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The Effect of Storage Condition on Biodiesel

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1. Introduction

Biodiesel is an alternative diesel fuel derived from the varied processes of vegetable oils, animal fats, or waste frying oils to give the corresponding fatty acid methyl esters (Chang et al., 1996; Schmidt & Van Gerpen, 1996). In the transport sector it can be used blended with fossil diesel fuel and in pure form. The major chemically bound oxygen component in the biodiesel fuel has the effect of reducing the pollutant concentration in exhaust gases due to better burning of the fuel in the engine (Kahn et al., 2002). It is also described as an alternative fuel which improves environmental conditions and contributes to gaining energy sustainability (Edlund et al., 2002).

As biodiesel fuels are becoming commercialized and with its biodegradability, it is important to examine their properties as respect to transport, storage, or processing. Demirbas (Demirbas, 2007) has summarized the biodegradability data of petroleum and biofuels available in the literature and showed heavy fuel oil has low biodegradation of 11%, in 28 day laboratory studies while biodiesels have 77%–89% biodegraded, and diesel fuel was only 18% biodegraded.

Some studies have been conducted focusing on how biodiesel stimulated the degradation of petrol–diesel in varied environments. However, there are very few studies concentrated on biodiesel degradation under different storage temperatures and storage environments such as in a sealed or ambient environment, and in an environment with or without the presence of water moisture. Mittelbach and Gangl (Mittelbach & Gangl, 2001) studied the degree of physical and chemical deterioration of biodiesel produced from rapeseed and used frying oil under different storage conditions. They found there has severe effects when the fuel was exposed to daylight and air. But they found there were no significant differences between undistilled biodiesel made from fresh rapeseed oil and used frying oil. In their study, the viscosity and neutralization numbers rose during storage and did not reach the specified limits for over 150 days.

Zullaikah et al. (Zullaikah et al., 2005) examine the effect of temperature, moisture and storage time on the accumulation of free fatty acid when they used a two-step acid-catalyzed process to produce the biodiesel from rice bran oil. Their results showed rice bran stored at room temperature showed that most triacylglyceride was hydrolyzed and free fatty acid (FFA) content was raised up to 76% in six months. Leung et al. (Leung et al., 2006) divided twelve biodiesel samples into 3 groups and stored at different temperatures and environments to monitor the regular interval over a period of 52 weeks. Their results showed that the biodiesel under test degraded less than 10% within 52 weeks for those samples stored at 4 and 20 ^{o}C while nearly 40% degradation was found for those samples stored at 40 ^{o}C.

Bouaid et al. (Bouaid et al., 2007) used four different vegetable oils: high oleic sunflower oil (HOSO), high and low erucic Brassica carinata oil (HEBO and LEBO) respectively and used frying oil (UFO) to produce biodiesel through the process of transesterification. These biodiesels were then used to determine the effects of long storage under different conditions on oxidation stability. Their samples were stored in white (exposed) and amber (not exposed) glass containers at room temperature for a 30-months study period. Their results showed that acid value, peroxide value, viscosity and insoluble impurities increased, while iodine value decreased with increasing storage time. They also found there has slight differences between biodiesel samples exposed and not exposed to daylight before a storage time of 12 months and after this period the differences were significant.

Karavalakis et al. (Karavalakis et al., 2011) investigated the impact of various synthetic phenolic antioxidants on the oxidation stability of biodiesel blends with the employment of the modified Rancimat method. Their experimental results revealed Butylated hydroxytoluene (BHT) and butylated hydroxyanisol (BHA) showed the lowest effectiveness in neat biodiesel, whereas their use in biodiesel blends showed a greater stabilizing potential. Propyl gallate (PG) and pyrogallol (PA) additives showed the strongest effectiveness in both the neat biodiesel and the biodiesel blends. They conducted an ageing process-- a naturally ageing process of the biodiesel blends for a period of 10 weeks; samples were taken every 2 weeks to simulate the automotive biodiesel stored in the fuel tank of a vehicle. Their results showed a sharp decrease in fuel stability, significantly increased in acid value but limited effects in viscosity over time. The addition of antioxidants resulted in some increases in viscosity and acid value of the biodiesel blends.

In this study, one commercial biodiesel and three laboratory-produce biodiesels were used to verify the effect of storage temperature, type of storage container, storage time as well as the moisture content on the properties of the biodiesel. The major properties analyzed in this study include acid value, iodine value, viscosity, flash point, and heating value. The variation of the chemical species in the tested biodiesel were also analyzed and compared.

2. Materials and methods

The laboratory-produce biodiesel fuel used in this study were produced from the transesterification of vegetable oil with methanol (CH_3OH, Malliuckrodt Baker Inc., USA) catalyzed by sodium hydroxide (NaOH, Shimakyu, Osaka, Japan). The reaction scheme of the methanolysis of triacyloglycerols can be found elsewhere (Komers et al., 1998; Wu et al., 2007). Three types of vegetable oil, soybean oil, peanut oil, and sunflower seed oil, were converted into biodiesels- soybean oil methyl ester (SBM), sunflower seed oil methyl ester (SFM), and peanut oil methyl ester (PNM). A titration was performed to determine the amount of NaOH needed to neutralize the free fatty acids in each vegetable oil. The amount of NaOH needed as catalyst for every liter of soybean oil, sunflower seed oil, and peanut oil were determined as 4.4g, 4.3g, and 4.1g, respectively. For transesterification, 200mL CH_3OH plus the required amount of NaOH were added for every liter of cooking oil, and the reactions were carried out at 65°C. A total of 50L of each vegetable oil was used to produce biodiesel. The water wash process was performed by using a sprinkler which slowly sprinkled water into the biodiesel container until there was an equal amount of water and biodiesel in the container. The water/biodiesel mixture was then agitated gently for 10 min., allowing the water to settle out of the biodiesel. After the mixture had settled, the water was drained out.

A series of tests were performed to characterize the properties of the produced biodiesel. These properties include density (ASTM D 1298), kinematic viscosity (ASTM D445), acid value (ASTM D664), iodine value (CNS 15060), flash point (ASTM D 93), water and sediment (ASTM D 2709), and heating value (ASTM D 240). The heating values of biodiesels were measure by bomb calorimeter (PAAR 6200, USA). The chemical components in the biodiesels were also analyzed by a gas chromatograph/mass spectrometry (ThermoQuest Trace MS) with a 1.0□□m, 0.25mm × 30m DB-1 column (J & W Scientific).
There was another 50L of commercial biodiesel (NJC) obtained from Taiwan NJC Corp. used for this study. The experiments use NJC, SFM, SBM, and PNM as the biodiesels to examine the effects of storage condition. The biodiesels were stored in the polypropylene bottle (PP) and stainless steel container (ST), respectively. Each container contains 500mL of biodiesels, there were three groups of water contents contained in two different containers, which include the pure biodiesel storage in the PP bottle (ppB100) and ST cup (stB100), 98% biodiesel + 2% distilled water storage in PP bottle (ppB98) and ST cup (stB98), and 95% biodiesel + 5% distilled water storage in PP bottle (ppB95) and ST cup (stB95), and stored at 0°C, 25°C, and 40°C, respectively. The major properties of every sample were measured at the time interval of 0, 1st, 2nd, 4th, 8th, 16th, and 32nd week.

