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Study on Hazard of Biodiesel

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Abstract : Hazard of Biodiesel (BDF) was studied. Biodiesel is a name for a variety of ester-based fuel made from vegetable oils. Recently importance of biodiesel is increasing, and its fires were sometimes reported. Therefore we studied on hazard of biodiesel comparing (petroleum) diesel oil and vegetable oil, raw materials of biodiesel. We found that biodiesel is auto-oxidized easily and ignites, and its flash point decreases when even small amount of methanol exists. And there are various raw materials to manufacture biodiesel, so we studied the difference of these materials, and their aging on safety.

Key words : biodiesel, oxidation, flash point, boilover

1. Introduction

Biodiesel (BDF=Biodiesel fuel) is an alternative fuel, a variety of ester-based fuel made from vegetable oils, such as soybean, rapeseed or sunflower oil [1,2]. Recently crude oil price increasing and environmental problem, such as global warming and reduction of amount of waste make importance of biodiesel increasing. Therefore its demand is increasing, and its safety issue in regard to manufacture, consume, is much important now. Pure biodiesel (B100) or blended biodiesel (for example, B20, mixture of 20% Biodiesel and 80% Petroleumdiesel) are most available. However it often made fires [2,3,4], and fires in biodiesel tanks were reported in Korea, July 2005 [5], and other places.

Therefore we studied on hazard of biodiesel comparing (petroleum, petro) diesel oil and vegetable oil which is one of raw material of biodiesel [3,4]. And then we studied effects on combustion properties with raw materials because varieties of raw materials are proposed to reduce manufacture cost.

2. Samples

Waste edible oil base biodiesel, A, B, used in this study was bought through local governments which arrange re-cycling of used vegetable oil. We got from two different sources and compared the difference. Petro-diesel oil and rape seed oil were also used for reference. Distribution curves of two biodiesels, (petro) diesel oil, and rape seed oil, are shown in Fig. 1.

Rape seed oil is one of the major raw materials of biodiesel. Its boiling point is much higher than that of biodiesel. There is no large difference between two biodiesels. Most of biodiesel boil at around 320-360°C, very uniform. Properties of biodiesel B are shown in Table 1.

Recently, to reduce cost of manufacture of biodiesel, various types of raw materials were proposed, such as Jatropha curcas oil, Palm oil, and sunflower oil. So difference on combustion property among these produc-

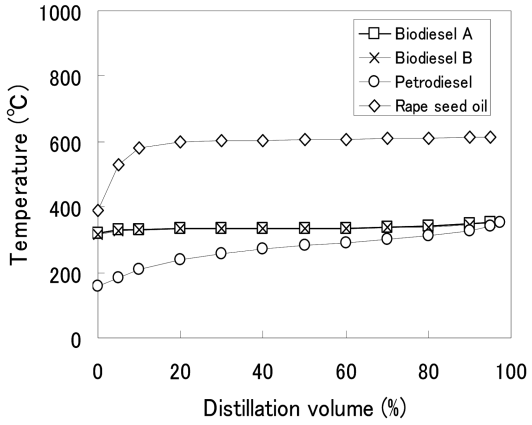

Fig. 1. Distribution of biodiesel, diesel and rape seed oil.

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Table 1. General properties of biodiesel, petro diesel and rape seed oil

Item	Unit	Bio diesel B	Diesel oil	Rape seed oil
Density	kg/m^3	883	890*	906~920
Dynamic viscosity	Mm^2/s	4.53	-	-
Pour point	°C	-5.0	-	-
Clogging point	°C	-6	-	-
10% residual carbon	%	0.71	-	-
Cetane number	-	52.3	-	-
Water content	ppm	297	-	-
Flash point**	°C	198*	70*	321
Ignition point	°C	255	316,225	405
Methanol	%	<0.01	-	-
Boiling point	°C	370~400	200~350	400~620
Heat of combustion	kJ/g	40.2	42.9	39.7
Iodine value		128	0	95~127

*: Tag closed cup, **: Cleveland open cup (authors measured) Data are from references or regulation except our data.

tions was studied, too.

3. Chemical of Biodiesel

3.1 Biodiesel

Biodiesel is made of glyceride and methanol with the following chemical reaction (Fig. 2). Rape seed oil is one of major base oil of vegetable oil base-biodiesel. Generally, NaOH is used as catalyst. So some amount of methanol and glycerol may exist in biodiesel. It produces less smoke than petro diesel.

Table 1 shows general properties of biodiesel, (petro) diesel oil and rape seed oil. Generally biodiesel is safer than diesel oil because of its high flash point. Because its pour point is -5°C, it may be solid-state in winter in cold area.

