The Effect of Storage Degradation of Palm- Stearin Biodiesel on Engine Performance and Exhaust Emission

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Abstract

The main objective of this experimental study is to determine the effects of biodiesel degradation on the fuel properties, the engine performance and exhaust emissions of a diesel engine by keeping biodiesel in closed containers at room temperature for different storage times. In this work, the biodiesel derived from palm stearin was investigated. The study was conducted for a period of 6 months. At the beginning of the study and at end of every month, the stored biodiesel was analyzed for changes in acid value (AV), iodine value (IV), peroxide value (PV), viscosity and methyl ester content. Results showed that AV and PV increased, while methyl ester content decreased with storage time upto 6 months. Viscosity changes were not significant within the 6-month storage time. The engine performance and exhaust emission results indicated that, the brake power of petroleum diesel was comparable to those of fresh and stored biodiesels, while the fuel consumption of biodiesel was higher than petroleum diesel by about 5 % and this trend increased slightly as the biodiesel degraded. Furthermore, the fuel conversion efficiency of degraded biodiesel continually decreased with storage time. In terms of emission, fresh biodiesel produced half the CO pollution compared to petroleum diesel and, as the biodiesel storage time increased, the emission of CO was even lower. On the other hand, the NO_x emission increased with longer biodiesel storage time.

Keywords: Degraded biodiesel, Chemical properties, Engine Performance, Emission, Storage time

1. Introduction

Nowadays, biodiesel is one of the most popular alternatives derived from tran-sesterification of vegetable oils or animal fats. The chemical structure of biodiesel is composed of saturated and unsaturated long-chain fatty acid alkyl esters. Thus, biodiesel is biodegradable, non-toxic and has low emission compared to petroleum diesel. However, the weak point of biodiesel for engine fuel is that it is sensitive to degradation because it contains unsaturated methyl esters, which can be easily oxidized, such as methyl linoleate (C18:2) and methyl linolenate (C18:3). The formation of degraded products of biodiesel includes insoluble gums, organic acids and aldehydes. These products are claimed to not only degrade the properties of biodiesel, but also build problems in engine operation [1].

As the degree of degradation increases with biodiesel age, some of the degraded products of biodiesel may cause negative effects to engine performance. Therefore, the main objective of this experimental study was to determine the effects of biodiesel storage degradation on the fuel properties as well as the engine performance and exhaust emissions. So far, there have been several reports on storage degradation of biodiesel [2-4]. However, there has been only one study on the effect of storage degradation on engine performance of biodiesel [19]. Besides, the report was for rapeseed biodiesel, not the palm-stearin one. In this work, the biodiesel produced from palm stearin was chosen for our investigation because palm stearin has become more and more popular as raw material for biodiesel production in Thailand.

2. Experimental

2.1 Raw Materials and methods

The biodiesel produced from palm stearin used in this study was kindly supplied by Prathum Vegetable Oil Co., Ltd. (Thailand). The petroleum-base diesel fuel used as a reference fuel was purchased from PTT Public company Ltd. (Thailand). In the experiment, the biodiesel was stored in closed containers at room temperature (temperature variation between 25 – 30 ºC) during the whole experiment. The period of biodiesel storage was 6 months, during which the chemical properties of biodiesel was analyzed every month. The biodiesel was also tested for the engine performance and exhaust emissions initially and after 3, 4, 5 and 6 months, respectively.

2.2 Analysis of chemical properties

The biodiesel was characterized for methyl ester content, acid value, viscosity, peroxide value, iodine value and high heating value. The purity of biodiesel was determined using Fison's GC 8000 series gas chromatography equipped with flame ionization detector. The capillary column was a DA-WAX column with a length of 30 m., a film thickness of 0.25 μm and an internal diameter of 0.32 mm. Methyl heptadecanoate was introduced as an internal standard. The methyl ester sample was tested with temperature program ranging from 160 °C up to 240 °C to detect the full length of fatty acid methyl ester. The acid value was determined by titration method according to ASTM D 664. Viscosities of biodiesels were tested using Cannon Fensky Routine No.75 P 573 viscometer at 40 ° C according to ASTM D 445. The peroxide and iodine values were approximated by titrating with sodium thiosulfate solution following ISO 3960 and EN 14111 standards, respectively.

2.3 Engine performance and exhaust emission testing

The short term engine test was carried out in a 4-cylinder, 4-stroke, direct injection Nissan diesel engine. The main specifications of the engine are given in Table 1. The engine performance test was measured by Eddy current dynamometer. In this work, the tests of diesel and biodiesel fuels were performed at variable loads and engine speeds. The engine was tested at speeds between 1,800 and 4,000 rpm. The performance parameters obtained from the engine test included brake power (P), brake specific fuel consumption (bsfc) and brake fuel conversion efficiency (η_{bf}). The exhaust emissions of engine were measured by Madur GA-40T Plus fuel gas analyzer.

