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Study of the Effect of Storage Time on the Oxidation and Thermal Stability of Various Biodiesels and Their Blends

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ABSTRACT: Biodiesel can be described as a safe alternative fuel, which can replace petroleum diesel in the future. It consists of long-chain fatty acid methyl esters (FAME). Biodiesel has high lubricity and is a clean burning fuel. It also produces less air pollution, is renewable biodegradable, and is safer for the environment. Since biodiesel is produced from vegetable oil, animal fats, used cooking oil, and so forth, which may contain more or less unsaturated fatty acids that are prone to oxidation accelerated by exposure to air during storage and at high temperature, it may yield polymerized compounds. The oxidation and thermal stability of the fuel changes with storage time due to the formation of oxidation. Therefore, the aim of this study to evaluate the stabilities of biodiesel according to measured fuel properties, such as density, viscosity, flash point, total acid number (TAN), and total base number (TBN), by using various methodologies. In addition, oxidation stability of the samples was measured by the induction period using a Rancimat instrument. In this experiment, palm oil methyl ester (PME), palm biodiesel blend (40% PME and 60% diesel fuel), jatropha methyl ester (JME), jatropha biodiesel blend (40% JME and 60% diesel fuel), coconut oil methyl ester (COME), and conventional diesel fuel were used. Experiments were carried out at intervals over a 12-week test period. The experimental results for JME and PME showed similar performance in terms of flash point. All samples met the standard specification of the American Society for Testing and Materials (ASTM) D6751 (3 h) regarding the induction period, except for JME and its biodiesel blend, which did not meet the EN 14214 (6 h) standard specification. Among the fuel samples giving the worst results for TBN value due to oxidation, overall, among the biodiesels, PME and COME were found to give better results with respect to oxidation and storage stabilities.

1. INTRODUCTION

Biodiesel is an alternative fuel source which is produced by using simple chemical processes on waste vegetable oils or fat oils. It can be used in a diesel engine without needing any engine modification. It is also known as a green fuel because the advantages include renewability and the reduction of most regulated exhaust emissions (it does not contribute to carbon dioxide (CO_2) emissions).[1] Biodiesel is safer for both the air and water. In its pure form, it is nontoxic and biodegradable, which is especially important in sensitive or protected waterway areas. It is also free from sulfur and aromatics, which reduces harmful emissions. When added to petroleum diesel, it makes fuel burn more cleanly.[2] However, biodiesel has the prominent technical problems of oxidation and thermal and storage instability.[3] Biodiesel is produced using the transesterification process. This process involves a reaction between triglycerides with an alcohol in the presence of base-catalyzed.[4] Short-chain alcohols, such as methanol and ethanol, can be used in the transesterification process. Based on lower-cost and faster-reacting characteristics, methanol is typically preferred. Alkyl ester and glycerol are the primary products of the reaction. Oxidative stability is defined as the ability of biodiesel to resist oxidization when exposed to factors such as air, water, and certain metals. Normally during long-term storage, biodiesel is more sensitive to oxidation than petroleum derivate diesel. The oxidation stability of biodiesel normally depends on the fatty acid profile of the parent feedstock. Thus, biodiesel that consists of high concentrations of unsaturated fatty acids, such as linoleic and linolenic, will tend to oxidize.[5] Oxidation stability is an important parameter that generally describes the degradation of biodiesel and is quite familiar in the context of problems with engine parts.[6] Peroxides and hydroperoxides are the main products of the oxidation process. The products produced from degradation normally have shorter-chain compounds, such as low molecular weight acids, aldehydes, ketones, and alcohols.[7] The presence of alcohols and acids will decrease the flash point and increase total acidity and the risk of corrosion. In addition, high molecular weight materials are formed through reactions of unstable hydroperoxide species with another fatty acid chain.

Thermal stability can be described as the ability of biodiesel to resist breakdown or change in the chemical structure if exposed to heat over a long period of time. The overall stability of biodiesel will be reduced when it is exposed to UV irradiation, high temperature, and the presence of metal traces (contaminants). Therefore, it will affect quality and, hence, marketability. During oxidative degradation, biodiesel parameters, such as kinematic viscosity, cetane number, and acid value, are affected.[8] Temperature had a significant effect during oxidation degradation. When biodiesel is exposed to high temperature conditions, thermal stability involves the measurement of the tendency of a fuel to produce asphaltenes.[9]

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2. MECHANISM OF OXIDATION AND THERMAL STABILITY

The oxidation mechanism of fatty acid methyl ester (FAME) is generally well understood. Basically, a fatty acid alkyl chain consists of a varying number of double bonds. The number of double bonds and position on the chain affects the rate of oxidation of the fatty acid alkyl. The primary products of oxidation are unstable allylic hydro peroxides, which easily form secondary oxidation products. Initiation, propagation and termination are involved in the primary oxidation.[10] Figure 1

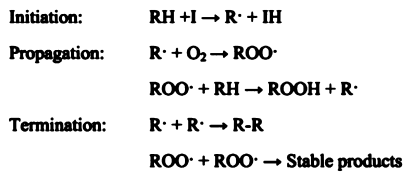

Figure 1. Primary oxidation reaction.[12]

shows that produced carbon-free radical hydrogen is removed from the carbon atom. If diatomic oxygen is present in that reaction, a subsequent reaction takes place extremely quickly from the peroxy radical, even preventing significant alternatives for the carbon-based free radical.[11] Peroxy-free radicals are not reactive compared to carbon-free radicals but are sufficiently reactive to abstract hydrogen from a carbon to from hydroperoxide (ROOH) and another carbon-free radical. The new form of the carbon-free radical reacts with the diatomic oxygen to continue the propagation cycle. This reaction is terminated when both free radicals react with each other to yield stable products. The ROOH concentration remains very low during the initial period of oxidation. The end of this period can be determined by the oxidation stability of the biodiesel under stressed conditions. The ROOH induction period can also change other properties of biodiesel fuels in a similar way.

