Chapter 4

Biodiesel Fuel Quality

Benchmarking of Biodiesel Fuel Standardization in East Asia Working Group

July 2010

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4. BIODIESEL FUEL QUALITY

4.1 Oxidation Stability

4.1.1 Introduction of Oxidation Stability

Compared to petroleum based diesel fuel, FAME oxidizes easily and forms reaction products shown to have unfavorable effects on vehicle fuel systems. Therefore, oxidation stability is one of the most important characteristics for practical use of FAME. FAME molecules typically have several double bonds, and oxidize fairly easily. Initially, the oxidation process generates peroxides (hydrogen peroxide), which subsequently forms acids, as shown in Table 6. The acid itself also plays a role in the acceleration of oxidation. In the end, the acid reacts with sludge, deposits, or other undissolved chemical compounds and accumulate as deposits.

Table 6 Organic acids formed by heat exposure (110℃)

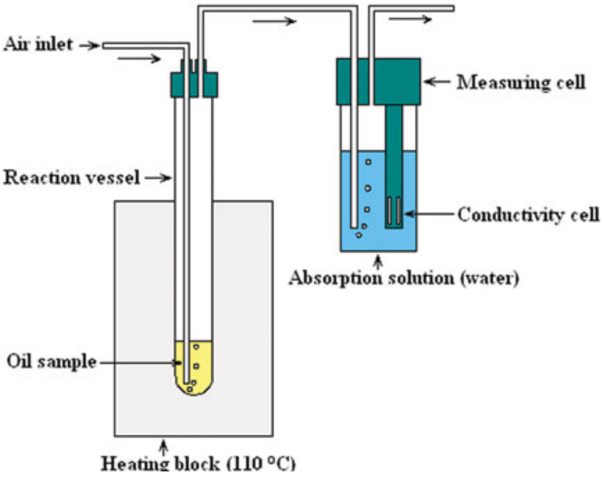
(ppm)

	FAME A B100	FAME B B5	FAME C B5	Petroleum Based Diesel
Heating Duration (h)	32	64	64	64
Formic Acid	620	180	190	120
Acetic Acid	410	190	170	170
Propionic Acid	160	89	78	43
Butyric Acid	1	38	23	36
Caproic Acid	50	316	289	47
Caprylic Acid	2	52	66	19
Capric Acid	<1	27	53	17
Lauric Acid	1	19	27	16
Myristic Acid	2	26	39	12
Palmitic Acid	95	280	374	16
Stearic Acid	27	51	253	28
Oleic Acid	354	304	388	2
Linoleic Acid	78	54	145	<1
Linolenic Acid	<1	<1	23	<1
Oxalic Acid	10	4	<1	<1
Malonic Acid	<1	<1	<1	<1
Succinic Acid	<1	6	4	5

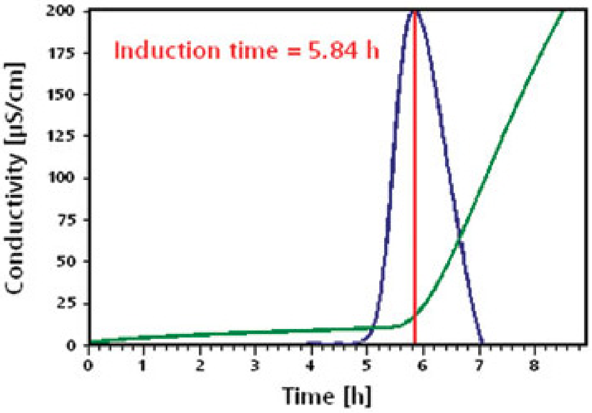
▒ : heat degradation

🟪 : hydrolysis

Rancimat method, provided in EN 14112, is the most popular test method of oxidation stability. The Rancimat method is an accelerated oxidation test that is run at elevated temperatures and exposes the sample to air. This results in auto-oxidation in a



(a)



(b)

(Source: http//www.biodieselmagazine.com)

(c)

Figure 12 (a) Principle of Rancimat method with (b) its conductivity measurement and (c) experimental setup

few hours, instead of weeks or months. Figure 12(a) shows the principle of the Rancimat method. Air is blown through the tested sample (approximately 3 g in weight) which is heated to a specified temperature (110 °C) in order to oxidize it. The stream of air then carries over the volatile oxidation products which normally formed at the end of the oxidation process to a measuring vessel containing deionized water. The readings of the conductivity measurement can be plotted as a function of the time required for the oxidation as shown in Figure 12(b). The inflection point of this oxidation curve is known as the induction time which serves as a measure of quality of the oil tested. Figure 12(c) is an example of Rancimat test equipment (743 Rancimat). With standard EN 14214 Minimum Racimat oxidation stability period of 6 hours at 110 °C is defined for biodiesel samples. In EAS-ERIA Biodiesel Fuel Standard: 2008, the oxidation stability is specified 10 hours minimum for B100 aimed for low level blending with diesel fuel.

Peroxides deteriorate plastic and elastomers, particularly at high temperatures. Acids corrode metal, which is used in vehicle fuel systems and fuel supply systems. The acids' effects on a metal fuel tank are particularly severe. Even though only light corrosion forms there, the resultant organic acid salts agglomerate and produce deposits inside the fuel pump and injector. The metallic and organic acids react again and form a metallic salt. These salts (which precipitate in fuel) pass through the fuel filter, and adhere to the fuel pump and fuel injector surfaces. These salts also form an injector deposit like sludge. Other immiscible substances formed include polymer, sludge, and oxidation products, which sometime cause fuel filter blockage, as shown in Figure 13.

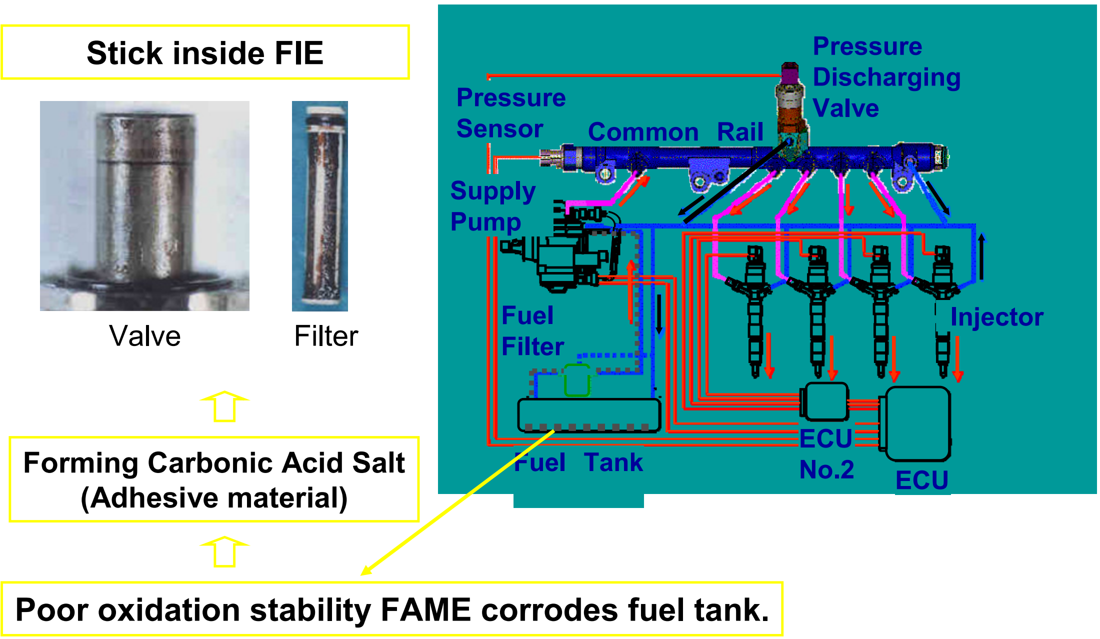


Figure 13 Example of market experience with problem from poor quality FAME

Past experience has shown that petroleum based diesel fuel can be stored without oxidation for a very long time. FAME, however, even at low blend levels, deteriorates the oxidation stability of the final FAME-diesel fuel blend. Depending on the storage condition (for example, temperature and air volume), unacceptable deterioration may occur. Thus, it is necessary to develop countermeasures to allow storage stability for a minimum of six months.

In order to prevent consumer problems, the oxidation stability of FAME must exceed a standard value. In other words, it is necessary to have more than a certain oxidation induction or delay period. Antioxidant additives can help maintain the necessary oxidation stability.

(1) Iodine Number

The iodine number indicates the total number of double bonds in a molecule (or its saturated level). In general, low oxidation stability correlates with a high iodine number, therefore the iodine number is considered as an index of oxidation stability, as shown in Figure 14. However, oxidation stability cannot be solely determined by the iodine number. Moreover, it is known that fatty acids with many double bonds are preferable to saturated fatty acids in terms of low temperature flowability.

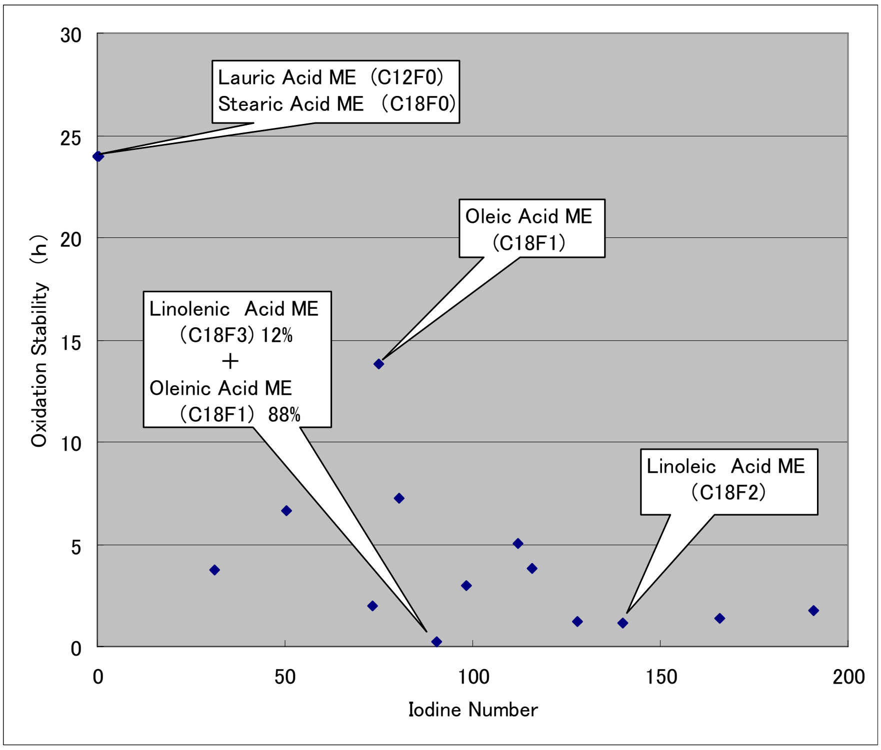
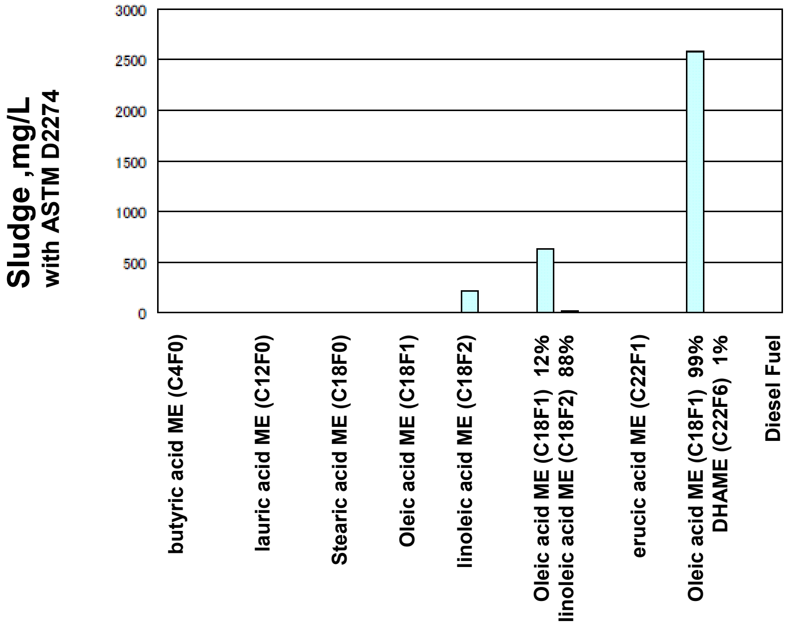


Figure 14 Relationship between oxidation stability and iodine number

In order to maintain oxidation stability, one suggestion was to establish a limit for the iodine number. In that case, it could mean elimination of FAME from raw materials which result in high iodine numbers, such as soybean, sun flower and other oils with many unsaturated bonds. If good oxidation stability can be maintained by countermeasures like the use of antioxidants, it may be not necessary to stipulate iodine numbers. A test method for oxidation stability which has been widely used at present (Rancimat Method: EN14112) can measure the induction period for acid to occur under conditions of accelerated deterioration. However, it is not fully known whether or not this method can predict sludge occurrence, or other properties. From this standpoint, and for sludge formation control, there is a thought that a certain maximum iodine number is necessary.

