Chapter 3

Trend of Biodiesel Fuel in Japan

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3. TREND OF BIODIESEL FUEL IN JAPAN

3.1. The governmental target for introducing biodiesel fuel in Japan and its actual situation

Biofuels (Organic compounds derived from plants and other biomass except for derivatives of crude oil, petroleum gas, natural gas and coal) like bio ethanol and FAME (Fatty Acid Methyl Ester; a product derived via chemical treatment from fatty oils like plant oils) play an important role as a measure to mitigate global warming, because the biofuels can be treated as carbon neutral materials according to the Kyoto protocol. The logic is that the amount of carbon dioxide generated from the combustion of biofuels is canceled out the amount of carbon dioxide absorbed during the growth of plants and other biomass.

The Japanese government has committed to the Kyoto protocol, meaning that the amount of green house gas emissions shall be reduced by six percent in 2010 from the 1990 emission level. To comply with its own plan to meet the Kyoto protocol, it has a target to introduce a 500,000 kl-crude oil equivalent of biofuels (including bio ethanol) by 2010.

The introduction of 500,000 kl-crude oil equivalent of biofuels is crucial to meet the commitment, as this measure alone could contribute to one percent reduction in greenhouse gases, out of a total target of six percent.

In a New National Energy Strategy issued by the Ministry of Economy, Trade and Industry in May 2006, the Ministry raised the target for the reduction of crude oil dependence in the country's transportation sector to ca. 80% in 2030, compared to 100% at present, with the aim to reduce in carbon dioxide emissions and its huge dependence on fossil fuels.

Electric vehicles and hydrogen-fuel cell vehicles and intelligent transportation system could be promising mid- and long-term measures to reduce carbon dioxide emissions and the dependence on oil.

Those next generation vehicles are, however, still in their research and development stage. On the other hand, bio fuels are liquid, can be used in existing vehicles and have an immediate effect on carbon dioxide emission reduction and oil dependence. Hence biofuels are useful.

Ethanol, ETBE (Ethyl Tertiary Butyl Ether) and FAME are under consideration as biofuels. The PAJ (Petroleum Association of Japan, a Japanese oil industry body) have committed themselves to introduce 210,000 kl-crude oil equivalent of ETBE into gasoline. Regarding the remaining 290,000 kl-crude oil equivalent, discussions are still ongoing

3.2. Situation and Future for Biodiesel fuel Penetration in Japan

To promote biomass energy and material, “Biomass Nippon Comprehensive Strategy” was established in 2002 by the Cabinet which was jointed by some Ministries; the Ministry of the Environment, the Ministry of Economy, Trade and Industry(METI), the Ministry of Agriculture, Fishery and Forest(MAFF) etc.

The MAFF promotes the “Biomass Town Concept” with cities, towns and villages playing a central role, an overall plan for using regional biomass as shown in Fig.3.2.1. As of March 31, 2007, 90 cities, town and villages have announced this concept. In these biomass towns, resources from cattle excrement or food waste, etc. are converted into energy at biomass conversion facilities such as power generation facilities or composting facilities to ensure that biomass is effectively used inside and outside of the regions.

The METI was established the “Law on the Quality Control of Gasoline and Other Fuels” (“Quality Assurance Law”). The Quality Assurance Law has been amended to allow up to 5% Fatty Acid Methyl Esters (FAME) by mass (in the USA and Europe, blending is by volume) and to prevent the use of unprocessed vegetable oils. The requirements take effect in March 2007. The diesel fuel properties specified in this law are sulfur, cetane index, T90 distillation temperature and upper limits on FAME and triglicerides. For biodiesel fuel, additional requirements include limits for methanol, total acid number (TAN), low molecular weight acids and oxidation stability as acid value growth. Both diesel fuel and biodiesel fuel/diesel blends have limits on FAME and triglycerides to clearly distinguish between the two and to prevent the use of unprocessed triglycerides.