Thermal oxidation is the oxidation reaction rate which increases the oil and fat weight when exposure to cooking temperature (high temperature) conditions.[8,13−15] Due to higher temperature conditions, the methylene obstruct poly-unsaturated olefin structure initiates the isomerize structure. This isomerization forms a cyclohexene ring, conjugated with the diene group, from one fatty acid chain to a single olefin group from another fatty acid chain.[10,16,17] This reaction is called a Diels−Alder reaction, and this reaction is important at temperatures of 250−300 °C or more. Products formed from this reaction are called dimers.[18,19] The Diels−Alder reaction is as shown in Figure 2. Aldehyde or high molecular weight polymers are the carbonyl compounds formed from the Alder reaction, which increases the biodiesel viscosity. The oil stability index (OSI) of biodiesel is affected by the temperature,

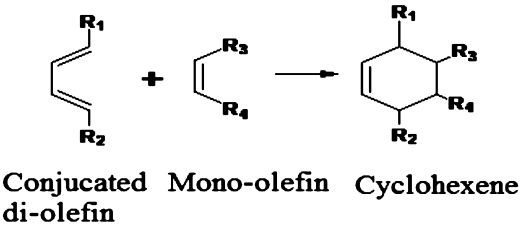

Figure 2. Diels−Alder reaction.[9]

the OSI of the FAME decreases and the oxidation reaction is accelerated when the temperature increases.[14] Many researchers have found that biodiesel stability is affected by temperature.[8,15,20]

3. EFFECT OF OXIDATION AND THERMAL INSTABILITY ON BIODIESEL PROPERTIES

3.1. Density. Density is the measure of the mass per unit volume, which is expressed in kilograms per cubic meter (kg/m^3). The molecular weight of biodiesel is one of the factors that contributes to increasing its density.[21] The stability of biodiesel blends would decrease with increases in the biodiesel content.[22] The density of biodiesel blends slightly changes since the density of methanol and oil are close to the density of the produced biodiesel blends.[23] The density of the biodiesel is also influenced by the temperature effect.[24]

3.2. Viscosity. Viscosity is another property of fuel that needs to be considered in order to maintain engine performance. It is defined as the resistance of fuel to flow and the strength of the oil film between the surfaces. Higher viscosity will cause a poor fuel flow into the engine during the intake stroke, and it will also take a long time for that fuel to mix with air, therefore delaying combustion.[25] The viscosity of a fuel is important in determining the operating temperature as the fuel flows into the engine from the fuel tank. In previous studies, it has been proved that the viscosity of fuel will decrease with an increase in the operating temperature.[26] The viscosity of the biodiesel also increases when the biodiesel is stored for a period at the same temperature.[3,6] In general, viscosity begins to increase when the formation of peroxides reaches a certain level, and the oxidized polymeric compounds can lead to the formation of gums and sediment.[6] The viscosity of biodiesel is less affected in the presence of antioxidant.[27]

3.3. Flash point. The flash point is defined as the lowest temperature at which liquid vaporizes to form an ignitable mixture in air. It is only one of a number of properties that must be considered in assessing the overall flammability hazard of a material. At this temperature, the vapor would stop burning if the source of the ignition is removed. Many factors contribute to the change in flash point of biodiesel. Each biodiesel has its own flash point. Residual alcohol content in biodiesel results in different values of the flash point.[28] The flash point of biodiesel is also influenced by the chemical properties of that biodiesel, that is, the number of double bonds and number of carbon atoms.[29]

3.4. Total Acid Number (TAN). TAN is defined as the mass of potassium hydroxide (KOH) (milligram) that is required to neutralize one gram of a chemical substance. It is also called the acid value or acidity number. Generally, the TAN describes the amount of acid in the oil. There are many factors that influence the value of TAN, such as the temperature, storage time, and so forth. The TAN of biodiesel will increase with the increase in storage time, and as a result, the oxidation stability of biodiesel will decrease.[9,22,30] This result depends on the biodiesel content, which means that the biodiesel consists of monoalkyl esters of long-chain fatty acids made from biolipids that tend to suffer from less oxidative stability.[30]

3.5. Total Base Number (TBN). The measurement of the capacity of engine fuel to neutralize strong acids from combustion fuel is called the TBN. It can also be described as the measurement of reserve alkaline additives in a lubricant in order to neutralize the acid to avoid oxidation and corrosion.