(2) Linoleic Acid Methyl Ester and Multi-Unsaturated Fatty Acid Methyl Esters

The linoleic acid methyl ester molecule contains three double bonds, and has very high oxidation instability. Therefore, these molecules can easily be oxidized to react, and as a result, form sludge. In addition, methyl esters with many unsaturated bonds form sludge very easily, as shown in Figure 15. It is known that fish oil contains many fatty acids which contain more than four unsaturated bonds per molecule (quite unlike plant oils). Fish oil is thus not suitable as a raw material for automobile fuels.



(Source: METI FAME Conformity Test)

Figure 15 Effects of poly-unsaturated methyl esters on sludge formation

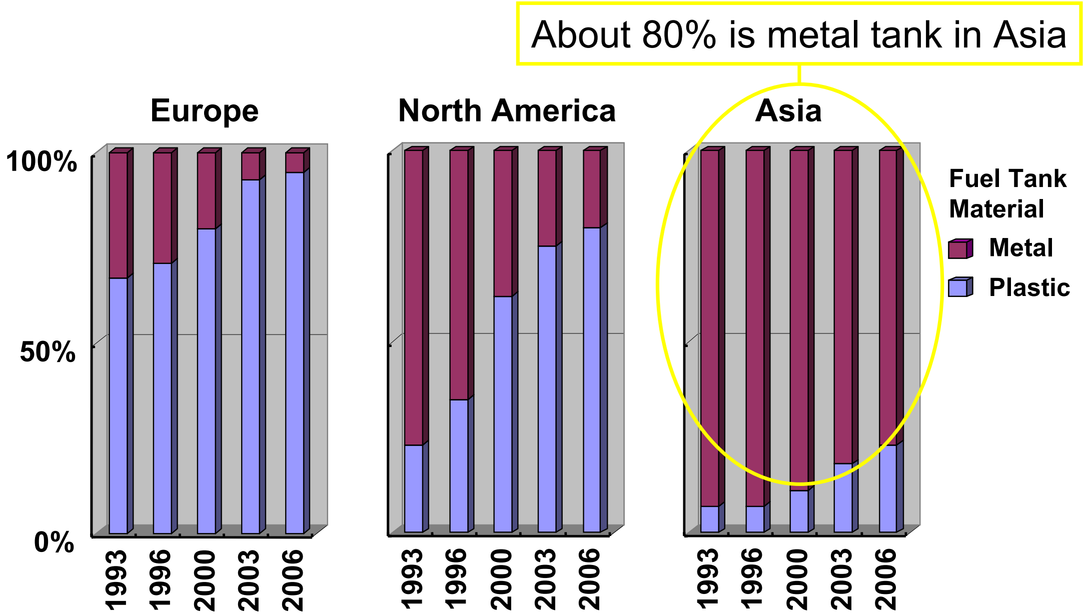
(3) Metal Corrosion

When FAME thermally oxidizes, it decomposes and produces organic acids. When plant oils or fats, which are now widely used as a biofuel, thermally oxidize and decompose, formic acid, acetic acid, propionic acid, and caprionic acid are mainly formed. Metals, particularly copper, copper alloys, lead, zinc, and tin corrode easily by these organic acids. A series of tests performed by the Japan Ministry of Economy Trade and Industry, showed remarkable effects on a galvanized steel plate placed in a fuel tank. This type of metal is commonly used for automotive fuel system components. Particularly in the lead - tin galvanized steel plate (trade name: Turne sheet), lead reacts with the highly reactive organic acids present, such as formic acid and acetic acid. The products react with caprionic acid (a larger molecule), and then are deposited as a metallic salt of caprionic acid. A large quantity of this caprionic acid salt can accumulate in the fuel tank and filter, as shown in Figure 16. However, part of it goes through the fuel filter, and is accumulated as an injector deposit. As shown in Figure 17, there is widespread use of metallic fuel tanks of varying material quality in East Asian countries, thus metal corrosion is an important problem compared to other regions.

Test Fuel: Commercial diesel fuel blended the FAME meets EN14214 by 5vol%

Test Fuel: Same FAME above with 400ppm of anti-oxidant (20ppm as B5)

Figure 16 Effects of oxidation stability on fuel tank corrosion



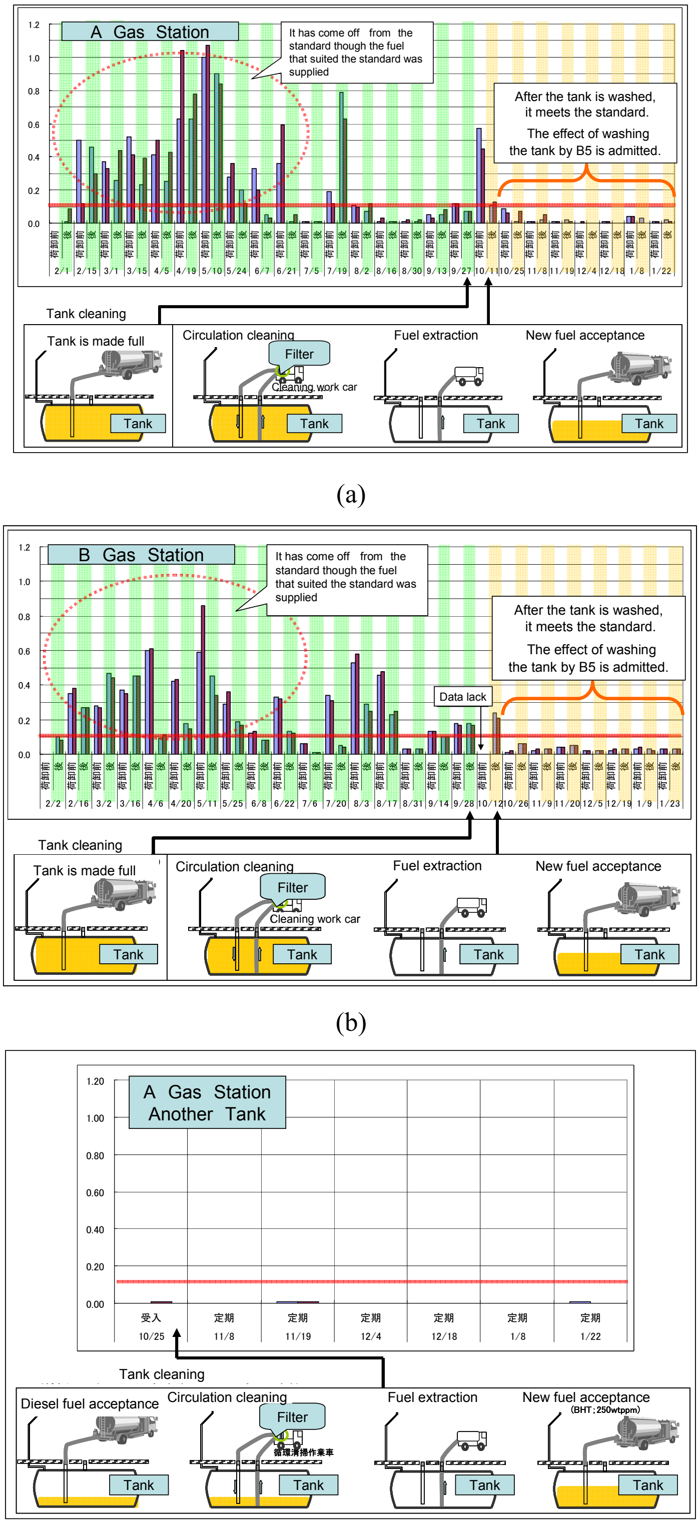
(Source: Data from Website of Plastics Fuel Systems Manufactures Association and in-house information of a material company.)

Figure 17 Fuel tank materials in Asia

(4) Storage Stability

The Japan Ministry of Economy Trade and Industry endeavored to identify problems involved with flow and storage processes of FAME blended with petroleum based diesel fuel. Several validation tests were carried out in this study, as shown in Figure 18. Two fuels were compared in the storage test. One was FAME blended with petroleum based diesel fuel, while the other was an identical blend ratio but mixed after a certain period. Both were stored for the same amount of time. Results showed that the latter case had better storage stability. Since 100% FAME has very poor storage stability, it would be desirable to add the appropriate amount of oxidation inhibitor in the production process, right after manufacturing, if possible.

Moreover, upon examination of the actual fuel transport path, it was found out that moisture typically remains inside the underground tank at a gas station. This significantly reduces FAME blend's oxidation stability. In Japan many of the underground tanks are made of steel or iron products, and do not have any surface treatment. Fuel tanks are open to the outside air for breathing. With the outside temperature changes, condensation collects at the bottom of the tank. This condensate contains oxidized metal, which works as a catalyst. It then lowers the oxidation stability of the FAME blend fuel stored in the tank.



(a)

(b)

(c)

Figure 18 Oxidative stability in circulation proof examination effect confirmation by (a) transition tank washing A, (b) transition tank washing B and (c) Antioxidant Additive

As a countermeasure, before storage of a FAME blend fuel, the fuel tank should be fully washed. At this time, a conventional fuel oil or a mineral type solvent is not sufficient. It is desirable to wash with FAME blend fuel itself. Alternatively, for the initial storage period, FAME blended with petroleum based diesel fuel with more oxidation inhibitor than usual should be used. It was confirmed that after it is stored for a certain period, the condensed water is gradually removed, which helps maintain better oxidation stability.

(5) New test method of oxidation stability: PetroOXY method

The PetroOXY method is a new test method to evaluate the oxidation stability of FAME and FAME-blended diesel, which has been investigated in the EU and Japan, as shown in Figure 19(a). The principle of the test method is simple. The following gives a summary of the test method:

(1) Measure 5 ml of sample in the pressure vessel and close the lid of the vessel tightly. Pressurize the vessel with oxygen from a gas cylinder to the predefined pressure for the room temperature.

(2) Heat up the vessel rapidly to the predefined temperature and then maintain the temperature.

(3) Monitor the pressure in the vessel during the heating and at the subsequent constant temperature condition (At first, the pressure rapidly goes up with the rapid heating. Then, the pressure gradually goes down, depending on the oxidation stability of the sample. This is because bulk oxygen reacts with the sample and is consumed.)

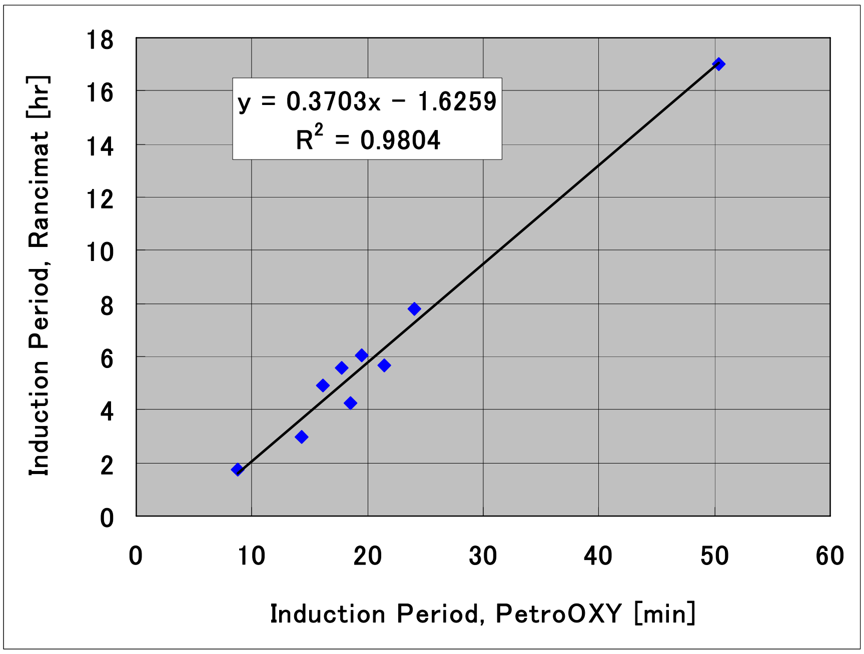
(4) The oxidation stability is expressed by the induction period, which is defined as the elapsed time from when the pressure reaches the maximum to when the pressure is decreased by 10% from the maximum. The longer the induction period, the better the oxidation stability.

