

SPONTANEOUS IGNITION OF BIODIESEL: A POTENTIAL FIRE RISK

by

Yasuhito SHIBATA, Hiroshi KOSEKI, and Okiyasu SHIMIZU

Original scientific paper

UDC: 621.43.041.6:665.3:544.332

BIBLID: 0354-9836, 12 (2008), 2, 149-158

DOI: 10.2298/TSCI0802149S

The spontaneous ignition of biodiesel was for the first time suspected to be the cause of a recent fire in Japan. We herein present experimental evidence implying this potential risk of biodiesel. Thus, three independent biodiesel samples were subjected to a series of experiments, including a thermogravimetry-differential thermal analysis, a differential scanning calorimetry analysis and a modified wire basket test. The results were comparatively evaluated with reference to vegetable oils, of which spontaneous ignition has been well reported as a cause of fires.

The heat onset temperature of biodiesel samples was determined to be ~100 °C, which was ~45 °C lower than those of vegetable oils. Furthermore, under the isothermal condition at 100 °C, the inner temperature of biodiesel samples rose rapidly with the generation of smoke after short induction periods owing to their exothermal decomposition, whereas for vegetable oils neither change in the inside temperature nor generation of smoke was observed even after 10 hours. It was therefore concluded that biodiesel possesses the higher risk of spontaneous ignition than vegetable oils. This is very important information to minimize the fire risk in biodiesel production facilities and so on.

Key words: *biodiesel, spontaneous ignition, fire, autoxidation*

Introduction

Over the past several years biodiesel has gained increasing interest as a clean-burning alternative fuel [1, 2]. Biodiesel is produced in a simple transesterification, whereby methanol and oils from renewable plants or animals are combined to make fatty acid methyl esters (FAME's) (the chemical name of biodiesel) and glycerin (a valuable by-product used in soaps and other products of higher value).

A recent fire at a biodiesel production facility in Nagoya, Japan, in August 2005 was believed to have started from a piece of work rag in a cardboard box. Since a trace amount of FAME's was extracted from the rag, it was speculated that biodiesel might have initiated the fire via spontaneous ignition. Although fires caused by the spontaneous ignition of vegetable oils have been well reported in Japan, no such incidents associated with biodiesel have ever been reported [3, 4]. Herein we present our experimental evidence indicating that biodiesel could undergo spontaneous ignition more readily than vegetable oils.

Experimental

Materials

Three biodiesel samples (A, B, and C) were examined by reference to vegetable oils such as soybean and rapeseed. Biodiesel sample A was sampled at the place of the recent fire and believed to be the cause of the fire. Biodiesel samples B and C were produced from waste vegetable oils at other two independent manufactures in Japan.

Gas chromatography (GC) analysis of biodiesel samples A, B and C

An 1% (v/v) sample solution in ether (1 μ L) was analyzed on a Shimadzu GC-17A FFWV3 gas chromatography equipped with a Shimadzu HiCap-CBP1 capillary column (25 m \times 0.32 mm) under the following condition: oven temperature 50 $^{\circ}$ C (for 5 min.) \rightarrow 300 $^{\circ}$ C at 10 $^{\circ}$ C/min., injector temperature 300 $^{\circ}$ C, flame ionization detector (FID) temperature 320 $^{\circ}$ C, carrier gas N_2 , and split ratio 50/1.

Gas chromatography-mass spectrometry (GC-MS) analysis of biodiesel sample A

A 0.025% (v/v) sample solution in benzene (1 μ L) was analyzed on a JOEL JMS-K9 instrument using a DB5MS capillary column (25 m \times 0.25 mm) under the following condition: oven temperature 100 $^{\circ}$ C \rightarrow 300 $^{\circ}$ C at 5 $^{\circ}$ C/min., injector temperature 300 $^{\circ}$ C, carrier gas He, split ratio 100/1, ionization voltage 70 eV, ionization current 200 μ A, mass range m/z 30 to 350, cycle time 400 m/s, and ionization chamber temperature 230 $^{\circ}$ C.

Measurements of flash point, autoignition temperature, and iodine value (= iodine number)

These measurements were carried out according to the Cleveland open cup method of “Testing Methods for Flash Point of Crude Oil and Petroleum Products (JIS K 2265-1989)”, “Standard Test Method for Autoignition Temperature of Liquid Chemicals (ASTM E659-1978)” and the Wijs method, respectively.

Thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC) analysis

A TG-DTA was performed using the TG-DTA6300 instrument (Seiko Instruments Inc., Japan). A sample (3-4 mg) was placed in an open aluminum sample cell and analyzed under the following condition: heating temperature 50 $^{\circ}$ C to 500 $^{\circ}$ C (10 $^{\circ}$ C/min.), and air flow rate 300 ml/min.

A DSC analysis was carried out in the DSC6200R instrument (Seiko Instruments Inc., Japan). A sample (8-9 mg) was placed in a sealed stainless steel sample cell and heated from 50 $^{\circ}$ C to 300 $^{\circ}$ C at a scanning rate of 10 $^{\circ}$ C/min.

Heating test in accordance with wire basket test (WBT)

The WBT (or wire mesh test) [5] measures the ability of a substance in a volume to undergo oxidative self-heating on exposure to air at given temperatures. Since sample container is made of stainless steel net with a mesh opening of 0.05 mm, a liquid sample cannot be analyzed by this test. Therefore, the modified WBT was carried out for this work.

A sample (30 g) was absorbed on an absorbent cotton sheet. The cotton sheet was wrapped with an additional absorbent cotton sheet and placed in a cylindrical sample container made of stainless steel net (diameter 15 cm, height 15 cm). The container was then introduced into a hot air circulation oven (Yamato Fine Oven DF 42, Yamato, Japan). Two chromel-alumel thermocouples (1.8-mm diameter) were embedded, respectively, in the centre of the sample and between the sample container and the oven wall. The measurements were carried out at both 100 °C and 120 °C for 3-10 hours.

Results and discussion

Composition of biodiesel samples

The biodiesel samples A-C were found to contain 4 identical components with the retention time of 21.4 min. (peak a), 23.1 min. (peak b), 23.2 min. (peak c), and 23.5 min. (peak d) (fig. 1). The identity of each peak was determined based on the GC-MS data of biodiesel sample A. The total ion chromatogram of biodiesel sample A is shown in fig. 2. Searching for the MS profile of each peak through the NIST database identified the peaks a, b, c, and d as methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate, respectively (figs. 3-6).

As reported by Porter *et al.* [6], exothermic decomposition can be initiated by the formation of allyl radicals through either thermal or photochemical reaction. Therefore, among the FAME's identified, the unsaturated FAME's, namely methyl linoleate and methyl oleate, are rather susceptible to exothermic

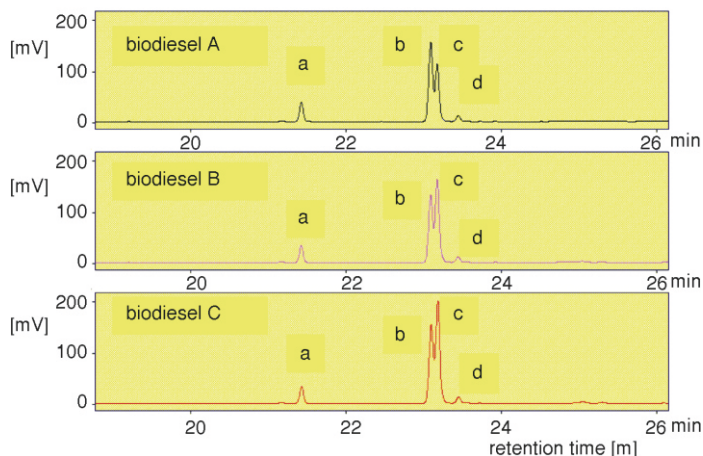


Figure 1. GC chromatograms of biodiesel A, B, and C (color image see on our web site)