3. Results and discussions

As similar in our previous study (Wu et al., 2007), after the transesterification process, there was a nearly 90% volume ratio of methyl ester phase to a 10% volume ratio of glycerol phase during the separation process. In this study, the volume ratios of methyl ester phase were 91.98%, 89.63%, and 91.33% for SBM, SFM, and PNM, respectively, which yielded nearly 45L of each biodiesel for the use in this study. A total of 50 L of each vegetable oil was used and converted into biodiesel. After the transesterification process, there was a nearly 90% volume ratio of methyl ester phase to a 10% volume ratio of glycerol phase during the separation process, which gave nearly 45L of sunflower seed oil biodiesel (SFM) for the use in this study. Table 1 gives some of the major properties of the NJC, SFM, SBM and PNM biodiesels. As observed form these data, the NJC has higher acid value and gross heating value but lower iodine value, kinematic viscosity, and density than the laboratory-produce biodiesels.

Property	NJC	SFM	SBM	PNM	Method
Acid value (mg KOH/g)	0.685	0.145	0.267	0.154	ASTM D664
Iodine value (g I_2/100g)	103.37	137.81	129.1	130.52	CNS 15060
Kinematic Viscosity (mm^2/s) at 40°C	4.103	5.251	5.171	5.390	ASTM D445
Density (g/cm^3) at 15°C	0.884	0.897	0.896	0.896	ASTM D1298
Flash point (^{o}C)	172	172	184	176	ASTM D93
Heating value (cal/g)	9529	9464	9460	9420	ASTM D240
Water content (ppm)	—	—	1699	1768	CNS 4446

Table 1. Original major properties of the NJC, SFM, SBM, and PNM used in this study.

Table 2 compares the initial major chemical composition of the commercialized biodiesel (NJC) and the laboratory-produce biodiesels. NJC contained 19.69% saturated fatty acid methyl esters (FAMEs) and 79.92% unsaturated FAMEs, SFM contained 12.38% saturated

Name	Formula	NJC	SFM	SBM	PNM
2-Methyl pentane	C_6H_{14}		0.373%		
3-Methyl pentane	C_6H_{14}		0.254%		
Hexane	C_6H_{14}		0.585%		
Methylcyclopentane	C_6H_{12}		0.172%		
Cyclohexane	C_6H_{12}		0.033%		
Methyl enanthate	$C_8H_{16}O_2$	0.001%			
Methyl caprylate	$C_9H_{18}O_2$	0.033%	0.022%		
2,4-Decadienal	$C_{10}H_{16}O$	0.011%	0.023%		
Methyl caprate	$C_{11}H_{22}O_2$	0.012%			
9-Oxo-nonanoic acid methyl ester	$C_{10}H_{18}O_3$	0.004%			
Butylated Hydroxytoluene (BHT)	$C_{15}H_{24}O$	0.168%			
Methyl laurate	$C_{13}H_{26}O_2$	0.114%			
Methyl 8-(2-furyl)octanoate	$C_{13}H_{20}O_3$	0.002%			
Methyl Z-11-tetradecenoate	$C_{15}H_{28}O_2$	0.008%			
Methyl myristate	$C_{15}H_{30}O_2$	0.626%	0.064%	0.005%	0.010%
Methyl cis-4-octenoate	$C_9H_{16}O_2$		0.002%		
Methyl (9E)-9-dodecenoate	$C_{13}H_{24}O_2$		0.005%		
Methyl pentadecanoate	$C_{16}H_{32}O_2$	0.030%	0.011%		
3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	0.034%			
Palmitoleic acid methyl ester	$C_{17}H_{32}O_2$	0.437%	0.094%	0.004%	0.011%
Methyl hexadecanoate	$C_{17}H_{34}O_2$	14.568%	6.911%	9.640%	10.579%
Ethyl palmitate	$C_{18}H_{36}O_2$	0.020%			
Methyl 8-(2-hexylcyclopropyl)octanoate	$C_{18}H_{34}O_2$	0.046%	0.025%		
Methyl margarate	$C_{18}H_{36}O_2$	0.071%	0.036%		0.022%
Methyl linileate	$C_{19}H_{34}O_2$	36.450%	57.762%	64.183%	61.332%
Methyl oleate	$C_{19}H_{36}O_2$	42.631%	26.186%	22.268%	22.386%
Methyl stearate	$C_{19}H_{38}O_2$	3.777%	4.129%	2.835%	3.986%
Methyl cis-9,cis-15-linoleate	$C_{19}H_{34}O_2$		0.014%		
Methyl linolelaidate	$C_{19}H_{34}O_2$		0.099%		
Dimethyl 9-oxoheptadecanedioate	$C_{19}H_{34}O_5$		0.027%		
Methyl linolenate	$C_{19}H_{32}O_2$	0.031%	0.034%	0.016%	
Methyl (6E,9E,12E)-6,9,12-octadecatrienoate	$C_{19}H_{32}O_2$		0.046%		
Methyl ricinoleate	$C_{19}H_{36}O_3$	0.022%			
Methyl (11E,14E)-11,14-icosadienoate	$C_{21}H_{38}O_2$	0.031%			
Methyl (11E)-11-icosenoate	$C_{21}H_{40}O_2$	0.274%	0.152%	0.106%	0.122%
Methyl 9-hydroxystearate	$C_{19}H_{38}O_3$	0.016%			
Methyl arachisate	$C_{21}H_{42}O_2$	0.256%	0.235%	0.224%	0.281%
Methyl heneicosanoate	$C_{22}H_{44}O_2$			0.014%	
Methyl 9,10-dihydroxystearate	$C_{19}H_{38}O_4$		0.008%		
2-Monopalmitin	$C_{19}H_{38}O_4$		0.024%		
Methyl behenate	$C_{23}H_{46}O_2$	0.136%	0.693%	0.255%	0.299%
Methyl tricosanoate	$C_{24}H_{48}O_2$	0.011%	0.024%	0.015%	
Glycerol 1-monolinolate	$C_{21}H_{38}O_4$	0.030%	0.896%	0.193%	0.442%

Name	Formula	NJC	SFM	SBM	PNM
Monoolein	$C_{21}H_{40}O_4$	0.057%	0.537%	0.127%	0.311%
Monostearin	$C_{21}H_{42}O_4$		0.035%		
Methyl (15E)-15-tetracosenoate	$C_{25}H_{48}O_2$	0.009%			
Methyl lignocerate	$C_{25}H_{50}O_2$	0.047%	0.253%	0.072%	0.105%
Squalene	$C_{30}H_{50}$	0.011%	0.018%		
Methyl pentacosanoate	$C_{26}H_{52}O_2$	0.004%			
Methyl hexacosanoate	$C_{27}H_{54}O_2$	0.004%			
Vitamin E	$C_{29}H_{50}O_2$		0.039%		
Stigmasterol	$C_{29}H_{48}O$		0.041%	0.013%	
β-Sitosterol	$C_{29}H_{50}O$	0.016%	0.138%	0.028%	0.117%

Table 2. Initial chemical compositions of NJC, SFM, SBM, and PNM.