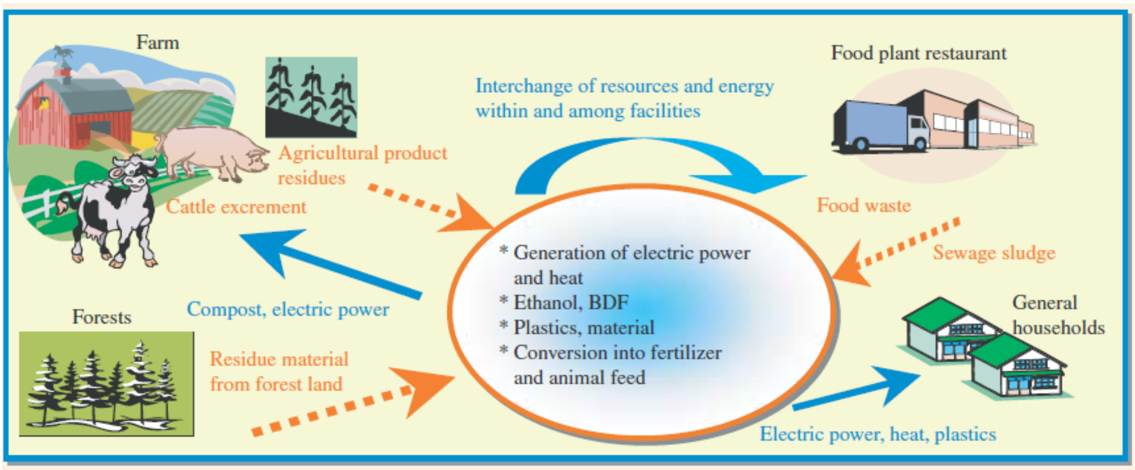
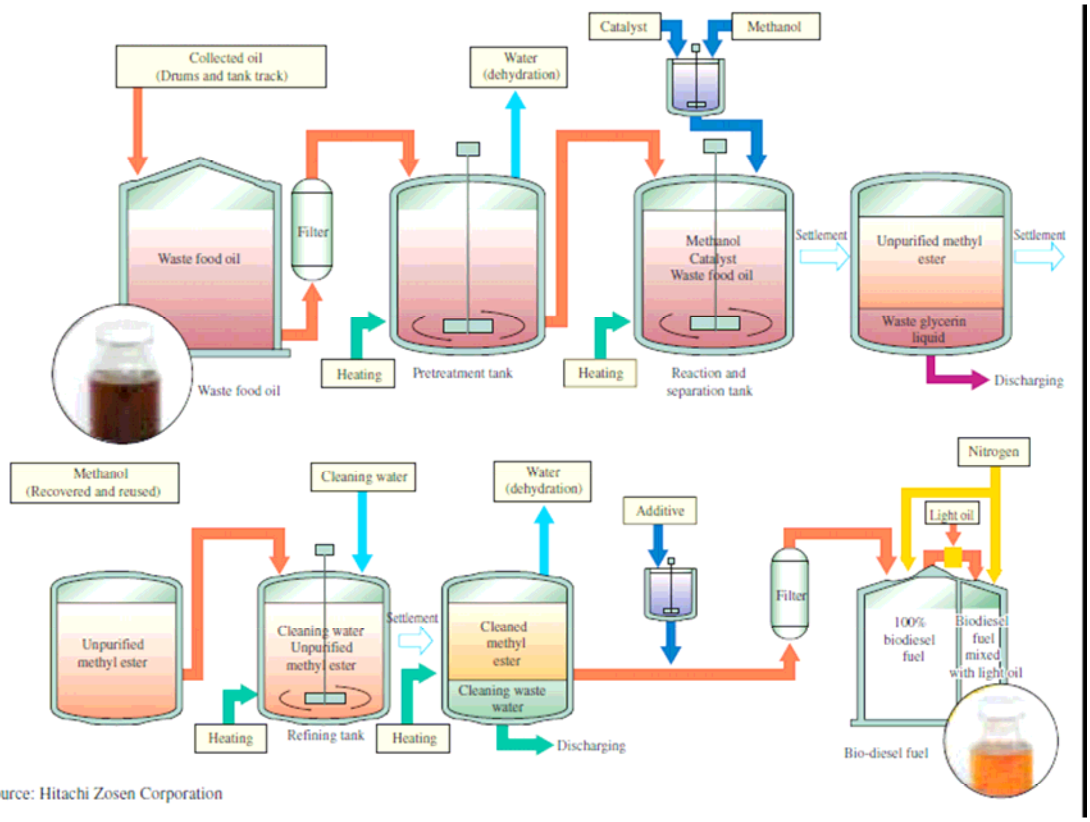


Fig.3.2.1 Biomass Town Concept in Japan

In this concept, Biodiesel fuel (BDF) is used in public automobile, such as garbage truck and city bus as the fuel of “production and consumption at regional area”.

Biodiesel fuel (BDF) can be substituted for light oil and used in automobile diesel engines. It is made from biomass materials such as waste food oil. BDF has low sulfur content, so the exhaust contains low concentrations of sulfur oxides. Since it is an oxygen-containing fuel it promotes engine combustion, making it a clean fuel characterized by low carbon monoxide and dark smoke emissions. The process of producing biodiesel fuel involves first causing fats (triglycerides) in waste food oil to react with methanol (transesterification) to produce fatty acid methyl esters. Glycerin and other byproducts produced at the same time are separated out from the obtained reaction oil. The remaining oil is then refined into biodiesel fuel.

Kyoto City collects about 125 kiloliters of waste food oil annually at about 1,000 collection sites in the city in cooperation with members of unit communities. The collected oil is made into biodiesel fuel at a dedicated plant with a capacity of 5,000 liters per day. The fuel is used in garbage trucks (equivalent to 210 trucks) and city buses.



Source: Hitachi Zosen Corporation

Fig.3.2.2 Biodiesel fuel production process in Kyoto City Plant

3.3. Regulation in Japan

3.3.1. Outline of Fuel Regulation in Japan

Fuel quality has a significant impact on vehicle performances. So it is very important to control the quality of fuels at the pump from the viewpoint of safety, Environment and customer protection. If inadequate fuels are distributed and fueled in vehicles, serious trouble may happens. Fig.3.3.1 shows an example of actual market trouble cased by in adequate fuel. High content alcohol fuel corrodes metals in fuel line parts. As a result, fuel leakage happened.

Fig.3.3.1 Example of Market Trouble Caused by fuel

In Japan, Ministry of Economy Trade and Industry (METI) is responsible for fuel quality in the market. By The Fuel Raw in Japan, METI is obligated to do next four items;.

- ✓ Registration of gas stations
  Gas stations are required to register to METI
- ✓ Developing fuel quality standard (mandatory and voluntary)
- ✓ Requiring gas stations to report quality check of gasoline once in:
  10 days, or a year if supply chain is approved by METI
- ✓ Fuel quality monitoring at pump
  Check work can be outsourced to the four registered testing organization

Table 3.3.1 Quality standard items for gasoline and diesel fuel

Items	Level	
Lead	No detection	*
Sulfur	< 10 ppm	*
MTBE	< 7 vol%	*
Oxygen Content	< 1.3 wt%	*
Benzene	< 1 vol%	*
Kerosene	< 4 vol%	*
Methanol	No detection	*
Ethanol	< 3 vol%	*
Existent Gum	< 5 mg/100mL	*
Color	Orange	*
Octane	Regular > 89	
	Premium > 96	
Density	< 0.786 g/cm3	
Distillation Temp.	(specified)	
Copper Corrosion	< 1 max	
RVP	44 - 65 kPa (Summer)	
Oxidation Stability	> 240 min	

Items	Level	
Sulfur	< 10 ppm	*
Cetane Index	> 45	*
90% distillation temp.	< 360 deg.C	*
Flash Point	> 45 deg.C	
Pour Point	Depend on region and month	
CFPP		
10% Carbon Residue	< 0.1%	
Kinematic Viscosity	> 1.7 mm2/s	

Note: * = mandatory

Table 3.3.1 shows a current fuel quality standard in Japan. Asterisk (*) in the table is mandatory items because these properties directly relates to issues of safety and environmental. There are about 50,000 filling stations in Japan. METI gathers about 200,000 fuel samples/year and investigates the quality. If METI finds any off-spec fuels, METI instruct fuel suppliers to follow fuel regulations. If they do not follow, METI order to suspend business up to 6 months and in some case, fuel distributors will be given criminal penalty.

