

FAME Blended Diesel Fuel Impacts on Engine/Vehicle Systems

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ABSTRACT

The impact of fatty acid methyl ester (FAME) blended diesel fuel on engine/vehicle systems was comprehensively investigated by vehicle, laboratory and engine tests. In this study, 20% FAME blended fuel (B20) was mainly used and soy bean oil methyl ester (SME) was primarily selected as the FAME. Vehicle testing with long-term fuel storage in vehicle fuel tanks was conducted, considering the most severe conditions in market use. Laboratory and engine tests were also conducted to better understand the vehicle test results.

In the vehicle test, engine startability, idle roughness and fuel injection control were evaluated using nine vehicles with plastic or metal fuel tanks. All vehicles showed no problems up to 7 months. While five vehicles with plastic fuel tank did not show any problems throughout the test period up to 18 months, four vehicles with metal fuel tanks experienced malfunctions in engine start or fuel injection control following 8, 13, 13 and 18 months respectively. All problems experienced in the vehicles with metal tanks resulted from insufficient and unstable fuel pressure at common-rail of fuel system. The insufficient and unstable fuel pressure was caused by sticking of the suction control valve (SCV) in the fuel pump unit due to compounds accumulated on the SCV needle surface. Ester compound which is considered to be polymerized FAME was commonly observed in the accumulated compounds. Carboxylic acid salt was also detected as a component of the accumulated compounds. In one vehicle, rust was also detected in the accumulated compounds on SCV as well as inside of fuel injector. The five vehicles with plastic fuel tanks demonstrated no problems up to 18 months, though small amount of ester compounds, carboxylic acid salts and rust were detected on the inner surface of the SCV body of one of the plastic fuel tank vehicles.

From the laboratory tests, it was found that carboxylic acids, carboxylic acid salts and polymerized SME can be formed when SME-blended diesel fuel was oxidized. Regarding the potential metal sources of the carboxylic acid salts, it was found that not only metal components but also some elastomers used in the fuel system release metals to the fuel.

From the engine testing based on an industrial standard test protocol to assess engine torque loss owing to deposit formation, no significant engine torque loss was observed among fuels with various oxidation conditions regarding acid concentrations and Rancimat Induction Period values.

INTRODUCTION

The use of biomass-derived fuels is promoted by governments to enhance diversification of energy resources and potentially help reduce green house gas emissions. FAME is an option of biomass resources as well as ethanol to be used for automotive fuels. There are three major FAMEs currently used in the world, namely soy bean oil methyl ester (SME) in the US, rape seed oil methyl ester (RME) in Europe and palm oil methyl ester (PME) in Asia Pacific area. Depending on the fat sources, FAMEs have unique characteristics corresponding to the fatty acid chemistry. In general, FAMEs with unsaturated carbon bond are susceptible to degradation.

Specifications of FAMEs which can be used as blend stocks for diesel fuel have been set in each countries/regions. For example, ASTM D6751 [1] is set in USA, EN14214 [2] in EU and JIS K 2390 [3] in Japan. Upper limits of FAME blend ratio in the ordinary diesel fuels are defined as 5% in USA [4], 7% in EU [5] and 5% in Japan [6]. FAME concentrations higher than those upper limits are planned in some countries/regions. In ASTM, FAME blended diesel fuel

covering fuel blend grades ranging from 6 to 20 volume % biodiesel has been defined as D7467 [7].

Regarding FAME blended diesel fuel use, concerns or problems such as injector deposits and/or fuel system plugging, etc. have been recently reported [8-11]. Studies on the degradation of FAME as well as the compatibility of FAME blended diesel fuels to engine / vehicle systems have been carried out [12-27] and it is commonly recognized that further extensive study is still required.

In this study, comprehensive study consist of vehicle, laboratory and engine tests were conducted by collaborative joint research between oil company and auto manufacturer in order to better understand the impact of FAME blended diesel fuel on engine/vehicle systems. SME was primarily selected as the FAME to be tested considered that SME is susceptible to degradation owing to its chemical structure in which poly-unsaturated carbon bonds are largely contained.