FAMEs and 84.42% unsaturated FAMEs, SBM contained 13.06% saturated FAMEs and 86.58% unsaturated FAMEs, and PNM contained 15.28% saturated FAMEs and 83.85% unsaturated FAMEs. The major species in NJC's saturated FAMEs were Methyl hexadecanoate (Hexadecanoic acid methyl ester, $C_{17}H_{34}O_2$, 14.57%) and Methyl stearate (Octadecanoic acid methyl ester, $C_{19}H_{38}O_2$, 3.78%), while Methyl linoleate (9,12-Octadecadienoic acid methyl ester, $C_{19}H_{34}O_2$, 36.45%) and Methyl oleate (9-Octadecenoic acid, methyl ester$C_{19}H_{36}O_2$, 42.63%) were the major species in NJC's unsaturated FAMEs. These four species were also the major species in SFM, SBM, and PNM. SFM contained 6.91% $C_{17}H_{34}O_2$, 4.13% $C_{19}H_{38}O_2$, 57.76% $C_{19}H_{34}O_2$, and 26.19% $C_{19}H_{36}O_2$. SBM contained 9.64% $C_{17}H_{34}O_2$, 2.84% $C_{19}H_{38}O_2$, 64.18% $C_{19}H_{34}O_2$, and 22.27% $C_{19}H_{36}O_2$. PNM contained 10.58% $C_{17}H_{34}O_2$, 3.99% $C_{19}H_{38}O_2$, 61.33% $C_{19}H_{34}O_2$, and 22.39% $C_{19}H_{36}O_2$. Also, there was one species, Butylated hydroxytoluene ($C_{15}H_{24}O$, BHT), which can be uses as antioxidant, detected in NJC.

3.1 Acid value

The freshness of the oil is related to acid value of the oil, while the oil may generate the free fatty acids during longer storage due to the hydrolysis reactions. Hence the acid value becomes one of the important quality targets to determine the purity of oil. Acid value, which defined as the amount of the free fatty acids contained in each gram of the oil determined by the neutral reagent, KOH, denoted as mgKOH/g.

The acid values determined from the four tested biodiesels stored in varied types of container under different temperatures as well as the various moisture contents as a function of storage time are shown in Figure 1. As shown in Figures 1(A), 1(B), 1(C), and 1(D), the acid values of NJC, SFM, SBM, and PNFM remain at a stable range at the lowest storage temperature (0°C). As the storage temperature rose, as shown in Figure 1(E) to Figure 1(L), there shows an acid value increases for these four tested biodiesels with the storage time increased, which suggests the storage temperature did affect but will increase the acid value of the biodiesel if storage temperature increased. Also, as the storage time increased, there shows obvious acid value differences for laboratory-produce biodiesels which stored in ST cups, while the acid value of NJC in ST cups only shows a slightly increase for storage temperatures at 25°C and 40°C. The NJC biodiesel is a commercial product with antioxidant BHT added while SFM, SBM, and PNM are laboratory products

with no additive. However, there was a small amount of Vitamin E (0.039%), which can be considered as a natural antioxidant, detected in SFM. This tiny amount of Vitamin E may have the retardation effect on oxidation of SFM at the beginning of study. Another difference is the storage container, the PP bottle has a screw-on lid which has a better sealing than the ST cups did. The effect of antioxidant can be observed from the results shown in Figures 1(A), 1(E), and 1(I). These three figures showed NJC kept in varied oxygen exposure environments (PP and ST) but show similar trend on the change of the acid value, which suggest the antioxidant can slow the degradation of biodiesel. These results show the oxygen in the air performed the oxidation and do affect the acidification of the biodiesel with the temperature acceleration. Among the three laboratory-produce biodiesels, there has a higher non-FAMEs observed for SFM (as shown in Table 2) which might caused the higher acid value change of SFM under oxygen contact environments. Also, the results observed, as shown in Figures 1, show the moisture content has no obvious effect on the acid value of tested biodiesels during the tested period in this study.

3.2 Iodine value

The iodine value is an index used to express the number of unsaturated bonds of the oil, the oil with higher iodine value implies it has higher number of unsaturated bonds. The measured iodine value from the NJC, SFM, SBM, and PNM which stored in PP and ST containers under varied temperatures and moisture contains as function of the storage time are shown in Figure 2. As observed from Figures 2(A), 2(E), and 2(I), the iodine value were stayed in a stable range regardless with the temperature changes, storage time or storage bottles. For iodine value observed from the sample of SFMs, as shown in Figures 2(B), 2(F), and 2(J), the iodine value stably remains for SFM stored at $0^{o}C$, and also stably remains for those kept in PP bottles as storage temperature increased, but decreased with increasing storage temperature and time for those stored in ST cups. The decreased iodine values of SFM stored in ST with increased storage time imply the effect from oxidation. As previous discussed, the NJC biodiesel contains the antioxidants which can prevent the oxidation of the fuel and kept the iodine value in a stable range. The laboratory-produce biodiesels with no oxidation inhibitor in the ST cups contact more oxygen at higher temperature and hence shows the effect on the difference of iodine value.

3.3 Viscosity

Viscosity is the important property that affects engine performance. Higher viscosity interferes with injector operation, resulting in poorer atomization of the fuel spray, and has been associated with increased engine deposits.

