

Influence of Base Diesel Fuel upon Biodiesel Sludge Formation Tendency

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ABSTRACT

With the rise in the introduction of biodiesel fuel throughout the world, there has arisen the technical issue of sludge formation due to oxidation degradation. The main causes of this phenomenon are the methyl ester degradation products such as short-chain organic acids and oligomer compounds such as dimer, trimer and tetramer acids, caused by the cleavage of the double bond in the fatty acid methyl esters (FAMES) at high temperatures, and by the occurrence of polymerized matter. The authors focused on this sludge formation and carried out forced thermal oxidation with various combinations of diesel fuel (aromatic content about 20 vol%) with Rapeseed Methyl Ester (RME) and Soybean Methyl Ester (SME). As the results, the settlement of viscous sludge was observed. It was found that this phenomenon was pronounced with the low concentration blend (around 20 to 40 vol%) biodiesel at which the maximum value was indicated.

Also, as the results of examination of hydrocarbon blends (cetane and binary aromatic hydrocarbons) as well as commercially available diesel fuels, it was found in laboratory experiments that if the aromatic ratio of the base diesel fuel was lower than approximately 30 vol%,

sludge formation became significant. Alternatively, if the aromatic ratio of the base diesel fuel was raised above approximately 30 vol%, the sludge was greatly reduced.

On the other hand, upon confirming the solubility in hydrocarbons of sludge created by the thermal degradation of the fuel, it was found that the sludge was more soluble in aromatics or methyl ester than in paraffin. In addition, by adding the correct amount of butylated hydroxytoluene and observing the sludge creation, it was found that it was possible to achieve reductions. That is to say, the implications were that the occurrence of this sludge was from the FAME radical reaction in high temperature oxidation, and solubility of the formed fuel sludge. From the above, it can be reasoned that effective countermeasures would be the addition of antioxidant to suit the biodiesel concentration, adjustment of the aromatic structure of the base diesel oil, and temperature reduction (load reduction) of the automobile fuel system.

INTRODUCTION

In automobile development, in addition to the existing demand for low emissions and high power/high torque, there is an increasing demand for lower fuel

consumption in order to reduce CO₂ emissions. There is growing expectation in the clean diesel car fitted with a common rail system to satisfy all these requirements. Also, as can be seen in Figure 1, recently there has been increased interest in the application of FAME blended diesel (biodiesel) in diesel cars. The characteristics of biodiesel vary according to their raw materials (vegetable oil, animal fat) and they comprise Fatty Acid Methyl Ester (FAME) of around C16 - C20.

In EU, where they have already been introduced, rapeseed oil is used for the raw material, in the United States, soybean oil, and in the Far East, palm oil is mainly used or development is under consideration. These methyl esters are almost never put into cars as is; FAME is what is blended in low concentrations to normal diesel fuel.

The characteristics of FAMES are shown in Table 1. Due to the fact that FAMES are saturated or unsaturated oxygenated compounds, accompanying issues exist, such as the calorific value being low compared to diesel oil, and the oxidation stability and low temperature fluidity are poor.

In the past, the alarm whistle to through and oxidization degradation of biodiesel has been made through the many reports and papers [1,2,3,4]. Fang et al. [5] and Ogawa et al. [6,7] did the laboratory tests centering on thermal oxidation degradation of B100, using various analysis equipments, and they proposed that the degradation materials of FAMES were the decomposed and the polymerization matters of FAMES. Especially the latter made reference also about the effect of Butylated hydroxytoluene (BHT, 2,6-di-tert-butyl-4-methyl phenol). Anyway, the oxidation stability would be one of key issues for the proper use of biodiesel.

Of these issues, this research concentrated on the occurrence of sludge due to low oxidation stability of FAMES. The various types of oxygen stability evaluation were conducted in the laboratory, and the effect of the sludge quantity and composition of the base fuel were investigated, using modified ASTM and EN methods.