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Table 1. Standard Specification for Biodiesel Properties and Test Methods[1,3]

property	units	ASTM test method	ASTM-D6751	EN test method	EN-14214
density	kg/m^3	ASTM D341		EN ISO 3675	860−900
kinematic viscosity @40 °C	cSt	ASTM D445	1.9−6.0	EN ISO 3104	3.50−5.00
flash point	°C	ASTM D93	130 min	EN ISO 3679	120 min
total acid number (TAN)	mg KOH/g	ASTM D664	0.5 max	EN ISO 14104	0.5 max
total base number (TBN)	mg KOH/g	ASTM D2894		EN ISO 3771	

Table 2. Impact of Storage Time on Various Properties of Biodiesel

parameter	time of storage, (weeks)	palm methyl ester (PME)	palm biodiesel blend (PME 40)	jatropha Methyl ester (JME)	jatropha biodiesel blend (JME 40)	coconut methyl ester (COME)	diesel
density (kg/m^3)	1	864.9	793.9	870.2	808.7	875.0	767.3
	3	865.4	794.3	870.6	809.1	875.3	767.8
	6	866.2	795.2	871.3	809.9	876.1	768.5
	9	866.9	796.3	872.0	810.8	876.8	769.3
	12	868.1	797.3	873.1	811.8	877.6	770.3
viscosity @40 °C (cSt)	1	4.03	3.84	3.01	4.21	4.58	2.54
	3	4.12	3.95	3.15	4.33	4.74	2.63
	6	4.38	4.14	3.33	4.50	4.85	2.73
	9	4.45	4.32	3.49	4.71	4.92	2.84
	12	4.59	4.49	3.64	4.89	4.99	2.87
flash point (°C)	1	321	196	261	199	293	67
	3	315	191	258	196	290	64
	6	308	185	250	191	284	58
	9	300	176	242	183	278	56
	12	296	174	237	178	276	51
TAN (mg KOH/g)	1	1.03	3.17	1.01	1.97	1.25	0.59
	3	1.49	3.51	1.37	2.34	1.65	0.85
	6	1.91	4.11	1.79	2.81	2.15	1.17
	9	2.43	4.60	2.35	3.37	2.55	1.56
	12	3.01	5.13	2.84	3.76	3.11	1.93
TBN (mg KOH/g)	1	12.23	12.52	8.91	11.97	7.83	13.41
	3	12.19	12.39	8.85	11.89	7.81	13.32
	6	11.97	12.25	8.72	11.78	7.71	13.21
	9	11.74	12.11	8.61	11.65	7.63	13.07
	12	11.64	12.02	8.51	11.55	7.56	13.0
induction time (h)	1	19.56	15.31	3.67	2.78	17.78	24.76
	3	18.52	14.93	3.06	2.19	16.88	23.87
	6	17.34	13.76	2.12	1.24	16.06	22.98

In addition, it will also improve the lubricity and viscosity characteristics. In basic terms, tests that check its ability to neutralize corrosive acids were made during normal operation.[31] According to the formation of acidic products with regard to the oxidation of the biodiesel fuel, the TBN increases due to the instability of the biodiesel oxidation.[30] Therefore, the TBN will decrease as the oxidation stability of biodiesel decreases. The components of the engine, such as those around the piston ring pack, piston ring lands and the top the end bearing, tend to corrode due to using a lower base number fuel.[32]

3.6. Induction Period. The induction period can be defined as the length of time before the rapid acceleration of oxidation. It is the measure of resistance to oxidation. The induction period is also known as the oxidative stability index. Generally, every fuel has its own induction period. Based on several studies using the Rancimat test at various temperatures, the induction period is a linear function of the test temperature.[33−35] In order to avoid degradation, the biodiesel must be stored at a low temperature for a long storage time. During the storage time, the samples are easily oxidized and will cause a reduction in the induction period.[9]

4. METHODOLOGY

4.1. Sample Preparation. Three types of biodiesel, two types of biodiesel/diesel blend, and diesel fuel samples were analyzed in this study. Each sample has a different chemical composition and properties. The samples that were analyzed were palm methyl ester (PME), palm biodiesel blend (40% PME, 60% diesel), jatropha methyl ester (JME), jatropha biodiesel blend (40% JME and 60% diesel), coconut oil methyl ester (COME), and diesel (100% diesel). The fuel samples were stored at a room temperature of approximately 25 °C and relative humidity 65% in a 200 mL glass bottle and were tightened with a cap to ensure that the fuel samples were free from air contact. All samples were tested and analyzed by using different tests and experimental procedures. The experimental work was carried out every week throughout a 12-week test period in order to achieve the objective, which was to analyze the thermal and oxidation stability of biodiesel. All properties of biodiesel must follow the standards of the American Society for Testing and Materials (ASTM) and European standards (EN) for biodiesel. Table 1 refers to the ASTM and EN standard for each of the selected properties that will be analyzed in this study.

4.2. Density Determination. Fuel density was determined using a DM40 liquiphysics density meter based on standard ASTM D341. The 25 mL beaker was weighed using a digital microbalance. The 20 mL samples were poured into a 25 mL beaker by using a piston-driven air

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displacement pipet and then weighed using a digital microbalance. Thus, the mass of the samples can be calculated by this formula:

$$M = m_1 - m_2 \quad (1)$$

where M is mass of sample, m_1 is mass of beaker containing 20 mL sample, and m_2 is mass of empty beaker.

