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Guidelines for handling and blending FAME

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ABSTRACT

This report provides guidance on the handling and blending of Fatty Acid Methyl Esters (FAME), as a neat product and at concentrations up to 10% v/v in diesel fuel. The major challenges associated with diesel fuels containing FAME are discussed as they relate to the conformity of the finished fuel to typical specifications, especially those in the European standard for automotive diesel (EN 590). This report focuses on the production, blending, distribution, and supply of diesel containing up to 10% v/v FAME as well as the storage and handling of neat FAME but does not address vehicle-related issues with the use of diesel fuels containing FAME. The potential future production and use of Fatty Acid Ethyl Esters (FAEE) in diesel fuel is also discussed.

KEYWORDS

Fatty Acid Methyl Ester, FAME, Fatty Acid Ethyl Ester, FAEE, biodiesel, diesel, B100, EN 590, EN 14214

INTERNET

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CONTENTS

SUMMARY

The production of diesel fuels containing FAME is increasing in Europe as a consequence of several EU Directives: 2003/30/EC (Biofuels), 2009/28/EC (Renewable Energy Directive) and 2009/30/EC (Fuel Quality Directive). The increased use of FAME introduces new challenges to the refinery and requires strict application of good housekeeping practices throughout the fuel supply and distribution system.

This report provides guidance on the production, blending, distribution, and supply of automotive diesel fuels containing up to 10% v/v FAME and for the storage and handling of neat FAME[1] (B100). Vehicle-related issues with the use of diesel fuels containing FAME are not discussed, however. Some information is also provided on the future production and use of Fatty Acid Ethyl Esters (FAEE) for diesel fuel blending.

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[1] Terminology:
- In this report, the terms ‘FAME’, ‘B100’, and ‘biodiesel’ all refer to the same product, that is the 100% Fatty Acid Methyl Ester complying with EN 14214. If a distinction is made among these terms, ‘B100’ and ‘biodiesel’ are most frequently used to describe the 100% FAME product when it is used as a neat diesel fuel.
- The term ‘diesel blend’ refers to a blend of hydrocarbon-only diesel fuel and up to 10% v/v FAME.

1. INTRODUCTION

European experience with diesel fuels containing bio-components is largely based on FAME manufactured from a limited number of locally grown crops, most notably rapeseed and sunflower. The diversity and volume of biomass feedstocks used for manufacturing FAME is increasing rapidly, however, as a consequence of several EU Directives: 2003/30/EC (Biofuels), 2009/28/EC (Renewable Energy Directive) and 2009/30/EC (Fuel Quality Directive). Imported FAME products are also increasing, manufactured from palm oil, soya, tallow, and other plant and animal feedstocks. The FAME products sold today for fuel blending are most commonly a mixture of different FAME products manufactured from different feedstocks, where the final FAME composition is a complex function of cost, availability, and performance.

The maximum FAME content allowed in EN 590 [1] diesel fuel is now 7% v/v FAME so most European experience is with comparatively low level blends of FAME in diesel fuel. In order to increase the use of renewable products in road fuels, the European Committee for Standardization (CEN) is improving the EN 590 diesel fuel specification to allow blending of up to 10% v/v FAME complying with the EN 14214 [2] specification.

The increased use of FAME in the fuel market, however, introduces new challenges to the refinery and fuel supply and distribution system as well as an increased need for good housekeeping practices. Although other renewable blending components for distillate fuels (e.g. hydrotreated vegetable oils (HVO) and Biomass-to-Liquid (BTL)) may become more common in the future, they are not considered in this report because they are not widely available today and are not expected to demonstrate the same product quality issues as FAME products. Fatty Acid Ethyl Esters (FAEE) are also not yet available on a large scale but this could change if they become more economically attractive. The future production and use of FAEE for diesel fuel blending is discussed in a later section.

1.1. CHALLENGES FROM FAME USE

The chemistry and composition of FAME is different from that of hydrocarbon-only fuels. As a result, blending FAME into hydrocarbon fuels introduces some specific challenges that must be carefully addressed in the production, blending, distribution, and supply of diesel fuels. These include the effect of FAME as a neat product and as a blend component in diesel fuel on:

- Oxidation stability, under both thermal and longer-term storage conditions
- Cold flow properties and filterability behaviour
- Propensity for supporting microbiological growth
- Tendency to increase the dissolved water content and degrade the water-shedding ability of diesel fuels
- Compatibility with materials commonly used in refinery, distribution, and fuel supply systems
- Removal of dirt, rust, and other solid contaminants in the supply and distribution system

- Transport of FAME/diesel blends in multi-product pipelines and other distribution systems
- Safety, fire-fighting, and waste handling measures
- Performance and compatibility of additives commonly used in distillate fuels.

All of these challenges can be effectively managed by proper fuel blending and experienced product quality specialists supported by robust specifications, sound procedures, and good housekeeping practices throughout the fuel supply chain.