Although the measurement time depends on the oxidation stability of the sample, in the case of B5, it is ca. 2-3 hrs under initial vessel pressure of 700 kPa and measurement temperature of 140 ^{o}C.

On the other hand, it is said that the EU is going to replace its existing oxidation stability test method, EN ISO 12205, with the modified Rancimat method, EN 15751. The specification with EN 15751 is min. 20 hrs, which means a much longer test duration than the PetroOXY method.

Figure 19(b) shows the relationship between results obtained using the Rancimat and PetroOXY methods [4]. Although only B100 samples were tested in this case, it can be seen that there is a good relationship between the two methods.

(a)



(b)

Figure 19 (a) PetroOXY equipment and (b) the relationship between Rancimat and PetroOXY with B100 samples

4.1.2 Antioxidant Additives

Although Fatty Acid Methyl Ester (FAME) or biodiesel has many benefits over fossil fuel including cleaner emission in terms of soot and carbon monoxide, biodiesel inherently suffers from its poor cold-flow properties and inferior oxidation stability to mineral diesel.

The cold-flow performance of biodiesel is derived from its constituent fatty acid composition, which varies among various feedstock. The superior cold-flow performance requires high fraction of unsaturated fatty acids. However, if it is inevitable to use biodiesel with inferior cold-flow properties in the cold atmosphere, the biodiesel must be treated a priori. Two approaches are available via additization and winterization process. The former is more common but is only effective for biodiesel with low saturation content. The latter is more effective for biodiesel with high saturation content because winterization process can remove high melting-point saturated esters. The remaining lower saturated fatty acids then give rise to improvement in cold-flow performance, but may reluctantly worsen oxidation stability.

It is generally known that biodiesel is more susceptible to oxidative degradation than mineral diesel. Typically, oxidation stability determined by the induction period is an indicator for the stability or shelf-life of the fuel during its storage. According to the European standard (EN 14214), an induction period of minimum 6 hours at 110°C with Rancimat test is specified for biodiesel. The oxidation stability of biodiesel depends not only on feedstock, processing condition and contaminants, but also storage condition such as storage duration, temperature, exposure to air and light and presence of metals and impurities.

Since oxidation stability of biodiesel depends on the unsaturated fraction of its fatty acid composition from the feedstock, the less stable biodiesel is most likely found in biodiesel with high polyunsaturated fatty acids. Figure 20 [5] shows the fatty acid composition of various biodiesel fuels in terms of saturated and unsaturated fatty acids of various fats and oils. Biodiesel from soybean and sunflower oils with higher fraction of polyunsaturated fatty acids are thus less stable than that from palm and coconut oils with less fraction of polyunsaturated fatty acids.

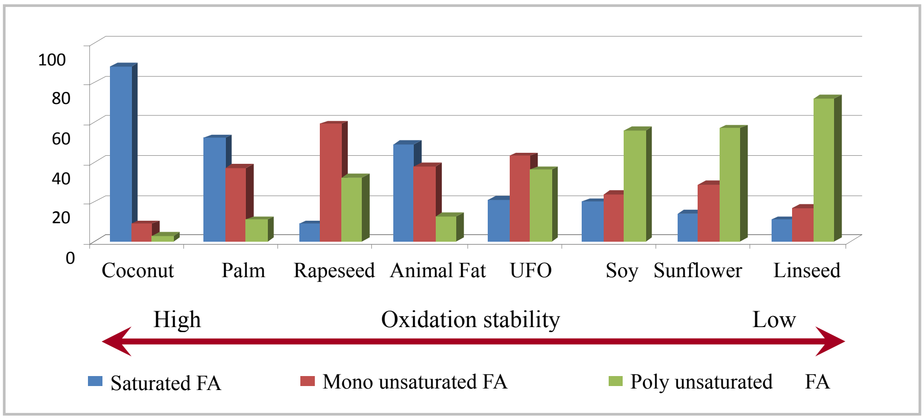


Figure 20 Fatty acid profile of various biodiesel feedstocks

The more popular countermeasure to improve oxidation stability is via natural or synthetic antioxidant additives. Hence, there is a wealth of antioxidant information in the literature from the research conducted in governmental agencies, research institute and chemical companies.

Several informative results from available literatures [6]-[13] regarding the type and effectiveness of antioxidant additives in various biodiesel were reported, as shown by various additive names in Table 7. Mittelbach [6], [7] reported that the undistilled biodiesel fuels from rapeseed oil show their induction period of 9 hours. When adding PY, PG or BHA in the amount of 250 ppm, their induction period increased to 17-22 hours. Similarly, the distilled biodiesel fuel from rapeseed oil show their induction period of 3.5 hours and increased to 6-11 hours when adding PY, PG or BHA in the amount of 250 ppm.

The biodiesel fuels from undistilled sunflower oil and soybean oil show their induction periods of lower than 6 hours. The oxidation stability can be greatly improved by various synthetic antioxidants like pyrogallol (PY), propylgallate (PG), TBHQ and BHA, but its effectiveness depends on the kind of feedstocks and biodiesel processing conditions. The palm oil methyl ester shows its good oxidation stability. Its induction period is over 10 hours without any antioxidant addition and increases to 14 and 21 hours with the addition of 50 ppm of PY and TBHQ, respectively.

The synthetic antioxidants have been continuously developed and introduced, as listed in Table 7. Several antioxidants have been experimented on the biodiesel blend in diesel oil. The recommendation of the highest amount of 500 ppm of antioxidants such as Kerobit 3627, Chimec CH 4636, IRGASTAB BD 100, Baynox plus can increase the oxidation stability of B10 to 8 hours. Nonetheless, too high dosage of antioxidant additive may deteriorate other fuel properties, such as the investigations of Baynox, DTBHQ, Vulkanox ZKF, Ionox 220, Vulkanox BKF as antioxidants in rapeseed oil methyl ester, distilled cooking oil methyl ester and tallow methyl ester as described below [14];

- With the use of 1,000 mg/kg Vulkanox ZKF antioxidant, only acid value may be affected while the viscosity, density, CFPP, carbon residue and sulphated ash content remain unaffected. However, if Vulkanox ZKF is additized into the biodiesel of high acid value, its acid value strongly increases beyond a standard limit of 0.5 mg KOH/g.
- With the use of 250 mg/kg of antioxidants, all parameters including acid value remain unchanged. All properties were within the standard specification even with the biodiesel of high acid value up to 0.42 mg KOH/g.

Table 7 List of various additives reportedly used in biodiesel

Acronyms	Explanation
BAYNOX	20% 2,6-di- *tert*-butyl-4-methylphenol (Brand of Bayer AG, Leverkusen, Germany)
Baynox plus	Product of Lanxess Deutschland GmbH
BHA	3-*tert*-Butyl-4-hydroxyanisole
BioStable ™ 403E	Product of Innospec Ltd.
Chimec CH 4636	Product of Chimec SpA
DTBHQ	2,5-Di- *tert*-butyl-hydroquinone (Brand of AECI-Aroma and Fine Chemicals_Richards Bay, South Africa)
Ionox 220	4,4'- methylene-bis-(2,6-di-*tert*-butylphenol) (Brand of Degussa Sant Celoni, S.A., Spain)
IRGASTAB BD 100	Product of Ciba Corporation
Kerobit 3627	Product of BASF SE
ppm	parts per million
PY	Pyrogallol
TBHQ	*tert* Butyl hydroquinone
UFO	Used Frying Oil
Vulkanox BKF	2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol) (Product of Bayer AG, Leverkusen, Germany)
Vulkanox ZKF	2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol) (Product of Bayer AG, Leverkusen, Germany)

4.1.3 Upgrading of FAME by hydrogenation

(1) Oxidation Stability of Fatty Acid Methyl Ester (FAME) Components

Unsaturated bonds (double bonds) contained in fatty acid methyl esters influence their oxidation and thermal stability. In fact, the influence of the number of double bonds on oxidation stability is dramatic. It has been reported that as the number of double bonds increases from 1 to 2 to 3, the oxidation rate increases about 10 times each step [15]. Because of this, the oxidation stability of each type of FAME depends highly on its unsaturated fatty acid composition (see Figure 21). In fact, Figure 22 shows the Rancimat test result for B100 using a high purity "model" FAME composed of fatty acid methyl chemical compounds (Aldrich reagent, purity>99%): stearic acid methyl ester (C18:0), oleic acid methyl ester (C18:1), linoleic acid methyl ester (C18:2), linolenic acid methyl ester (18:3), all with a carbon number of 18. Stearic acid methyl ester that does not contain unsaturated bonds shows extremely high oxidation stability. On the other hand, as the number of double bonds increases, the induction time decreases rapidly. This characteristic time delay is taken as an index of oxidation stability (values inside parentheses in the figure). Note that the oxidation stability of multi-unsaturated fatty acid methyl ester is remarkably low.

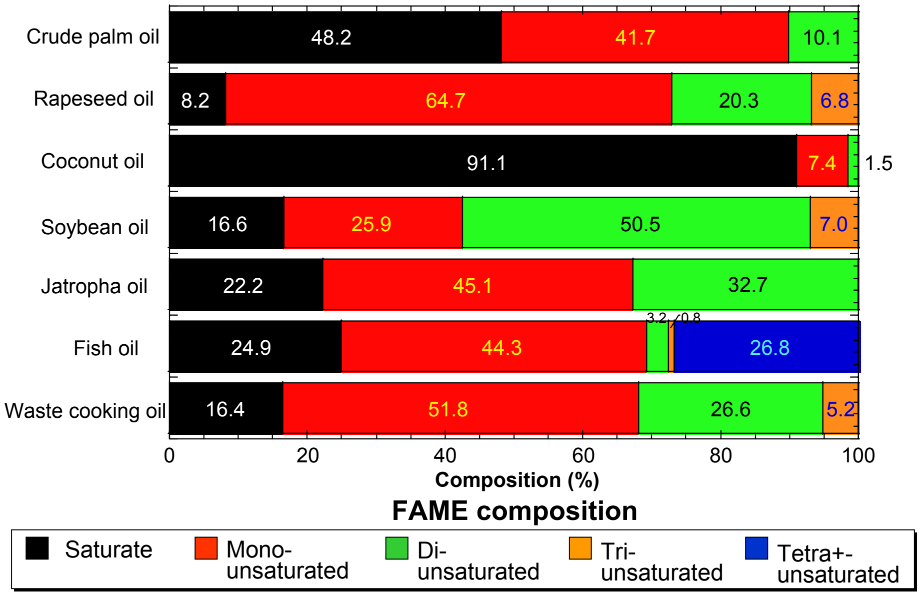


Figure 21 Composition of FAME derived from various biodiesel feedstocks

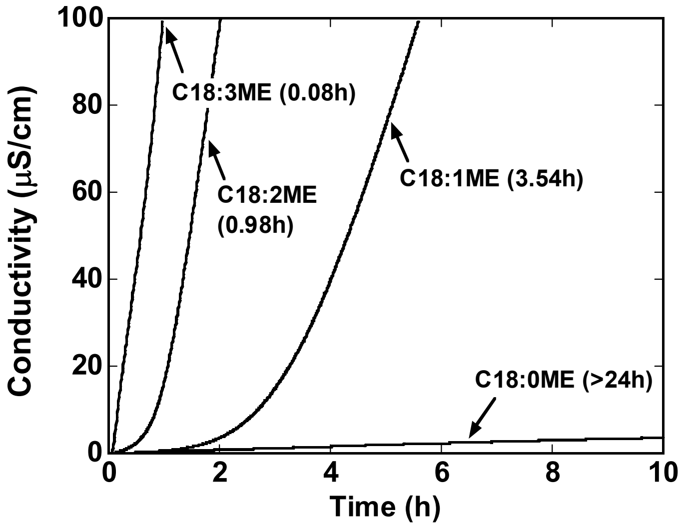


Figure 22 Oxidation stability of model FAME compounds after Rancimat tests

The oxidation stability of B100 naturally has an influence on the oxidation stability of blended diesel fuel Bx (conventional petroleum based diesel fuel blended with x% FAME) Bx supplied nationwide as a fuel. Since there is a limit when the Rancimat test method is used as the Bx oxidation stability evaluation method, the oxidation stability evaluation method in Japan for B5 blended fuel is governed by quality assurance laws. The magnitude of acid value increase (ΔAV) can be obtained from the difference between the final and initial values, when B5 is made to oxidize in a pure oxygen environment at 115ºC for 16h. It has been determined that with this amount, the oxidation stability can be evaluated, and the magnitude of increase should be below 0.12mgKOH/g. Under this assumption, a model B5 fuel was made from the pure FAME chemical compounds given above, blended with normal tetradecane (n-C14). The oxidation stability of this model FAME based biodiesel fuel was evaluated with the oxidation method underlying the above quality assurance law. As shown in Table 8, as the number of double bonds increases, the acid value increases in a similar way to the Rancimat test results for B100 mentioned above. The degree of increase for multi-unsaturated fatty acid methyl esters (e.g. C18:2 and C18:3) is significant. Moreover, for C18:3 linolenic acid methyl ester, it was observed that large amounts of acidic sludge formed after the oxidation test. It was discovered that organic acid was generated by oxidative degradation, which catalyzed the thermal oxidative polymerization in the presence of oxygen.