4.3. Viscosity Determination. An Anton Paar Stabinger viscometer (SVM 3000) was used to determine the viscosity of the biodiesel samples in this project based on standard ASTM D445. The mode viscosity index was chosen from this device to determine the kinematic viscosity at two different temperatures of the biodiesel.

4.4. Flash Point Determination. In this study, we used the NPM 440 Pensky–Martens flash point tester based on the standard ASTM D93 to determine the flash point of each sample.

4.5. Total Acid Number (TAN) and Total Base Number (TBN) Determination. An automation titration rondo 20 analyzer (Mettler Toledo, Switzerland) was used to determine the TAN of all the biodiesel blend samples based on standard ASTM D664. Operation of this device is controlled by a computer by using Metrohm TiNet software. All calculations were undertaken in that software, and all the results are shown on the computer. The TAN values of the prepared solvent, in the mixing ratio toluene 500 mL IPA and water 5 mL, were analyzed. Then, 5–10 g of the fuel sample were mixed with 125 mL of that solvent in a white beaker of the analyzer. Similarly, the TBN value was analyzed using the same instrument with 120 mL of solvent formed by the mixing of 80 mL chlorobenzene and 40 mL glacial acetic acid, which was then mixed with 5–10 g of the fuel sample.

4.6. Rancimat Method. In determining the oxidation stability of biodiesel, a 743 Rancimat was used. This device is controlled by a computer. The induction time or oil stability index (OSI) was determined using the 743 Rancimat instrument with an air flow rate of 10 L/h at a constant temperature of 110 °C. The Rancimat method is also called the automated Swift test or oxidation test.

5. RESULTS AND DISCUSSION

The properties of the biodiesel samples were determined continuously over a 12-week test period. The results of these analyses are provided in Table 2.

5.1. Investigation of Biodiesel Density. Figure 3 illustrates the density of diesel and several biodiesel blends

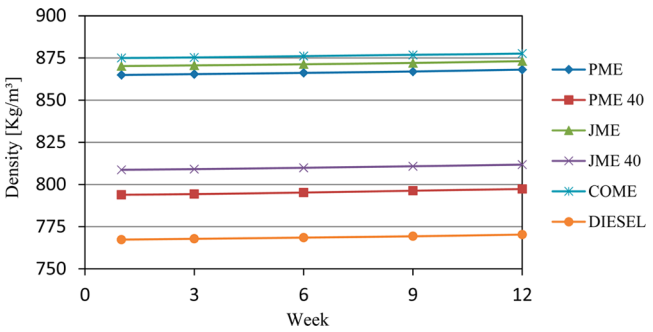

Figure 3. Density of different fuels for 12 weeks storage.

over the 12-week test period. Thus, it can clearly be seen that the density of all samples is directly proportional to storage time. However, the density of COME was significantly higher than the others. In addition, the increasing trend of the palm biodiesel blend was most noticeable whereas JME showed the least increment in density. The main cause of the increase in density of the fuel was oxidation and the presence of a percentage of fatty acid in the fuel. The factor that contributes to the increasing density was the thermal instability of the biodiesel, which, as the rate of oxidation increases, increases the mass of oil and fat due to the formation of insoluble sediments at the bottom of the bottle. Studies in the literature review have shown that the oxidation rate suddenly increases at higher temperatures. The residue due to oxidation stored at the bottom of the storage bottles was measured by the weight measurement method. Since, the density is directly proportional to mass, when the mass of fuel increases, then the density of the fuel also increases.[36]

5.2. Investigation of Biodiesel Viscosity. According to the experimental results for each sample, the graphs of kinematic viscosity against storage time at 40 °C, viscosity against storage time at 100 °C, and viscosity index against storage time are plotted in Figures 4, 5, and 6, respectively. The values of the viscosities were analyzed and can be measured in centistokes (cSt).

The kinematic viscosity of the fuel is closely related to the fuel flow, fuel spray and atomization in the combustion chamber. Lower atomization characteristics lead to several effects on engine performance due to the higher viscosity.[37] The line graphs demonstrate the changes in kinematic viscosity over the storage time at 40 °C. It can be seen that the viscosity of jatropha biodiesel blend significantly increased from 3.15 cSt to 3.64 cSt over the storage time of the 12-week test period, and the stability of the graph also means that the viscosity is steadily increasing. Even the palm biodiesel blend has a significant viscosity increment from 3.84 cSt to 4.49 cSt over the storage time compared with other samples. Moreover, the kinematic viscosity of the other fuels shows oxidation effects due to storage. Diesel fuel showed good characteristics in terms of viscosity and it has little effect on oxidation. The viscosity of diesel fuel was slightly increased (from 2.54 cSt to 2.87 cSt). Hence, it can be stated that diesel is a suitable fuel to be used in engines due to having the lowest viscosity compared to the other samples. Knothe et al.[26] also found similar results by analyzing different biodiesel viscosities at low temperature.