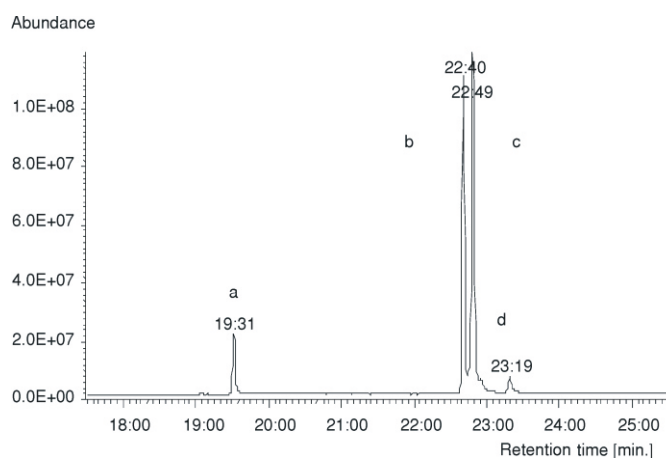


Figure 2. GC-MS total ion chromatogram of biodiesel A

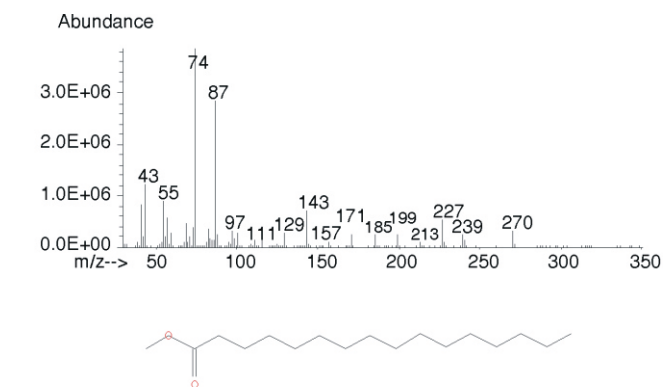


Figure 3. Mass spectrum of peak a (upper site) and methyl palmitate (lower site)

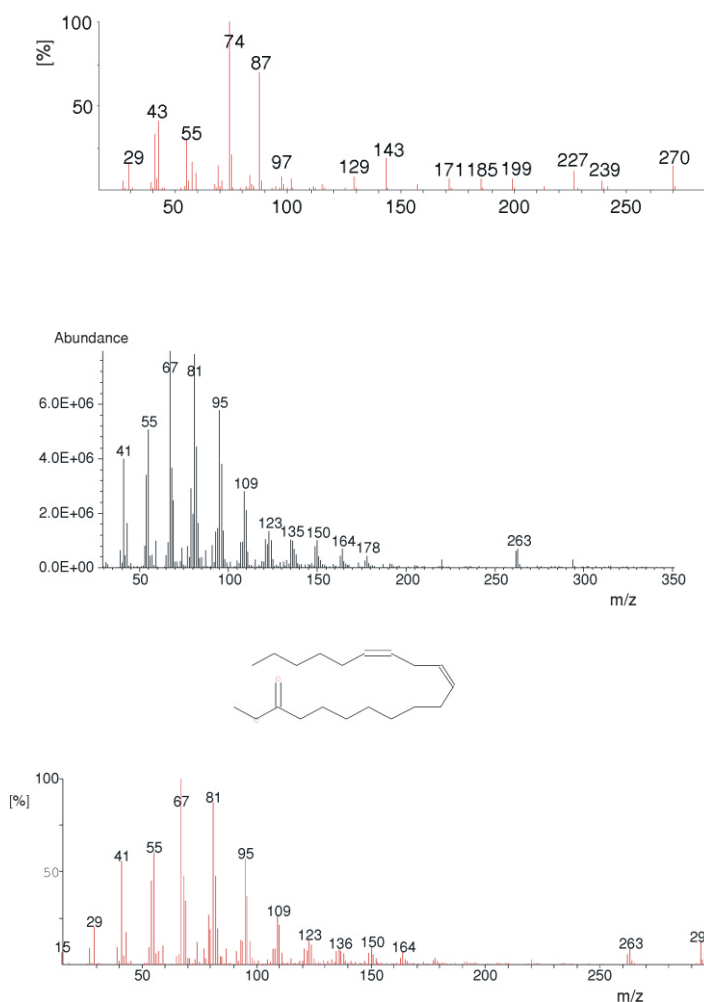


Figure 4. Mass spectrum of peak b (upper site) and methyl linoleate (lower site)

decomposition. Moreover, methyl linoleate having a bisallyl position should be the most labile FAME. Since both unsaturated FAME's are the major components, all biodiesel samples are considered to undergo exothermic decomposition with considerable ease [6].