Table 8 Oxidation stability of a B5 blend of model FAME with tetradecane

Model FAME compounds	Increment in acid value* (mgKOH/g)
Stearic acid methyl ester (C18:0 ME)	0.07
Oleic acid methyl ester (C18:1 ME)	0.66
Linoleic acid methyl ester (C18:2 ME)	20.3
Linolenic acid methyl ester (C18:3 ME)	152.5

*Acid value difference before and after oxidation at 115°C for 16h under the blowing of pure oxygen. Increment in acid value for n-C14 was 0.10 mgKOH/g

From the oxidation stability evaluation test results using the above model FAME chemical compounds, it was determined that:

(1) The oxidation stability of multi-unsaturated FAME (containing more than two double bonds in the fatty acid part) is extremely bad.

(2) Multi-unsaturated FAMEs containing more than three double bonds in the fatty acid part easily form organic acid accompanied by oxidative deterioration and at the same time sludge due to thermal oxidation polymerization catalyzed by acids.

(3) Oxidation stability of fatty acid ME with one double bond is worse than saturated fatty acid ME. However, compared to the oxidation stability of multi-unsaturated fatty acid ME, oxidation stability is extremely high.

(2) Improvement of Oxidation Stability using Partial Hydrogenation of FAME

As the number of double bonds contained in the fatty acid part in FAME decreases, oxidation stability improves. The cold flow property of FAME, however, deteriorates because oxidation stability and cold flow property have a tradeoff relationship, as shown in Figure 23. Because of this, when improvement of FAME's oxidation stability is given a higher priority and the low temperature flowability is improved with a cold flow improver, the partial hydrogenation technology that converts multi-unsaturated FAME produced with the current method to singly unsaturated molecules is considered to be a high quality FAME technology [16]. An approach to high quality biodiesel production via partial hydrogenation of currently available FAME has merits. It is not necessary to significantly redesign or revise FAME production equipment already in place. By installing partial hydrogenation apparatus as supplementary equipment, it is possible to utilize all the current process equipment, as schematically shown in Figure 24. However, to obtain the highest bio-diesel quality from oil crops, the current petroleum products and similar hydrocarbon fuels not having double bonds or oxygen are preferable. Because of this, in environments where incoming oil crop feedstocks are fully maintained, and high pressure equipment for oil refinery processes can be utilized, an approach to produce a high quality fuels (second generation bio-diesel) [17] via hydrodeoxygenation of triglycerides would be promising. Figure 25 shows characteristics of the partial hydrogenation method of FAME and the hydrodeoxygenation method of triglyceride.

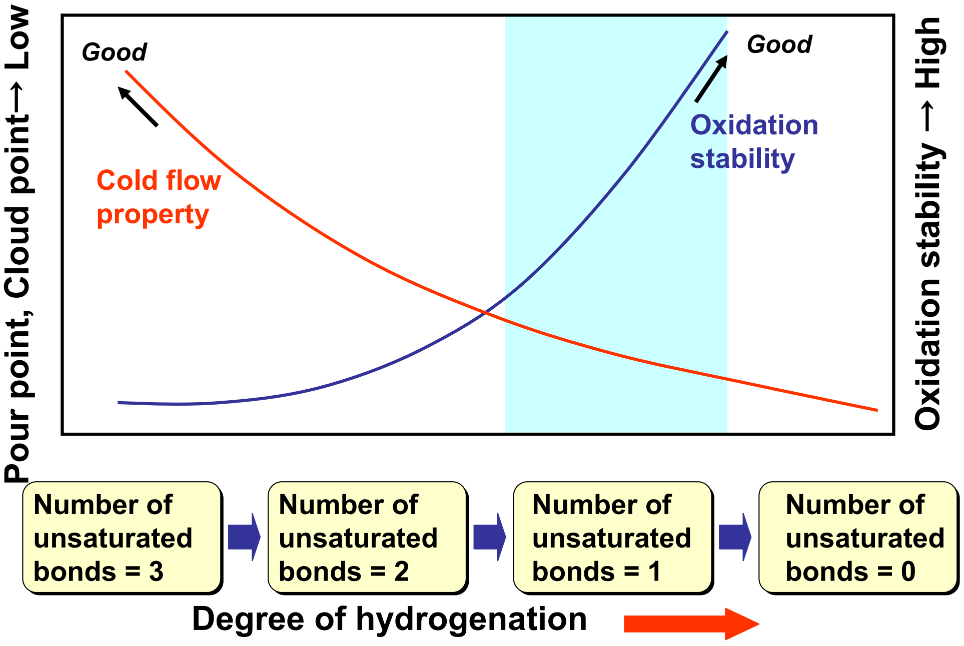


Figure 23 Concept for partial hydrogenation of FAME

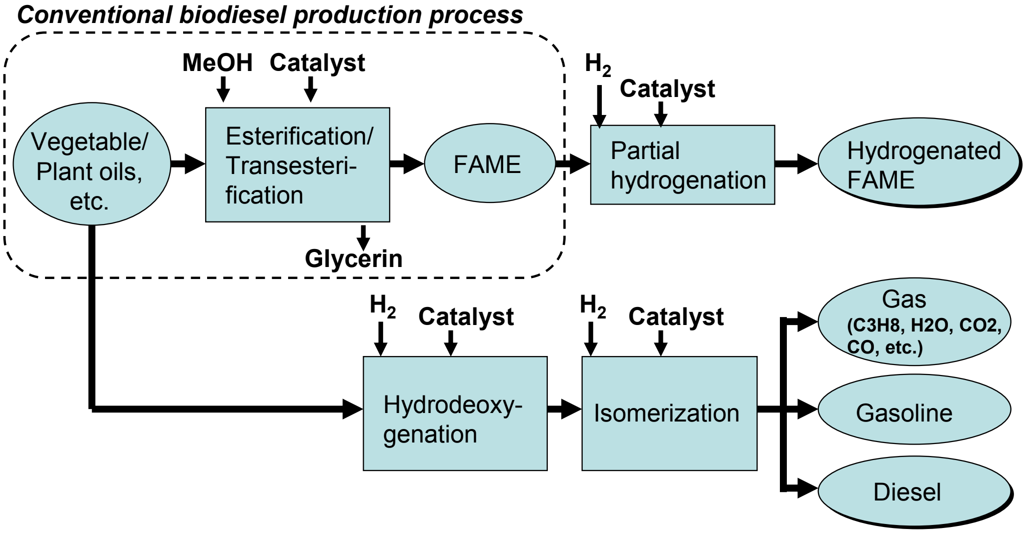


Figure 24 Partial hydrogenation for upgrading conventional FAME

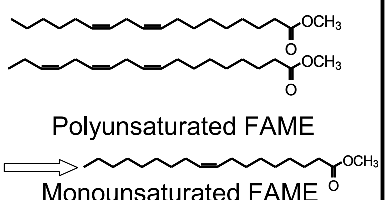
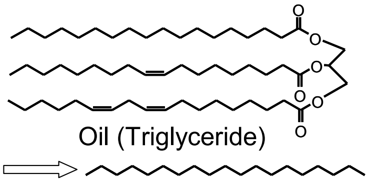
	Partial hydrogenation	Hydrodeoxygenation
Reaction	 Polyunsaturated FAME Monounsaturated FAME	 Oil (Triglyceride) Hydrocarbons
Oxidation Stability	Relatively high	High
Reaction Conditions	Low pressure (atmospheric~0.5MPa) Low temperature (80~120°C)	High pressure (>5MPa) High temperature (>300°C)
Catalysts	Ni catalysts, Noble metal catalysts, etc.	Water (steam)-tolerant NiMo catalysts, CoMo catalysts, etc.
Further processing	None	Isomerization for conditioning cold flow property and cetane number
Location of processing facility	Local Community (small ∼ large plants)	Petroleum refinery (Neat ∼ Coprocessing)

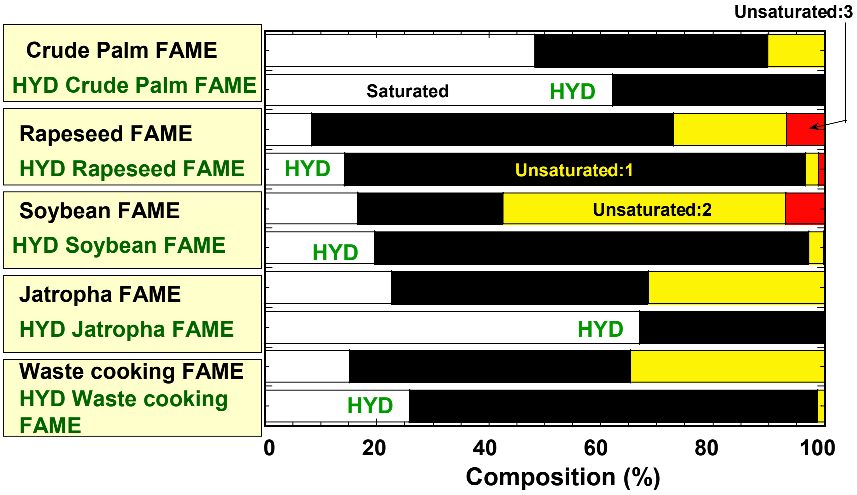
Figure 25 Comparison of partial hydrogenation for FAME upgrading and hydrodeoxydation (HDO) for second generation biodiesel production

(3) Characteristics of Partial Hydrogenation of FAME

When oxidation stability improvement via partial hydrogenation of FAME (B100) is attempted, as shown in Figure 24, the optimal hydrogenation level varies depending on the unsaturated chemical compounds present. This is because hydrogenation reactions proceed in a serial manner, for example: Trivalent unsaturated

FAME → Bivalent unsaturated FAME → Mono-unsaturated FAME → Saturated FAME. In addition, the higher the unsaturation level is, the faster the hydrogenation reaction rate is. Figure 26 shows a breakdown of saturated and unsaturated components of five types of FAME. The companion bar graph shows the corresponding composition after hydrogenation treatment. It was obtained at atmospheric pressure and 100ºC, with a 1 hour hydrogenation treatment time, in order to compare the reactivity of each type of FAME. Under the hydrogenation conditions used here, reaction selectivity to a mono unsaturated FAME is high, except for Jatropha FAME.

Crude palm oil ME and soybean oil ME (B100) that had been partial hydrogenated were blended with sulfur free diesel fuel (S = 6ppm) with 5% mass to obtain a B5 blend. Then the oxidation stability was evaluated using the accelerated oxidation method used with the Japan quality assurance law described earlier. Table 9 shows the results obtained. Antioxidants for all cases are non-additives. Oxidation stability of B5 obtained via partial hydrogenation FAME is good ($\Delta AV<0.12$mg KOH/g). Even for B10 with 10% FAME, the level of acid value increment is under 0.12mgKOH/g. When other hydrogenated FAMEs shown in Figure 26 were used as the blend material, even without an antioxidant, the amount of acid value increment after accelerated oxidation of B10 was below 0.12mg KOH/g. This means that more than one type of FAME can be fed into this partial hydrogenation method. That is, the partial hydrogenation method has the flexibility to handle not only FAME obtained from virgin raw materials, but also FAME obtained from mixtures of waste cooking oil and raw materials containing fish oil, for example. These materials can have high variability in feedstock composition and characteristics. Besides, it shows that with this quality improvement method, the Japan quality assurance levels required for B5 biodiesel can be maintained even with B10.



