

OXIDATION STABILITY AND RISK EVALUATION OF BIODIESEL

by

Takashi HOSHINO, Yusaku IWATA, and Hiroshi KOSEKI

Original scientific paper

UDC: 662.754

BIBLID: 0354-9836, 11 (2007), 2, 87-100

This review describes oxidation and thermal stability and hazardous possibility of biodiesel by auto-oxidation. As it can be distributed using today's infrastructure biodiesel production has increased especially in the European Union. Biodiesel has many surpassing properties as an automotive fuel. Biodiesel is considered safer than diesel fuel because of the high flash point, but it has oxygen and double bond(s). Fatty acid methyl esters are more sensitive to oxidative degradation than fossil diesel fuel. The ability of producing peroxides is rather high, therefore we should care of handling of biodiesel.

Key words: *biodiesel, oxidation stability, thermal stability, Rancimat, pool fire*

Introduction

Biodiesel is a name for a variety of ester-based fuel made from vegetable oils, such as soybean, rapeseed or sunflower oil, or from animal fats, using transesterification process. This renewable source is as efficient as petroleum fuel in unmodified diesel engines [1-3]. The concept of using vegetable oil as engine fuel dates back to 1895 when Rudolf Diesel developed the first engine to run on peanut oil, as he demonstrated at the World Exhibition in Paris in 1898. He said "The use of vegetable oils for engine fuels may seem insignificant today. However such oils may become in the course of time as important as the petroleum and coal products of the present time [1]".

Biodiesel can be distributed using today's infrastructure and has become a rapidly growing market of renewable biofuels especially in the European Union and has been studied on characteristics of fuel for vehicles, but also it is important to study in regard to fire safety.

Biodiesel chemistry

Table 1 shows general properties of biodiesel [3]. Biodiesel (virgin) is made of raw vegetable oil, and biodiesel (used) is made of used vegetable oil, mostly used for

Table 1. Properties of biodiesel [3]

		Unit	Virgin biodiesel (rapeseed)	Used biodiesel I	Used biodiesel II
Density	@15 °C	g/cm ³	0.8824	0.8856	0.8825
Viscosity	@30 °C	mm ² /s	5.555	5.407	5.927
	@40 °C	mm ² /s	4.456	4.411	4.726
Flash point	COC ⁽¹⁾	°C	186	184	186
Pour point		°C	-7.5	-2.5	-2.5
CFPP ⁽²⁾		°C	-12	-4	-1
Ash		wt.%	0.001	<0.001	0.001
Water		wt.%	0.01	0.03	0.04
10% carbon residue		wt.%	0.29	0.21	0.32
Sulphur		wt. ppm	2	<1	4
Cetane index		—	58.0	52.2*	56.5
Distillates	Ignition point	°C	322.5	294.0	135.5
	10 vol%	°C	335.0	332.5	329.5
	50 vol%	°C	338.0	336.5	333.5
	90 vol%	°C	351.0	decomposed	347.5
	95 vol%	°C	decomposed	—	decomposed
Total acid value		mg KOH/g	0.23	0.19	0.34
Iodine number		mg/100 g	111	124	98.9
Methanol		wt./vol.%	0.04	<0.01	0.07
Phosphorus**		wt. ppm	no detect	no detect	no detect
Metals	Na	wt. ppm	<1	<1	<1
	K	wt. ppm	1	<1	4
Gums		g/100 ml	—	2.2	—
Elements	C	wt.%	77.1	77.1	76.8
	H	wt.%	12.1	12.0	12.1
	O	wt.%	10.5	10.7	10.9

* Calculated from JIS K2204-92; ** Limit of detection is 10 wt. ppm
⁽¹⁾ Cleveland open cup; ⁽²⁾ Cold filter plugging point

cooking. Biodiesel is biodegradable and non-toxic, has significantly fewer emissions than petroleum diesel fuel. Flash point is about 130-200 °C, and it is defined as a non-flammable liquid by the U. S. Occupational Safety and Health Administration

(OSHA) [4, 5]. This property makes a vehicle fueled by pure biodiesel far safer in an accident than one powered by petroleum diesel or explosively combustible gasoline. But biodiesel easily produces peroxides and the vigorous combustion may occurs compared with diesel fuel. Methanol is used in the manufacturing, and the concentration of methanol effects on the flash point. This review describes the possibility of hazard, the oxidation and thermal stability of biodiesel from recent papers.