The kinematic viscosity of the NJC, SFM, SBM, and PNM stored in PP and ST bottles with varied moisture contents and stored at $0^{o}C$, $25^{o}C$, and $40^{o}C$ with respect to storage time were shown in Figure 3. Similar with the results of acid value and iodine value sections, the viscosity of NJC biodiesel, as shown in Figures 3(A), 3(E), and 3(I), remain constant with respect to storage time. The viscosities of laboratory-produce biodiesels shows varied results. For SFM, SBM, and PNM stored in PP bottles, the viscosity remains constant as storage time changed. However, the viscosity of SFM, SBM, and PNM kept in ST bottles increased as storage temperature increased and also increased as storage time increased. Allena et al. (Allena et al., 1999) has point out the viscosity of biodiesel fuels reduce considerably with increase in unsaturation. Prankl and Worgetter (Prankl & Worgetter,

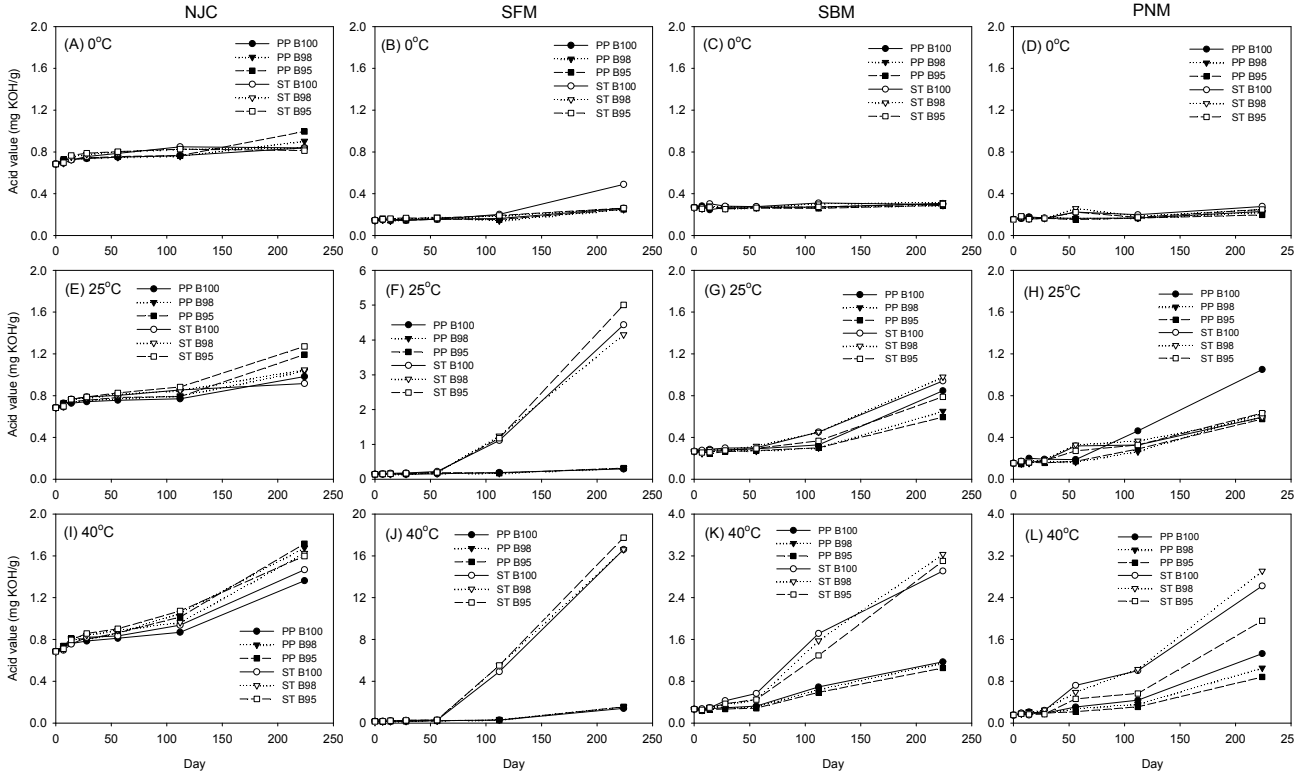

Fig. 1. The acid values determined from the NJC, SFM, SBM, and PNM stored in varied types of container under different temperatures and the various moisture contents as a function of storage time.

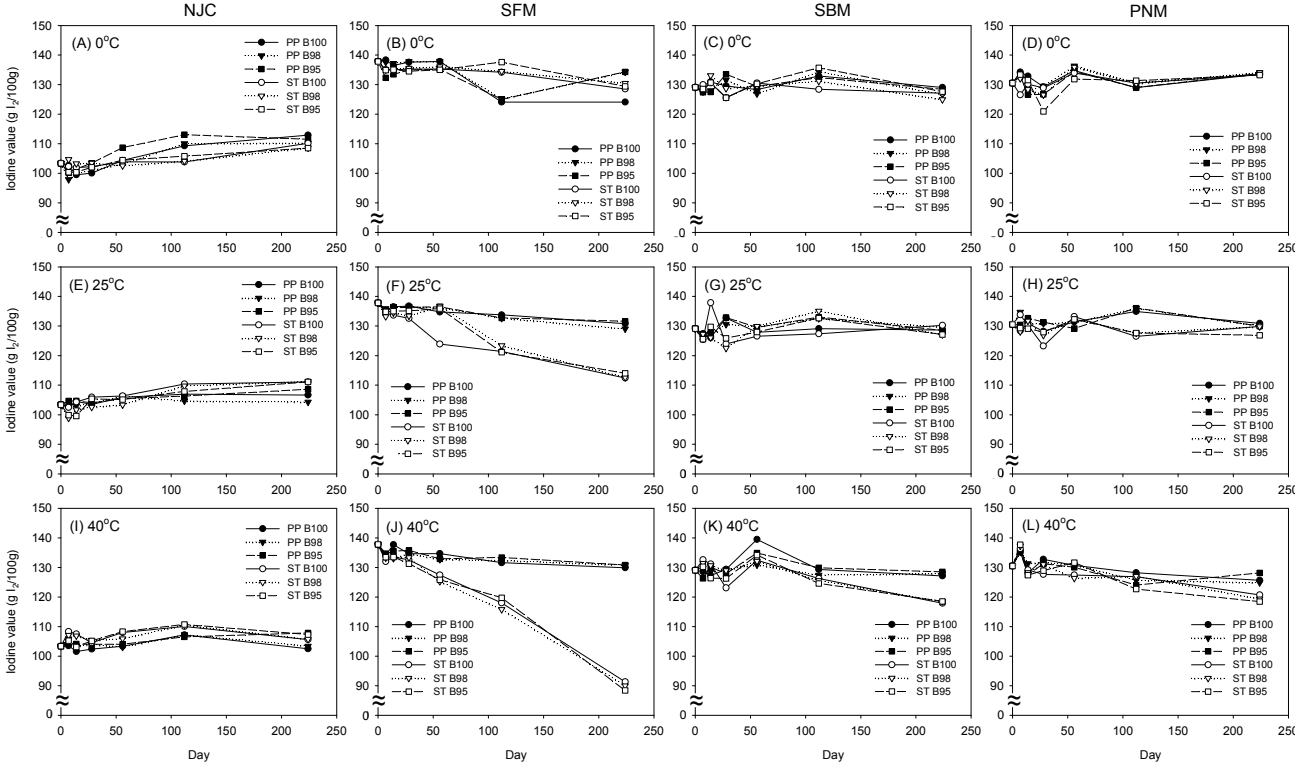

Fig. 2. The iodine values determined from the NJC, SFM, SBM, and PNM stored in varied types of container under different temperatures and the various moisture contents as a function of storage time.