Hydrogenation conditions: H_2 pressure = atmospheric, Temperature= 100 °C, Reaction time = 1h

Figure 26 Changes in composition of FAME derived from crude palm oil, rapeseed oil, soybean oil, jatropha oil and waste cooking oil after partial hydrogenation

Table 9 Oxidation stability and cold flow properties of Bx

Bx*	blending components	Increment in acid value (mgKOH/g)	pour point (°C)
B5	CPO-ME**	0.21	-14
	Hydrogenated-CPO-ME	0.02	-13
B10	CPO-ME	1.63	-11
	Hydrogenated-CPO-ME	0.04	-8
B5	RSO-ME***	3.47	-18
	Hydrogenated-RSO-ME	0.01	-17
B10	RSO-ME	9.38	-20
	Hydrogenated-RSO-ME	0.02	-15

* X mass % of FAME blended with petrolem diesel (S=6 ppn

** Crude palm oil derived methyl ester

*** Rape-seed oil derived methyl ester

When hydrogenated crude palm oil ME was used as the blend material, the oxidation stability was good up to a FAME blended ratio 20 mass % (ΔAV=0.05mg KOH/g < 0.12mg KOH/g after accelerated oxidation). However, the pour point of B20 deteriorated to only -2ºC, which means the cold flow property will be an issue in many areas. In warm regions where oxidation stability improvement receives a higher priority, it is possible to use a higher concentration of the partially hydrogenated FAME.

Table 10 shows fuel characteristics of crude palm oil ME (B100) before and after partial hydrogenation. After treatment of the raw FAME which clears the relevant EN standard (EN14214), as the density decreases and cold filter plugging point deteriorates. However, oxidation stability is greatly improved, and there was no influence on other FAME components and characteristics. The cetane value of hydrogenated FAME is still unmeasured, however it is known that the cetane value increases as the fatty acid unsaturation level decreases. Thus the cetane value is assumed to exceed 64. In other words, the FAME partial hydrogenation method negligibly changes the fuel characteristics, and it is the preferred quality improvement method to improve FAME's oxidation stability. For comparison, also shown are characteristics of triglyceride oils obtained by hydrodeoxygenation[18], which are expected to be a second generation biodiesel fuel.

Table 10 Properties of hydrogenated FAME and hydro-deoxygenated (HDO) palm oil

	FAME	Hydrogenated FAME	Hydrodeoxy-genated palm oil*
Feedstock	Crude Palm oil	Crude palm oil	Refined palm oil
Density at 15 °C (kg/m^3)	876	857	785
Viscosity at 40 °C (mm^2/s)	4.4	4.7	4.2（at 30 °C）
Flash point （°C）	168	176	132
Centan Number （-）	64	-	101
Sulfur content （massppm	＜3	＜1	＜1
Oxidation stability (h)	9.7	＞24	＞24
Acid value (mgKOH/g)	0.34	0.27	0.00
Acid value after oxidation** （mgKOH/g）	0.55	0.30	0.03
Increment in acid value （mgKOH/g）	0.21	0.03	0.03
CFPP (°C）	9	13	22

* A. Koyama et. al., SAE 2007-01-2030.

* Accelerated oxidation at 115 °C for 16h under the blowing of pure oxygen.

(4) Method of FAME Partial Hydrogenation

As shown in Figure 25, partial FAME hydrogenation is possible under reaction conditions of 0.1~2MPa hydrogen pressure and 80~120°C temperature, using a hydrogenation catalyst. A typical Ni type catalyst, which has been used for conventional oil and fat hydrogenation, has merits for catalyst cost, but it is necessary to use a hydrogen reaction pressure of several atmospheric pressure (>0.3~0.5MPa). On the other hand, noble metal catalysts like Pd and Pt are disadvantageous compared to Ni catalysts in terms of their cost. However, they have some merits in that their reaction pressure is lower – low enough that hydrogenation treatment is possible under atmospheric pressure. This means that expensive high-pressure process equipment is unnecessary. The sulfur content of the raw material FAME is less than in conventional diesel fuels. However if one takes the catalyst lifetime duration into consideration, sulfur resistance countermeasure for the selected catalysts would be necessary. FAME hydrogenation is possible using supplementary equipment along with conventional FAME production equipment. Batch type and continuous type reaction methods are possible, while slurry bed and fixed bed types of catalyst reactors can be used. The volume recovery yield of hydrogenated FAME can exceed 100% because FAME hydrogenation accompanies a volume increase.

(5) Characteristics of Triglyceride Hydrodeoxygenation

Hydrodeoxygenated (HDO) oils that are expected as the second generation bio-diesel contain negligible aromatics or sulfur. They are composed of straight-chain hydrocarbons with carbon number 15~18. As shown in Table 10, characteristics of HDO oils include a high cetane value, a lower density, and a lower viscosity, compared to FAME and partial hydrogenated FAME. The most significant difference from FAME is this: Since negligible oxygen is contained in HDO oil, the acid value is extremely low, and since unsaturated bonds are very sparse, the oxidation stability is extremely high. HDO oil has some demerits in cold flow property (Table 10Table shows the cold filter plugging point), however with current isomerization techniques used in oil refineries, it is possible to improve the low temperature flowability and optimize the cetane value.

(6) Method of Triglyceride Hydrodeoxydation

It is possible to achieve hydrodeoxydation of triglycerides, as shown in Figure 25, at high temperature conditions (>300ºC), high hydrogen pressure (>5MPa), using the appropriate hydrodeoxydation catalyst. Hydrodesulfurization reactions are similar to hydrodeoxydation reactions, therefore it is possible to use NiMo and CoMo type hydrodesulfurization catalysts for HDO reaction. However in terms of the catalyst lifetime, it has been found necessary to take countermeasures for keeping the proper sulfide conditions of supported metals and increasing the water (steam) resistance of the catalyst supports. A wide range of process methods have been reported for triglyceride hydrodeoxygenation, from a single neat treatment process, to a co-processing treatment method were triglycerides blended with petroleum fractions are hydrotreated. In addition, recalling that hydrocarbon components obtained by HDO are mainly a straight-chain hydrocarbons, the cold flow property and cetane value can be modified by secondary isomerization treatments. In the process of hydrodeoxygenation and isomerization, decomposition of straight chain hydrocarbons and over-hydrocracking reactions proceed simultaneously. Therefore, diesel fuel fraction yield improvement is one area of future work. For both hydrodeoxygenation and isomerization processing mentioned above, high-temperature high-pressure equipment is necessary. One merit is that we can use current oil refinery equipment. Moreover, methanol is not necessary for this hydroteatment method. CO_2 formation accompanying methanol production is thus not a concern. In LCA compared to the conventional FAME production technology it is said to be advantageous [17], [18].

4.2 Fluidity

4.2.1 Introduction of Fluidity

(1) Low Temperature Flowability

There are two types of fat and oil that are made into FAME: one liquid (oil) and one solid (fat) at room temperature (~ 20°C), depending on the degree of saturation as shown in Figure 27. FAME made from room-temperature solid raw materials is also solid at room temperature. When mixing these FAMEs with petroleum based diesel fuel and using them, low temperature flowability worsens. Even pure petroleum based diesel fuel has different low temperature flowability depending on the amount of wax it contains. In general, in order to use FAME during cold seasons or in a cold region, a low temperature flowability improver is added. The low temperature performance of FAME blended with petroleum based diesel fuel depends not only on the low temperature performance of FAME but also on the low temperature blend characteristics, type of improvers, and the amount of low temperature flowability additive used.

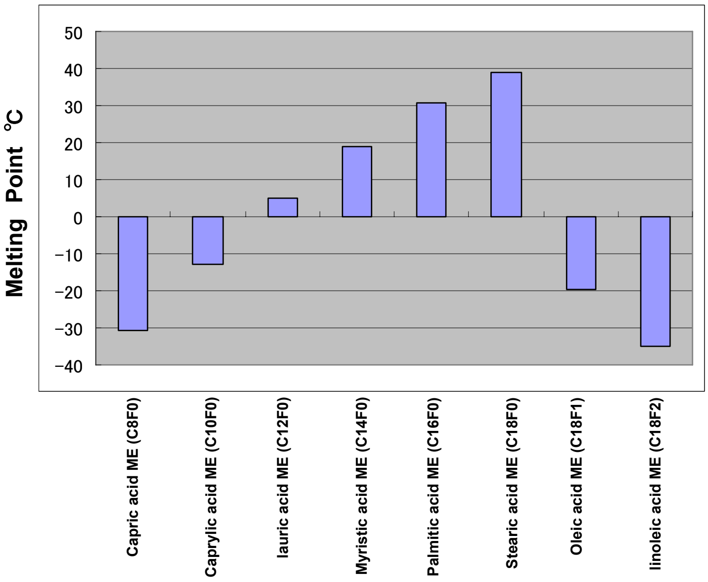


Figure 27 Melting point of FAME

(2) Low Temperature Characteristics of Fatty Acid Methyl Esters

FAME made from animal and plant oils or fats is a mixture of each kind of fatty acid methyl ester. Each component fatty acid methyl ester is a pure material, for which a solidification point exists. The bigger the FAME molecule is, the higher the solidification point is, and the more unsaturated bonds it has, the lower the solidification point is. Ordinary FAME is a mixture, therefore it does not have a solidification point but it does have a cloud point, a clogging point, and a pour point (see Figure 28). For example, palm oil methyl ester and animal oil/fat methyl ester containing many saturated bonds both have poor low temperature performance. By comparison, soybean oil methyl ester and canola seed oil methyl ester, containing a high level of unsaturated bonds, both have good low temperature performance. Moreover, compared to palm oil methyl ester, coconut methyl ester contains high levels of fatty acids with relatively low diversity of molecules and also has good low temperature performance.

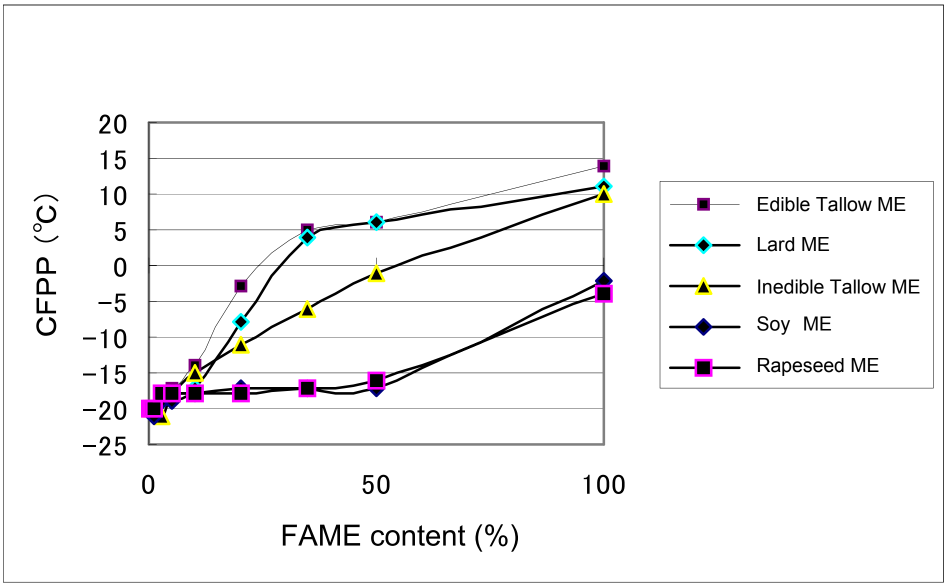


Figure 28 CFPP of Biodiesel / Diesel blend

(3) Influences of Vehicles

When using FAME blended with petroleum based diesel fuel, the low temperature performance of FAME before blending is sometimes below a certain value. However, depending on the diesel blend fuel, it does not always meet the standard for low temperature FAME characteristics that are being sought. A low temperature flowability improver, even for diesel fuel, is an effective additive, but the exact additive level depends on the composition. The specific additive and amount required do not always effectively function with FAME blended with petroleum based diesel fuel. Because of this, those who blend FAME with petroleum based diesel fuel are required to adjust the final blend such that it has the proper cloud point, clog point, and pour points.