The objective of this report is to highlight some of the characteristics of neat FAME and of FAME in diesel fuel that must be recognized and managed in order to ensure on-specification and fit for purpose diesel blends in the marketplace. This report complements others that have been published recently [3,4,5,6]

2. FAME PRODUCTS AND PROPERTIES

2.1. SOURCES AND COMPOSITIONS OF NATURAL OILS

The European specification for FAME (EN 14214) allows the use of many different feedstocks and manufacturing processes as long as the finished FAME product meets certain minimum specifications. Feedstocks that are used to manufacture FAME include:

- Vegetable oils, e.g. rapeseed, palm, soy, sunflower, corn, cottonseed, jatropha, and many other oils derived from edible and inedible seeds;
- Animal fats, e.g. tallow, lard, poultry fats, fish oils, etc.;
- Waste oils and fats, e.g. used cooking oils.

At a molecular level, each oil or fat triglyceride molecule consists of a three-carbon glycerol backbone to which three fatty acids are esterified, one to each carbon in the glycerol backbone. The ester functionalities in the triglyceride molecule can readily undergo a trans-esterification reaction with methanol, displacing the fatty acid from the glycerol backbone and forming the fatty acid methyl ester (FAME). This FAME product is frequently called B100 or biodiesel.

Because the natural oils and fats listed above are derived from different biological feedstocks, the fatty acids comprising the fats and oils will be slightly different, typically ranging from 8 to 22 carbon atoms in the fatty acid carbon chain. Some of these fatty acid chains are fully saturated while others may be mono-unsaturated or poly-unsaturated (i.e., contain one or more than one carbon-carbon double bond, respectively). Fatty acid chains having more than one double bond, especially those having conjugated (adjacent) double bonds, are usually more chemically reactive and can be susceptible to oxidative degradation.

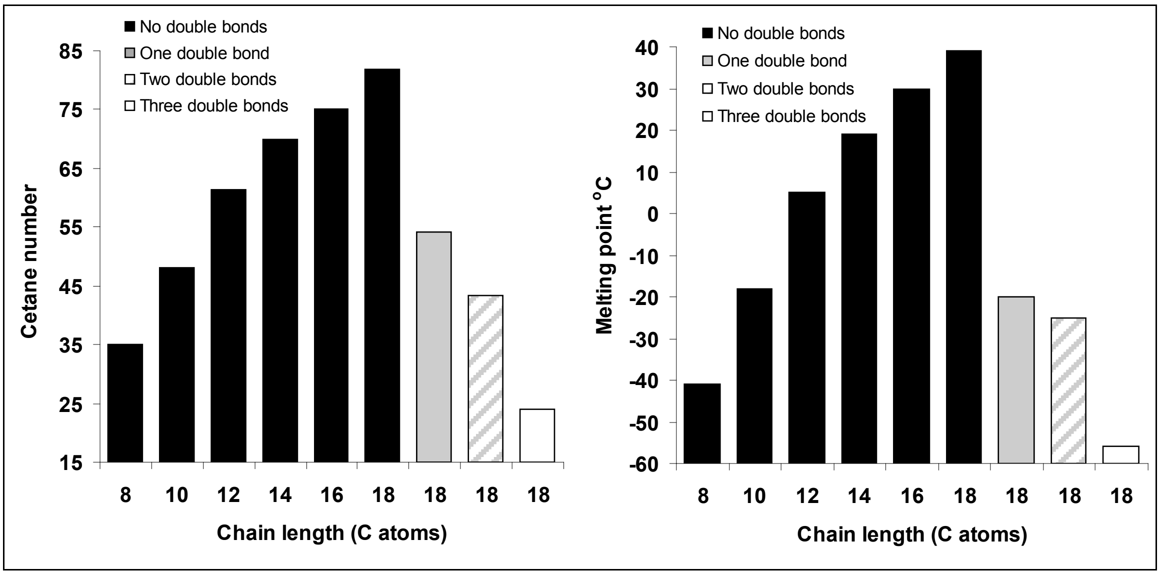
The carbon number distribution of the fatty acid makes the FAME products manufactured from one feedstock different from those derived from another feedstock. The fatty acid composition also determines the physical and chemical properties of the FAME product, most notably its cetane number, cold flow, filterability, and oxidation stability properties. The properties of FAME and FAME/diesel blends can also be affected, however, by natural or added antioxidants as well as by the presence of low level contaminants left behind from the FAME manufacturing process.

Table 1 and **Figures 1** and **2** demonstrate the impact of the fatty acid composition on different physical and chemical properties of the FAME product.

Table 1 Impact of fatty acid composition on the properties of the FAME product

	Impact on oxidation stability	**Impact on cold flow properties**	**Impact on cetane number**
Increasing the number of carbon atoms in the fatty acid chain	Not significant	Poorer	Better
Increasing the number of unsaturated double bonds in the fatty acid chain	Poorer	Better	Poorer
Increasing the number of double bonds in the fatty acid chain: - None (saturated) - One (mono-unsaturated) - More than one (poly-unsaturated)	Relative oxidation rate: Low Medium High		

Figure 1 Properties of FAME derived from some specific fatty acid molecules[1] [3,7]