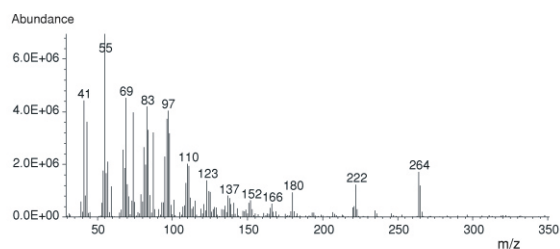


Figure 5. Mass spectrum of peak c (upper site) and methyl oleate (lower site)

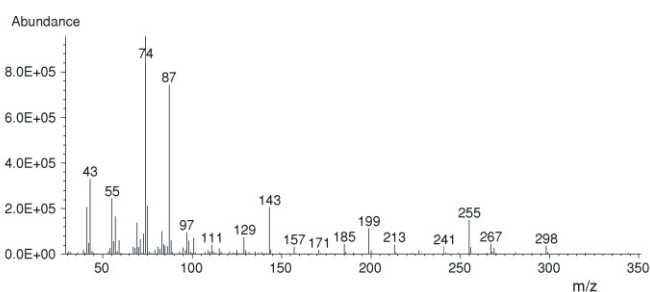
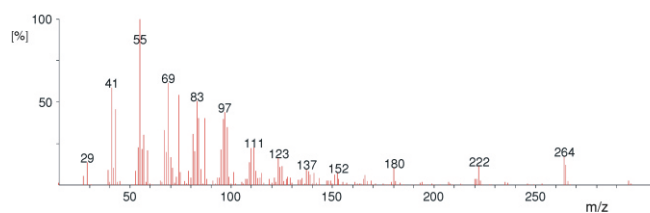
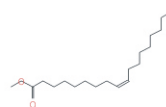
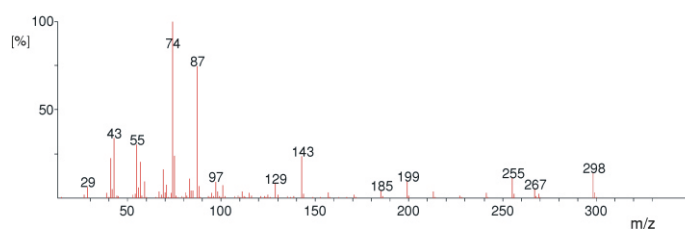


Figure 6. Mass spectrum of peak d (upper site) and methyl stearate (lower site)



Combustibility of biodiesel samples and vegetable oil

The results are summarized in tab. 1. With regard to the flash points and autoignition temperatures, little differences were found among biodiesel samples. However, these values were at least 75 °C or 163 °C lower than that of vegetable oil, indicating the higher combustibility of biodiesel samples. On the basis of the iodine values (IV's), biodiesel samples and vegetable oil were classified as a group of semi-drying oil (IV = 100–130). It was however noted that the IV's for both biodiesel sample A (IV = 128) and vegetable oil (IV = 127) were somewhat closer to that for a group of drying oil (IV >130).

Table 1. Characteristics of biodiesels and vegetable oil

	Biodiesel A	Biodiesel B	Biodiesel C	Vegetable oil
Flash point [°C]	176	185	182	250
Autoignition temperature [°C]	255	242	242	418
Iodine value	128	115	119	127

Thermal stability of biodiesel samples and vegetable oil

The TG-DTA curves of biodiesel samples and vegetable oil are shown in figs. 7-10. The biodiesel samples underwent thermal decomposition in a similar fashion as expected from their similar composition. The thermal decomposition temperatures (TG curves) of biodiesel samples were ~100 °C lower than that of vegetable oil. This finding further suggested that biodiesel samples were more combustible than vegetable oil.

The DSC curves of biodiesel samples and vegetable oil are shown in figs. 11-14. Each sample displayed a characteristic DSC curve. For biodiesel samples, the DSC curves consisted of two or three peaks attributable to their two- or three-step thermal decomposition. The first decomposition started at ~100 °C, which was ~45 °C lower than that of vegetable oil. Therefore, it is almost certain that biodiesel samples are more prone to thermal decomposition than vegetable oil.