Due to the chemical composition, fatty acid methyl esters (FAME) are more sensitive to oxidative degradation than fossil fuel. This is especially true for fuels with a high content of twice and more fold unsaturated esters, as methylene groups adjacent to double bonds have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation. An understanding of biodiesel stability requires knowledge of the chemical make up of biodiesel and its parent, vegetable oils. Fats/oils contain a glycerol molecule bonded to three fatty acid chains. This structure can be called triester or triglyceride. These chains differ in the number of carbon atoms and the number of carbon-carbon double bonds in the chain. For example, in soybean oil, there are four types of chains that contain 18 carbon atoms. So biodiesel with esterification of soybean oil contains stearic, oleic, linoleic, and linolenic methyl esters. A double bond normally introduces a “kink” in the chain and plays an important part in the stability of biodiesel.

Stearic acid is saturated, but oleic, linoleic, and linolenic acid are unsaturated. The location and number of double bonds influence reactions to destabilize fatty acid chain. The interaction of oxygen molecules with the fatty acids chain, called “oxidation”, destabilizes oil/biodiesel. Relative rates of oleic, linoleic, and linolenic fatty acids with oxygen are known as 1, 41, and 98 times, respectively [6]. By oxidation, hydroperoxides are attached to the fatty acid chain. In food oil this leads to rancidity. In biodiesel these degraded chains can polymerize, hooking together into substances including insoluble gums that clog up parts.

Mechanisms of auto-oxidation of methyl oleate and methyl linoleate were studied by many researchers [7, 8]. The primary products formed from auto-oxidation of lipids can be understood based upon five different reaction types: reaction of carbon radical and molecular oxygen, atom transfer of a hydrogen from substrate to the chain carrying peroxy, fragmentation of the chain carrying peroxy to give oxygen and a carbon radical, rearrangement of the peroxy, and cyclization of the peroxy. Porter reviewed this subject regarding with the mechanisms of primary reaction steps which had been studied over the past fifty years [7].

Evaluation of stability in European Union

Standardization and quality assurance are the key factors in the market introduction of biodiesel [9-11]. In 1997 the European Commission gave a mandate to the European Committee for Standardization (Comité Européen de Normalisation – CEN) to develop standards for biodiesel as fuel. Minimum requirements and test methods are included in the standards, pr EN 14214 (automotive fuel) and pr EN 14213 (heating fuel).

Summary of EU project

In 2001 the European project Stability of Biodiesel (BIOSTAB) started [12-14]. The program was divided into four packages to evaluate and to develop accurate methods for the oxidation, storage, and thermal stability. Concerning oxidation stability the Rancimat test (pr EN 14112) has already been chosen. The relationship between the induction period provided by this test and other quality parameters has to be clarified. For thermal and storage stability no test method has been chosen, but one of the main goals is to select and develop a method for each item considering criteria such as reflection of real conditions, correlation with quality parameters of biodiesel, precision, and cost.

Oxidation stability (presence of oxygen)