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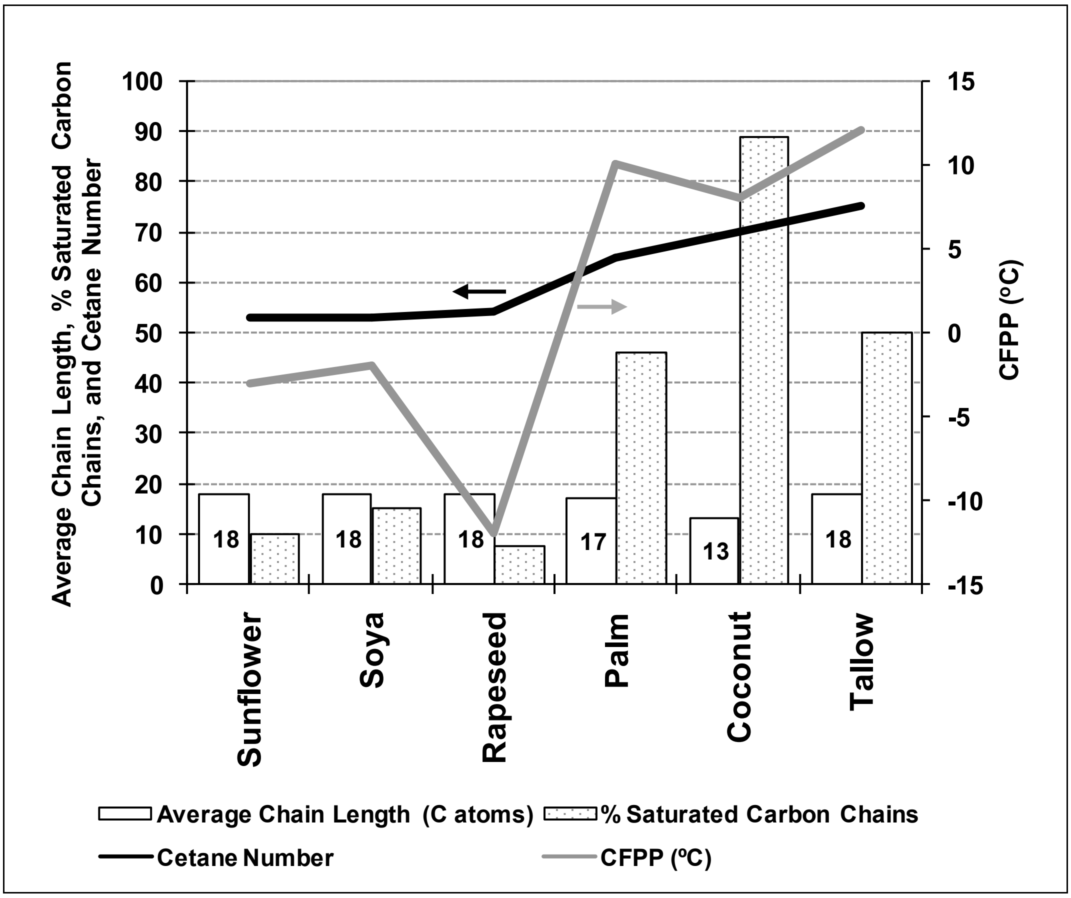
[1] The most common unsaturated C18 chains in natural products are: oleic (one double bond), linoleic (two double bonds), and linolenic (three double bonds).

Figure 2 Properties of FAMEs derived from different feedstocks



In **Figure 2**, the Cold Filter Plugging Point (CFPP) is a measure of the cold flow properties that has been useful for judging the low temperature performance of conventional diesel fuels. Lower CFPP temperatures represent better cold temperature performance.

Most commercially available FAME products are either manufactured from a blend of different oils or fats or are blended from different FAME products. This allows FAME producers and fuel blenders to optimise the properties of the FAME and the blended diesel fuel to meet the requirements of the finished fuel blend. Regardless of the FAME source, composition, or manufacturing process, the marketed FAME product must comply with the EN 14214 specification in order to manufacture EN 590 diesel fuel.

2.2. ESTERIFICATION OF NATURAL OILS AND FATS

There are three main reaction pathways to manufacture FAME from natural oils and fats [8]:

- Base-catalysed trans-esterification
- Acid-catalysed trans-esterification

- Hydrolysis of the oil or fat to its fatty acids and then esterification of the resulting fatty acids to produce FAME

These processes can be catalysed either heterogeneously or homogeneously. Most of the FAME on the market today is manufactured by means of the homogeneous base-catalysed reaction for several reasons:

- the reaction can be carried out at low temperatures and pressures;
- high conversion yields (98%) with minimal side reactions and short reaction times are typically achieved;
- FAME is produced in a one-step reaction without intermediate products;
- exotic construction materials are not needed for the reaction vessel and associated equipment.

The trans-esterification reaction for base-catalysed biodiesel production is shown in **Figure 3**. In this reaction, one molecule of oil or fat reacts with three molecules of a low carbon number alcohol in the presence of a base catalyst. Three molecules of fatty acid esters and one molecule of glycerol[2] by-product (also called glycerine) are produced. The low carbon number alcohol is usually methanol, but can also be ethanol or higher alcohols. The R_1, R_2, and R_3 shown in **Figure 3** represent the fatty acid carbon chains associated with the natural oil or fat and are typically 16 to 18 carbons (C16 to C18) on average.