In the vehicle test, engine startability and idle roughness were evaluated when FAME blended fuels were stored in vehicle fuel tanks for a long-term over 7 months up to 18 months at the maximum. Here, period over 6 months is recognized as a long-term storage time as defined in the Appendix X2.2.4 in ASTM D7467 [7]. The National Biodiesel Board and companies of diesel engine, fuel injection and vehicle stated that "Avoid long term storage of B20 to prevent degradation. Biodiesel should be used within six months." in the "Technical Recommendations for B20 Fleet Use Based on Existing Data" [28]. Effects of parameters consist of FAME species, use of cetane improver fuel additive, materials of vehicle fuel tank and vehicle operating conditions were studied in this vehicle test. The vehicles in which problems were noted were investigated in detail to identify the failure mode and the root cause.

In the laboratory study, degradation phenomena of SME were investigated to better understand potential malfunction of engine/vehicle system.

In the engine test, effects of oxidation status of FAME on engine performance were examined.

This paper provides information regarding the impact of FAME blended diesel fuel on engine / vehicle systems when the biodiesel fuel was stored in vehicle fuel tanks.

EXPERIMENTAL PROCEDURES

VEHICLE TEST

Long-term vehicle testing up to 18 months were conducted to study impacts of FAME blended fuel on vehicle performance. Four types of B20 fuels were prepared: "20% SME-1", "20% SME-1 with 600 mass ppm of a cetane improver (2-ethylhexyl nitrate)", "20% SME-2" and "20% RME". Major properties of the FAMEs as well as a base fuel (petroleum based fuel) used for the blending are respectively shown in Table A1 and Table A2 in Appendix part.

Two types of operation procedures, Procedure-A and Procedure-B, were developed to provide conditions that fuel was stored in a vehicle fuel tank for a long period. Procedure-A simulated operation modes of vehicles left in long-term parking facilities. Vehicles tested according to Procedure-A were operated on a chassis dynamometer for 80 minutes at 2730 rpm and around 2500 N condition at the beginning of the test, except vehicle #6. In vehicle #6, the load was limited about 1000 N during the last 30 minutes in the 80 minutes operation because the engine control was happen to be engaged to DPF regeneration mode. Then the vehicles under the Procedure-A were parked outside for a maximum of 18 months. Procedure-B simulated operation modes of vehicles with short mileage trips at low load conditions. Vehicles under Procedure-B were operated twice a week on road with a mileage of 4.4 km at each time for the entire test period of 7 months without refueling. Schematic diagram of these two procedures is given in Figure 1.

Nine light duty diesel vehicles consist of SUVs, vans and pickup trucks were used for the long-term test. These vehicles comply with an emission standard of Euro-IV or Japanese Long-term regulation corresponding to the destination market region. All vehicles were equipped with Toyota 1KD-FTV engines with displacement of 2982 cc. Four vehicles out of nine had metallic fuel tanks and other five had plastic fuel tanks. Test matrix of vehicles, fuels, operation procedures and period is shown in Table 1.

Vehicle performances of startability and idling roughness were evaluated every month. When a vehicle experienced problems, operation for that vehicle was terminated to examine. If detailed investigation on parts in fuel system was necessary, FT-IR for chemical structure analysis and/or EPMA and ICP for elemental analysis were carried out.