The results of the modified WBT are shown in figs. 15 and 16, and compared with results of TG-DTA, DSC in tab. 2. WBT gives the lowest onset temperature and the DSC gives next one. The WBT is the most similar to natural conditions. On standing at 120 °C in WBT all samples began to generate smoke over a period of 8 hours. At 100 °C only vegetable oil re-

Table 2. Summary of the results of TG-DTA, DSC, and WBT

	TG [°C]	DTA [°C]	DSC [°C]	WBT	
				100 °C hour	120 °C hour
Biodiesel A	190.0	159.3	107.0	5.7	3.0
Biodiesel B	190.8	150.4	97.5	7.4	4.3
Biodiesel C	192.7	165.6	112.1	9.9	5.0
Vegetable oil	294.7	178.4	143.1	—	7.6

mained unchanged even after 10 hours. The rapid increase in the sample temperature was attributable to the exothermic decomposition. As expected, the higher atmospheric temperature accelerated the decomposition. Bio-diesel sample A was found to be the most heat sensitive sample tested and thereby could hold the highest risk of spontaneous ignition.

Since the constituent of FAME's in biodiesel samples A-C were found to be identical, the observed difference in the heat sensitivity was probably derived from various additives (*e. g.*, antioxidant additives).

Possible mechanisms of spontaneous ignition of biodiesel

The surface area per unit volume of biodiesel increases with its size, and absorbs much more onto fibrous material (*e. g.*, a piece of cloth and paper), metal/wood powders and porous material (*e. g.*, activated clay). The increased surface area also results in more contact with air, thus facilitating exothermic auto oxidation, which is very similar situation with Nagoya biodiesel fire in 2005, where biodiesel was absorbed with rag.

Under the well-insulated condition, nearly adiabatic condition, such as in a tightly closed container with poor thermal conductivity, the heat caused by exothermic decomposition will be built up inside. Once reaching the heat onset temperature, the inner temperature will rise rapidly and subsequently a fire could start [7].

Conclusions

A series of experiments were carried out to investigate the possibility of spontaneous ignition of biodiesel. The experimental results can be summarized as follows.