Table 1: Engine specifications

Engine model	Nissan BD-30
Engine type	4 cylinder, 4 stroke, in - line
Displaced volume	2,953 cc.
Bore	96 mm
Stroke	102 mm
Compression ratio	18.5 :1
Maximum power	70.8 kW (95 HP)

3. Results and Discussion

The results will be discussed in 3 parts including chemical characteristics, engine performance and exhaust emissions. The changes in several chemical properties over time were analyzed and correlated with engine performance and exhaust emissions.

3.1 Chemical characteristics

In this experiment, the degradations of biodiesel at various storage time up to 6 months were indicated by the changes in several properties including acid value, kinematic viscosity, iodine value, peroxide value, methyl ester content and high heating value.

3.1.1 Change in acid value

The acid value is a measure of the amount of acidic substances in fuel. Fig. 1 shows the acid values of biodiesel derived from palm stearin at all storage periods. As can be seen, the acid values of biodiesel derived from palm stearin increased with storage time from 0.14 to 0.59 mg KOH/g within 6 months. One reason for the increase in acid value is the hydrolysis of methyl ester by the reaction of moisture in the ambient air with methyl ester [5]. Another reason is that, as the biodiesel is kept for a long time without antioxidant, the biodiesel undergoes oxidation by the reaction of ambient oxygen with double bonds of biodiesel causing it to form peroxides as the first product. These peroxides then undergo complex reactions including a split into more reactive aldehydes, which further oxidize into acids, leading to an increase in acid value [3-5].

3.1.2 Changes in viscosity

Another possible degradation pathway is to form a larger molecule like polymers or gums. This type of degraded products can be indicated by changes in kinematic viscosity. Kinematic viscosity is an important property of fuel as it indicates the ability of fuel to atomize into small droplets in the combustion chamber. Fig. 2 indicated that the changes in the fuel viscosity were not significant within the 6 - month storage time. This means that degradation of palm stearin biodiesel into polymer products was not significant in the period of this study.

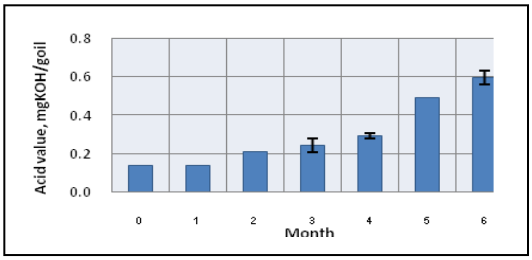

Fig. 1 Acid values of degraded biodiesels at various stored periods.

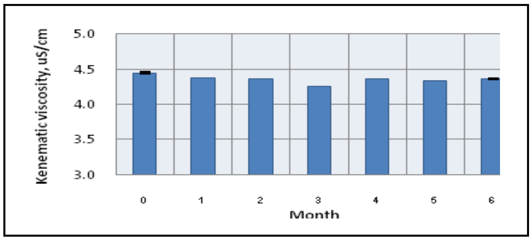

Fig. 2 Kinematic viscosities of degraded biodiesels at various stored periods.

3.1.3 Changes in iodine and peroxide values

Iodine value is a measure of the quantity of double bonds in biodiesel, whereas peroxide value indicates the amount of peroxide in biodiesel. Fig. 3 shows the iodine values of biodiesel obtained from palm stearin during long term storage. The iodine values of biodiesel continued to decrease with storage time to the end of month 6 from 32.99 to 21.89 g / **100** g oil. The decrease in iodine value indicated the reduction of double bonds in biodiesel molecules by the degradation process. The decrease in double bonds was consistent with increase in peroxide values as illustrated in figure 4, implying that the reduction in the double bonds was due to oxidation. As a result of oxidation, double bonds of biodiesel broke apart and reacted with oxygen to form hydro- peroxides. The peroxide value parameter helps to indicate the initial oxidation step of oil. Hydro peroxides are unstable and easily form a variety of secondary oxidation products which can further undergo two major types of degradation, which are fission to give shorter-chain compounds and polymerization [6-10]. Although peroxide value is not specified in the biodiesel fuel standard, this parameter influences cetane number, a parameter that is specified in the fuel standard. Increasing peroxide value increases cetane number, an effect that may reduce ignition delay time [11].

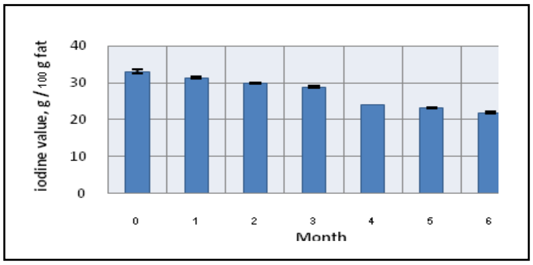

Fig. 3 Iodine values of degraded biodiesel at various stored periods.