Based in Figure 5, the line graphs of all samples at a temperature of 100 °C over the storage time are mostly similar to the previous analysis at a temperature of 40 °C. The viscosities of all samples at 100 °C were directly proportional to the storage time, which means that the viscosity increased over the storage time. Observation of all the fuel sample trends clearly shows that palm oil biodiesel blend has the most incremental slope at about 0.0003. In contrast, other fuels, such as jatropha biodiesel, have an incremental slope of about 0.00027. Compared to the other samples, coconut oil methyl ester still has the highest viscosity value, while diesel has the lowest viscosity value. The viscosity of the biodiesel blends starts to increase only after the peroxides reach a certain level, which means the oxidation of the biodiesel blends occurs at this time. The formation of an oxidized polymeric was the main contributor to the increase in viscosity of the biodiesel during the storage time. It can also lead to the formation of gums and sediments that clog filters. Higher molecular weight species possess higher viscosity; for that reason, the viscosity specification in biodiesel blend standards can be used to assess the fuel quality status of stored biodiesel. Fuel viscosity must be low enough for the fuel to flow freely at its lowest operational temperature and yet high enough to provide lubrication to the moving parts of the finely machined injectors. Based on the previous discussion, it can be stated that viscosity is one of the properties that contributes to problems of using biodiesel blends in diesel engines. Higher viscosity affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel.[38]

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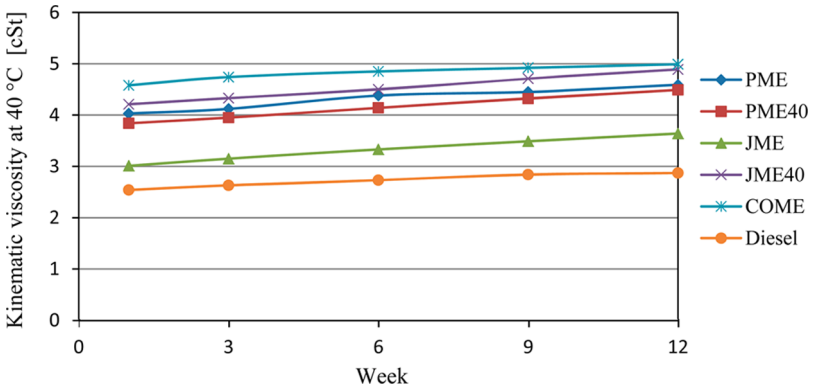

Figure 4. Kinematic viscosity at 40 °C of different fuels for 12 weeks storage.

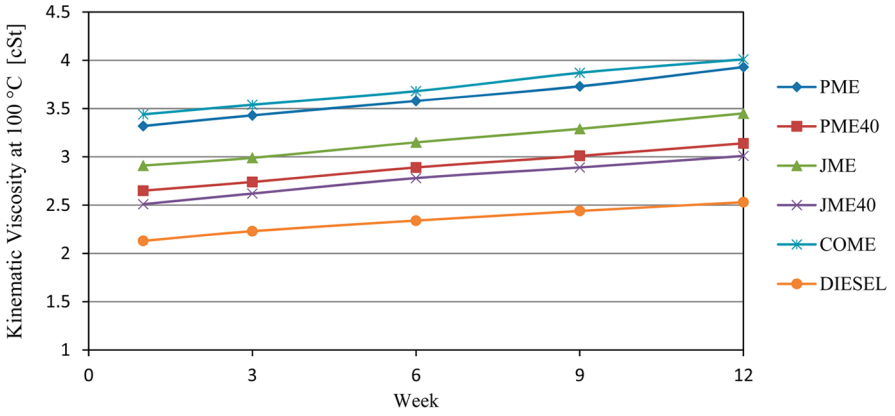

Figure 5. Kinematic viscosity at 100 °C of different fuels for 12 weeks storage.

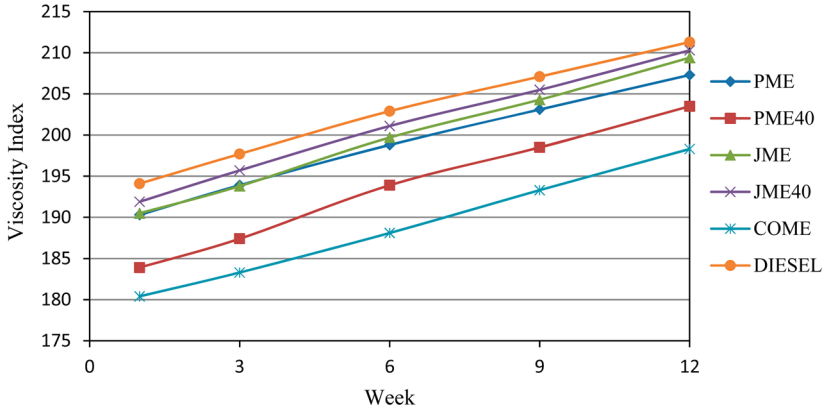

Figure 6. Viscosity index of different fuels for 12 weeks storage.

Moreover, high viscosity may lead to the formation of soot and engine deposits due to insufficient fuel atomization.

Figure 6 illustrates the viscosity index over the storage period. It can be seen that the viscosity index of all fuel samples has a positive value slope, which means that the relationship between the viscosity index and storage time is directly proportional. The viscosity index, commonly designated VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. A high viscosity index indicates small changes in oil viscosity with temperature. A low viscosity index indicates higher changes in oil viscosity with temperature. Therefore, a fluid that has a high viscosity index can be expected to undergo very little change in viscosity with temperature extremes and is considered to have a stable viscosity.