When mixing FAME with petroleum based diesel fuel, the cloud point, clogging point and pour point generally increase with diesel fuel concentration. These sometimes change linearly, but they exhibit different characteristics depending on the FAME type. For example the effect may be large at low concentrations, or it may hardly change at low concentration but change dramatically when the concentration exceeds 50%, as shown in Figure 28.

In the past, low temperature engine starting and driving characteristics in automobiles were considered to depend on the clogging point. For current high-pressure common rail injection systems it is necessary to design the fuel filter with sufficient porosity and flow area for effective system protection. This tends to depend on the cloud point rather than the clog point. Particular attention has to be given when using palm and animal oil methyl esters, which are both prone to phase separation.

(4) Influences of Storage

Problems of low temperature flowability become apparent not only in vehicles but also in storage and flow processes as well. In storage and flow processes the temperature increases and decreases repeatedly during the daytime and night. As a result, there are several concerns:

(1) Wax separates at low temperatures, causing deposits inside the fuel tank,

(2) Wax separated at low temperatures does not melt when the temperature increases.

After the temperature repeatedly increases and decreases, the amount of separated wax gradually increases. Actually, when the test conditions are determined and tests are conducted, high pour point FAME results in wax separation, causing differences in composition between the upper and lower part of the test container, as shown in Figure 29.

From this behavior, for trouble-free flowability of FAME blended with petroleum based diesel fuel, it should be kept in mind that its possible for the composition to degrade when the temperature repeatedly fluctuates, as well as when the temperature is simply too cold.

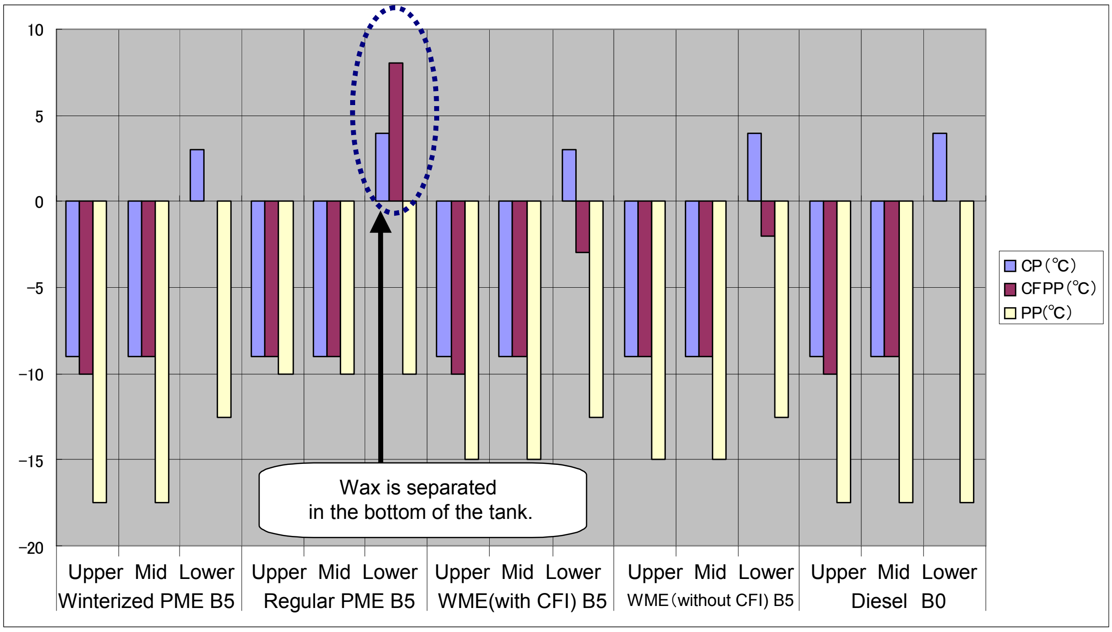


Figure 29 Wax separation of temperature circulation test

(5) Influences of Impurities

When FAME is produced, triglyceride are the raw material, and reaction intermediate products like diglycerides and monoglyceride remain as impurities. It is known that these impurities influence sludge formation, and also cause deterioration of low temperature flowability. Some saturated fatty acids like glycerides have a high pour point. For example, the pour point of stearic acid is about 40°C, while stearic acid monoglyceride, diglyceride, and triglyceride fall into the range of 50 ~ 80°C, and monoglyceride has the highest pour point of them all.

In the European FAME standard (EN14214), an upper concentration limit for these glycerides was determined. It has recently been shown that petroleum based diesel fuel blended with FAME may surpass this upper limit, and problems may occur. That is, at low to moderate temperatures the fuel filter of vehicles and also on refueling equipment can clog. When analyzing the substances plugging these filters, it was found out that monoglycerides of saturated fatty acid was the main element. Further details are still under research. It is assumed that methanol being used as a raw material acted as a co-solvent to aid dissolving these compounds, and during flow process or in the vehicle’s fuel supply system, the temperature increased and methanol evaporated, resulting in decreasing dissolving performance, and phase separation. In Europe, canola oil is the most commonly investigated FAME raw material. As FAME has been widely utilized worldwide, oils and fats containing saturated fatty acids, like palm oil and beef oil, have started to be used as raw materials. When using FAME produced from these high saturated fatty acid materials in a cold region or season, it is necessary to be particularly careful and investigate further countermeasures.

4.2.2 Fluidity Improvers for Biodiesel Fuels

The low temperature fluidity of FAME is related to the specific saturated fatty acid methyl ester's (FAME) content, while the amount of saturated fatty acid methyl esters in a given FAME depends on the fat and fatty oil as the original source of the FAME. Figure 30 shows the cloud point and cold filter plugging point (CFPP) of various FAMEs in terms of the mass ratio of saturated to unsaturated fatty acid methyl esters, for each type of FAME. From Figure 30, we see that as the ratio of saturated to unsaturated fatty acid methyl esters increases, the cloud point and CFPP both increase, and for palm stearin methyl ester, with a ratio of 1.5, the cloud point and CFPP reach 15ºC and 21ºC respectively.

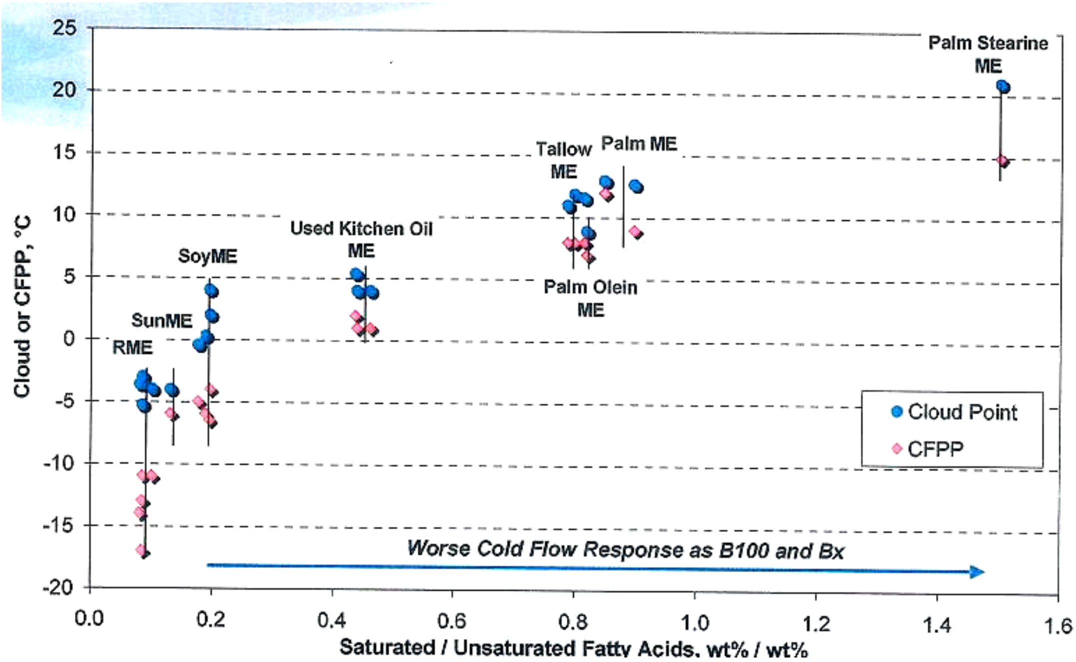


Figure 30 Cloud point and CFPP of various FAMEs

Figure 31 shows the effect of the addition of a cold flow improver for several types of FAME. The effect is indicated as the amount of the additive required to achieve a CFPP of -10ºC. For rapeseed, the addition of the cold flow improver was not necessary. However, as the amount of saturated fatty acid methyl esters in FAME increased, the required amounts of the cold flow improver were increased. Note that for palm olein and palm oil, even though a large amount of the cold flow improver was added, it was not possible to achieve the CFPP of -10ºC.

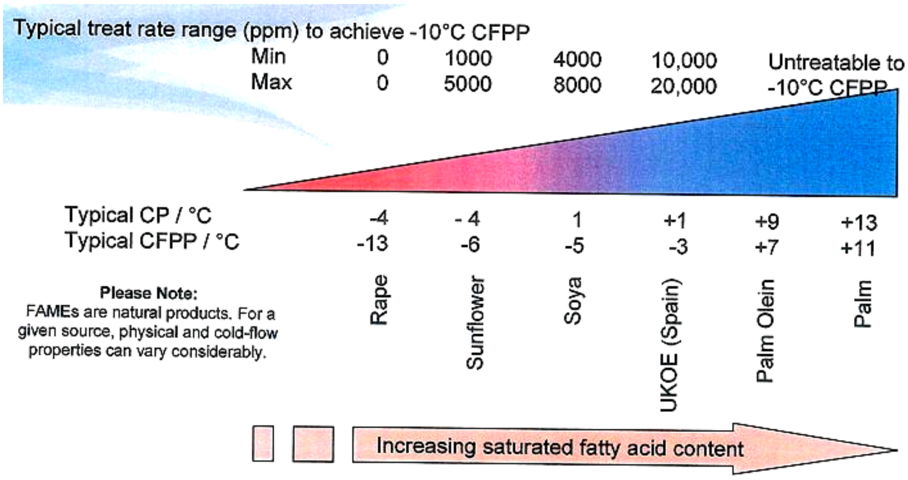


Figure 31 Treatability of FAME B100 with cold flow additives

Infineum Co. Ltd., a maker of cold flow improver additives, identifies the following four points regarding effective utilization of cold flow improvers in FAME blended petroleum diesel fuel.

- The cold flow improver should work even in base petroleum diesel fuel.
- The proper cold flow improver should be selected, depending on the kind of FAME and the amount of blending.
- FAME should be properly blended with base petroleum diesel fuel, and the blends should be in a homogenized and stable condition.
- The cold flow improver should be properly added to FAME or FAME blended petroleum diesel fuel to obtain the desired results.

Figure 32 shows an example of how a cold flow additive improves the fluidity for a range of B5, prepared by blending various FAMEs with a UK petroleum diesel fuel (B0). The effectiveness is shown as a function of the additive dosage rates to achieve CFPPs of –15 °C and –17 °C. Compared to B0, B5s was made with palm ME and tallow ME, which contain high levels of saturated fatty acid methyl esters, require twice the amount of the cold flow improver.