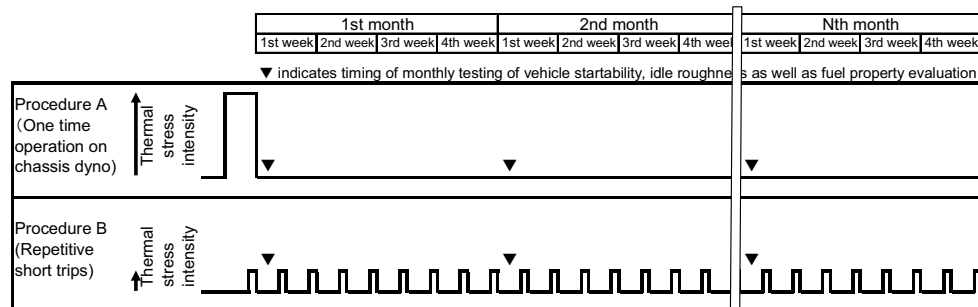


Figure 1 Schematic diagram of vehicle test patterns indicating thermal stress intensity and the frequency

Table 1 Vehicle test matrix

Vehicle number	Vehicle category	Model year	Destination market region	Tank material	Fuel	Cetane improver dose	Test procedure (*1)	Test period [month]
#1	SUV	2007	Europe	Metal	20% SME-1	No	A	14
#2	SUV	2007	Europe	Plastics	20% SME-1	No	A	18
#3	Pickup truck	2008	Thailand	Plastics	20% RME	No	A	17
#4	Van	2007	Hong Kong	Metal	20% RME	No	A	13
#5	Pickup truck	2008	Thailand	Plastics	20% SME-1	600 mass ppm	A	17
#6	Van	2007	Japan	Metal	20% SME-1	600 mass ppm	A	18
#7	Pickup truck	2008	Europe	Plastics	20% SME-1	No	B	7
#8	Pickup truck	2008	Europe	Plastics	20% SME-1	600 mass ppm	B	7
#9	Van	2007	Hong Kong	Metal	20% SME-2	No	A	8
*1 A: One time relatively high load operation followed by storage B: Periodical low load operation throughout storage period								

LABORATORY TESTS

FAME has several characteristics different from conventional petroleum based fuel. The chemical structures have double bonded carbon-carbon combination as well as ester function. In order to understand vehicle test results better and to consider potential problems which the characteristics may cause, following four kinds of laboratory tests were carried out. The first one is acid formation test at high temperature condition as the FAME would experience in diesel engine system. FAME is generally susceptible to oxidation owing to unsaturated double bonded structure, and as a result carboxylic acids are formed. The second one is materials elution test. FAME is supposed to have relatively stronger effect of elution due to the polarity of ester function compared to conventional petroleum diesel fuel. The third one is a test for carboxylic acid salts formation. Carboxylic acids formed by the oxidation of FAME can react with metal to form carboxylic acid salts, which are insoluble to fuel. The last one is a test for polymerization of FAME. Double bonded carbon can be bridged each other cross-linked by oxygen to form larger molecule [20], which could be a potential deposit precursor.

Acid formation test

Acid formation was studied from the following two points of view. One is the effect of SME concentration on increase of acid concentration after oxidation. The other is components of acids after oxidation. Apparatus shown in Figure 2 was used for the oxidation, which is similar to that



Figure 2 Apparatus used in acid formation study

used in the ASTM D525 "Standard Test Method for Oxidation Stability of Gasoline" [29].

SME blended fuels of three concentration levels, 10, 20 and 50 volume % were prepared by blending SME-1 with a base fuel (petroleum based fuel). Characteristics of SME-1 and the base fuel are respectively shown in Table A1 and Table A2 in Appendix part. One hundred milliliter (100 ml) of each sample fuel was held in a glass vessel and stored in a pressure tight metal container. The container was connected to pure oxygen gas line and fed up to 0.5 MPa-absolute (0.4 MPa-gauge) through check valve. Then the container was immersed into an oil bath to raise the temperature up to 110 deg C and kept for 16 hours. Test condition is summarized in Table 2. The temperature was set to 110 deg C based on the temperature that diesel fuel would usually experience in the fuel system of diesel engines. Ambient condition, pure oxygen 0.5 MPa-absolute, was set in order to accelerate the oxidation process. When oxygen was consumed due to the oxidation reaction of SME, oxygen was made up to keep the total pressure 0.5 MPa. After the 16 hours oxidation, the fuel samples were collected from the glass vessels to evaluate the oxidation status.