Figure 3 The trans-esterification reaction for producing biodiesel from a vegetable oil

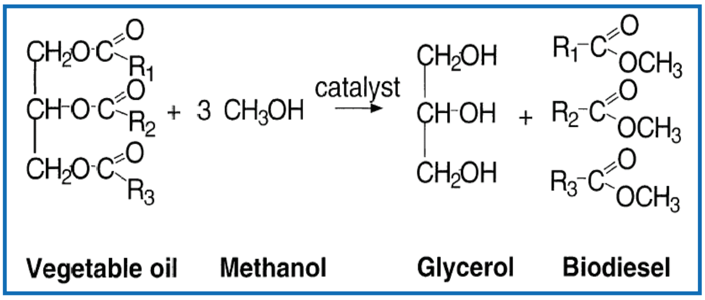


Figure 4 is a schematic of the biodiesel production process, starting with a natural oil or fat that has been purified sufficiently from primary biomass through prior processing steps.

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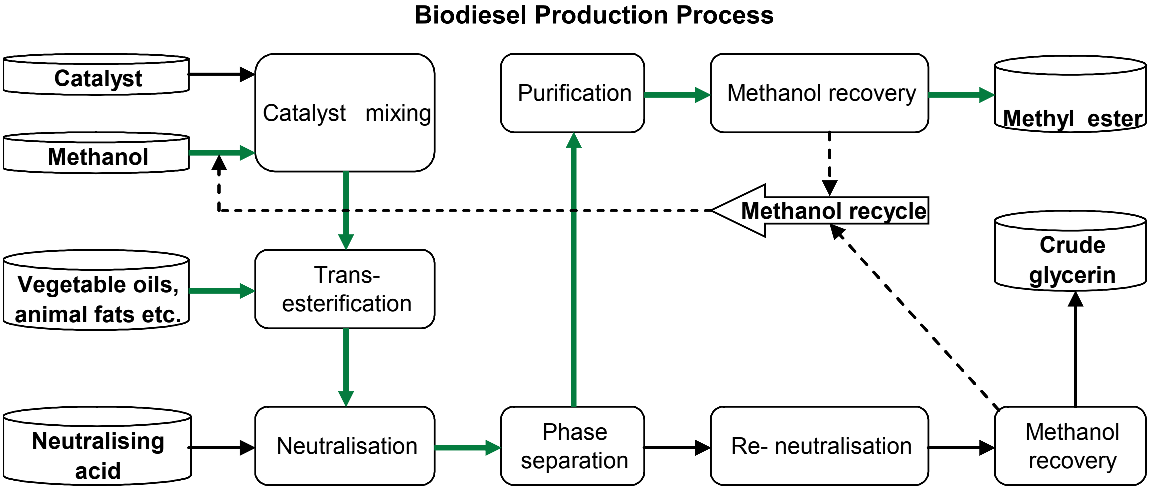
[2] The term ‘glycerol’ as used in this document is consistent with the terminology in EN 14214.

Figure 4 Schematic of the biodiesel production process [8]



The base-catalysed production of FAME generally occurs with the following steps:

- *Mixing of alcohol and base catalyst.* The catalytic base is typically sodium- or potassium hydroxide.
- *Reaction.* The alcohol/catalyst mix is charged into a reactor and the oil or fat is added. Excess alcohol is normally used to ensure total conversion of the fat or oil to its corresponding esters.
- *Separation.* Once the reaction is complete, there are two major products: glycerol and biodiesel. The reacted mixture is sometimes neutralised at this step. Because the glycerol phase is more dense than the biodiesel phase, the two products can be separated by gravity or centrifuge.
- *Alcohol Removal.* Once the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. The recovered alcohol is re-used in the process.
- *Glycerol Neutralization.* The glycerol by-product usually contains residual base catalyst and soaps that are then neutralised in order to produce crude glycerol.
- *Methyl Ester Purification*. Once separated from the glycerol, the biodiesel is sometimes purified by washing with warm water to remove any residual catalyst or soaps and is then dried and sent to storage. This is normally done at the end of the production process resulting in a clear amber-yellow liquid. In some processes, the biodiesel is distilled in a final step to remove small amounts of colour bodies, producing a colourless FAME product. Purification, where residual soaps, mono-glycerides, and sterol glucosides are removed, is a critical process step in order to ensure acceptable performance of the FAME in the blended diesel fuel.

There are several aspects of the biodiesel production process that are very important in order to ensure good performance of the FAME or FAME/diesel blend in diesel engines and in the fuel distribution system:

- Complete reaction of the fatty acids to produce FAME
- Removal of the glycerol co-product

- Removal of residual catalyst
- Removal of excess alcohol.

2.3. PHYSICAL AND CHEMICAL PROPERTIES OF FAME

Although FAME has many physical properties that are similar to hydrocarbon-only diesel fuel, there are differences that must be taken into consideration when handling or blending FAME. For example, FAME, when compared to hydrocarbon-only diesel fuel:

- Has a higher viscosity, density, and distillation profile;
- Has a lower energy content resulting in a higher volumetric fuel consumption for diesel fuels containing FAME;
- Is a better solvent that may loosen and/or dissolve sediments in fuel tanks and fuelling systems, contributing to filter plugging;
- Has different cold flow properties than most hydrocarbon-only diesel fuels, usually a higher pour point, cloud point, and CFPP, that are not as easily predicted as in conventional diesel fuels;
- Can contain impurities that have poor solubility in the FAME and in the blended diesel fuel contributing to poor cold temperature and filterability performance;
- Generally has lower oxidation and thermal stability compared to hydrocarbon-only diesel;
- Is not compatible with some metals, plastics, and coatings that are typically used in fuel supply and distribution systems.