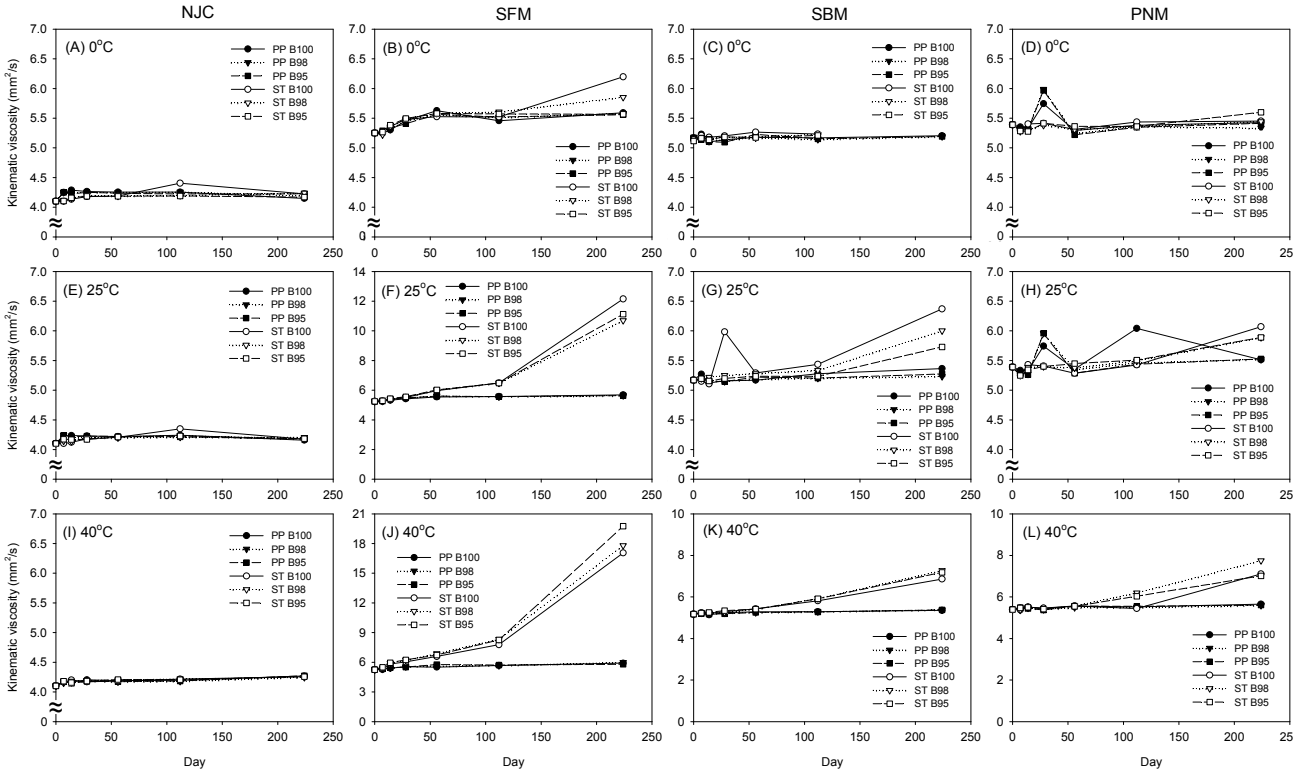

Fig. 3. The viscosities determined from the NJC, SFM, SBM, and PNM stored in varied types of container under different temperatures and the various moisture contents as a function of storage time.

1996) showed that the lower iodine value of biodiesel fuel gives higher viscosity. Compare the results show in Figures 2(F) and 2(J), and Figures 3(F) and 3(J), the viscosity of SFM in ST cups increased match up with the decreased iodine value with increasing storage time. Similarly, there are same trend can be observed from Figures 2(G) and 2(K), and Figures 3(G) and 3(K) for SBM, and from Figures 2(H) and 2(L), and Figures 3(H) and 3(L) for PNM. Here, again, the results show that storage temperature accelerates the degradation and adding antioxidants can prevent the biodiesel degradation.

Viscosity increases with chain length and with increasing degree of saturation (Knothe, 2007). Free fatty acids have higher viscosity than the corresponding methyl or ethyl esters. Since oxidation processes lead to the formation of free fatty acids, double bond isomerization, saturation and products of higher molecular weight, viscosity increases with increasing oxidation.

3.4 Density

Density has importance in diesel-engine performance and is required for the estimation of the Cetane index since fuel injection operates on a volume metering system. (Demirbas, 2008a, as cited in Song, 2000; Srivastava & Prasad, 2000). This study also measured the density of NJC, SFM, SBM, and PNM stored in PP and ST bottles with varied moisture contents and stored at 0°C, 25°C, and 40°C with respect to storage time and shown in Figure 4. Similar with the results of the properties discussed earlier, the density of tested biodiesels remain stable at 0°C. The density of NJC remains constant with regardless with the difference of storage temperature, time, or containers. The density of the SFM, SBM, and PNM kept in ST cups increased with increased storage temperature and storage time.

3.5 Flash point

Flash point is an important property for determining the flammability of a fuel and can be used as a safety indicator for the storage and transportation of a fuel. Biodiesel with a higher flash point indicates the methyl esters transesterification have been properly treated, eliminating any remaining alcohols.

The flash point of the NJC, SFM, SBM, and PNM stored in PP and ST bottles with varied moisture contents and stored at 0°C, 25°C, and 40°C with respect to storage time were shown in Figure. 5. Among these figures, the flash point of the tested biodiesels tends to decrease with increasing storage time at higher storage temperature. The flash point of SFM stored in ST cups show a larger difference with respect to storage time (Figures 5(F) and 5(J)). The FAMEs in biodiesels will get hydrolyzed to alcohols and acids in contact with air. Sharma et al. (Sharma et al., 2008) has point out the oxidation of biodiesel is dependent on the total number of bis-allylic sites. The conversion of FAMEs into alcohols will lead to the reduction of flash point which can easily observed from the results showed in Figures 5(F), 5(G), 5(J), 5(K), and 5(L).