If FAME bended diesel fuel is commercialized in Japan, The Fuel Raw has to be modified that it can be included FAME components.

3.3.2. Developing Biodiesel fuel Standard in Japan

Currently biodiesel fuel has not been introduced commercially. However bio fuels like bio ethanol and biodiesel fuel has been discussed for reducing CO_2 from the transportation section. In order to use bio fuels for automobile, developing adequate specification is essential. METI organized Fuel Policy Sub-committee which is a kind of advisory committee of METI, to discuss biodiesel fuel specification.

There are many kinds of biodiesel fuel like crude vegetable oil, refined vegetable oil, FAME (Fatty Acid Methyl Ester), hydrogenated vegetable oil and BTL (bio mass to liquid). First, it was agreed to select FAME as biodiesel fuel we should develop standard because FAME was used as fuel for fleet use in some area governments and was expected to be used in Japan.

FAME has quite different character from fossil derived diesel fuels. As shown in Fig.3.3.2, the character of FAME is different by raw materials. For example, SME (Soya Methyl Ester) has a tendency to be easy oxidized. FAME from fish oils produces sludge easily. PME (Palm Methyl Ester) and TME (Tallow Methyl Ester) are easy to form wax. Refining process also influences to quality of FAME. If washing process is not enough, some impurities like methanol, glycerin and so on remain in FAME.

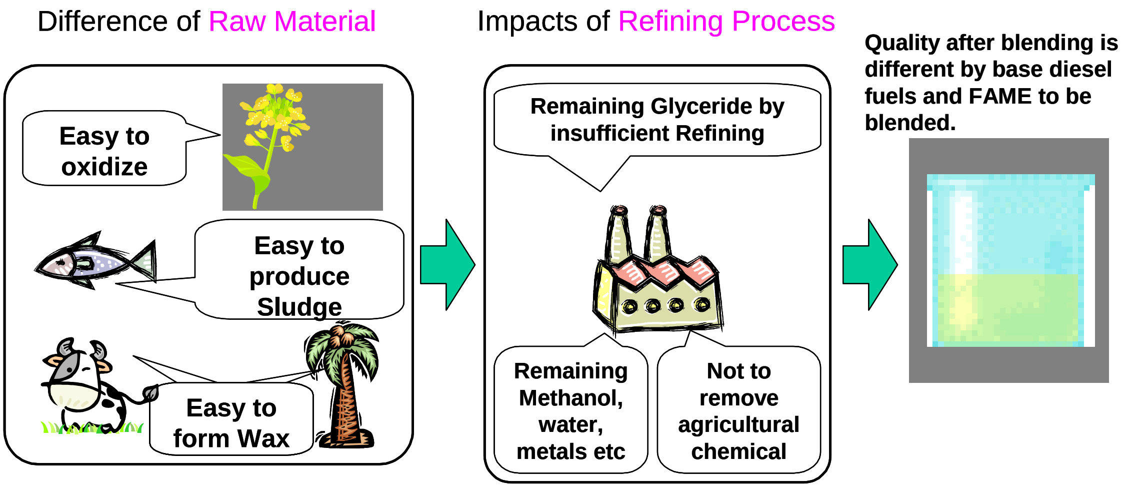


Fig.3.3.2 Characteristics of FAME ; Effects of Raw Materials and Refining Process

These characteristics relates to vehicle performance closely as shown in Fig.3.3.3. If quality of FAME is not controlled properly, serious trouble and/or fatal damage in vehicles may be expected.