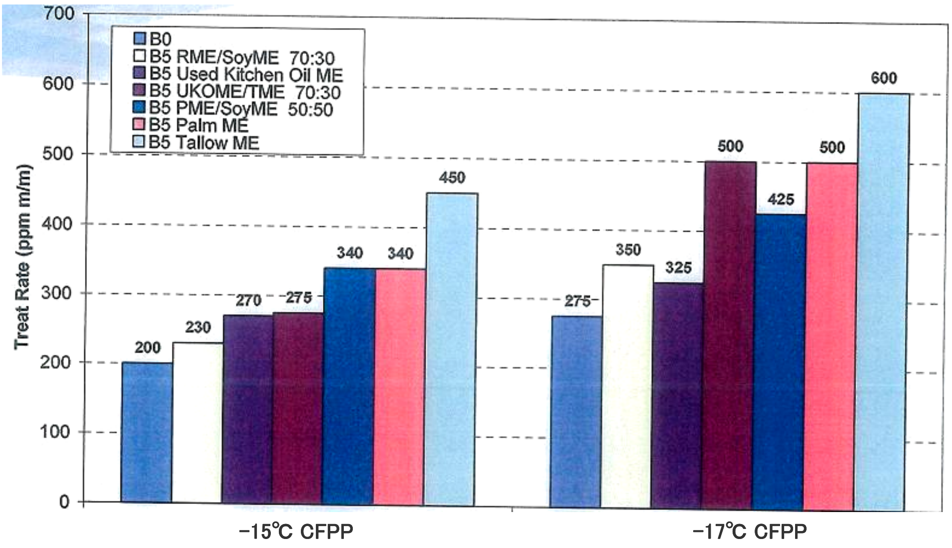
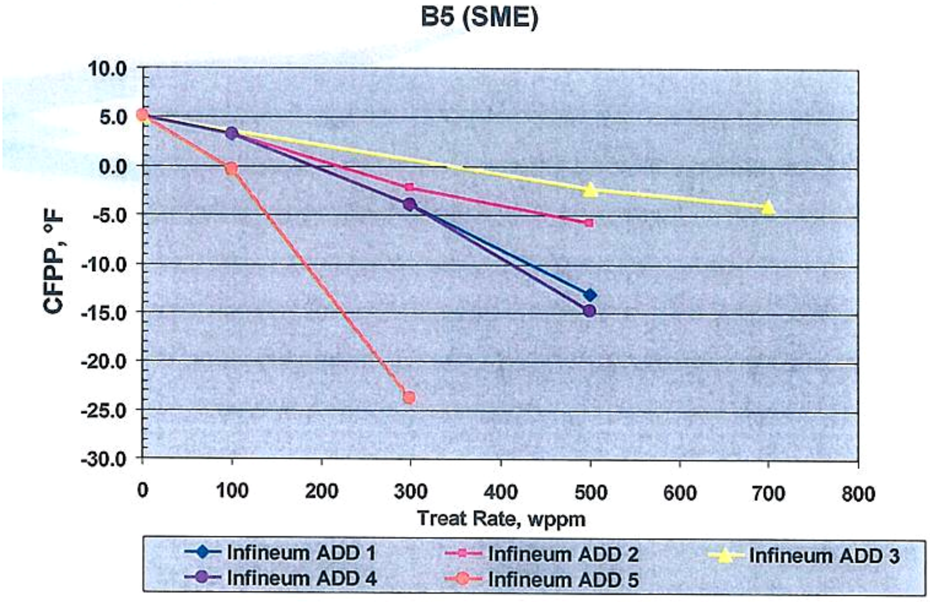


Figure 32 Impact of various FAMEs on cold flow performance

Moreover, Figure 33 shows the effects of various cold flow improvers to a common B5, made from soybean methyl ester (SME). It can be observed that the effects are remarkably different, and depend on the specific additive. Thus, proper selection of the optimal cold flow improver is important.



Additive	Rate, wppm	Cloud, °C	Cloud, °F	CFPP, °C	CFPP, °F	PP, °C	PP, °F
ULSD Base Fuel	0	-11.5	11.3	-13	8.6	-21	-5.8
B5	0	-9.1	15.6	-15	5.0	-21	-5.8

Figure 33 An example of the effectiveness of cold flow improvers for an SME blended B5

Infineum Co. Ltd. mentions the following points regarding the proper application of a cold flow improver to FAME blended petroleum based diesel fuel.

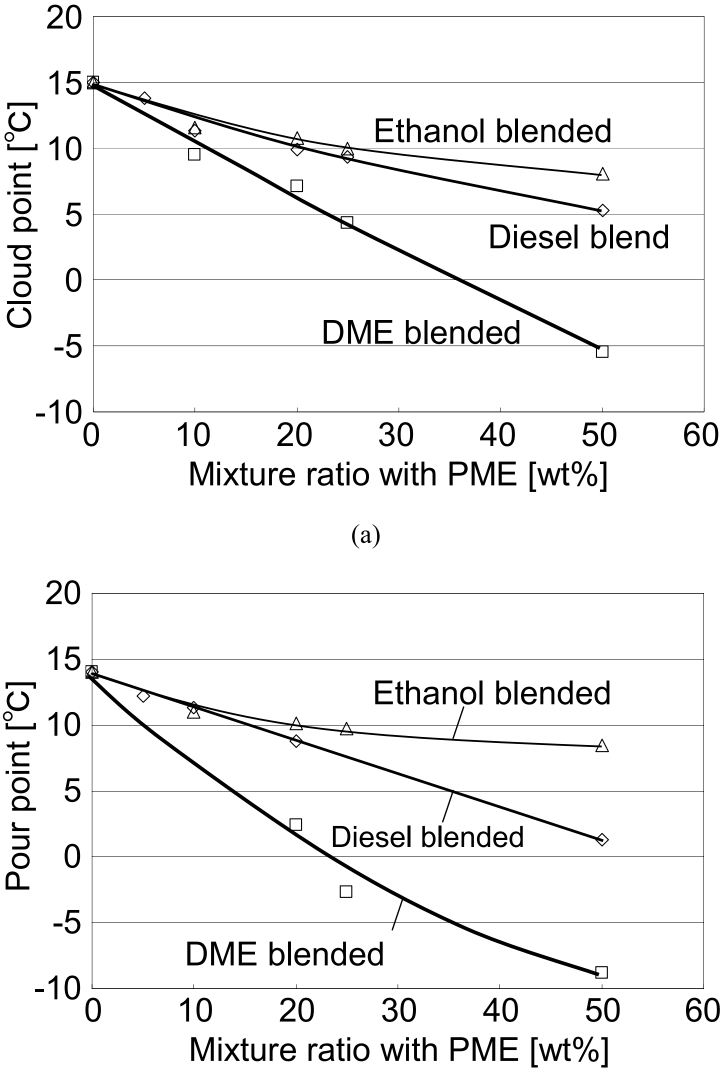
- Blending FAME with petroleum diesel fuel can result in considerable challenges for fuel suppliers and end users regarding low temperature fluidity.
- Biodiesel blends up to B5 are sometimes possible to treat with existing cold flow improvers.
- As the FAME blend ratio increases, it may be necessary to use further advanced additive technologies.
- Additive technology solutions depend on the characteristics of FAME and petroleum diesel fuel, and their combination.

4.2.3 Other Countermeasures

(1) Blending another fuels to FAME

Biodiesel fuel is a multi-component mixture of fatty acid esters, and its solidification characteristics are correspondingly complex. However, in many cases it is possible to improve the low temperature fluidity by blending with substances having a lower solidification point. Figure 34 shows the cloud point and pour point when JIS #2 diesel fuel, ethanol and dimethyl ether (DME) were blended with palm methyl ester (PME). Also, Table 11 shows the main properties of fuels used for these tests.

The cloud point and pour point of PME used in the current tests were 15ºC and 14ºC, respectively. It is understood that the solidification point of PME will decrease when blended with other fuels such as diesel fuel, ethanol and DME. For example, when 20% of diesel fuel or ethanol is blended with PME, the cloud point and the pour point is decreased by about 5ºC. When 20 % of DME blended with PME they decrease by about 10ºC. The effect of DME blending is quite large. When blended 50% of DME with PME, the pour point reaches -8.8ºC, which is equivalent to the low temperature fluidity of JIS #2 diesel fuel. It should be noted that the improvement effect is not be directly related with a solidification point of blended substances. The solidification point of ethanol is -114ºC. This is substantially lower than the pour point of diesel fuel, however diesel fuel has even better low temperature fluidity improvement effects than ethanol. When diesel fuel is blended 50/50 with PME, the pour point becomes 1.3ºC, which is equivalent to JIS #1 diesel fuel, while the low temperature fluidity improvement effects of ethanol decrease gradually with mixture ratio.



(a)

(b)

Figure 34 Effect of diesel fuel, ethanol and DME blend ratios on the (a) cloud point and (b) pour point of PME

Table 11 Fuel properties of test fuels

Fuel	PME	RME	JIS No.2 diesel fuel	Ethanol	DME
Density [kg/m^3]	873.8	880.5	822.6	789.3	667
Kinetic viscosity [cSt]	4.455	4.309	3.259	1.373	0.197
Pour point [°C]	14	-10	<−7.5	−114	−141.5
Oxygen content [wt%]	13.2	10.8	0	34.8	34.8
Low heat value [MJ/kg]	37.11	37.14	42.7	26.82	28.43

(2) Characteristics of Pressure Solidification

From a thermodynamics viewpoint, a high cloud point means that standard pressure and temperature conditions are close to the location of a solidification line at phase equilibrium diagram. Thus it is possible that wax occurs at relatively low pressures when the pressure is increased. A fuel injection pressure of current diesel engines can reach 100 to 200MPa. So even though the fuel is used at temperatures above the cloud point, it can be considered that biodiesel fuels form wax in the high-pressure fuel lines. There is thus the possibility of negative influences on the fuel injection system. The cloud point and pour point describe solidification characteristics at atmospheric pressure and have typically been used as an index of low temperature fuel fluidity. Considering the above arguments, however, it is necessary to take into consideration the solidification characteristics along with local fuel pressure.

Using a test cell, Figure 35 shows the PME solidification process when pressure was gradually increased at a constant 20°C temperature. At pressure of 56MPa, frame 2 shows that wax occurred in part of the sample. The wax that occurred first became a center for further growth of filaments. Then as the core regions became solid with filamentation, in frames 3 to 11, eventually the test cell became completely solid with wax filaments.

Figure 36(a) shows the measured solidification pressure as a function of sample temperature for PME and RME. As the temperature is increased, the solidification pressure increases quickly at first and more slowly later. The solidification point (a cloud point) of PME at standard pressure (0.1MPa) is 15°C, at 20°C the solidification pressure increases to 56MPa, at 25°C it increases to 83MPa, and then at 40°C it rises all the way to 145MPa. For diesel engines with high-pressure fuel injection systems able to reach 200MPa, PME solidification can thus occur even if the fuel temperature is kept at 40°C. With a current design common rail fuel injection system, the fuel temperature rises relatively soon after start-up, thus it is thought that problems of PME pressure solidification are limited to cold start and operating in low temperature environments.

The situation with RME is quite different. Its solidification point (cloud point) at 0.1MPa is -2.7°C. Then, at 5°C the solidification pressure increases to 115MPa, at 10°C it rises to 150MPa, and at 20°C it reaches 180MPa. So with typical fuel injection systems it is unlikely that solidification will occur. Considering temperatures from the East Asia region to the South East Asian region, RME solidification due to pressure in this area does not seem like it would be a problem.

Pressure solidification characteristics can be improved by blending with high-grade substances for improved low temperature fluidity, as at standard pressure.

Figure 36(b) shows the solidification pressure when DME is blended with PME at ratios of 10 to 25% by weight, and diesel fuel is blended with PME at ratios of 5 to 20% by weight. As the blend ratio increases, the solidification pressure increases. Looking at which substance has a more powerful improvement effect on the solidification pressure, DME appears to be stronger than diesel fuel. For example, at 20°C, when 20% diesel fuel is blended with PME, the solidification pressure increases from 56MPa to 95MPa. On the contrary, when 20% DME is blended with PME, the solidification pressure rises all the way to 140MPa.