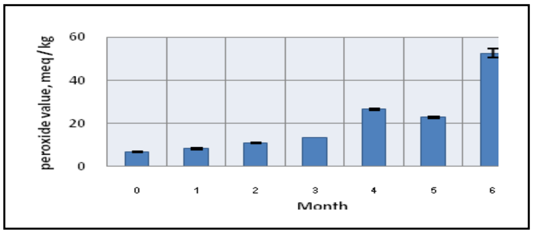

Fig. 4 Peroxide values of degraded biodiesel at various stored periods.

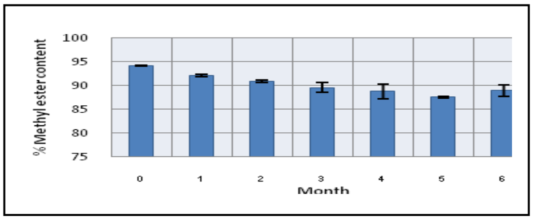

Fig. 5 Methyl ester content of degraded biodiesel at various stored periods.

3.1.4 Changes in methyl ester content and heating value

The methyl ester content in fig. 5 indicates that the purity of biodiesel continued to decrease with storage time. This result is consistent with the change in peroxide value and acid value, implying that the methyl ester continued to convert to peroxides and acids. We found that these degraded products also contributed to the reduction in the biodiesel's heating values, as shown in fig. 6.

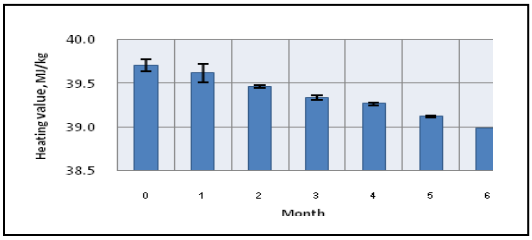

Fig. 6 High heating values of degraded biodiesel under the stored periods.

3.2 Performance characteristics

The engine performances of the fresh and stored biodiesels were evaluated based on brake power, brake specific fuel consumption and brake fuel conversion efficiency by comparing with petroleum diesel. All tests were performed at various engine speeds ranging from 1,800 to 4,000 rpm.

3.2.1 The effect on brake power

The brake power of the test engine when using petroleum diesel were compared to those using up to 6-month-old biodiesels. The variations of brake power with engine speed for all types of fuels are shown in figure 7. As can be seen, all types of fuels provided the maximum brake power at the engine speed of 3,600 rpm. The average values of brake power over the range of speeds from 1,800 to 3,900 rpm in figure 8 indicates that the brake power of biodiesel increased slightly with storage time up to the end of month 6. The result is consistent with the decrease in the amount of double bonds, as indicated by iodine value in figure 4. The reduction in double bonds, led to higher cetane number, thus reducing ignition delay [12, 16 and 17].

3.2.2 Effect on brake fuel conversion efficiency

The brake fuel conversion efficiency (η_{bf}) indicates the engine's ability to convert chemical energy of fuel into mechanical power. Fig. 9 shows the average brake fuel conversion efficiency values for all types of fuels. As can be seen, the brake fuel conversion efficiency of all types of biodiesel was higher than that of petroleum diesel. However, the fuel conversion efficiency decreased slightly for degraded biodiesel.

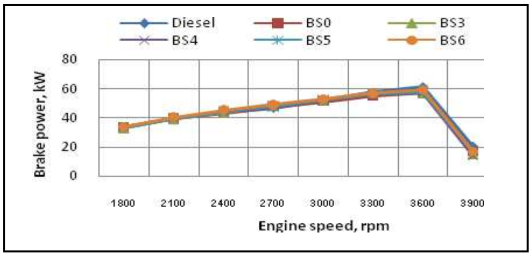

Fig. 7 The variation of brake power with engine speed for petroleum diesel (Diesel), fresh biodiesel (BS0), and biodiesels kept for 3 months (BS3), 4 months (BS4), 5 months (BS5) and 6 months (BS6).

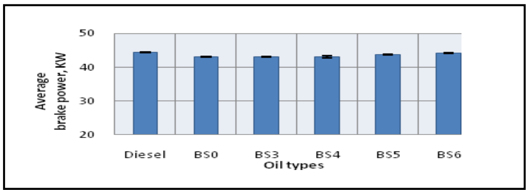

Fig. 8 The average values of brake power for all types of fuels

3.2.3 Effect on brake specific fuel consumption

The brake specific fuel consumption (bsfc) indicates the consumption rate of fuel per unit power by the following equation:

$$bsfc = \frac{fuel\ consumption\ rate}{brake\ power} = \frac{fuel\ consumption\ rate}{\eta f \times heating\ value}$$

From fig. 10, the consumption of fresh biodiesel was about 5% more than that of petroleum diesel and became slightly higher as the biodiesel storage time increased. This relates directly to the heating value of biodiesel reported in fig. 6 [12-15].