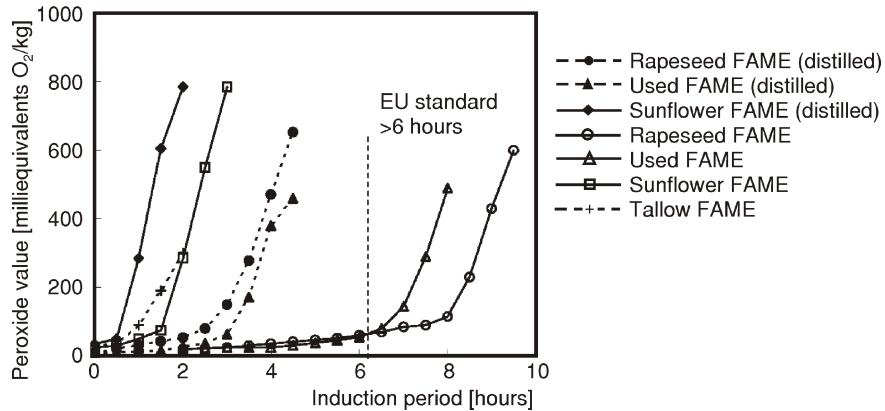
The standard analytical method oxidation stability (EN 14112) is derived from food chemistry. In this Rancimat procedure a sample is aged at elevated temperatures (110 °C) by passing air through it at a constant rate. The effluent gases are collected in a measuring cell filled with distilled water, of which the conductivity is constantly recorded. When the sample breaks down, a sharp increase of conductivity can be observed. The period of time up to this point is called induction period (IP), whereby the temperature at which the measurements were conducted needs to be specified. Every each half an hour, air flow was switched off and cool down the tube quickly using tap water for 5 minutes and quality parameter analysis is carried out immediately.

The Rancimat test was evaluated for seven methyl esters from rapeseed oil, sunflower oil, used frying oil and tallow, and each distilled and undistilled. For each quality parameter studied, a ranking of samples was obtained based on their resistance towards oxidation. This ranking was compared to the one provided by the Rancimat IP. Conclusion was that peroxide value, anisidine value, acid value, kinematic viscosity at 40 °C, ester content, linolenic acid content, UV absorbency at 232 nm, and polymer content, give similar ranking of samples with the conductivity of the Rancimat test. Only evolution of absorbency at 270 nm does not present a visible variation. This result in EU concluded that Rancimat is well correlated to other biodiesel quality parameters, so that fuels artificially oxidized to give IP values below the limit tend to be out of specification regarding the limited parameters.

Figure 1 shows the peroxide values [12]. It was concluded that samples of a holding time over six hours could be good. The EU standard for biodiesel has a stability specification of a minimum induction period of 6.0 hours.

Thermal stability (absence of oxygen)

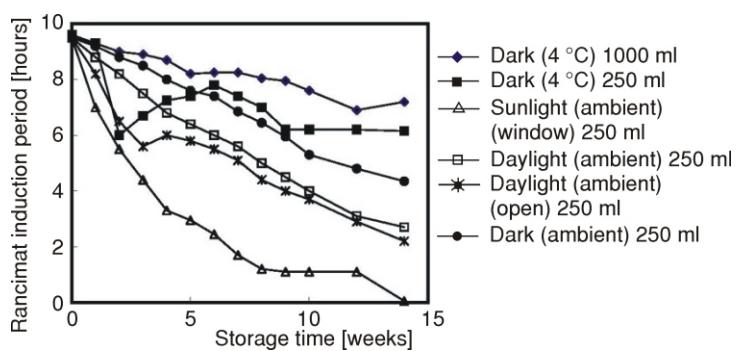
At the beginning of the project it was decided to keep ageing conditions of ASTM D 6468 (150 °C, 180 or 90 min.) considered not too far from the real conditions. The variation of quality parameters (acid value, Rancimat, ester content) after ageing was too low to be measured correctly. Thermal stability tests at 200 °C (oil bath) during 5 hours applied to all samples demonstrates that samples coming from European produc-

**Figure 1. Accelerated oxidation test (Rancimat) [12]**

tions are really stable when heated at a high temperature without air flow. Viscosity and acid value were chosen to evaluate the ageing effect. But repeatability results were not acceptable. So, it was decided to use Rancimat apparatus with a procedure specially modified for the thermal stability evaluation. Sample is aged for 6 hours at 200 °C in open tubes with air exposure. After ageing and cooling, polymer content is determined by high performance liquid chromatography (HPLC). The modified Rancimat test is suitable for use in terms of repeatability and easy to handle.