Total acid number (TAN) was measured by potentiometric titration method [30]. Compositional analysis for lower carboxylic acids, such as formic acid, acetic acid, propionic acid and oxalic acid, was performed by ion chromatography method. The other higher carboxylic acids were measured by gas chromatography mass spectroscopy apparatus equipped with selected ion monitoring detector after derivatized with Bis (trimethylsilyl) - trifluoroacetamide (BSTFA) reagent. The compositional analysis for carboxylic acids was conducted only with the 20% SME blended fuel.

Table 2 Condition of acid formation test

Fuel	Temperature	Atmospheric gas	Total pressure	Period
SME-1 10%	110 deg C	Pure oxygen 100%	0.5 MPa-abs.	16 hrs
SME-1 20%				
SME-1 50%				

Table 3 Materials used for elution test

No.	Materials (3 types, 16 kinds)	Materials ID	Surface area immersed [cm ²]	Test temperature [deg C]
1	Elastomers (7 kinds)	HNBR-1	58	120
2		HNBR-2		120
3		FKM-1		120
4		FKM-2		120
5		NBR-1		80
6		NBR-2		80
7		NBR with PVC composite		80
8	Resins (2 kinds)	Nylon (PA66) with glass-fiber	66	80
9		Polyacetal (POM) with glass-fiber	57	80
10	Metals (7 kinds)	Sn-Zn coated Steel-1	12	80
11		Sn-Zn coated Steel-2		80
12		Sn-Zn coated Steel-3		80
13		Zn-Ni coated Steel		80
14		Aluminum alloy (A3003)		80
15		Brass alloy		80
16		Terne sheet (Sn-Pb coated steel)		80

Table 4 Condition of materials elution test

Fuel	Temperature	Atmospheric gas	Total pressure	Period
SME-1 50%	80 deg C for Elastomers (except HNBR and FKM) or 120 deg C for HNBR, FKM, Resins and Metals	Air	0.1 MPa-abs. (atmospheric pressure)	168 hrs

Table 5 Condition of carboxylic acid salt formation test

Fuel	Temperature	Atmospheric gas	Total pressure	Period
SME-1 100%	140 deg C	Pure oxygen 100%	0.5 MPa-abs.	16 hrs

Table 6 Condition of polymerization test

Fuel	Temperature	Atmospheric gas	Total pressure	Period
SME-1 100%	80 deg C	Pure oxygen 100%	0.5 MPa-abs.	16 hrs
	110 deg C			
	140 deg C			

Materials elution test

Immersion tests with FAME blended diesel fuel were carried out to identify components eluted from typical materials used in fuel system of diesel engine.

Sixteen materials were evaluated, which consisted of 7 types of elastomers, 2 types of resins and 7 types of metals as shown in Table 3. As to elastomers, two pieces of rectangular shaped sample were used in each immersion test. As to resins, one piece of dumbbell shaped sample was used. As to metals, one piece of rectangular shaped sample, of which the side edges and the back surface were covered by epoxy coating, was used. The epoxy coating can stably mask the material beneath and does not contain metal elements. Surface areas of the test material pieces immersed were summarized in Table 3.

Immersion test was conducted with 150 ml of mixture of 50 volume % of SME-1 and 50 volume % of the base fuel. SME 50 % blended fuel was used considered that elution behavior is affected by both properties of SME and the base fuel. B0 fuel was also applied as a reference.

Each material was immersed to 150 ml of the SME-1 50 % fuel in a test tube. Then the test tube was heated in an oil bath to raise the temperature up to 80 deg C or 120 deg C, corresponding to the maximum service temperature of each material. Each immersion test lasted for 168 hours under air of 0.1 MPa. A condensation tube was installed on to the each test tube so that evaporative components such as lower carboxylic acids, etc. would return to the fuel during the immersion test. The test conditions are summarized in Table 4. After the immersion test, each fuel sample was evaluated by appearance and analyzed by ICP method to detect metallic elements eluted from the materials.