EXPERIMENTAL FUELS EVALUATED

The fuels that were evaluated in this research are shown below. These fuels were variously blended and tested. Below, the FAME content of the FAME-blended diesel will be expressed as Rxx in the case of RME, and Sxx for SME. And referring to some fuel standards [8,9,10,11,12], the following fuels were obtained. Basically, R100 and S100 without anti-oxidation additive such as BHT were used in the main tests to examine the oxidation tendency (S100 imported from US meets BQ9000. Since some SME samples had a good numerical value of Rancimat, a certain anti-oxidation additives may have been contained.). But in case of anti-oxidation additive addition, the sample conditions are mentioned in each test result.

FAME-1 ; RME from the EU was referred to as "R100".

FAME-2 ; SME from the US was referred to as "S100".

Diesel fuel from EU ; Base diesel from the EU was referred to as "B0(EU)". This was used as a main base fuel in this research.

Diesel fuel from US ; Base diesel from the US was referred to as "B0(US-1)" and "B0(US-2)". These were used to test the influence of base fuels for sludge formation.

The basic characteristics of the above fuels are shown in Table 2 and Figure 2, and they are listed as an average value for each fuel characteristics. Although sterols are sometimes present in market FAMES, they were hardly detected in the FAMES supplied in laboratory tests of this research from the result of GC/MS.

Paraffin, aromatic hydrocarbon reagents, FAME reagents such as oleic acid methyl ester (OME), linoleic acid methyl ester (LME), and linolenic acid methyl ester (LnME) were prepared as the simulated fuels and the simplified evaluation performed. The particulars are explained in details in the results.

Table 1. General and Presumed Feature of Biodiesel

General Characteristics	Concerns to be investigated for vehicle development
Unstable oxidation	→ Increased sludge Materials compatibility FIE reliability deterioration
Low elastomer	→ Rubber and Plastics deterioration
Low evaporativity	→ Oil dilution
Low cloud point	→ Worse cold startability, Waxing
Oxygenates, Ester structure	→ Change of ignition characteristic Foaming by surface activity effect
Low energy density	→ Worse fuel economy Poor post-processing reproduction
Na, Glyceride, Fatty acid	→ Metal corrosion, Increased sludge
Contaminations (Metals, Sterols, Methanol, Glycerin, etc.)	→ Injector coking Material deterioration

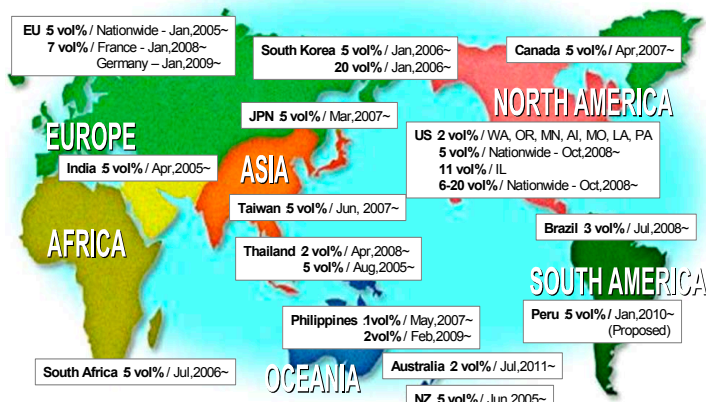


Figure 1. Movement of FAME blended diesel introduction* (Standard establishment)

*Created referring to IFQC website etc.

Table 2. Characteristics of Test Fuels

<Base FAME>				
Items	Unit	R100 (Ave.)	S100 (Ave.)	
Cetane number	—	52.5	48.5	
Water content	ppm $\mu\text{g/kg}$	250	270	
Contamination	ppm $\mu\text{g/kg}$	3.8	2.0	
Viscosity @40°C	mm ² /s	4.41	4.23	
Density @15°C	kg/m ³	0.883	0.884	
Ester content	% $\mu\text{g/m}$	98.0	97.8	
Linolenic acid methyl ester	% $\mu\text{g/m}$	10.1	8.8	
Rancimat @110°C	hours	6.3	3.0	
Acid number	mg KOH/mg	0.13	0.19	