Storage stability

To determine the change of oxidation stability during storage the Rancimat test has successfully applied [13]. Results of 14 weeks storage test shows that the IP decreased rapidly, sunlight having the strongest influence on the fuel. Viscosity and acid number were found to correlate with the IP shown in fig. 2 [14]. After the one year storage study carried out on eleven different biodiesel samples, Prankl found that it was not

**Figure 2. Result of storage test (14 weeks) [14]**

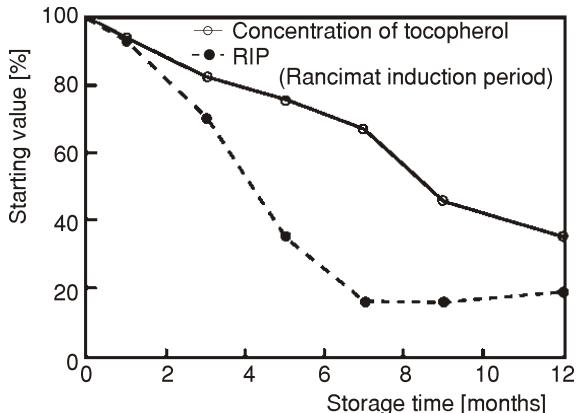


Figure 3. Storage time vs. starting value [12]

Figure 3 shows the dramatic decrease in tocopherol content in rapeseed oil (undistilled) and the decrease of Rancimat IP [12]. After a short initial period of parallel decrease IP decreases with a higher rate than tocopherols content.

The accelerated storage stability test was done at several methods and was correlated with ASTM D 4625. Using the modified Rancimat apparatus the selected experimental conditions based on IP48/IP306 were done with a stream of purified air (10 L/h), heated at 80 °C during 24 hours. The repeatability was carried out for 3 parameters (polymer content, ester content, and PV) on the 8 samples and showed good results for each parameter.

Evaluation of stability in United States

In US the fleets of biodiesel fueled cars have been progressing, and in 2001 handling and use guidelines were established by the National Renewable Energy Laboratory (NREL) [5, 6]. NREL further has studied biodiesel by accelerated stability test methods [15]. Users re-concerned that fuel does not form sediments in storage and also interested in knowing what precautions can be taken to ensure satisfactory storage characteristics.

Accelerated stability test

In NREL three accelerated stability methods were performed: (1) ASTM D2274, Standard Test Method, Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method), (2) ASTM D6468, Test Method for High Temperature Stability of Distillate Fuels, and (3) EN 14112 (Rancimat). D2274 and the Rancimat test are designed to predict storage stability, and D6468 test provides an indication of thermal or in-use stability. A simple procedure for measuring the total antioxidant content was developed and applied in this study.

possible to observe strong changes in 15 monitored characteristics. All samples met the specification limits even the end of storage period, with the exception of IP. Changes of peroxide value (PV) are different depending on samples. For samples initially not too oxidized, PV increase is slow and for samples initially oxidized, PV first increases and then decreases due to the formation of secondary oxidation products. Generally, biodiesel includes natural antioxidants such as tocopherols.

In the Rancimat method, the sample is exposed to a stream of air. The volatile carboxylic acids (primarily formic acid) are formed in the oxidation reaction into an absorber section that contains demineralized water. And in the D2274 method, the sample is heated to 95 °C and exposed to pure oxygen for 16 hours. After this reaction time, the amount of sediment (filterable insoluble) and gum (adherent insolubles) are determined. The D6468 test exposes the sample to air at a temperature of 150 °C for 3 hours. Then sediments formed are captured on a filter paper, and the reflectance of sediments of a particular light source is measured [15].