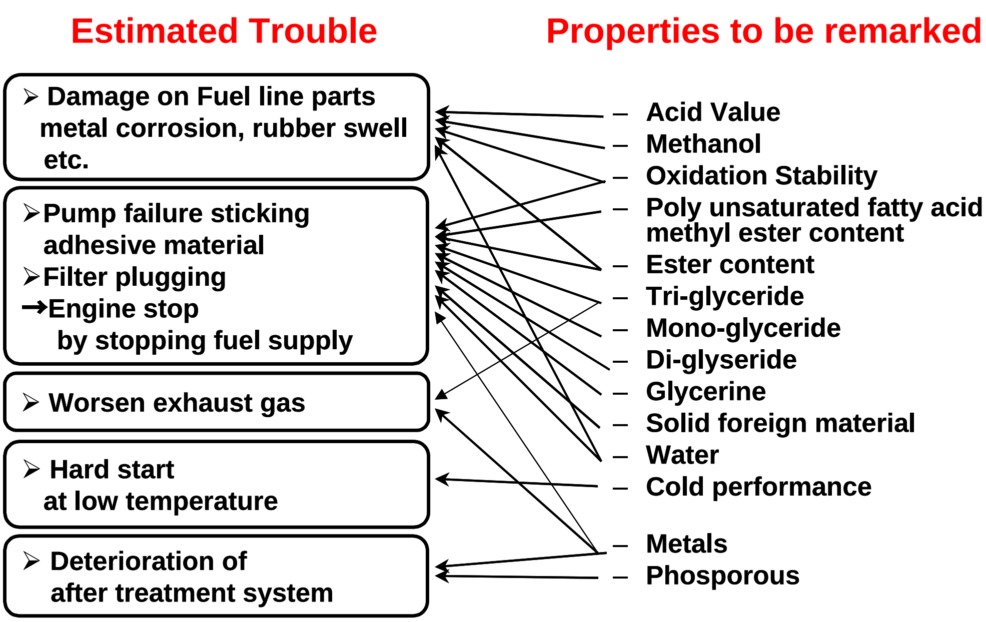


Fig.3.3.3 FAME Properties to be Remarked and Estimated Impacts

For developing biodiesel fuel specification, METI has conducted the FAME conformity tests to gather technical knowledge about FAME. In order to shorten the period for developing the specification, European FAME specification, EN14214 was selected as a base specification. Even though starting from EN14214, more than two years and about four hundred million JPY were spent.

Table 3.3.2 is a summary result of the conformity tests. In the conformity tests, the testing FAME which completely meets EN14214 was prepared and was blended into Japanese JIS No.2 diesel fuel by 5vol%, and then was used in each test. Corrosion was observed in the fuel tank tests and metal dipping tests as the problem related to FAME properties even though the testing FAME used in the conformity tests met European requirements.

Table 3.3.2 Summary of METI Conformity Test Results

Test Items	Results	Summary
Material Compatibility		
Metals	**Fail**	**Corrosion in Tern Sheet**
Rubber & Plastics	Pass	No effects of Ester as far as less than 5v%
Cold Performance	–	Poor Startability
Long Storage Test	Pass	Slight Degradation
Fuel Line Parts Test		
Fuel Filter Test	Pass	Same as diesel fuel with B5
Fuel Tank Test	**Fail**	**Corrosion and melting plating in lead-tin alloy coated and electrolytic zinc-coated steel sheets**
Fuel Pipe Test	Pass	Same as diesel fuel with B5
Fuel Hose Test	Pass	Same as diesel fuel with B5
FIE Durability Test	Fail	Wear in Injectors with B5
Engine Durability Test		
LD, ID&DI	Pass	Observation of no trouble with B5
HD, DI	Fail	Flow loss and Wear in Injectors with B5
Vehicle Durability Test (LDV, IDI)	Pass	Observation of no trouble with B5
Emission Test	Pass	Little Impact with up to 10v%

Note) Test FAME consists of PME:RME:SME=60:38:2 and is blended in commercial diesel fuel by 5%. Test FAME completely met EN14214.

Figure 3.3.4 is an example of corrosion observed in the fuel tank test. The cause of corrosion was lack of oxidation stability. FAME blended diesel fuel was oxidized during tests and produced corrosive acids. No other problems related to FAME were observed. These results suggested that only oxidation stability requirement in EN14214 is not enough for ensuring the performance of vehicles. As the next step, the effect of improving oxidation stability was investigated. Oxidation stability is easily improved with anti-oxidant agents as shown in Fig.3.3.5. The oxidation stability of the testing FAME was improved to 10 Hrs with Rancimat method using additive technology and then blended into JIS No2 diesel fuel by 5vol %. Fig.3.3.6 shows the photograph of the fuel tank inside after finishing the test. No corrosion was observed and the effectiveness of improving oxidation stability was confirmed. Based on the conformity tests, Japanese biodiesel fuel specification was developed.