<Base Diesel fuel>					
Items	Unit	S10-B0(EU)	S15-B0(US-1)	S15-B0(US-2)	
Cetane number	-	53.8	44.6	53.5	
Water content	ppm (mg/kg)	49	40	47	
Contamination	ppm (mg/kg)	6.8	1.3	0.3	
Cloud point	°C	-12	-24	-11	
CFPP	°C	-32	-25	-12	
Viscosity @40°C	mm2/s	2.72	2.14	2.43	
Density @15°C	kg/m3	0.831	0.841	0.825	
Distillation 90%	°C	328	295	321	
Aromatics	1 ring	% (v/m)	18.1	30.2	10.9
	2 ring	% (v/m)	2.4	5.9	1.3
	3 ring	% (v/m)	0.3	0.4	0.2
	Total aromatics	% (v/m)	20.8	36.5	12.4
HFRF @60°C	um	355	593	390	

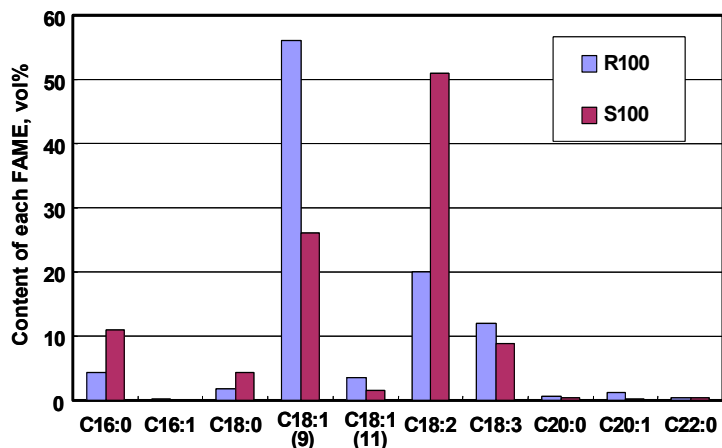


Figure 2. Composition of FAME used as Test fuels

SLUDGE FORMATION TEST METHOD

First, the induction period method was performed to confirm the thermal oxidation tendency modified from JIS K2287[13]. To evaluate sludge (Total insoluble) formation in laboratory mainly, the evaluation was performed with reference to ASTM D2274 [14] with allocated FAME concentrations. The test temperature specified by ASTM is 95°C; however, for sludge formation tests, the fuel temperatures were performed from 95 to 150°C arranged in order to grasp temperature dependency of sludge formation and so on. The authors defined these temperature conditions as “Modified-ASTM D2274”. After each oxidation test, the cooling of sample was carried out in the ice bath[15] based on ISO 12205[16].

While performing above mentioned sludge evaluation, also Modified-EN14112 (pr-EN15751) based on EN14112 [17] and correlation with the change in Delta TAN (Total Acid Number) at 115°C [18] referring to Modified ASTM D2274 procedure were confirmed if necessary.

After carrying out the laboratory fuel-only degradation test described above, an FIE test rig was made, and filter sludge trap tests were performed. Regarding this rig test performed in the bench, the fuel temperature of an actual engine, 25 to 115°C, were used. And this test was performed under heat-cooling environment cycle.

Conditions and details of the above tests are shown in Figure 3.

On the other hand, also the actual vehicle test for filter plugging was performed besides these sludge formation tests.