Rancimat test

At the Rancimat test only one sample among 27 samples passed the European specification [15]. The European standard for biodiesel has a stability specification of a minimum IP of 6.0 hours [12]. Typical biodiesel has a short Rancimat IP of less than 1 hour, and generates roughly 5 mg/100 mL of total insolubles in the D2274 test. The main factors affecting insoluble formation were antioxidants, polyunsaturates, and total glycerins. Additionally, there was no correlation of the Rancimat results with the initial acid values. Based on results for the D2274 test the average value of filterable was 2.46 mg/100 mL, and the average value of adherent insolubles was 2.47 mg/100 mL. Rancimat and D2274 results are not well correlated. The Rancimat test seems more suited to predicting how long a material can withstand oxidative conditions, not its inherent tendency to form polymers. The D2274 method exposes the fuel for a too long period of time to highly oxidizing conditions (at 95 °C), and the Rancimat test, on the other hand, measures the length of time before volatile acidic oxidation products begin to form [15].

Oxidizability

There is a significant effect of antioxidant content on the D2274 test results. The antioxidant content of biodiesel had a range of roughly one order magnitude (less than 0.5 to nearly 6). They derived oxidizability for C₁₈ methyl esters as:

$$\text{Oxidizability} = [0.02(\% \text{ oleic}) + 1(\% \text{ linoleic}) + 2(\% \text{ linolenic})]/100$$

Coefficients are induced from rate of oxidation at the room temperature [15]. For grease and tallow-based biodiesel this oxidizability is correlated to the Rancimat IP, but for the soy biodiesel it isn't correlated.

Thermal stability

The D6468 test exposes sample to air at a temperature of 150 °C for 3 hours. After this reaction sediments formed captured on a filter paper, and the reflectance of sediments with a particular light source is measured. The amount of sediments determined by gravimetry, and the acidity of the sample is determined. But it is difficult to interpret

these results without reference to gravimetric data on petroleum diesel fuel. Clearly additional work is required to fully quantify biodiesel thermal stability [15].

Stability index

Iodine number (= Iodine value)

Currently the most common method for doing this measurement to evaluate the chemical stability against oxidation is called the Iodine Number (IN). IN measures the reaction of iodine with double bonds of fatty acids. Fats with a greater number of double bonds provide more sites for oxidation. But IN does not necessarily make the best measurement for stability as it does not take into account the positions of the double bonds available for oxidation, so does not correlate well with the oxidative stability [16].

Peroxide value

One of the most widely used tests for oxidative rancidity, peroxide value (PV) is a measure of the concentration of peroxides and hydroperoxides formed in the initial stages of lipid oxidation. Milliequivalents of peroxides per kg of fats are measured by titration with iodide ion. PV is not static and care must be taken during testing. It is difficult to provide a specific guideline relating to rancidity. High values are definite indication of a rancid fat, but moderate values may be the result of depletion of peroxides. PV may not be a suitable indicator of biodiesel oxidation because fatty acids with higher unsaturation appear to produce hydroperoxides in lower yields as they are readily decomposed [17].

Oxidation stability index

The Oxidation Stability Index (OSI) is similar to the Active Oxygen Method (AOM), but it is faster and more automated. Air is passed through a sample held at a constant temperature. After the air passes, it is bubbled through a reservoir of de-ionized water. Volatile acids produced are dissolved in the water increasing its conductivity monitored continuously and OSI is defined as the hours required for the rate of conductivity change to research a predetermined value. This method has been collaboratively studied and accepted by American Oil Chemists Society, and determines the relative resistance of oil/fats samples to oxidation and replaces the outdated AOM. These measurements of stability are available which do take into account double bond position and is termed Oil Stability Index [18].

Knothe *et al.* [17] studied the influence of structure and concentration of individual fatty compounds. The most common fatty acid esters were investigated. Another stability specification is known as APE and BAPE for allylic and bis-allylic position equivalents which takes into account both the number and position of double bonds in the chains [19]. Knothe suggested APE and BAPE to correlate better the mixtures [17]. The calculation APE and BAPE values of the mixtures are given by Knothe [16]. One APE is

the equivalent of one allylic position contained in a fatty compound of concentration 1% in a mixture. The same holds for one BAPE. However, since the common C_{18:1}, C_{18:2}, and C_{18:3} fatty compounds contain two allylic positions, the following equation holds for these fatty compounds:

$$\text{APE} = 2 \times (A_{\text{C18:1}} + A_{\text{C18:2}} + A_{\text{C18:3}})$$

$$\text{BAPE} = A_{\text{C18:2}} + 2 \times A_{\text{C18:3}}$$

Here A is the amount of each fatty compound, in weight percentage.