Carboxylic acid salt formation test

Oxidation of SME-1 under existence of a copper plate for 16 hours was carried out to identify possibility that carboxylic acid generated through degradation of SME-1 would form carboxylic acid salt with copper eluted from the plate.

In order to enhance carboxylic acid salts formation, temperature condition was set at 140 deg C, which would be the maximum temperature of the fuel in modern diesel engine systems equipped with a common-rail fuel injection unit. For the same reason, 100 % of SME-1 sample fuel was used. In addition, ambient condition was set to pressurized pure oxygen of 0.5 MPa-absolute in order to accelerate the oxidation process.

One hundred milliliter (100 ml) of 100 % SME-1 sample was held in a glass vessel with copper plate. The shape of copper plate was rectangular and the surface area immersed to the sample fuel was approximately 10 cm². The glass vessel was stored in a pressure tight metal container. Then the container was connected to pure oxygen gas line and fed up to

0.5 MPa-absolute (0.4 MPa-gauge) through check valve. The container was immersed into an oil bath to raise the temperature up to 140 deg C and kept for 16 hours. Test condition is summarized in Table 5. When oxygen was consumed due to the oxidation reaction of SME, oxygen was made up to keep the total pressure 0.5 MPa. After the 16 hours oxidation, the fuel samples were evaluated by TAN in addition to appearance inspection. TAN was determined by titration method [30].

Polymerization test

Severe oxidation testing with SME-1 for 16 hours was carried out to examine possibility of its polymerization.

In order to enhance polymerization of SME, 100 % SME-1 sample was used with pressurized pure oxygen of 0.5 MPa. Three temperature conditions of 80, 110 and 140 deg C were selected.

One hundred milliliter (100 ml) of 100 % SME-1 sample was held in a glass vessel and the glass vessel was stored in a pressure tight metal container. Then the container was connected to pure oxygen gas line and fed up to 0.5 MPa-absolute (0.4 MPa-gauge) through check valve. The container was heated up using oil baths to raise the temperatures to 80, 110 or 140 deg C and kept for 16 hours. The test conditions are summarized in Table 6. When oxygen was consumed due to the oxidation reaction of SME, oxygen was made up to keep the total pressure 0.5 MPa. After the 16 hours oxidation, the fuel samples were collected from the glass vessels. Molecular weight distribution of each sample was analyzed by GPC method before and after the oxidation.

ENGINE TEST

Engine test was carried out focusing on examining impact of oxidation status of FAME blended diesel fuel on engine system performance, especially maximum torque. In this paper, oxidation status is defined as the following two items. One is current concentrations of lower acids already existing in fuel. As the existing lower acids, formic, acetic and propionic acids were determined. The other is potential increase of acids when fuel is oxidized in engine system. Rancimat I.P. evaluated by EN 15751 method [31] was used as the index for the potential acid increase. Four B20 test fuels were prepared as shown in Table.7.

SME-3 with Rancimat I.P. of 4.4 hours was used to prepare No.1 fuel, of which Rancimat I.P. was measured at 14.3 hours. Characteristics of SME-3 are shown in Table A1 in Appendix part. Concentrations of formic acid, acetic acid and propionic acid in No.1 fuel were identified as less than 1 mass ppm. Two hundred liter (200 L) of the same SME-3 sample was treated at temperature of 100 deg C with introduction of air, of which flow rate was approximately 36 l/min, to have Rancimat I.P. of 0.6 hour. This degraded SME-3 sample was used to prepare No.2 fuel with Rancimat I.P. of 2.9 hours. Schematic diagram of the preparation procedure for No.1 and No.2 fuels is shown Figure A1 in Appendix part. Concentrations of