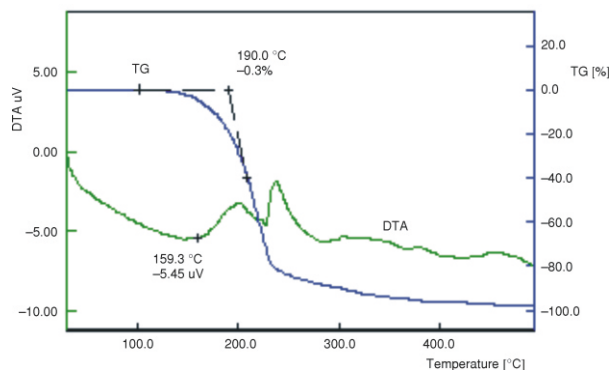


Figure 7. TG-DTA results of biodiesel A

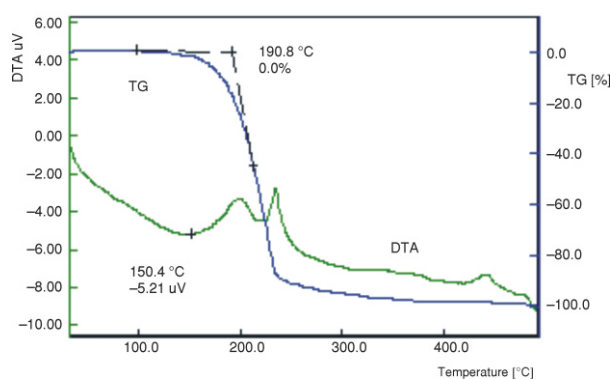


Figure 8. TG-DTA results of biodiesel B

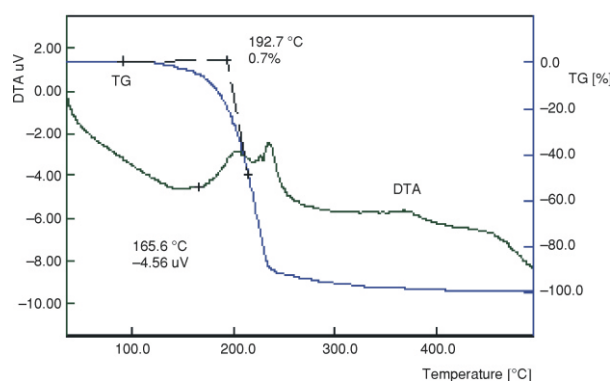


Figure 9. TG-DTA results of biodiesel C

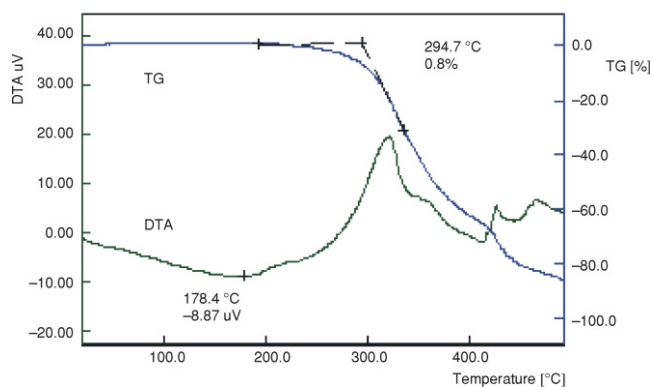


Figure 10. TG-DTA results of vegetable oil

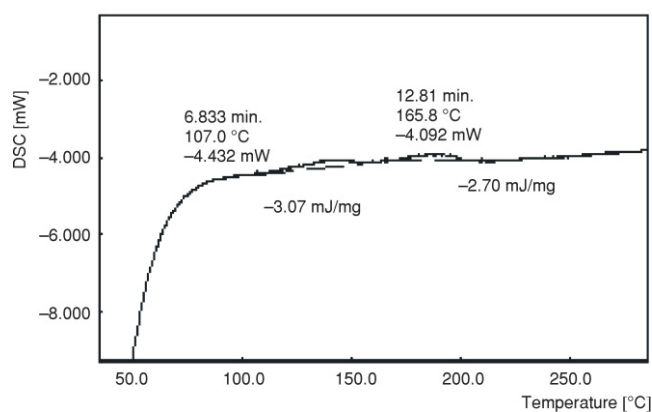


Figure 11. DSC results of biodiesel A

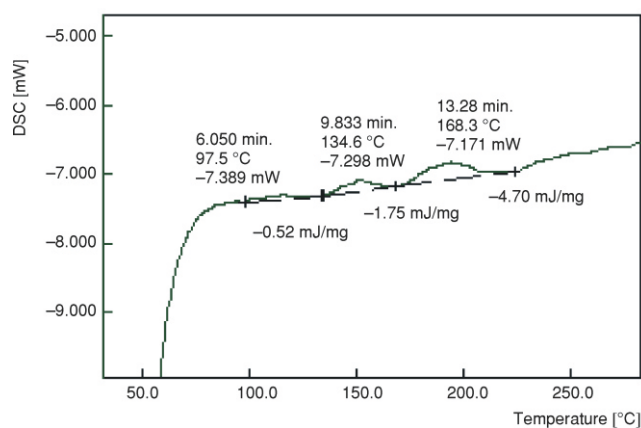


Figure 12. DSC results of biodiesel B

The major components found in biodiesel samples were unsaturated FAME's, namely methyl linoleate and methyl oleate, which were susceptible to exothermic decomposition. Biodiesel had a heat onset temperature of ~100 °C, which was ~45 °C lower than that of vegetable oils.