Lower Side of tank   Upper Side of tank

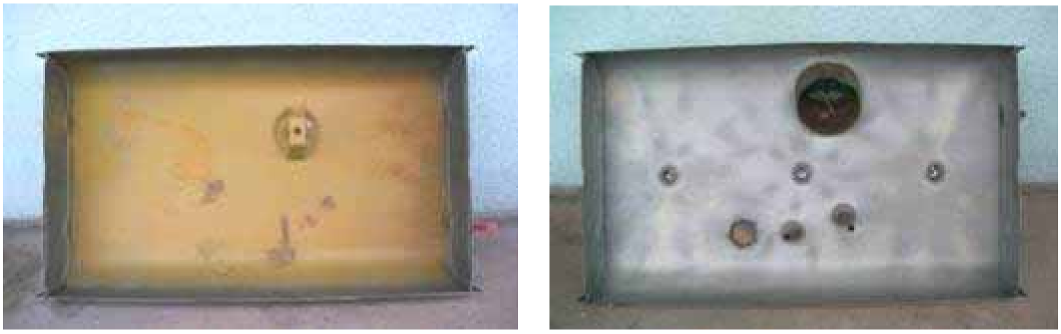


Fig.3.3.4 Results of Fuel Tank Test

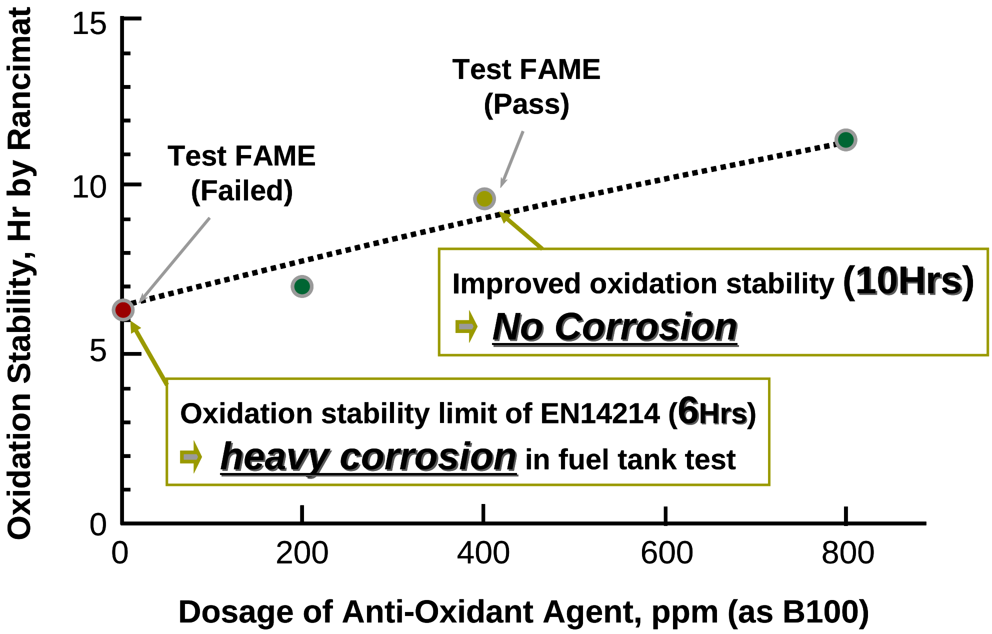


Fig.3.3.5 Effect of Anti-Oxidant Agent on Oxidation Stability

Lower Side of tank Upper Side of tank

Fig.3.3.6 Results of Fuel Tank Test : Effects of Improving Oxidation Stability

3.3.3. Japanese B5 diesel fuel specification

In Japan, the quality of FAME blended diesel fuel is regulated by The Fuel Raw as a compulsory standard as a compulsory standard. The standard of neat FAME (B100) for blending stock is not included the compulsory standard but it's as a voluntary specification.

Figure 3.3.7 shows the difference of fuel regulation in Europe and Japan. In Europe, there are two specifications for specifying the quality of FAME blended diesel fuels. That is, one is diesel fuel specification, EN590. The other is FAME (B100) specification, EN14214. EN590 refers to only ester contents as the properties related to FAME.

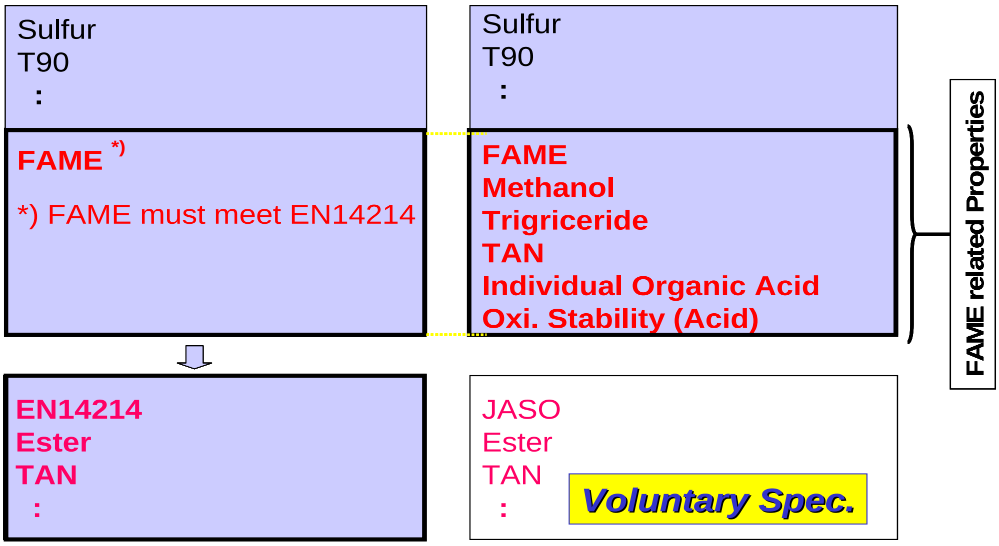


Fig.3.3.7 Difference of Fuel Regulation in Europe and Japan

It means that both EN590 and EN14214 are necessary to specify the quality of FAME blended diesel fuel, European governments regulated both specifications and monitor the quality of both diesel fuel and FAME before blending. There is no way to check the quality of FAME after blending, because no specifications related to FAME except for ester content in EN590.

In case of Japan, fuel quality is controlled at fuel pump. This principle is also applied to FAME blended diesel fuel. Then, the quality of FAME blended diesel fuel is regulated by The Fuel Raw as a compulsory standard as a compulsory standard which dose not include specification of neat FAME (B100) for blending stock. The specification of B100 for blending stock was developed as a "guideline for FAME producers", named JASO M360. In this paragraph, these two standardizations will be explained in details as follows.

(1) Compulsory Diesel Fuel Standard (Specification of The Fuel Raw)

METI developed the specification of FAME blended diesel fuel based on the conformity test results as shown in Table 3.3.3.

Existing items in the present diesel fuel standard are following 3 items.

- Sulfur Content should be 0.005 mass% or less.
- Cetane index should be 45 or more.
- 90% distillation point should be 360 deg.C or less.

New additional items are classified into two groups. Either of the following (i) or (ii) should be satisfied.

⇒Standard to be satisfied by Diesel Fuel in which FAME is not contained.

(i) FAME content is 0.1 mass% or less.

Triglyceride content is 0.01 mass% or less.

⇒ Standard to be satisfied by Diesel Fuel in which FAME is contained.

(ii) FAME content is 5.0 mass% or less.

Triglyceride content is 0.01 mass% or less.

Methanol content should be 0.01 mass% or less.

Acid value should be 0.13 mgKOH/g or less.

Total of formic acid, acetic acid and propionic acid should be 0.003 mass% or less.

Oxidative stability should be 0.12 mgKOH/g or less for acid value growth.

