropha oil 10vol%) and JO15 (jatropha oil
15vol%) storage at indoor condition and outdoor condition. The summary as follows:
1. It seems that the small changes in the physical properties of biodiesel when stored at ambient
temperature or low temperature. Biodiesel storage at room temperatures is suitable and more
advantageous because the impact on the physical properties is minimal and beneficial of slow
down the degradation of biodiesel and storage.
2. Indoor storage conditions which are less susceptible to delayed break light chain fatty acids. The
physical properties majorly affected by the blending ratio and type of derivation used.

Acknowledgements
The authors also would like to thank the Universiti Tun Hussein Onn Malaysia for the Ministry of Higher
Education, Malaysia for supporting this research under COE-MTUN Grant Scheme VOT.C009.

References
[1] Khalid, A., Yatsufusa, T., Miyamoto, T., Kawakami, J., Kidoguchi, Y., “Analysis of relation
between mixture formation during ignition delay period and burning process in diesel combustion”,
SAE Technical Papers, 2009, SAE International.
[2] 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
Process. Technol., vol. 99, pp. 56–63, 2012.
[3] 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, 2012.
[4] 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.
[5] C. Pattamaprom, W. Pakdee, and S. Ngamjaroen, “Storage degradation of palm-derived biodiesels:
Its effects on chemical properties and engine performance,” Renew. Energy, vol. 37, no. 1, pp. 412–
418, 2012.
[6] L. Natalie, “Study of hydrogenation derived renewable diesel as a renewable fuel option in North
America,” pp. 1–78, 2012.
[7] C. Y. Lin, H. A. Lin, and L. B. Hung, “Fuel structure and properties of biodiesel produced by the
peroxidation process,” Fuel, vol. 85, no. 12–13, pp. 1743–1749, 2006.
[8] S. M. Hafis, M. J. M. Ridzuan, R. N. Farahana, A. Ayob, and S. Syahrullail, “Paraffinic mineral oil
lubrication for cold forward extrusion: Effect of lubricant quantity and friction,” Tribol. Int., vol.
60, pp. 111–115, 2013.

[10] Khalid, A., Anuar, M.D., Ishak, Y., Manshoor, B., Sapit, A., Leman, M., Zaman, I., “Emissions characteristics of small diesel engine fuelled by waste cooking oil”, MATEC Web of Conferences, Volume 13, 2014, Article number 06006, 2014, DOI: 10.1051/matecconf/20141306006

[11] N. Kaushik, K. Kumar, S. Kumar, N. Kaushik, and S. Roy, “Genetic variability and divergence studies in seed traits and oil content of Jatropha (Jatropha curcas L.) accessions,” Biomass and Bioenergy, vol. 31, no. 7, pp. 497–502, 2007.

[12] E. Akbar, Z. Yaakob, S. K. Kamarudin, M. Ismail, and J. Salimon, “Characteristic and Composition of Jatropha Curcas Oil Seed from Malaysia and its Potential as Biodiesel Feedstock Feedstock,” Eur. J. Sci. Res., vol. 29, no. 3, pp. 396–403, 2009.

[13] M. H. Gordon, Chemistry of oils and fats – sources, composition, properties and uses, vol. 94, 2006.

[14] P. K. Sahoo and L. M. Das, “Combustion analysis of Jatropha, Karanja and Polanga based biodiesel as fuel in a diesel engine,” Fuel, vol. 88, no. 6, pp. 994–999, 2009.

[15] Khalid, A., Azman, N., Zakaria, H., Manshoor, B., Zaman, I., Sapit, A., & Leman, A. M. (2014). Effects of storage duration on biodiesel properties derived from waste cooking oil. doi:10.4028/www.scientific.net/AMM.554.494

[16] Khalid, A., Tamaldin, N., Jaat, M., Ali, M. F. M., Manshoor, B., & Zaman, I. (2013). Impacts of biodiesel storage duration on fuel properties and emissions. Paper presented at the Procedia Engineering, 68 225-230. doi:10.1016/j.proeng.2013.12.172