In other respects, FAME's properties can be more favourable than those of hydrocarbon-only diesel. For example, the cetane number and oxygen content are higher than for typical hydrocarbon-only diesel fuels. FAME meeting the EN 14214 specification also typically has better lubricity, a higher flash point, and no or only trace levels of poly-aromatic hydrocarbons (PAH) and sulphur compounds.

2.4. FAME SPECIFICATIONS

FAME used in the EU either as a neat diesel fuel or as a blend component for regular diesel fuel must comply with the European Standard EN 14214. In addition to the quality parameters incorporated in the EN 590 standard for regular diesel, EN 14214 contains specifications for properties addressing operability and environmental concerns that are specific for FAME. These include limits on the concentration of various impurities, fatty acid composition, and stability parameters.

Table 2 FAME properties specified in EN 14214

Property	**Property is intended to:**	**Units**	**EN 14214 Limit** (Maximum)
Ester content	Ensure purity and absence of high and low boiling components	% m/m	96.5% (min)
Methanol content		% m/m	0.20
Phosphorous content	Protect vehicle aftertreatment and emissions performance	mg/kg	4
Group I metals content (Na + K)	Ensure acceptable equipment operability and mitigate: + Engine wear + Corrosion + Fouling + Deposit formation + Sticking of moving parts + Filter plugging	mg/kg	5.0
Group II metals content (Ca + Mg)		mg/kg	5.0
Acid number		mg KOH/g	0.50
Mono-glycerides content		% m/m	0.8
Di-glycerides content		% m/m	0.2
Tri-glycerides content		% m/m	0.2
Free glycerol content		% m/m	0.02
Total glycerol content		% m/m	0.25
Oxidation stability at 110°C	Ensure acceptable oxidation stability and mitigate: + Fuel degradation + Fouling + Deposit formation + Filter plugging	h	6.0
Iodine value		g iodine/100g	120
Linolenic acid methyl ester content		% m/m	12.0
Polyunsaturated methyl ester content		% m/m	1

As more knowledge is gained on FAME properties and their impact on the performance of B100 and blended diesel fuel, it can be expected that the EN 14214 specification will continue to evolve, particularly with respect to parameters that impact the quality of the blended fuel, such as oxidation stability, handling, filterability and operability. The complete EN 14214 specification table, including test methods, is shown in **Appendix 1**.

In addition to meeting technical specifications, FAME used in the EU as a blending component for diesel fuel will also need to meet minimum sustainability requirements as defined in the 2009 EC Directives. Although the details for meeting these requirements are still being defined, companies marketing diesel fuels containing FAME will expect to receive certain information from the FAME supplier in order to certify that the FAME product meets or exceeds the regulated sustainability requirements.

2.5. B100 VERSUS EN 590 DIESEL FUEL CONTAINING FAME

The relevant standard for diesel fuels used in diesel engines is EN 590. This standard currently allows the blending of up to 7% v/v FAME but work is underway to extend this limit to 10% v/v FAME. **Table 3** compares the quality parameters that are included in both the EN 590 and EN 14214 specifications.

Table 3 Common properties in EN 14214 and EN 590 specifications

Property	**Units**	**EN 14214**	**EN 590**
Density	kg/m3	860-900	820-845
Flash point	°C	101°C min	55°C min
Distillation temperature	(% vol)	NA	85%: <350°C 65%: >250°C
Kinematic viscosity	mm^2/s at 40°C	3.5-5.0	2.0-4.5
Cold Filter Plugging Point (CFPP)		Climate dependent: + required for FAME used as B100 + not required for FAME used in diesel blends	Climate dependent
Ash content	% m/m	0.02 (Method 1)	0.01 (Method 2)
Water content	mg/kg	500 max	200 max
Oxidation stability (EN ISO 12205)	g/m^3		<25
Oxidation stability (EN 15751 Rancimat test)	h	6.0 min	20.0 min[3]
Lubricity (HFRR)	µm WSD		460 max
Cetane number		51.0 min	51.0 min

Unlike blended diesel fuel, FAME has a narrower distillation range, typically 300-360°C and a higher flash point, as long as unreacted methanol has been removed from the FAME during manufacturing. Because FAME has a higher water saturation limit, the maximum water content for FAME is higher than for diesel fuel.

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[3] The Rancimat oxidation stability limit in EN 590 only applies to diesel fuels containing 2% v/v FAME or greater

3. FAME QUALITIES AND GUIDELINES

3.1. OVERVIEW OF PRODUCT QUALITY CONCERNS

Due to the chemical composition of FAME, there are a number of product quality issues that must be considered and addressed when handling and blending FAME. The main concerns are: poorer fuel stability, an increased risk of deposit formation, poorer cold temperature handling, filterability, and operability, increased solvency, greater potential for microbiological contamination, poorer water shedding, different material incompatibilities, increased foam decay times, and impact on fuel additive performance. When FAME is blended into a diesel basestock at terminal locations, the properties of the hydrocarbon basestock must also be considered in order to ensure that the finished diesel fuel is on specification after blending with FAME.