formic acid, acetic acid and propionic acid in No.2 fuel were measured at 14 mass ppm, 4 mass ppm and 1 mass ppm respectively. No.3 fuel with Rancimat I.P. of 11.0 hours was prepared by adding 560 mass ppm of butylated hydroxytoluene (BHT), an antioxidant additive, to No.2 fuel. Concentrations of formic acid, acetic acid and propionic acid in No.3 fuel were supposed to be the same values as those in No.2 fuel. No.4 fuel with Rancimat I.P. of 2.8 hours was prepared by adding 11 mass ppm of formic acid to No.2 fuel. Hence, concentrations of formic acid, acetic acid and propionic acid in No.4 fuel were calculated as 25 mass ppm, 4 mass ppm and 1 mass ppm respectively. Total of these three acid concentrations in No.4 fuel was therefore 30 mass ppm. It coincided with the upper limit for sum of these three acid concentrations for the B5 fuel standard defined in the fuel quality law of Japan.

A light duty diesel engine of Toyota 1KD-FTV, the same model used in the vehicle test, was used in this study. It was a turbo charged 4 cylinder engine with displacement of 2982 cc, and had common-rail fuel injection system. Major specifications of the engine were summarized in Table 8.

Engine operation cycle was illustrated in Figure 3. One basic cycle lasted for one hour with 6 low load conditions and 6 high load conditions. This cycle was repeated 8 times a day, followed by 16 hours of engine soak period, and the testing continued until total engine operation time reached 32 hours. Coolant water temperature during engine operation was maintained between 87-94 deg C.

Engine torque was measured with 30 minute intervals at 100 % speed and 100 % load conditions. Final torque loss (FTL) was defined as torque reduction ratio, comparing a torque value measured at 0.5 hour of operation with an average of torque values measured at 31.5 and 32.0 hours. FTL can be expressed by Equation (1).

Table 8 Major specifications of engine used

Engine ID	1KD-FTV
Displaced volume	2982 cc
Cylinder configuration	Inline 4
Bore	96 mm
Stroke	103 mm
Compression ratio	17.9 : 1
Numbers of Valves	4 valves / cylinder
Air Intake system	Turbo with intercooler
Fuel injection system	Common-rail
Maximum Output	125 kW / 3400 rpm
Maximum Torque	352 Nm / 1800-3400 rpm

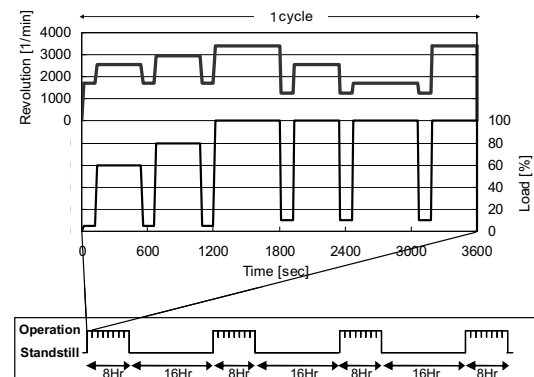


Figure 3 Engine test profile

$$FTL = 1 - \frac{\left(\frac{T(31.5) + T(32.0)}{2} \right)}{T(0.5)} \quad (1)$$

here T(x) = Engine torque at x hrs cumulative engine running time

Table 7 Fuels of engine test for oxidation status effect study

No.	Fuels	Additives	Acid concentration [mass ppm]			Oxidation stability (Induction Period by EN 15751) [hr]
			Formic acid	Acetic acid	Propionic acid	
1	Fresh SME-3 20%	NA	<1	<1	<1	14.3
2	Degraded SME-3 20%	NA	14	4	1	2.9
3	Degraded SME-3 20% + Anti-oxidant	BHT: 560 mass ppm in B20	14 ^(*1)	4 ^(*1)	1 ^(*1)	11.0
4	Degraded SME-3 20% + Formic acid	Formic acid: 11 mass ppm in B20	25 ^(*2)	4 ^(*2)	1 ^(*2)	2.8
(*1) Estimated values assuming that the acid composition of No. 3 fuel is equal to that of No. 2 fuel						
(*2) Calculated values from the acid composition of No. 2 fuel and 11 mass ppm of formic acid added						