3.6 FAMEs

The major FAME species of the NJC, SFM, SBM, and PNM with 5% water (ST95) in ST cups stored at 40°C was measured by GC/MS during the storage study. Figure 6(A) presents the major species detected in NJC at the beginning (0 week) and the end of study (48th week). This figure shows the shorter chain saturated FAME, Methyl hexadecanoate ($C_{17}H_{34}O_2$), slightly increased after the 48 weeks of durations, but the longer chain saturated FAME,

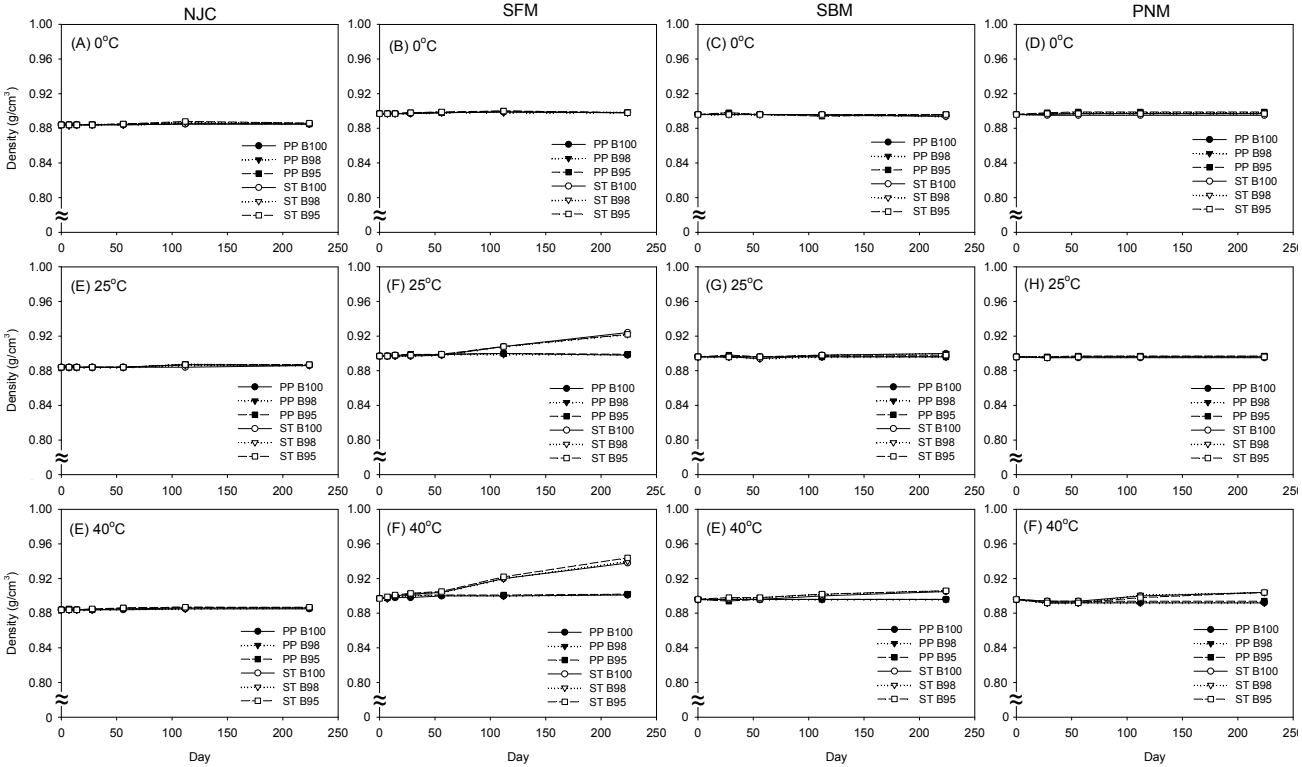

Fig. 4. The densities (15°C) determined from the NJC, SFM, SBM, and PNM stored in varied types of container under different temperatures and the various moisture contents as a function of storage time.

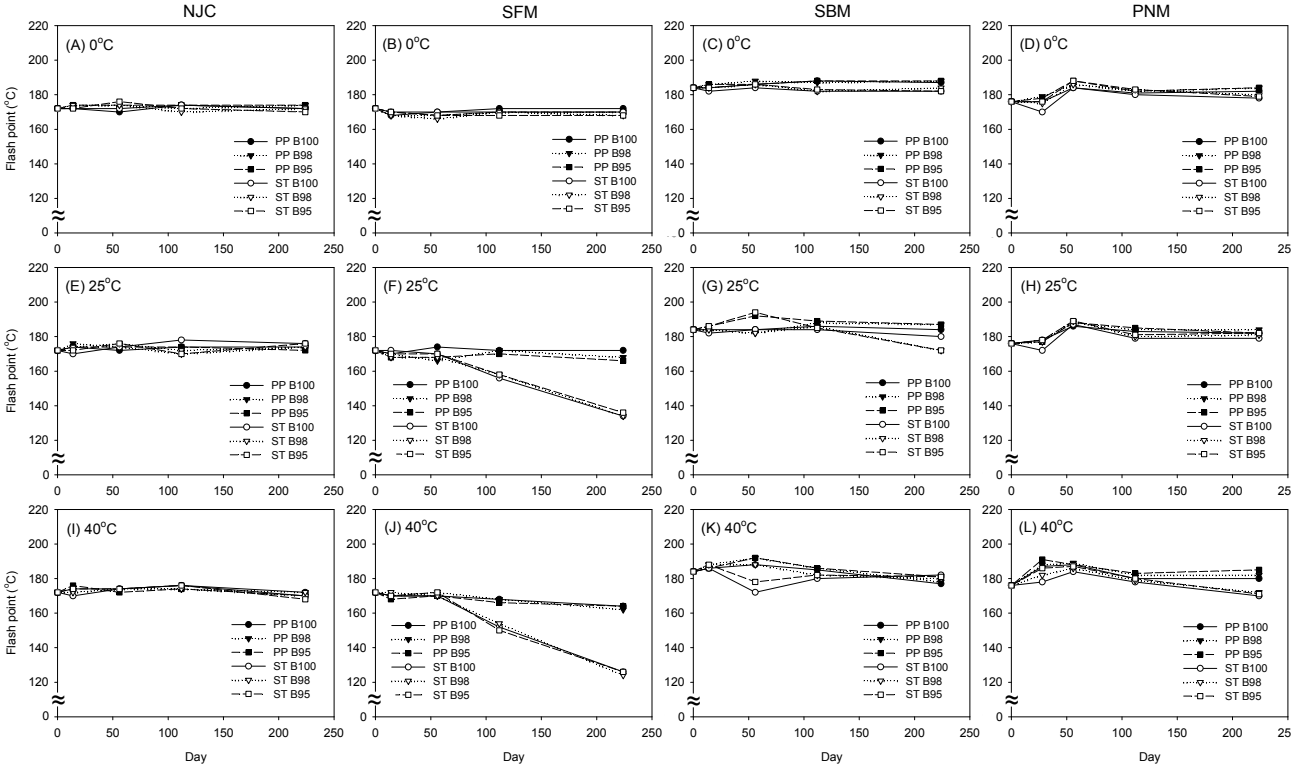

Fig. 5. The flash points determined from the NJC, SFM, SBM, and PNM stored in varied types of container under different temperatures and the various moisture contents as a function of storage time.