We studied difference among various types of biodiesel. Results are shown in Table 2. Based on the data of

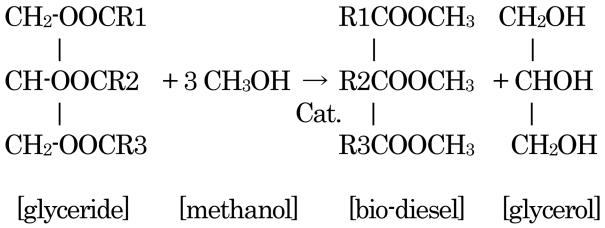

Fig. 2. Synthesis of biodiesel.

Table 2. Comparison of various type of biodiesels

	Bio diesel A	Jatropha curcas base	Palm oil base	Sunflower base
Flash point	186	176	174	186
Ignition point	249	248	239	253
Melting point	-5.5	-4.5	5	-6
Iodine value	116	99	52	129
DSC result, effect of aging	No change	No change	No change	No change

Table 2, there are not large difference in flash point and ignition point. Among them palm oil base biodiesel was slightly low. But the iodine value of palm oil base biodiesel was very low, which means little oxidation danger. Only sunflower oil base biodiesel had high iodine which means it was easy to be oxidized. Sunflower oil is used widely for vegetable oil. The melting point of palm oil base biodiesel was high, 5°C, though others were about -5°C. So to keep liquid state, palm oil base biodiesel has to be added proper material.

To study of thermal properties of bio-diesel and aging effect, the TG-DTA and DSC measurements were conducted using Rigaku Thermo plus 8120. Heat rate was 10 K/min. Samples for DSC were kept for 40 days at 20°C and 40°C. The results show no onset temperature change and no difference among these materials.

4. Results and Discussion

4.1 Flash point measurement

Flash points of sample biodiesel B and methanol added bio-diesel were measured following JIS K2265. The flash point of methanol is 12°C. When the flash point is expected more than 80°C, the Cleveland Open cup method is used, and when it is lower than 80°C, the Tag closed cup method is used. Results are shown in Table 1 and Fig. 3. The flash point of pure biodiesel B is 198°C, and much higher than diesel oil, 70°C. When its methanol concentration is larger than about 0.01% (Vol.), the flash point of biodiesel was lower than 50°C, and its flash point is about 165°C when its concentration is smaller than 0.01%. Therefore if methanol exists more than 0.01% in biodiesel, its flash point decreases drastically and it becomes easy to be ignited even at near room temperature. Therefore to reduce methanol concentration in biodiesel is very important to keep high flash point, safety. However to reduce viscosity of biodiesel, methanol sometimes may exist, in winter season or cold area.

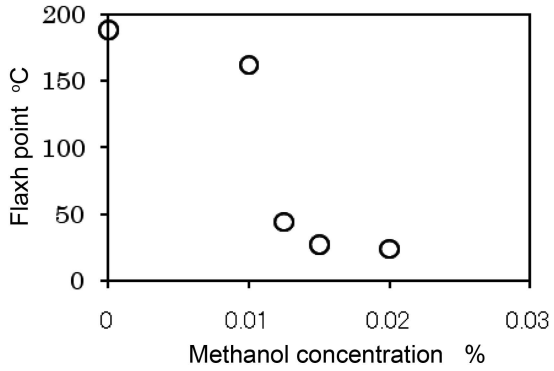

Fig. 3. Results of flash point measurement for bio-diesel B and methanol added bio-diesel.

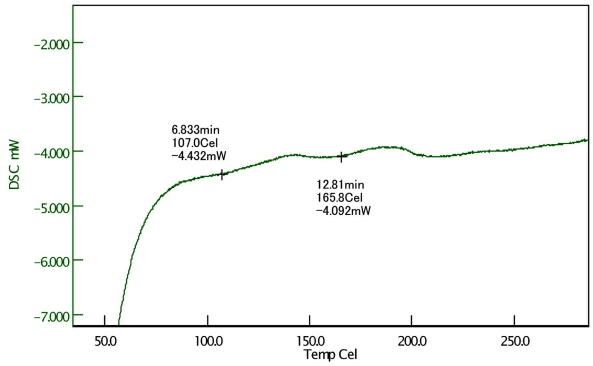

Fig. 5. DSC curve of Biodiesel A.

4.2 Oxidation of biodiesel

An iodine value is a parameter of oxidizing properties. According to the iodine value measurement, it is clear that biodiesel is easy to be oxidized except for palm oil base bio diesel (Tables 1 and 2). Generally when its iodine value is larger than 120, it is easy to be dried and easy to be ignited. And diesel oil has no oxidizing properties and palm oil base bio diesel had very low oxidizing property (Tables 1 and 2). In Japan, two fires occurred with biodiesel, and both fires were caused with oxidization of biodiesel reported by local fire departments. That is, the temperature of rags which included biodiesel was increased and then ignited suddenly and made a fire. These reasons are that; biodiesel was oxidized by strong sunshine. Fires by biodiesel were reported world-widely.