5.3. Investigation of Flash Point. Based on the data collected from the experiment for each sample, graphs of the flash point against storage time are plotted as shown in Figure 7.

The definition of flash point is the lowest temperature at which the fuel can vaporize to form an ignitable mixture in air under controlled laboratory conditions. In order to assess the overall flammability hazard of a material, the flash point must be taken into consideration.[38] The flash point, as in the scope of ASTM D93, is defined as a measure of the temperature to which a fuel must be heated such that a mixture of the vapor and air above the fuel is ignited. All conventional diesel fuels

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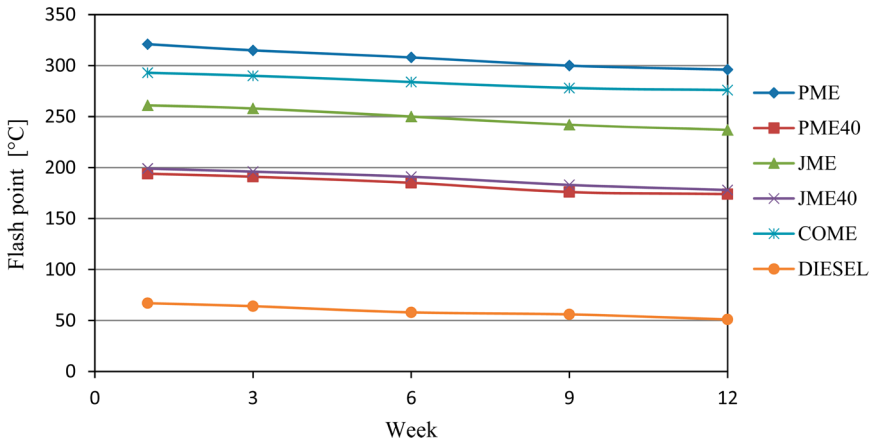

Figure 7. Flash point of different fuels for 12 weeks storage.

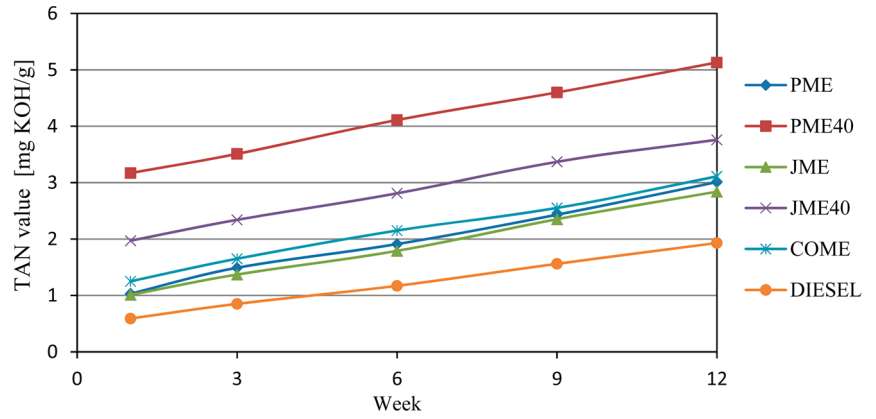

Figure 8. Total acid number (TAN) value of different fuels for 12 weeks storage.

have high flash points (54 °C minimum; 71 °C typical). The flash point of neat biodiesel is typically greater than 93 °C. The U.S. Department of Transportation considers a material with flash point of 93 °C or higher to be nonhazardous.[39] As can be seen in Figure 7, the pattern of the flash points of all the biodiesel samples slumped over the entire storage period. Thus, the relationship between the flash point of all samples and the storage time is inversely proportional. Among these fuel samples, the flash point decreased over the entire storage period; PME dropped by 29 °C (max. 325 °C; min 296 °C), followed by JME 24 °C (max 261 °C; min 237 °C), palm oil biodiesel 20 °C (max 196 °C; min 176 °C), jatropha biodiesel 19 °C (max 197 °C; min 178 °C), COME 17 °C (max 293 °C; min 276 °C), and diesel fuel 16 °C (max 67 °C; min 51 °C). It can be seen that these fuel sample flash points decreased and that the lowest value of the flash point is much higher than that of the standard limiting value. Conventional diesel fuel is the best sample to choose for engines in terms of flash point since it indicated the lowest flash point during the 12-week test period compared to the other samples. During the test period, the reduction in the flash point for the diesel sample was 16 °C from week 1 to week 12. The samples that have higher flash points are PME and JME. Based on the data, both samples have flash points exceeding 250 °C. Currently, in the new automotive sector era, most engine manufacturers have begun to realize and be concerned about the instability of the oxidation of some biodiesels that affect some properties, one of them being the flash point which reduces over the storage period due to the instability of biodiesel.

5.4. Investigation of total acid number (TAN). Experimental data of the TAN values for each sample over the storage time are plotted in the graph shown in Figure 8. The TAN values are measured in units of mg KOH/g.