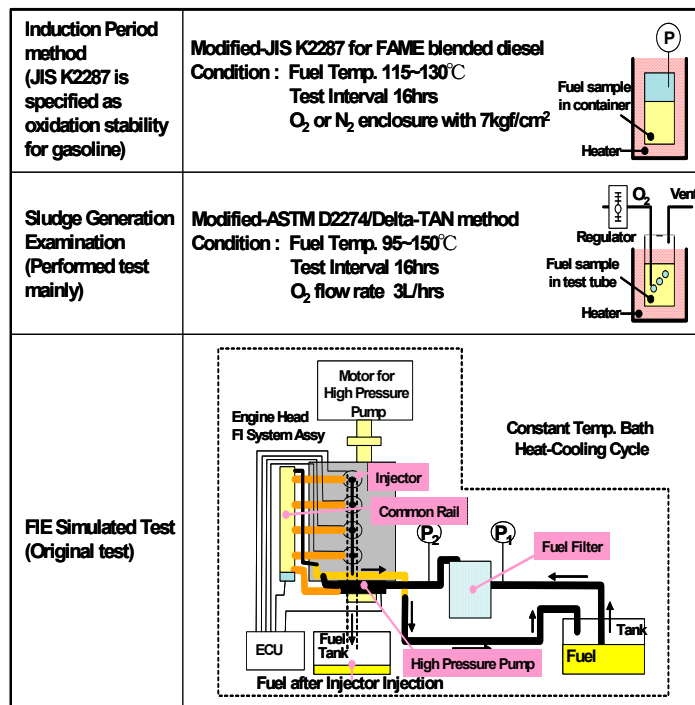


Figure 3. Sludge Formation Test Methods

SLUDGE EVALUATION

To decide the occurring sludge amount, as shown in Figure 4, with reference to the ISO 12205 sampling method [16], sludge was divided into filter-separated insoluble and viscous insoluble amounts, and their total represented as the “Total Insoluble Sludge Amount”. From here, “sludge” will be defined as “Total Insoluble Sludge” for the purposes of this paper. Insolubles were washed with a tri-solvent system followed by drying at 160°C. Alternatively, the insolubles were washed with a di-solvent system followed by air-drying. The latter technique was the author’s original method in order to avoid further decomposition and polymerization of sludge.

On the other hand, the sludge evaluation mentioned below, in the case of sludge occurring due to fuel-only degradation as well as sludge occurring in the FIE rig, the separation analysis was carried out according to the flow shown in Figure 5.