3.2. STABILITY AND DEPOSIT FORMATION

The degradation of FAME can be caused by several chemical and biological processes, including oxidation, reverse trans-esterification, hydrolysis, thermal polymerisation and microbial growth.

The most important cause of stability problems is the reaction of the FAME or petroleum diesel with dissolved oxygen, resulting initially in the formation of peroxides. These peroxides undergo subsequent transformation to produce alcohols, aldehydes, ketones, and carboxylic acids. The products formed during this transformation can catalyse the formation of gum, sludge and other insoluble compounds. Methylene carbons ($-CH_2-$) adjacent to unsaturated carbons in the fatty acid chains are a primary site for oxygen attack. When there are more unsaturated carbons in the fatty acid chains, the FAME will be more prone to oxygen attack and instability.

Reverse trans-esterification is the reaction of the methyl ester with residual glycerol or mono- and di-glycerides remaining in the FAME product. These reverse products can form intermediates that are highly reactive toward oligomer formation leading to insoluble products.

The hydrolysis of methyl esters by reaction with dissolved water can lead to acid formation. These acids can catalyse other degradation reactions such as reverse trans-esterification and oxidation. The water required for hydrolysis can be present as a contaminant.

In general, diesel fuels containing bio-components are stable in the absence of oxygen and water. However, elevated storage temperatures and prolonged storage times can increase the rate of other degradation processes. Polymerisation of fatty acid chains can occur if the fuel temperature reaches higher levels. FAME made from used cooking oils may also retain some residual products that were formed when the feedstock was heated for cooking and can increase thermal and oxidative instability.

The instability risks described above can be mitigated by maintaining the level of water, glycerol, glyceride and other impurities within the specification limits. Good housekeeping in the storage and distribution system is also important.

The addition of oxidation stability enhancing additives to the FAME product is strongly recommended in order to protect the product from oxidation and degradation. Antioxidant and similar additives should be added to the FAME product as soon as possible in the production stage and before storage. The stability of the FAME used in the EU after additive treatment should be similar to that achieved when 1,000 mg/kg (ppm) of butylated hydroxytoluene (BHT) is used.

3.3. COLD TEMPERATURE HANDLING, FILTERABILITY AND OPERABILITY

There are two different cold temperature performance concerns: handling and operability. Handling, including filterability, is the ability to store, blend and pump B100 or the resulting diesel blend. Operability refers to the use of the diesel blend in a vehicle's fueling system or in other equipment intended to be used with diesel fuel.

Several factors can impact the cold temperature handling and operability performance of FAME. The first is the type of feedstock used to produce the FAME. As shown in **Table 4**, the cold flow properties of FAME vary with the fatty acid composition of the feedstock and typical values for esters produced from single feedstocks are shown in the table. Feedstock selection also determines whether undesirable impurities must be removed during processing in order to improve the cold temperature performance (see below).

Table 4 Typical handling properties for FAME manufactured from different feedstocks

Feedstock	Cloud Point (°C)	CFPP (°C)	Viscosity (mm^2/s at 40°C)
Rapeseed	-5	-18 to -12	5.0
Sunflower	-1 to +3	-7 to -3	4.4
Soybean	-7 to + 3	-6 to -2	4.0
Coconut	+9 to +12	8	4.8
Palm	+13 to +16	+5 to +11	4.3-5.0
Tallow	+10 to +20	+9 to +14	4.8

Because individual FAME products have different cold flow properties, it is obvious that they will also impact the cold flow properties of the final diesel blend. This impact must be understood, especially when FAME is blended into a diesel basestock at terminal locations where options to correct the cold temperature properties may be limited.

It is recommended that FAME used for fuel blending should not contain any additives other than antioxidants used to improve the oxidation stability. This helps to avoid problems that could be caused by incompatibility of the FAME with the cold flow or performance additive package that is typically used in the final diesel blend. See **Section 3.10** for more information.

The second factor influencing cold temperature performance is the FAME manufacturing process and the resulting B100 purity. This is because some FAME impurities can promote the formation of precipitates and deposits. The two main impurities in FAME that can cause handling and operability problems are saturated mono-glycerides and sterol glucosides. Precipitation from B100 is thought to be associated with the presence of sterol glucosides while precipitation from diesel blends is more often linked to the presence of saturated mono-glycerides.

Sterol Glucosides

Sterol glucosides (SGs) occur naturally in vegetable oils and fats in a soluble (acylated) form. During the FAME manufacturing process, however, they are converted to non-acylated SGs. Due to the higher melting points of these SGs (~240°C) and their relative insolubility in B100 or diesel fuel, SGs can be considered to be dispersed solid particles in the FAME product. These dispersed particles may promote the crystallization and co-precipitation of other compounds.

Even at relatively low concentrations (~35ppm), SGs may promote the formation of aggregates in biodiesel, exacerbating problems caused by saturated mono-glycerides and other known cold-crystallizing components [7]. This may cause the formation of a cloud-like haze in FAME, even at room temperatures.