Referring to Figure 8, it can be seen that palm biodiesel leads the results in term of TAN values followed by jatropha biodiesel, PME, JME, COME, and diesel, respectively. On the basis of the pattern of the graph for each sample, that is, the slope of the graph, which is positive, we can state that the relationship between the TAN values for each sample and the storage time is directly proportional. On the basis of the observation of the TAN values for the samples COME, PME, and JME, they are similar but are slightly different for each week of the test period. The minimum TAN value for the palm biodiesel blend was 3.17 mg KOH/g, following by Jatropha biodiesel blend at 1.97 mg KOH/g, COME at 1.25 mg KOH/g, PME at 1.03 mg KOH/g, JME at 1.01 mg KOH/g, and diesel at 0.59 mg KOH/g, respectively, in week one of the test period. The maximum TAN value of palm biodiesel blend was 5.13 mg KOH/g, followed by Jatropha biodiesel blend at 3.76 mg KOH/g, COME at 3.11 mg KOH/g, PME at 3.01 mg KOH/g, JME at 2.84 mg KOH/g, and diesel at 1.93 mg KOH/g, respectively, in week 12 of the test period. A high TAN value is related to the potential acceleration of rust, corrosion, and oxidation. Based on the results, palm biodiesel has the worst results in terms of TAN values, since it indicates the highest TAN values during the 12-week test period compared to the other samples, while diesel has the best result showing the lowest TAN values. However, all samples indicate the same

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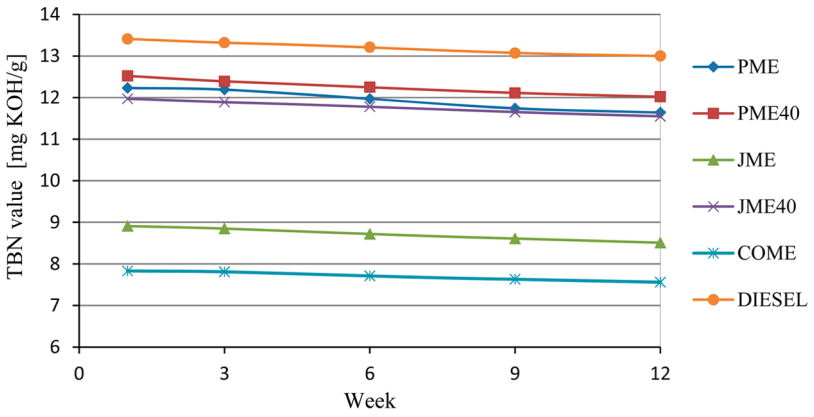

Figure 9. Total base number (TBN) value of different fuels for 12 weeks storage.

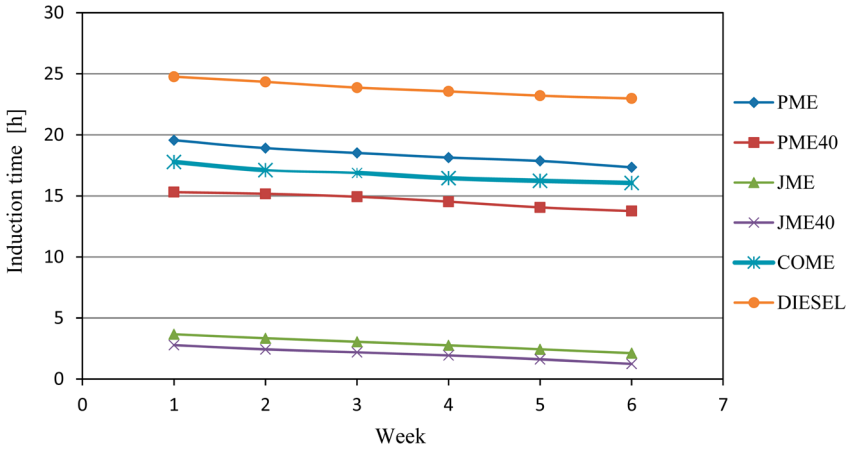

Figure 10. Induction period of different fuels for 6 weeks storage.

result, being increasing TAN values during the 12-week test period, which is shown by the negative effect of oxidation instability. Increases in the TAN are influenced by the increment of hydroperoxides, which may oxidize into acids. Oxidation begins when the ester is oxidized to form peroxides which then undergo complex reactions. Then, they also will split into more reactive aldehydes to form further oxidation into acids. Acids can also be formed when traces of water cause hydrolysis of the esters into alcohols and acids.[40] Due to its characteristics, acid is corrosive and conductive; hence, the TAN analysis may be the most important test that needs to be carried out in order to maintain the mechanical integrity of equipment and to prevent internal damage to components. Another factor that contributes to the increasing trend in the TAN values is the temperature as well as the storage time. Biodiesel tends to oxidize when it is exposed to high running temperatures due to the reaction of biodiesel molecules and oxygen within the air. In the samples, oxidization is easy so the TAN values increase with the temperature factor.

5.5. Investigation of Total Base Number (TBN). Figure 9 shows a graph of the TBN values plotted against the storage time. The TBN value is measure in units of mg KOH/g.