Table 3.3.3. Compulsory Diesel Fuel Standard

Regulatory Item		FAME Blended Diesel Fuel	Diesel Fuel
Existing Items	Sulfur	0.001mass% max	
	Cetane Index	45 min	
	T90	360 deg.C max	
Additional Items	FAME Content	5.0 mass% max	0.1 mass% max
	Triglyceride Content	0.01 mass% max	0.01 mass% max
	Methanol Content	0.01 mass% max	-
	TAN	0.13 mgKOH/g max	-
	Individual Organic Acid*)	0.003 mass% max	-
	Oxidation Stability (Acid Value Growth)	0.12 mgKOH/g max	-

*) Total Formic, Acetic and Propionic acids

Regulatory items should be added to the diesel oil standard in order to specify the upper limit of the FAME content in diesel fuel (up to 5% is allowed) and the properties of the fuel satisfying the aspect of 1, 2 and 3 based on the use of FAME satisfying the neat standard.

1. FAME sufficiently refined (purity is high) should be blended. (Triglyceride, Methanol)
2. FAME in fresh condition (not degraded with time) should be blended. (Acid value, Specific Acids)
3. Properties should be such that generation of acid and sludge from the heat and oxidative degradation is controlled (oxidative stability is established)

Differences from the regulated value of EN Standard are follows.

Content of the specific organic acid

Oxidative stability (acid value growth)

Items to study based on the regulated value of EN Standard are follows.

FAME blending ratio to diesel fuel

Acid Value

Methanol

Triglyceride

FAME Content

When the FAME blending ratio in diesel fuel (ester content) is increased, blotting of fuel from the fuel hose will take place. In the EN Standard (EN590), the blending ratio in diesel fuel is limited to 5 % or less.

As for the FAME blending ratio in diesel fuel, it can be used as the upper limit for the effect on safety and also in identifying diesel fuel containing FAME or not containing FAME.

When the compulsory standard for diesel fuel is simply increased, items investigated regarding fuel quality by producers and distributors will also increase whether or not FAME is contained n the diesel fuel In order to avoid increasing the burden unnecessarily when diesel fuel not containing FAME is handled, the FAME blending ratio should be used as criteria.

Conformity study was based on the fact that the FAME blending ratio is limited to 5% in Europe. A variety of test was conducted within the range where the FAME blending ratio was 5% or less. No phenomenon connected to problems and considered possible due to ester was confirmed. As to the soak test for plastics and rubber in which a significant effect was anticipated, no significant effect was observed for the FAME blending.

In the fuel filter durability test using the conventional test method, pressure tightness decreased after the durability test for the plastic filter case. It was considered an effect of FAME on rubber (NBR) and plastics (nylon 6). Effect from acid in addition to ester was also considered.

In the fuel filter test under the revised test conditions adjusted for actual in-use conditions, it was confirmed that no problems existed.

Triglyceride Content

Triglycerides are purely vegetable oil and animal fat. When blended with diesel fuel even in a concentration with impurities, it easily forms sludge from oxidative degradation and causes clogging of the fuel filter or improper sliding of parts. As to the measuring method of Neat FAME before blending with diesel fuel, 0.2 mass% or less is specified by the EN Standard (EN14214).

Provisions are necessary because triglycerides (the very fat) will blended with diesel fuel without forming methyl ether.

Triglyceride content is used as an index to measure the refinement level of FAME before blending with diesel fuel similar to methanol.

5% equivalent by EN Standard should be used as the standard value.

Conformity test result shows that combustion residuals are easily formed from triglyceride (increase of carbon residue). No problems caused by triglycerides occurred in the conformity test including the durability test using the triglyceride content equivalent to the EN Standard.

<u>Methanol Content</u>

Methanol aggressively corrodes metal.

The present quality law specifies that 'no methanol shall be detected' in the compulsory standard item for gasoline.

Currently, blending methanol in diesel fuel is not considered, but in the case of the FAME blended diesel fuel, methanol is used in the production of FAME, and methanol may be contained in the fuel.

It is appropriate that the standard value should be 'not detected,' the same as gasoline.

The level presently prescribed for 'not detected' for gasoline is 0.5 mass% or less.

In the case of FAME, methanol is not added intentionally but will be included as an impurity accompanying the synthesis process.

In this compulsory standard, only the critical items to be prescribed for FAME should be applied after it is blended with diesel fuel, and it is necessary to decide whether the quality of the FAME before blending was appropriate.

Among the items proposed as a compulsory standard, residual methanol and triglyceride (both are row materials for synthesis) should be a measure of the refinement level of FAME before blending.

Accordingly, it is considered appropriate to use the 5% equivalent to the European Standard.

<u>Acid Value and Content of Specific Acid</u>

When the acid value or the content of specific acid is increased, the metal of motor vehicle fuel system corrodes. By EN Standard (EN 14214), required acid value of 100% FAME is 0.5 mgKOH/g or less.

The cause of corrosion is the acid originated form FAME, and it is necessary to specify the combination with the acid value of FAME blended diesel fuel and concentration of specific acid.

When the acid value specified by EN 14214 (0.50 mgKOH/g) is applied to the 5%

FAME blended diesel fuel, the acid value should be 0.03 mgKOH/g.

There have been cases where fatty acid was added in diesel fuel to improve lubrication, it was confirmed that this additive would not cause corrosion with the present dosage, and the maximum available acid value in the existing diesel fuel is 0.10 mgKOH/g. Accordingly, 0.13mgKOH/g is caused as the upper limit for the standard.

Specifying the acid value only is not sufficient for corrosion, and it is necessary to specify the short chain fatty acid, which demonstrates strong corrosiveness. From the study of acids generated from FAME and from the results of corrosion tests for each acid, the specifications for formic acid, acetic acid and propionic acid should be provided.

Formic acid, acetic acid and propionic acid are important according to the results of the study of corrosive acids generated by FAME when showing oxidative degradation.

The evaluation results of corrosiveness from these acids confirmed that no corrosion would occur when formic acid, acetic acid and propionic acid is 0.003 mass% or less, and when caproic acid is 0.01 mass% or less in a system without moisture (tens of parts per million level).

A study of the method of analysis indicated that formic acid, acetic acid and propionic acid can be analyzed by a relatively easy method, but caproic acid cannot be analyzed with same test method.