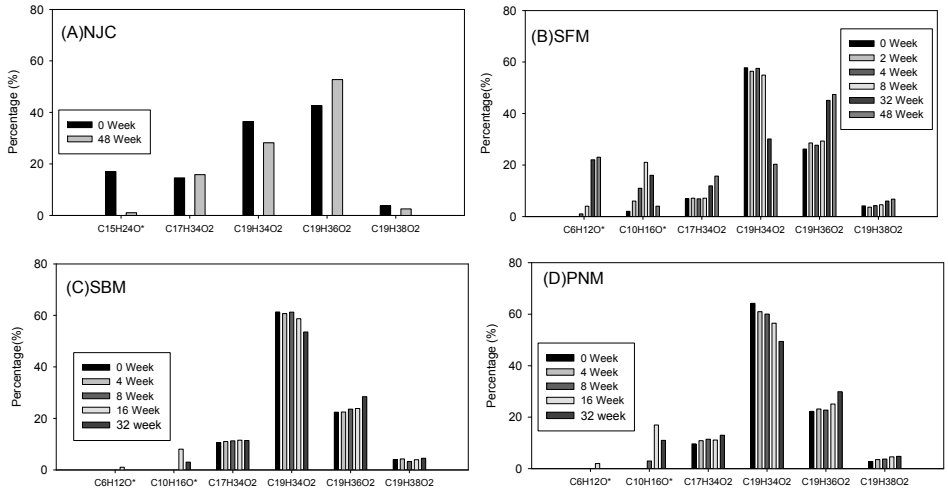

Fig. 6. The major FAME species of the NJC, SFM, SBM, and PNM with 5% water (ST95) in ST cups stored at 40°C.

Methyl stearate ($C_{19}H_{38}O_2$) decreased. For unsaturated FAMEs, the di-double bonds species, Methyl linoleate ($C_{19}H_{34}O_2$), decreased at the end of study and the mono-double bond species, Methyl oleate ($C_{19}H_{36}O_2$) increased. Figure 6(A) also presents the concentration difference of BTH between the beginning and the end of study. It shows the BTH concentration also decreased with increased storage time. Figure 6(B) shows the difference of the major FAME species during the study. As shown in the figure, the trends of the difference for the major FAMEs are similar with those in NJC. There were also have a small amount of alcohols, hexanal ($C_6H_{12}O$) and 2, 4-Decadienal ($C_{10}H_{16}O$), detected as storage time increased. It supports the hydrolysis reaction did occurs within the storage. Figures 6(C) and 6(D) present the major FAMEs analysis results from SBM and PNM but with a shorter period. The difference trends of the major FAMEs were similar with those of NJC and SFM.

3.7 Higher heating value (HHV)

The higher heating value (HHV) is an important property defining the energy content of fuels. The HHVs of the NJC, SFM, SBM, and PNM stored in PP and ST bottles with varied moisture contents and stored at 0°C, 25°C, and 40°C with respect to storage time were shown in Figure 7. The HHV remains at a stable level for NJC and for SFM, SBM, and PNM which stored at lower temperatures. The HHV of SFM stored in ST cups at higher temperatures, Figures 7(F) and 7(J), shows a larger decrease with respect to storage time. The HHV is the same as the thermodynamics heat of combustion with enthalpy change for the reaction of the compounds before and after combustion. Here, as refer to the species of the FAMEs from Figure 6, the formation of enthalpy ($H_{f,298}$) at 25°C were estimated by using the "THERM" computer code which is based on modified Group Additivity (Benson, 1976; Ritter & Bozzelli, 1991). The gross $H_{f,298}$ of each biodiesel at varied period were then calculated by assuming the $H_{f,298}$ is proportional to the fraction (x_i) of the species, that is

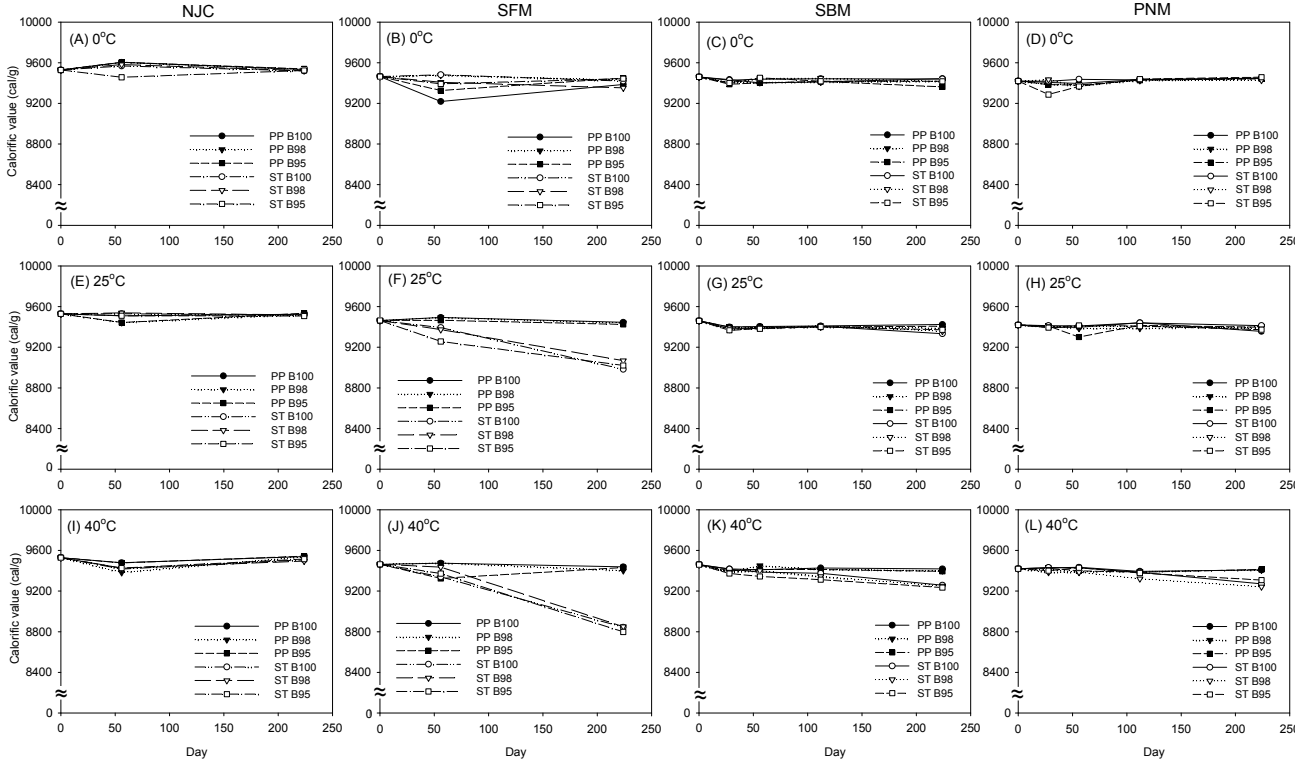

Fig. 7. The high heating values determined from the NJC, SFM, SBM, and PNM stored in varied types of container under different temperatures and the various moisture contents as a function of storage time.