Figure 9 shows that diesel leads the results in terms of TBN values, followed by palm biodiesel, PME, jatropha biodiesel, JME, and COME, respectively. On the basis of the pattern of the graphs for each sample, that is, the negative slope, it can be stated that the relationship between the TBN values for each sample and the storage time is inversely proportional. The reduction in TBN value for each sample during the 12-week test period is not significant, changing only slightly; see Figure 9. The maximum TBN values of diesel, palm biodiesel, PME,jatropha biodiesel, JME, and COME were taken in week one of the test period and were 13.41 mg KOH/g, 12.52 mg KOH/g, 12.23 mg KOH/g, 11.97 mg KOH/g, 8.91 mg KOH/g, and 7.83 mg KOH/g, respectively. The minimum TBN values of diesel, palm biodiesel, PME, jatropha biodiesel, JME, and COME were taken in week 12 of the test period and were 13 mg KOH/g, 12.02 mg KOH/g, 11.64 mg KOH/g, 11.55 mg KOH/g, 8.51 mg KOH/g, and 7.56 mg KOH/g, respectively. According to the previous discussions of the TAN analysis, the relationship between the TAN value and storage time is directly proportional which means that TAN values increase with the increase in storage time. Therefore, with the increase in storage time over the 12-week test period the samples tend to become more acidic due the oxidation of the samples. Hence, it will give the opposite result for the TBN analysis; the TBN value of all samples decreased as the storage time increased. This is due to the formation of acidic products as a result of oxidation of the fuel. Low TBN reserves provide insufficient neutralization capacity, leading to the corrosion of engine components.[36] In the analysis, diesel showed good results in terms of TBN values, since it has the highest value compared to the other samples while COME has the worst results.

5.6. Rancimat Test (Oxidation Stability of Biodiesel). Figure 10 shows the graph of the induction period plotted against the storage time for each of the samples. The induction time is measured in hours.

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According to studies in the literature review, induction time can be defined as the length of time before the rapid acceleration of oxidation and is a measure of the resistance to oxidation. Oxidation stability is the most valuable factor to appraise the fuel quality of biodiesel and is introduced by the chemical reaction between a free unsaturated fatty acid and a free radical. The elementary products of the oxidation reaction are involved in some complex reactions producing secondary products, including carbonyl compounds and alcohols, which are oxidized to form carboxylic acids.[41] Based in Figure 10 it can be seen that diesel leads the results in terms of induction time followed by PME, COME, palm biodiesel, JME and Jatropha biodiesel, respectively. The relationship between induction time and storage time is inversely proportional, and the slope of the graph dropped. Also seen from the figure is that diesel had the longest induction period at 23.87 h, followed by PME at 18.47 h, COME at 16.90 h, palm biodiesel at 14.66 h, JME at 2.95 h, and jatropha biodiesel at 2.07 h, respectively. It was also found that all fuel samples met the standard ASTM D6751 (3 h) specification, but JME and its biodiesel do not meet the EN 14214 (6 h) specification. For JME and its biodiesel blend to meet the standard specification, among several antioxidants, phenolic 2, 6-ditertiarybutyl hydroxytoluene antioxidants are the most effective at 200 ppm.[42] Furtherance of the induction period of JME and its biodiesel to above 6 h, as required by EN-14112, requires a minimum dosage of 300 ppm of tert-butylated phenol derivative and acetylated butyrate biphenyl amine antioxidants, while dosages of 200 ppm of tertbutylated hydroxytoluene and only 150 ppm of tert-butylhydroxquinone are required to achieve the same induction period of 6 h,[43] whereas oxidation stability and the cold filter plugging point of JME can be improved by using pyrogallol as an antioxidant with 100−250 ppm at a temperature of 25 °C ensuring storage stability for 2−3 years without degradation of the fuel quality.[44]

6. CONCLUSION AND RECOMMENDATIONS

Biodiesel stability is divided into two categories: oxidative stability related to long-term storage and thermal stability depending on the effect of temperature on the fuel. Biodiesel can oxidize due to the formation of gum and sediments in long-term storage. Biodiesel instability can lead to high density, high viscosity, and a high acid number due to the formation of gums and sediment. The gums and sediment will affect the engine by clogging the fuel filters. In addition, the increase in biodiesel density due to its instability will cause a problem with the operation of the fuel injection system as a result of the delivery of a slightly greater mass of fuel in the volume metering equipment.

Based on the observation of this experiment the following conclusions can be drawn:

1. Biodiesel properties and stability are influenced by the presence of unsaturated fatty acids and longer chain double-bonded hydrocarbons in the fuel. Increased storage periods reduce the fuel properties and stability.
2. Coconut oil methyl ester exhibits the worst results for oxidation stability due to several properties of the fuel compared to other biodiesels. Density, viscosity, and TAN increased over the time frame, while the flash point and total base number decreased.
3. The induction time for each sample, either diesel or biodiesel, reduced over the storage period. Since the induction period is the time taken by biodiesel to oxidize, the induction period will reduce over long storage periods due to oxidation instability, which is influenced by storage time.
4. The flash point properties showed positive results due to oxidation instability. The biodiesel flash point reduces over long storage periods due to the effect of oxidation instability. A low flash point is one of the good characteristics of fuel since the flash point indicates the lowest temperature at which the fuel will flash when a small flame is passed across it. Unfortunately, typical biodiesels have high flash points and are unsuitable to support the auto ignition process during the combustion cycle.

From these results, it can be concluded that fuel quality deteriorated with increasing storage time. Since the oxidation of fuels is dependent on the storage conditions, further study is required, applying several conditions, to investigate the biodiesel oxidation, thermal, and storage stabilities, which would help to improve fuel properties and quality.

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Notes

The authors declare no competing financial interest.

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