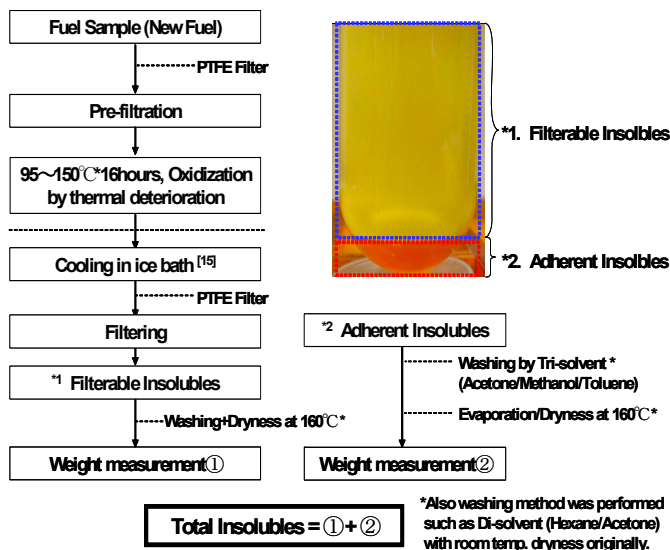


Figure 4. Sludge extraction conditions referring to ISO12205¹⁶⁾

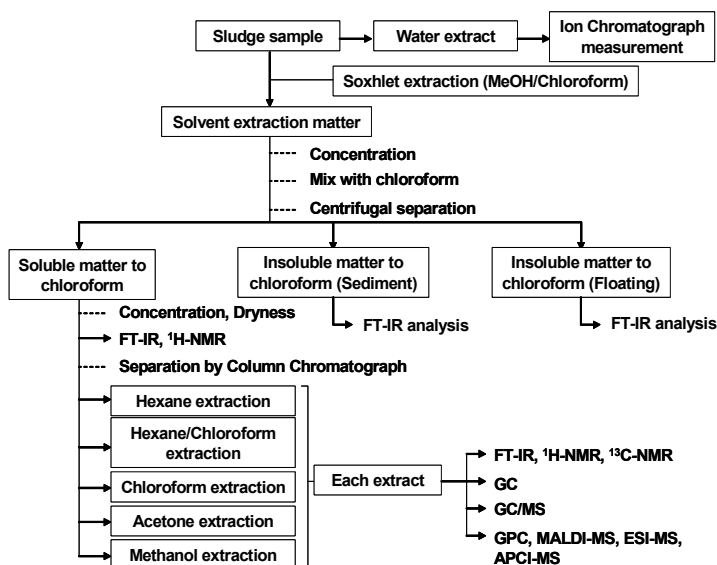


Figure 5. Separation method for sludge analysis

RESULTS AND DISCUSSION

Sludge Formation in Laboratory - As shown in Figure 6, the closed container tests at 115 and 130 °C for 16 hours modified from JIS K2287[13] were performed to confirm oxidation tendency of RME blended fuels by O₂ or N₂ pressurization atmosphere. The effect of thermal oxidation by O₂ and high temperature for acid number and peroxide was confirmed. And Figure 7 shows the results obtained from Modified- ASTM D2274 (temperature 115°C for 16 hours) with a mixed blend of sulfur-free diesel with RME and SME used as the FAME. Also shown in Figure 7 are the results obtained for Modified-EN14112 (as this is the same as prEN15751, it is indicated as prEN15751) that was performed concurrently.

As is well known, with an increase in the blend ratio in diesel fuel of either RME or SME, with the occurrence of light acids, prEN15751 shows a drop in value. Also, in the case of SME, which contains a lot of double-bond FAMES, oxidation degradation proceeded rapidly compared to RME. However, although there was no marked difference in the amount of sludge formed by RME or SME, maximum quantities were found to occur in both ester forms at FAME concentrations of around 20 to 40 vol%. In other words, no clear correlation could be confirmed between prEN15751 and the amount of sludge being formed.

On the other hand, with the original ASTM D2274 test conditions of 16 hours at 95°C, absolutely no sludge was confirmed for both tri-solvent dryness and di-solvent dryness.

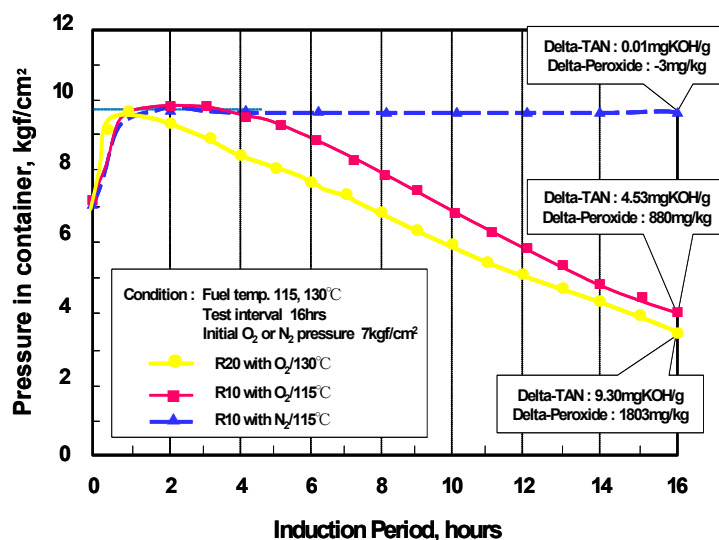


Figure 6. Induction Period by Mod.-JIS K2287

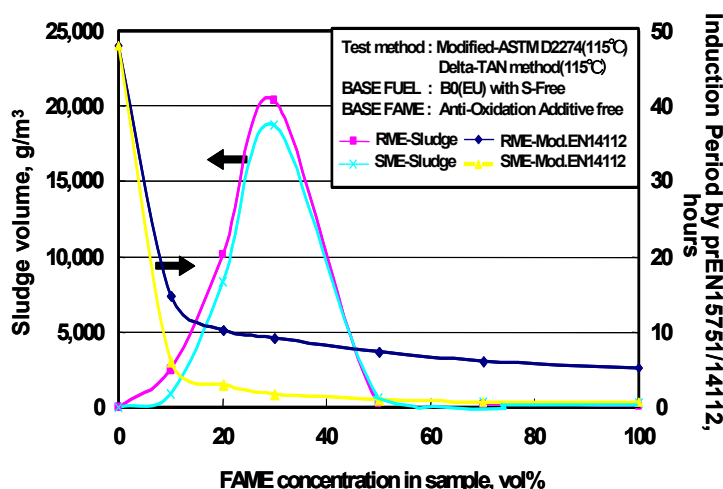


Figure 7. Relation between Sludge and Mod.-EN14112