$$H_{f,298} = \sum_i x_i H_{f,298,i} \cdot \quad (1)$$

The HHVs were then calculated by assuming the species is combusted completely to CO_2 and H_2O. Fig. 8 presents the calculated HHV of NJC, SFM, SBM, and PNM at varied storage time. Demirbas (Demirbas, 2008) presents several estimate methods for HHV in his study. One is using the correlation between flash point and HHV for biodiesels. The equation between flash point (FP) and HHV is

$$\text{HHV (MJ/Kg)} = 0.021 \text{ FP (K)} + 32.12 \quad (2)$$

Another equation from regression is between viscosity (VS) and HHV for biodiesels. The equation between VS and HHV is

$$\text{HHV (MJ/Kg)} = 0.4625 \text{ VS (cSt)} + 39.450 \quad (3)$$

There is a modified Dulong's formula may used to calculate the HHV for biomass fuels such as coal (Demirbas, 2008b, as cited in Perry & Chilton, 1973; Demirbas, 2008b, as cited in Demirbas *et al.*, 1997) as a function of the carbon (C%), hydrogen (H%), oxygen (O%), and nitrogen (N%) contents (wt.%).

$$\text{HHV (MJ/Kg)} = 0.335(\text{C\%}) + 1.423(\text{H\%}) - 0.154(\text{O\%}) - 0.145(\text{N\%}) \quad (4)$$

Figure 8 compares the HHV of NJC, SFM, SBM, and PNM from the methods described above with the experimental values. Among this figure, all the estimating HHVs were higher than experimental results. As shown in Figure 8(A), the estimated HHVs of NJC stay in a small variance range. For the other biodiesels, as shown in Figures 8(B), 8(C), and 8(D), the estimated methods giving an order of VS > Flash pt > Dulong's > THERM on giving the value of HHV. There has an exception on these estimations, as shown in Figure 8(B), there has large HHV difference for SFM at the end of storage study. The method using VS equation gives an extreme high HHV due to the high viscosity detected in the sample.

4. Conclusions

The acid values of tested biodiesels remain at a stable range at lowest temperature (0^oC). As the storage temperature raised the acid value increases with the storage time increased, which suggests the storage temperature did affect but will increase the acid value of the biodiesel. Also, the results show the oxygen performed the oxidation and do affect the acidification of the biodiesel with the temperature acceleration. The laboratory-produce biodiesels with no oxidation inhibitor in the ST cups contact more oxygen at higher temperature and hence shows the effect on the difference of iodine value. The viscosity of SFM, SBM, and PNM kept in ST cups increased as storage temperature increased and also increased as storage time increased. These results suggesting the storage temperature and the degree of oxygen contact will affect the degradation of biodiesel. The water content shows no significant effect on the biodiesel storage in this study. There still have some research topics, for example, the ageing effect of natural or artificial antioxidants on the chemical composition of biodiesels, the proper amount of antioxidants if needed, and the quick analysis method for determining the degree of degradation, can be considered for helping us has better understanding on biodiesel storage.

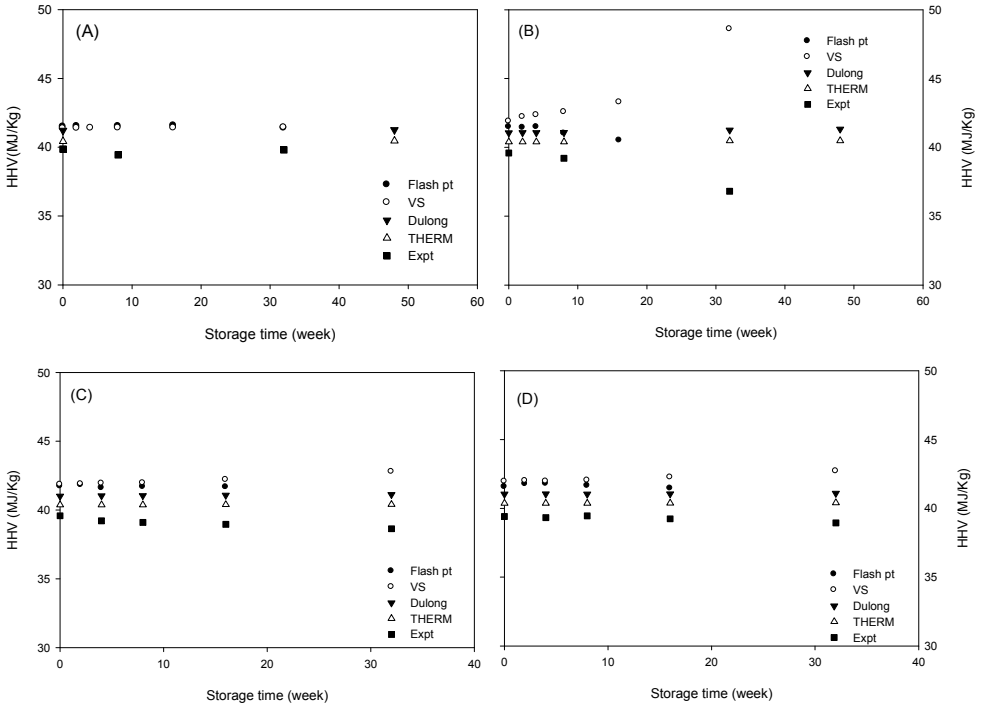

Fig. 8. Comparison of estimated higher heating values of NJC, SFM, SBM, and PNM with experimental results.

5. Acknowledgement

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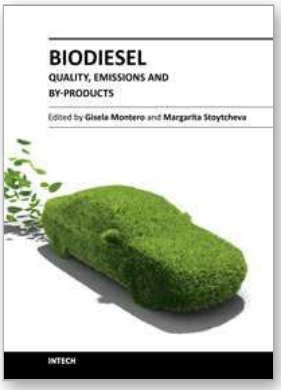

Biodiesel- Quality, Emissions and By-Products

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This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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