Because it is known that caproic acid is generated by oxidative degradation of methyl linolenate and acetic acid is also generated, it is possible to restrict the caproic acid content to a certain level or less by restricting the acetic acid content.

It was confirmed that no problem such as a decrease in durability would occur in fuel filter durability test using FAME blended diesel fuel with acetic acid 0.003 mass% or less and acid value of 0.13 mgKOH/g.

<u>Oxidative Stability</u>

Organic acid, fatty acid and moisture are generated and during the process FAME undergoes oxidation degradation, and these corrode metals. Furthermore, when oxidative stability is decreased, polymer (sludge) is generated to cause failure in sliding of the fuel pump and injector.

As to measuring method of the neat FAME before blending with diesel fuel oxidative stability of 6 hours or more of the organic acid is required by EN Standard (EN14214).

No measuring method and standard value for neat FAME are provided with respect to sludge; however, in the European Diesel Fuel Standard (EN590), 25 g/m3 is specified in accordance with ISO 12205 (ASTM D2274). This will remain the same when it is amended in 2004 to allow 5% FAME blending.

A study on oxidation stability was conducted based on the concept that it is necessary to specify both acid value (yield of organic acid) and yield of sludge as FAME blended diesel fuel.

Because it is considered appropriate to evaluate the oxidative stability after thermal oxidation degradation progress to some extent, a study was conducted on the method by which the yield of sludge and acid value can be measured at the same time by reviewing test conditions and referencing the existing oxidation test method, for example oxidation stability test for gasoline, lubricant and so on.

Although corrosion occurred in the fuel tank circulation test conducted with the fuel used for the fuel system rig durability test, corrosion did not occur with fuel in which oxidative stability was established (fuel with antioxidant added) in the fuel tank circulation test conducted with the test method partially reviewed.

While the difference in the results is significant, according to the testing laboratory, in both yield of sludge and acid value growth, even if the same sample was used, the difference remarkably reduced for fuel for which the oxidative stability was established (with antioxidant added).

There was some correlation between the yield of sludge and acid value growth as a whole, and it was decided that the restriction of yield of sludge can be controlled by specifying the standard value on acid value growth.

Because the average acid value growth for fuel assumed to be border in the fuel tank circulation test was 0.06 mgKOH/g, the standard value was determined as 0.12 mgKOH/g considering the 95% confidence level.

As a result of the fuel simulation test, in a high temperature and common pressure rail system, it was confirmed that the degradation of the fuel accelerated and problems like corrosion and deposit build-up also occurred.

Build-up of deposits was observed in the suction control valve (a valve to regulate supply and pressure of fuel) of the supply pump (a pump to boost fuel pressure and to supply fuel to injection nozzles) in fuel system rig durability test and in the fuel system pipe in vehicle endurance test. While it may not be a problem in practical use, it was considered necessary to maintain the level of fuel used for the durability test this time as the minimum.

Although corrosion occurred in the fuel tank circulation test using the conventional test method, it was confirmed that no problem existed by conducting the fuel thank durability test again using the fuel in which oxidative stability was reviewed (fuel with antioxidant added).

Polyunsaturated Fatty Acid Methyl Ester Content

Because polyunsaturated acid methyl ester, such as methyl linolenate, has many unsaturated bonds in the same molecules, a large amount of sludge is easily generated from oxidative degradation, and blocking of the fuel system is likely for occur, even if the content is small.

As to the content of methyl ester with unsaturated bonds, some are provided with the metrology and the standard value for neat FAME according to the EN Standard (EN14214). Specifically, the metrology and the standard value exist for the content of methyl linolenate with three unsaturated bonds. As for polyunsaturated fatty acid methyl ester with four or more unsaturated bonds, the standard value exists while the metrology did not exist. In the EN Standard (EN14214), the content of methyl linolenate should be 12 mass% or less, and the content of polyunsaturated fatty acid methyl ester with four or more unsaturated bonds should be 1 mass% or less.

While it was confirmed that the yield of the sludge increase when the content of methyl linolenate was substantial, it was determined that yield of sludge can be controlled by the standard value of oxidation stability (acid value growth).

As polyunsaturated fatty acid methyl ester with four or more unsaturated bonds, analysis was extremely difficult after blending with diesel fuel, and it was considered appropriate to specify it according to the Neat FAME Standard.

Yield of sludge in the simulation test increased when the content of methyl linolenate in FAME blended diesel fuel increased.

It was found that the methyl linolenate significantly decreased oxidative stability. It was considered necessary to maintain the level of the durability test fuel as the minimum.

Build-up of deposits was observed in the suction control valve (a valve to regulate supply and pressure of fuel) of the supply pump (a pump to boost fuel pressure and to supply fuel to injection nozzles) in fuel system rig durability test and in the fuel system pipe in vehicle endurance test. While it may not be a problem in practical use, it was considered necessary to maintain the level of fuel used for the durability test as the minimum.

As to polyunsaturated fatty acid methyl ester with four or more unsaturated bonds, no confirmation was made through a simulation test or with a durability test, and no results sufficient to examine the presence of contents and the problem were obtained. However, the oxidative stability might decrease significantly to the same level oxidative stability as the FAME blended diesel fuel with which the problem is caused, even with a small quantity.

Cetane Index

Cetane number and the cetane index are indicators that show the ignitability of diesel fuel, and the engine cannot be operated unless they are above the appropriate value.

In compulsory standard cetane index 45 or more is required.

The cetane index is an indicator estimating the cetane value from the density and distillation characteristics. It is not always applicable when a substance with different composition is mixed, because it is based on mineral oil refined from crude oil.

While the variation is large to some extent when compared with conventional diesel fuel, the cetane index can be applied when the blending ratio is within 5%.