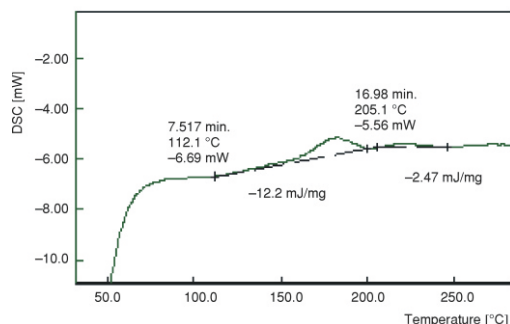


Figure 13. DSC results of biodiesel C

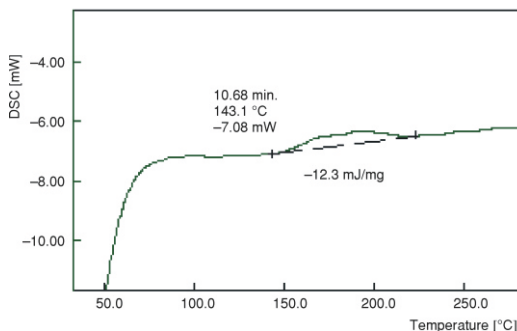


Figure 14. DSC results of vegetable oil

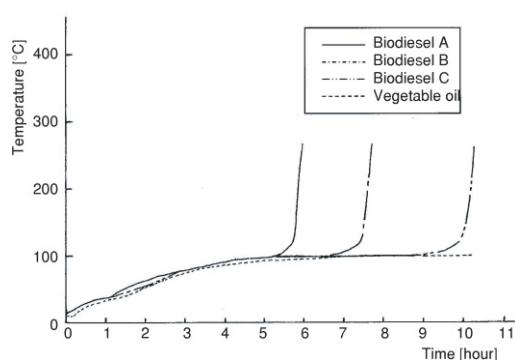


Figure 15. The results of biodiesel A, B, C, and vegetable oil by the modified WBT (100 °C)

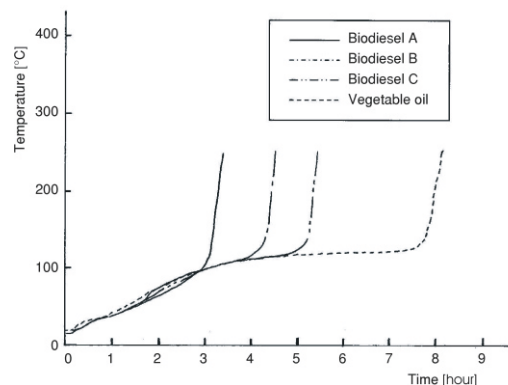


Figure 16. The results of biodiesel A, B, C, and vegetable oil by the modified WBT (120 °C)

Under the isothermal condition at 100 °C, the inner temperature of biodiesel rose rapidly after a short induction period (1–4 hours) with generation of smoke, whereas the inner temperature of vegetable oils stayed at 100 °C for more than 10 hours.

The main conclusion to be drawn from these results is that biodiesel has significantly higher risk of spontaneous ignition compared with vegetable oils. The biodiesel sampled at the fire site (*i. e.*, biodiesel sample A) has indeed the highest risk of spontaneous ignition. Accordingly, precautions must be exercised to minimize the fire risk in biodiesel production facilities and so on.

Acknowledgement

We thank Prof. Akio Kuwae, Dr. Yasuko Fukuda, and Dr. Tastushi Toyokuni for their invaluable guidance throughout this investigation. GC-MS analyses were carried out at JOEL Ltd.

References

- [1] Marlair, G., Rotureau, P., Automotive Biofuels Safety: INERIS Project "Biosafuls", OECD-IGUS-EOS Meeting, Washington D. C., USA, 2006

- [2] ***, Fire and Disaster Management Agency of Japan, White Book on Fire Service in Japan, 2005
- [3] Hoshino, T., Iwata, Y., Koseki, H., Oxidation Stability and Risk Evaluation of Biodiesel, *Thermal Science*, 11 (2007), 2, pp. 87-100
- [4] Koseki, H., Natsume, Y., Iwata, Y., Evaluation of the Burning Characteristics of Vegetable Oils in Comparison with Fuel and Lubricating Oils, *J. of Fire Science*, 19 (2007), 1, pp. 31-44
- [5] ***, American Society for Testing and Materials (1990b), Standard Test Method for Determining Material Ignition and Flame Spread Properties, ASTM E1321-90, ASTM, Philadelphia, Penn, USA
- [6] Porter, N. A., Caldwell, S. E., Mills, K. A., Mechanisms of Free Radical Oxidation of Unsaturated Lipids, *Lipids*, 30 (1995), 4, pp. 277-290
- [7] Komamiya, K., Self-Ignition from Large Pile of Solid Waste (in Japanese), *Safety Digest*, (2006), 50, pp. 30-38

Authors' addresses:

Y. Shibata

Nagoya City Fire Bureau
Graduate School of Natural Sciences,
Nagoya City University
Nagoya, Japan

H. Koseki

National Research Institute of Fire and Disaster,
4-35-3, Jindaijihigashi-machi, Chofu,
Tokyo 182-8508, Japan

O. Shimizu

Graduate School of Natural Sciences,
Nagoya City University
Nagoya, Japan

Corresponding author H. Koseki

E-mail: koseki@fri.go.jp