Literature data on the SG contents of natural oils and fats and of FAME products are very limited. For example, the SG content of soybean and palm oil (~2,300 ppm) can be higher than in other vegetable oils such as in oils from sunflowers and corn (~300-500 ppm). The manufacturing process for vegetable oils, or the pre- and post-processing done as part of the FAME production, may reduce SG levels to the point where they are no longer a problem.

If SGs are present at high enough levels, however, and have sufficient time in storage, they are likely to settle to the bottom of storage tanks and vessels. Cold temperatures can accelerate this process and increase the likelihood that SGs will act as nucleating agents for larger agglomerates which will also settle to the bottom of storage tanks and vessels. This potential settling effect may mask the real filter-clogging potential of SGs and SG-related agglomerates because the agglomerates may remain on the bottom of unstirred tanks. Draw-down of an unstirred tank to lower than normal levels could lead to sudden and unexpected operability problems even when the FAME in the tank has been within specification and trouble-free.

As a result, SGs in FAME used for blending may cause filter blockage at temperatures above the cloud point [9]. Cold temperatures are likely to exacerbate the effect of SGs in both B100 and in diesel blends, even in diesel blends containing low FAME contents. For this reason, the contribution of SGs to filter blocking should be considered when addressing filter problems with B100 and diesel blends. To better control this problem, it may be necessary to add an additional specification to the FAME product based on validated test methods, such as the maximum allowed SG level, a filter blocking test, or a particulate measurement.

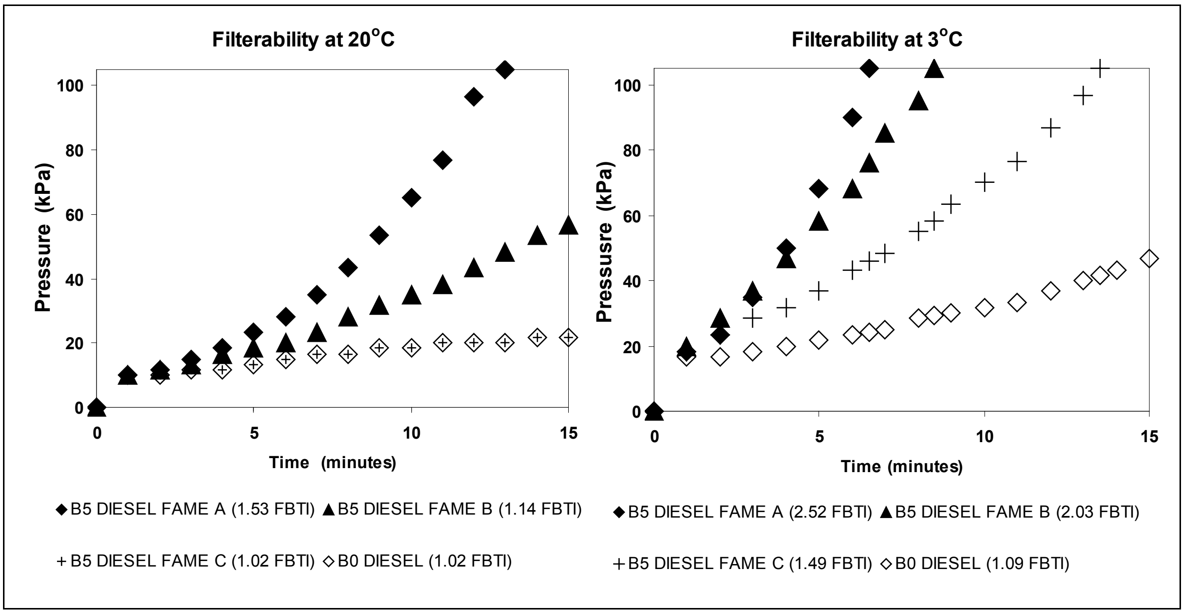
Mono-glycerides

The presence of impurities in FAME can also influence the cold temperature performance of the blended diesel fuel. Saturated mono-glycerides have been identified as one of the main problem species for blended diesel fuels. Saturated mono-glycerides are unreacted products retained from the FAME manufacturing process. The mono-glyceride content of the FAME product will depend on the success of the manufacturing steps taken to reduce their concentration (distillation, settling, etc.). As such, the mono-glycerides can vary from one manufacturer or supply point to the next.

These impurities have relatively poor solubility in diesel fuel and the solubility is temperature dependent. The current FAME specification only limits the total mono-glycerides and not the saturated fraction of mono-glycerides. The fraction of saturated mono-glycerides will depend on the feedstock used to manufacture the FAME.

Figure 5 shows the filterability of three B5 blends made from the same diesel basestock (B0) but using different FAME types. The results are based on the Filter Blocking Tendency Index (FBTI), as specified in method IP387. At room temperature, some blends are as good as the B0 diesel fuel but at lower temperatures all three blends exhibit poorer filterability performance.

Figure 5 Filterability of a B0 diesel fuel and three B5 blends at two different temperatures [10]



3.4. SOLVENCY

For many decades, methyl esters have been used as low volatility cleaning agents and solvents. Because B100 is a mixture of methyl esters, FAME products have some tendency to redissolve accumulated sediments in diesel storage tanks, vessels, and pipelines. These redissolved sediments can plug fuel filters. It is necessary therefore to ensure that the FAME storage and distribution system is clean and dry before use and that excessive deposits have been removed. In addition, the size and placement of filters throughout the supply chain should be reviewed.