4.3 TG-DTA and DSC measurements

Biodiesel A and diesel oil were measured in the TG-DTA. Biodiesel makes heat generation at more than 100°C, and its peak is at 260°C. The TG curve shows weight increasing of biodiesel very slightly at around 100°C which may mean production of peroxide. However diesel oil does not increase its weight, which means no peroxide production. The DSC curve shows small heat generation at 107°C, which is due to oxidation (Fig. 5)

Vegetable oil generally includes anti-oxidizer when it is used by consumers, but it is doubted that the anti-oxidizer keeps working after vegetable oil changes to biodiesel, so maybe we need to add anti-oxidizer into biodiesel.

5. Pool Fire Tests of Biodiesel

In order to know burning characteristics of biodiesel when it is involved in a fire, burning tests were conducted. Burning characteristics of biodiesel and diesel oil were studied in several different size pans which diameters are between 0.3 m and 0.92 m in the NRIFD large indoor test facilities (24 m square, 20 m high).

Biodiesel was floated above water and was ignited. Fig. 6 shows time history of external radiation of biodiesel burning. Radiations were measured by RE-3 type, low time constant (0.3 second). We found it is

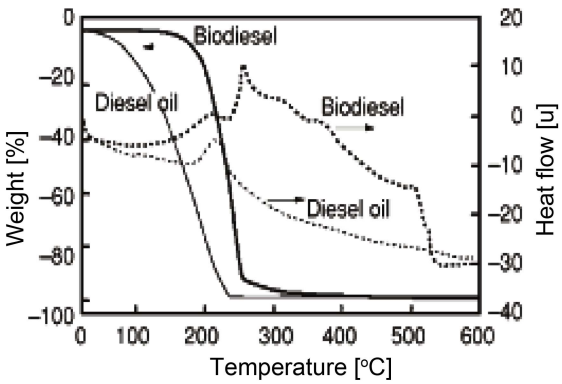

Fig. 4. TG-DTA Curves of Biodiesel A and diesel.

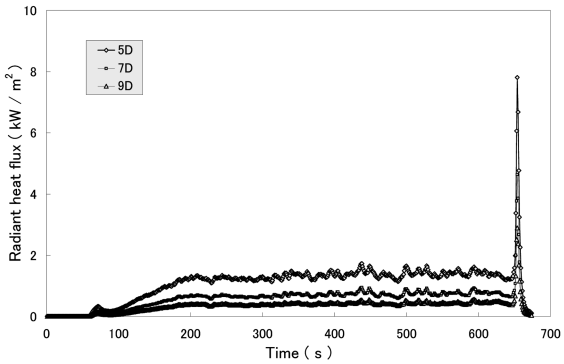

Fig. 6. Time history of radiant emittance in biodiesel burning (Pan diameter; 0.92 m, Fuel and water thickness; 0.1 m).

Table 3. Comparison of burning rate and radiation at steady state burning for various fuel (Pan diameter: about 1 m)

	Burning rate (mm/min)	Radiation (kW/m2)*	Ref.
Biodiesel	1.55	1.3~1.5	Present
Diesel oil	2.5~3	1.6~2	Present
Gasoline	4.5	2.2~2.7	7
Kerosene	3.4	1.88	7
Rape seed oil	1.2	1.2~1.8	8

*: Measured at L/D=5 from the center of the pan

safer than major fuel, gasoline, kerosene, diesel and fuel oil. Table 3 shows burning rate and external radiation during steady state burning in large pan (Pan diameter: about 1 m). External radiation of biodiesel is smaller than that of diesel oil. However it makes violent combustion after long burning. Its radiation increased very rapidly, about five times as much as that of steady state burning. And then the fire was extinguished even there was some fuel existed.

This kind of violent burning was not observed in diesel oil burning, which gave only water splashing at the end of burning. Burning of biodiesel might be involved in a kind of boilover, but classical theory of boilover [6] can not explain these phenomena, because to occur boilover fuel needs boiling point with wide range, like to crude oil, though the flashpoint of biodiesel is very uniform. And we did not observe isothermal zone (so-called hot zone) in the fuel layer.

6. Conclusion

Properties and burning characteristics of biodiesel are studied. Biodiesel (BDF) is a name for a variety of ester-based fuel made from vegetable oils, and expected to be used widely in the future.

We found that;,

1) The flash point of pure biodiesel is very high and biodiesel is safe, but its flashpoint decreases when even small amount of methanol exists.

2) Some biodiesel is to be oxidized in the air, and makes a fire. So anti-oxidizer should be added. However when it is kept at room temperature, aging may not affect so much.

3) Palm oil base biodiesel is low oxidizing properties, but melting pint is high, and is difficult to handle in winter.

4) Burning of biodiesel is low burning rate and low external radiation, but it makes violent combustion, like to boilover after long burning.

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