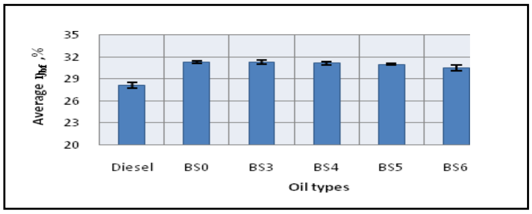

Fig. 9 The average values of the brake fuel conversion efficiency (η_{bf})

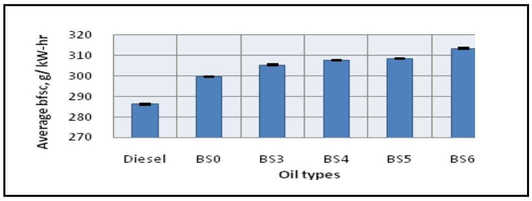

Fig. 10 The average values of the brake specific fuel consumption (bfsc)

3.3 Exhaust emission

The emission tests were carried out at a constant engine speed of 3,600 rpm and various loads ranging from 0 to 30 kg.

3.3.1 Carbon monoxide (CO) emission

High CO emission indicates degree of incomplete combustion. The average values of CO emission over the load range of 0 to 30 kg are shown in fig 11. Comparing use of petroleum diesel and biodiesel as fuels, it is obvious that CO emissions of all biodiesels were lower than petroleum diesel. This result was expected as the molecular structure of biodiesel contains oxygen atoms leading to more complete combustion compared to petroleum diesel. As the storage time of biodiesel increased, the degree of oxidative degradation also increased, leading to more oxygen atoms in the fuel molecules. The oxygen content of the degraded biodiesel enhanced the air/fuel ratio in the combustion chamber, leading to more complete combustion and lower emission of CO.

3.3.2 Oxides of nitrogen (NO_x) emission

The average NO_x emission values for all types of fuels are shown in fig. 12. As can be seen, the NO_x emissions for all biodiesels were higher than for petroleum diesel. High NO_x emission usually occurs when excessive amount of oxygen is used in the combustion engine at high temperature [18]. Since biodiesel contains higher oxygen content and even more in degraded biodiesel, we found that NO_x emission of biodiesel was slightly higher than that of petroleum diesel and continued to increase with storage time up to the end of month 6.

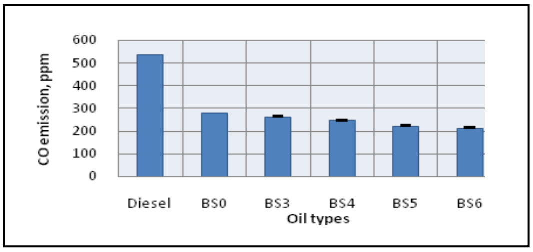

Fig. 11 CO emission of a diesel engine when using the same fuels as in figure 7.

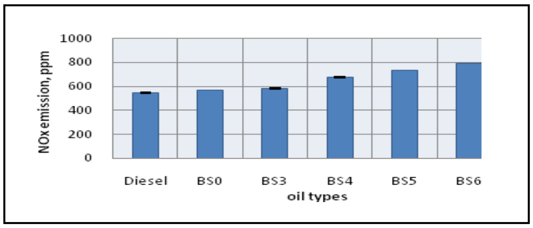

Fig. 12 NO_x emission of a diesel engine when using the same fuels as in figure 7.

By comparing our study with previous researches on storage degradation of biodiesel produced from rapeseed oil [19], we found that, for the 6-month storage period, the changes in acid value and peroxide value of palm stearin biodiesel were faster than rapeseed biodiesel, corresponding to a greater drop in heating value. However, we cannot compare the changes in the engine performance since the previous literature [19] did not report monthly changes in engine performance but only reported the engine performance after 2 years.

4. Conclusion

In this study, the effects of biodiesel storage degradation on engine performance and exhaust emissions were investigated. We found that the degradation of biodiesel kept in a closed and dark container at various storage times up to 6 months occurred mainly by oxidation process into acids, peroxides and other derivatives as indicated by higher acid and peroxide values, and lower methyl ester content. However, the changes in the fuel viscosity were not significant indicating negligible degree of polymerization. In terms of engine performance, we found that the storage degradation of biodiesel led to an increase in brake specific fuel consumption overall mainly due to the reduction in heating values of degraded biodiesel. However, this degradation assisted the more complete combustion inside the combustion chamber and lower CO emission. Another drawback of this degradation is that higher oxygen amount in the degraded biodiesel also led to higher NO_x formation.

5. Acknowledgement

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