When FAME is blended, the cetane index tends to be large compared with the cetane value. This tendency is more significant with the increase in the blending ratio of FAME.

Variation in correlation between cetane value and cetane index is significant compared with diesel fuel without blending of FAME.

Within the range of the FAME blending ratio 5%, the cetane index is higher than cetane value by 1.3 on average.

Test Method

FAME content and triglyceride content in diesel fuel are determined by using high performance liquid chromatography.

Methanol content in FAME blended diesel fuel are determined by using gas chromatography with oxygen detector (GC-AED), with head space, or with water extraction. Because the study was made to add the methyl linolenate as a standard item initially, the study on GC-AED method was examined as a test method to analyze methanol and methyl linolenate simultaneously. However, a more general test method can be considered to analyze methanol only. Water extraction – gas chromatography and head space – gas chromatography were studied and established the method.

Acid value are determined by potentiometric titration.

Formic acid, acetic acid and propionic acid in FAME blended diesel fuel are determined by using water extraction ion chromatography.

Oxidation stability of FAME blended diesel fuel is estimated by TAN growth after heat degradation. Increase of TAN after 16 hour heating to 115 deg.C while bubbling oxygen at 3.0 L/h through the sample is measured. The test apparatus used in this method is defined in ISO-12205-1995 ‘Petroleum Products – Determination of the Oxidation Stability of Middle – Distillate Fuels’.

<u>The other information</u>

The test method and the limit of the oxidation stability were newly developed by METI because current oxidation stability test method and the limit were not suitable for applying FAME blended diesel fuel. This diesel fuel regulation was come into effect from March 2006. For reducing the work of fuel distributors who will not blend FAME, two properties, ester content and triglyceride content are measured at first. If both were not detected, distributors do not need to measure other four properties.

(2) Neat FAME (B100) for blending stock (Specification of JASO 360)

Basically standard items and values were according to the FAME standard in Europe with EN 14214 as the starting point. The items especially focused are the following.

Oxidative stability

Acid value and content of specific acids

Cold temperature properties

<u>Oxidation Stability</u>

Standard value is not established but quality requirement is ‘In accordance with the mutual agreement between parties concerned’.

While a new evaluation method was established as the standard for the FAME blended diesel fuel, it was found that the oxidative stability was different for the same FAME depending on the diesel fuel based on the series of studies.

However, the properties of the diesel fuel that affect the oxidation stability after it is blended with FAME were not identified.

If the standard of the oxidative stability of FAME that is applicable for the mixture with any kind of diesel fuel is established, it will be an excessively strict standard.

Accordingly, the subject item was defined as ‘Based on mutual agreement between the manufacturer and the user’.

(However, “10 hours min.” of oxidation stability is needed to meet the Japanese Compulsory Diesel Fuel Standard (Specification of The Fuel Raw).)

<u>Acid Value and Content of Specific Acid</u>

Standard value is 0.5 mgKOH/g or less. This value is equal to the European Standard.

As to the acid value after blended with diesel fuel, a value in which 5% based on the

European Standard is added as contribution of the FAME origin acid to the acid value of the conventional diesel fuel was used.

When it is assumed that formic acid, acetic acid and propionic acid, which are specific acids, are contained FAME in the quantity equaling 0.5mgKOH/g, the concentration becomes 20 ppm, 27 ppm and 33 ppm, respectively. Because the total is 30ppm or less and the acid value of the FAME 0.5 mgKOH/g is almost equivalent, the standard for the content of a specific acid is not added to the neat standard.

Table 3.3.4 Japanese FAME Specification (JASO M360)

JASO M360 -Automotive fuel – FAME as blend stock

Item	Unit	Specification	
		Limit	Test Method
Ester content	mass %	96.5 min	EN 14103
Density (@15 deg.C)	g/cm^3	0.860-0.900	JIS K 2249
Kinematic viscosity (@40 deg.C)	mm^2/s	3.50-5.00	JIS K 2283
Flash point	deg.C	120 min	JIS K 2265
Sulfur content	mg/kg	10 max	JIS K 2541-1, -2, -6 or -7
10% carbon residue	mass %	0.3 max	JIS K 2270
Cetane number		51.0 min	JIS K 2280
Sulfated ash content	mass %	0.02 max	JIS K 2272
Water content	mg/kg	500 max	JIS K 2275
Total contamination	mg/kg	24 max	EN 12662
Copper corrosion	rating	1 max	JIS K 2513
Oxidation stability	hours	Agreement between producer and distributor	
Acid value	mgKOH/g	0.50 max	JIS K 2501or JIS K 0070
Iodine value	gl/100g	120 max	JIS K 0070
Methyl linolenate	mass %	12.0 max	EN 14103
Methanol content	mass %	0.20 max	EN14110
Monoglyceride content	mass %	0.80 max	EN 14105
Diglyceride content	mass %	0.20 max	EN 14105
Triglyderide content	mass %	0.20 max	EN 14105
Free glycerol content	mass %	0.02 max	EN 14105 or EN 14106
Total glycerol content	mass %	0.25 max	EN 14105
Metals (Na+K)	mg/kg	5.0 max	EN 14108 and EN 14109
Metals (Ca+Mg)	mg/kg	5.0 max	EN 14538
Phosporous	mg/kg	10.0 max	EN 14107
Pour point	deg.C	Agreement between producer and distributor	
CFPP	deg.C		

Cold Temperature Properties

Standard value is not established but quality requirement is ‘Based on the mutual agreement between parties concerned’.

Because the low temperature performance of the FAME blended diesel fuel significantly depends on the property of both FAME and diesel fuel to be blendes, it is difficult to specify the low-temperature performance of FAME.

Although specifications of the low-temperature performance (grading) are provided in European Standard similarly to the diesel fuel standard, this is intended for use with neat FAME, and it is difficult for use as the indicator when it is blended with diesel fuel.