Since C_{18:2} has only one bis-allylic position and C_{18:3} has two bis-allylic positions, regression of the BAPE values and the OSI times in fig. 4 gave the following correlation [16]:

$$\text{OSI} = 3.91 - 0.045 \times \text{BAPE} \quad (R^2 = 0.983)$$

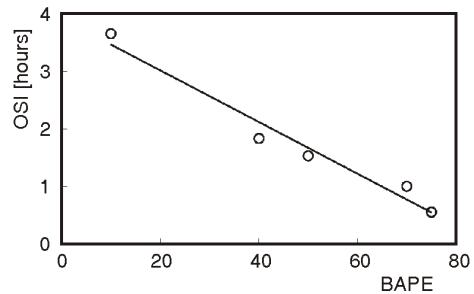


Figure 4. OSI values of some prepared mixtures at 90 °C [17]

Thermal stability (pyrolysis) by thermogravimetry

Oil and fats

Many kinds of oils/fats are used for foods over the whole world. The thermal stability of 11 vegetable oils and 2 animal fats was energetically evaluated by Ushikusa *et al.* [20, 21]. They reported the pyrolytical characteristics of various deteriorated oils and triglycerides investigated by thermogravimetry (TG), derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC). In auto-oxidized oil, an oxidative reaction occurred at 150~200 °C and could be detected more clearly during heating on TG and DSC curves with the progress of deterioration. In thermally oxidized oil, this reaction was not detected. But pyrolysis occurred more quickly than that of the unoxidized oil, the temperature at which the weight reduction accrued shifted to a lower region as deterioration proceeded [20].

Triglycerides and fatty acid esters

Ushikusa *et al.* [21] studied the pyrolysis characteristics of unsaturated polyglycerides (PG) and polyglycerol fatty acid esters (PGAE) by the dynamic programmed TG. They evaluated those of lauric acid (C₁₂), palmitic acid (C₁₆), and stearic esters (C₁₈) and those PGFE. They studied the temperature at weight loss initiation and the correlation of thermostability with the degrees of polymerization and esterification. The heat resisting time of PGFE was essentially independent of the carbon number of the

acyl group as was observed in the isothermal TG. But heat resisting time was reduced and thermostability decreased with increase in the degree of esterification.

Fukuda *et al.* studied the oxidative deterioration of edible oils by using TG [22]. As the measuring method to evaluate the oxidation deterioration for oils/fats, there are many methods, titration (acid value, peroxide value, iodine number, carbonyl value) and spectrometric analysis (thyocyanate method). However in case of brown oils from roasted seeds or carotene rich red oils, the degrees of deterioration could be determined only by the weighing method for the inhibition by the colored components. But it takes a very long term, for example, 6 months are needed at the temperature of 60 °C. Fukuda investigated the effectiveness of TG to evaluate the oxidation deteriorations and showed that TG would improve the accuracy by setting the proper condition (rate of temperature rise, oxygen flow) and has advantage of being able to use very small quantity of sample, 10 mg.

Dunn [23] studied the stability of fatty acids and biodiesel by the pressurized-differential scanning calorimetry (p-DSC). Curves were analyzed for the oxidation temperature of methyl soyate from four separate sources. Addition of antioxidants increased the oxidation temperature from 108.4-127.2 °C to 137.2-163.4 °C. Mixtures with t-butylhydroquinone consistently gave higher than those with α-tocopherol; therefore, the p-DSC may be useful for screening antioxidants. Though the p-DSC results were consistent with corresponding the OSI measured at 50 °C, no correlation for predicting OSI directly from oxidation temperature results was evident, with the possible exception of unmodified methyl soyate. This work establishes p-DSC as an analytical tool in evaluating the oxidative stability of biodiesel with and without antioxidants. Recently p-DSC is used in many studies to investigate the stability of fatty acids and esters [24-26].