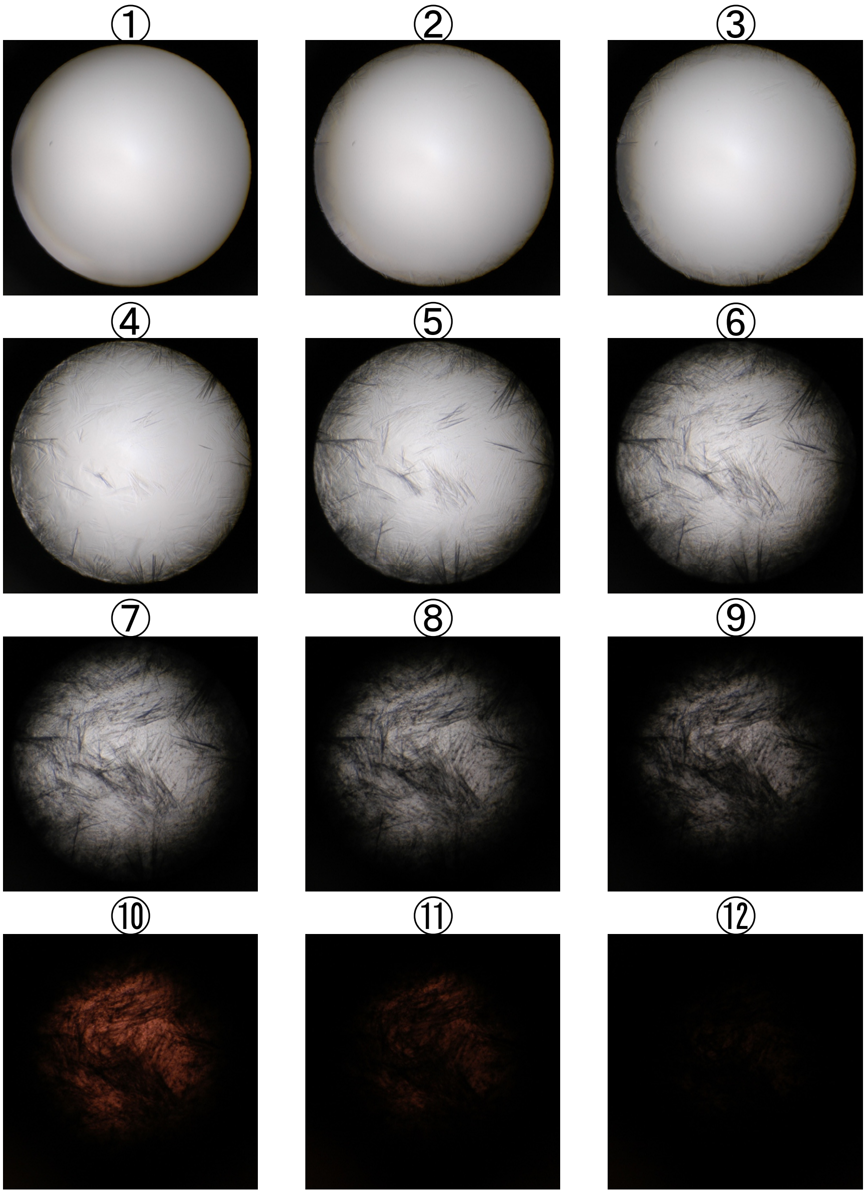
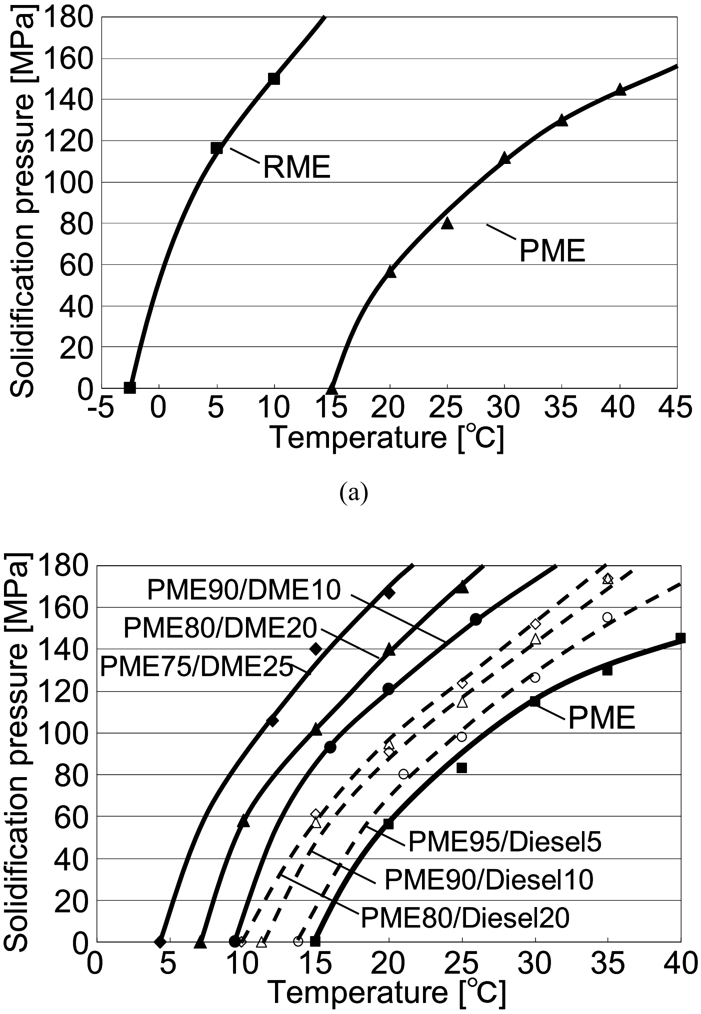


Figure 35 Pictorial solidification process of PME at 20℃



(a)

(b)

Figure 36 (a) Solidification pressure of PME and RME, and its effect by DME and diesel fuel blend ratios

(3) Winterization technology for PME

Normal grade palm biodiesel has typical pour point of about 15°C and can only be used in tropical countries. To enable palm biodiesel to be used as mineral diesel substitute in countries with cold climate, the Malaysian Palm Oil Board (MPOB) has developed a novel process to produce palm biodiesel with cold filter plugging point (CFPP) that meets the seasonal requirements of temperate countries (CFPP ranging from minus 20°C in winter to 0°C in summer). Winter-grade palm biodiesel (PME) with low CFPP and its production technology are filed under Malaysian Patent PI 20021157.

Winter-grade PME is produced by removing the high melting components from normal grade palm biodiesel. A physical separation process is used. This includes fractional distillation and/or crystallization of the esters followed by separation of the solids from the liquid fraction. Depending on the CFPP requirements, the yield of winter-grade PME is between 35 to 40% while the co-products find applications as summer grade fuel or as raw materials for the oleochemical / surfactant (α-sulphonated methyl esters) industry. The typical product specifications of winter Grade Palm Biodiesel produced by MPOB Technology is shown in Table 12

Table 12 Properties of normal and winter grades palm biodiesel

Property	Unit	EN 14214 (a)	Palm Biodiesel	
			Normal Grade	Winter Grade
Ester content	% weight	Min. 96.5	> 98.0	> 98.0
Density @ 15°C	kg/m³	860 - 900	878	870 - 890
Viscosity @ 40°C	mm²/s	3.5 – 5.0	4.4	4.0 - 5.0
Flash point	°C	Min. 120	182	150 - 200
Pour point	°C	--	15	-21 to 0
CFPP	°C	See note (b)	15	-18 to - 3
Iodine value	--	Max. 120	50 - 55	56 - 83
Cetane number	--	Min. 51	58 - 59	58 - 59
Sulphur	mg/kg	Max. 10	< 10	< 10
Phosphorous	mg/kg	Max. 10	< 10	< 10
Water	mg/kg	Max. 500	< 500	< 500
Linolenic acid methyl esters	% weight	Max. 12	< 0.5	< 0.5
Polyunsaturated methyl esters	% weight	Max. 1	< 0.1	< 0.1
Methanol	% weight	Max. 0.2	< 0.2	< 0.2
Monoglycerides	% weight	Max. 0.8	< 0.8	< 0.8
Diglycerides	% weight	Max. 0.2	< 0.2	< 0.2
Triglycerides	% weight	Max. 0.2	< 0.2	< 0.2
Free glycerol	% weight	Max. 0.02	< 0.02	< 0.02
Total glycerol	% weight	Max. 0.25	< 0.25	< 0.25

Notes :-

(a) EN 14214 : European Standard for Biodiesel

(b) CFPP (Cold Filter Plugging Point) requirements based on the German Annex to EN 14214 :-
- Summer : Grade B (Max. 0°C)
- Spring & Autumn : Grade D (Max. -10°C)
- Winter : Grade F (Max. -20°C)

Oiltek Sdn. Bhd. has technology licensing agreement with MPOB to supply full scale commercial production plants for normal grade as well as winter grade palm biodiesel, as shown in Figure 37. The first three commercial winter-grade PME plants were successfully construction in Malaysia and the first plant has been in operation since September 2006 until today.

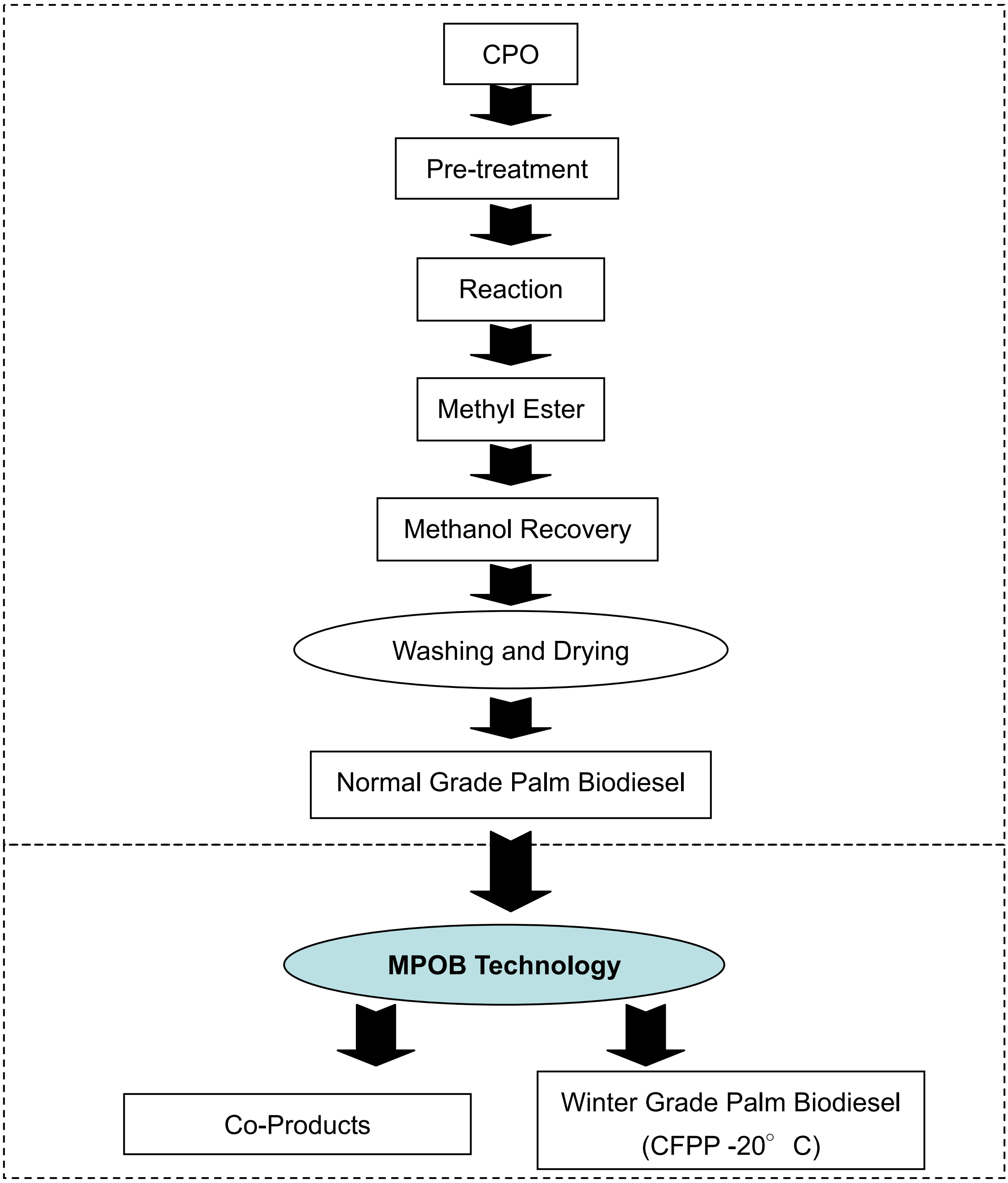


Figure 37 Process flow diagram of normal and winter grades palm biodiesel technology

Winter Grade PME has been produced and exported by Malaysia since the establishment of the commercial plant, as shown in Figure 38. Compared with other types of liquid oil derived biodiesel (e.g. rapeseed and soybean), the winter grade PME contains bulk of mono-unsaturated methyl ester (18:1) and thus, it is a premium grade biodiesel with good storage stability, low CFPP and able to decrease polymerization degree of biodiesel at high combustion temperature.

Integration of existing palm biodiesel production plant with winterization technology could provide the solution for palm biodiesel to be used in the temperate countries to suit the regional temperature requirement. MPOB is also able to provide technical know-how for helping the palm biodiesel producers to meet the cold soak filtration test specified in ASTM D6751 in 2009.

Figure 38 Palm biodiesel winterization plant at Sime Darby Biodiesel Sdn. Bhd., Malaysia.