Figure 5 shows the weight loss and the heat flux of biodiesel and diesel fuel which was examined with the thermogravimetry and differential thermal analysis (TG-DTA) [27]. Weight loss of diesel fuel occurred accompanying the increase of temperature, but for biodiesel, weight loss started at the temperature of 162 °C. And for diesel fuel the heat flux occurred at only one point of 200~210 °C, but for biodiesel several peaks (200, 260, 270, 500 °C) were shown. Further, authors [28] investigated the oxidation characteristics of biodiesel by used oils and its esterification products. Oil was almost mainly a rape-seed oil. Biodiesel was mixtures of the mono-, di-, tri-esters including a little raw material and other small compounds. To investigate the fundamental information of the effects of the number of double bonds in the branched hydrocarbons, the unsaturated aliphatic acid which has the same number of carbon atoms and its mono-methyl ester compounds were

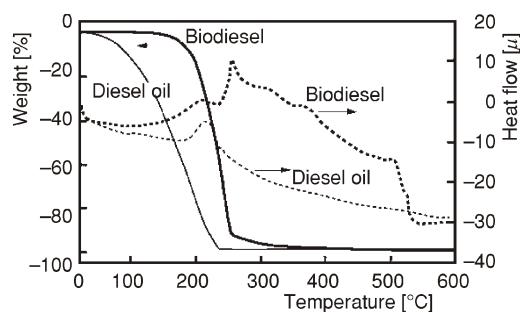


Figure 5. TG-DTA curves of biodiesel and diesel oil [27]

selected, that is, as C₁₈ fatty acid, oleic, linoleic, linolenic and stearic acid, and C₁₈ esters, each esterified compounds are selected.

Stearic acid is solid. But by heating, its phase transfer to liquid begins followed by the reduction of weight. The weight reduction of the stearic acid and oleic acid begins at 235 °C, but for linoleic acid and linolenic acid, about 225 °C. Esterification reduced these temperatures about 10 or 20 °C except the linoleic methyl ester.

Risk evaluation on auto-oxidation and combustion characteristics

Koseki *et al.* [29] studied the flash point and the ignition point of vegetable oils and evaluated the burning characteristics comparing with the petroleum fuel. Heat release rate, radiative heat loss, mass loss rate (burning rate) of vegetable oils are larger than petroleum fuel. And they concluded the ability of hazardous of most vegetable oils is greater than petroleum fuels. The reason is that vegetable oils include oxygen as 10~17 weight percents.

In August 2004 in Nagoya, Japan, a fire occurred from trash box due to the auto-oxidation of work rags which had been used for handling biodiesel. Shibata investigated scenario of this fire from the stored rags being stained with FAME for a long time with the sample oil composed mainly methyl oleate and linoleic methyl ester and small amount of linolenic acid methyl ester and stearic acid methyl ester by DSC [30]. Two stage exothermal phenomena occurred. The first point of temperature was 107 °C and the second one was 166 °C. Auto-oxidation of FAME gradually took place and continuously generated heat and at last a fire broke out at the ignition point. The ignition point of linoleic acid is 255 °C. In the isothermal test at 100 °C, vigorous combustion happened after 5 hours, fig. 6 [30]. The results mean that the FAME has the possibility of easily auto-oxidation during storage time.

To evaluate combustion characteristics of biodiesel, authors did pool fire tests in pans of 0.54 and 0.92 m in diameter floated above water [31]. Fuel layer depth was 13 or 30 mm, floating above 100 mm thick water. Table 2 show results. Relationship between irradiance and dimensionless horizontal distance, *I/D* during steady burning is shown in fig. 7. Radiant emittance of the flame, the flame temperature, the pulsation of the flame, and the phenomenon of boil-over were also evaluated. Radiative outputs and burning rate were smaller than those of diesel oil. However, burning of biodiesel seems to be more vigorous with the sounds of vaporizing water than those

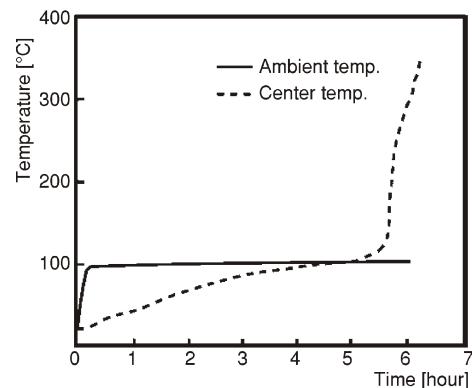
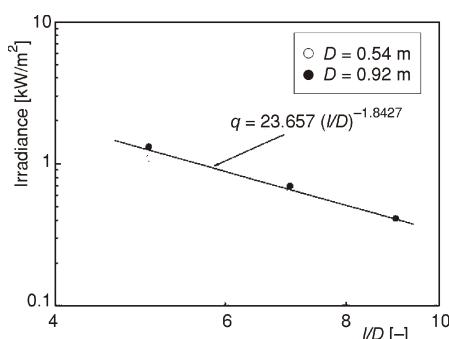


Figure 6. Time history of sample temperature in the isothermal test. Ambient temperature is 100 °C [30]

Table 2. Summary of results of burns [31]

Item	Unit	$D = 0.54 \text{ m}$	$D = 0.92 \text{ m}$
Mass loss rate	kg/sm^2	0.0204	0.0228
Burning rate	$\text{mm}/\text{min.}$	1.39	1.55
Radiant heat loss ($l/D = 5$)	kW/m^2	99.89	350.55
Averaged height of the flame (H/D)	Steady burning [-]	2.3	2.5
	Boilover [-]	7.4-8.3	8.6-9.7

**Figure 7. Relationship between irradiance and l/D during steady burning (D [m] is the pan diameter, and l [m] is the horizontal distance between pan axis and radiometer [31])**

of diesel fuel and crude-oil. Compared with vegetable oil, biodiesel gave larger burning rate and radiative outputs.

Very little is known about boilover of biodiesel, many studies are needed to establish the risk assessment of biodiesel at boilover. Droplet combustion of bio-oil was studied by Hristov *et al.* [32]. Bio-oil contains moisture and high content of moisture can promote the onset of microexplosions in the droplets during combustion than diesel fuel. Microexplosion and boilover are not the same phenomenon, but from these results the risk evaluation of fuel mixed with water is not always derived from flash point of fuel. In regard to extinguishment of biodiesel fires, research should be conducted.

Conclusions

In regard to the oxidation and thermal stability of biodiesel many investigation have been carried out. In EU and US Rancimat or modified Rancimat apparatus is fully adopted for evaluation of stability, but there is a difference between EU and US. In EU the induction period with Rancimat/modified Rancimat test is correlated to peroxide value by titration. However in US, oxidation stability index has been evaluated from many other views and recently APE and BAPE are adopted as most reasonable parameters for correlation with results of the Rancimat/modified Rancimat test.

Because the flash point of biodiesel is higher than that of diesel fuel, biodiesel is considered safety fuel. But biodiesel has double bond(s) and easily produces the peroxides, so might be considered to have the provability of cause of a fire during storage/handling. We have studied free burning of biodiesel. More study should be done in regard to the hazard possibility of biodiesel to consider of the future large demand.

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Authors' address:

T. Hoshino, Y. Iwata, H. Koseki
National Research Institute of Fire and Disaster
Higashijindaiji-machi 4-34-5, Chofu, Tokyo, 182-8508, Japan

Coresponding author H. Koseki
E-mail: koseki@fri.go.jp or wildstar@nyc.odn.ne.jp

Paper submitted: April 15, 2006
Paper revised: June 1, 2006
Paper accepted: June 15, 2006