The level of ‘cleaning’ action from FAME will depend on the amount of sediment that is already in the system as well as the blending level of FAME that is being used in the diesel blend. This also means that there should not be an effect from FAME use if the storage and distribution system is already free of sediment. The cleaning effect of FAME is much greater with B100 and with higher level diesel blends than it is with lower level blends, such as B7 to B10. While it may not be necessary to clean diesel tanks and lines before the transition to B7 use, it is still wise to monitor potential filter plugging and keep extra filters on hand when first starting work with B7 diesel blends.

3.5. MICROBIOLOGICAL CONTAMINATION

Due to its chemical structure, FAME and diesel blends are more susceptible to biological attack by micro-organisms. Microbiological activity in B100 is about twice that in diesel fuel and the activity is even higher in FAME blends [11]. Aerobic micro-organisms that consume hydrocarbons, such as fungi, bacteria, and yeast, usually grow at the interface between fuel and water in tanks and vessels [12]. Anaerobic species can actively grow on tank surfaces and can contribute to metal corrosion because they often chemically reduce sulphur, forming sulphur acids.

Proper control of water and sediments is therefore essential for preventing microbiological problems. This can be achieved by a combination of periodic sampling and testing of storage tanks and immediate removal of any water or sediment that is present. The sampling frequency may vary depending on local conditions.

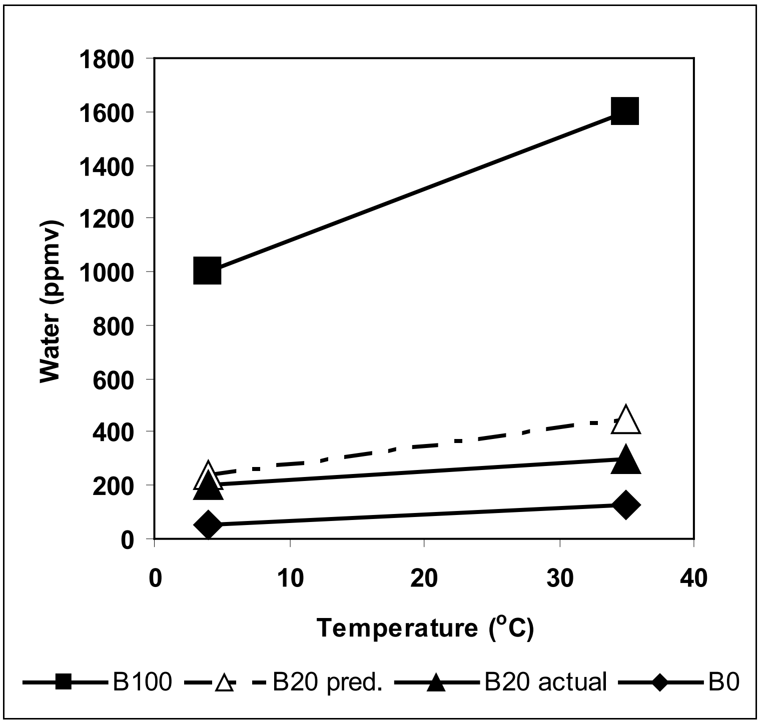
If microbiological growth remains unnoticed, it will eventually cause fouling and filter plugging. Field problems have been reported that have been associated with fungal growth in service station filters. Removal of water, sediment and contaminated product as well as a shock treatment with biocides is recommended in such circumstances.

3.6. WATER SEPARATION

Due to their hygroscopic nature, B100 and FAME/diesel blends can contain more water than hydrocarbon-only diesel fuels. Water separation is more difficult and can be manifested as an increased haziness in the fuel blend. Prolonged exposure to water is likely to facilitate microbial growth and/or hydrolysis and both of these can result in accelerated corrosion, sediment formation, and filter blocking.

Hydrocarbon-only diesel fuels reach water saturation at levels typically less than 100 ppm (volume basis) while B100 can reach saturation at water levels greater than 1,000 ppm (see **Figure 6**). Unfortunately, the solubility of water in blends of hydrocarbon-only diesel and in FAME does not blend linearly. For this reason, it is possible to end up with a FAME/diesel blend that has water above the saturation limit (i.e., free water) even if the FAME and diesel fuel themselves only contain dissolved water (i.e., no free water). This should not occur, however, if the water content of the FAME is below the specification limit.

Figure 6 Water content at saturation level for B0, B20 and B100 [7]



The water shedding characteristics of the diesel blend can be improved by using a fuel performance additive package, in conjunction with good housekeeping practices. However, there may be potential for higher water drop-out in service stations if a fuel that is already water saturated is exposed to a fuel containing an additive package.

3.7. MATERIAL COMPATIBILITY

Materials associated with the fuel distribution system are considered in this section and not the fuel system components that are commonly used on vehicles.

Regarding the compatibility with materials that are typically used in fuel supply and distribution systems, it is important to recognize that FAME is chemically different from fuel hydrocarbons due to its chemical functionality. Because of this chemical difference, various components in the fuel distribution system may be less compatible with FAME (B100) than they are with hydrocarbon-only fuels. Sensitive materials may swell or lose their integrity after prolonged contact with FAME. They may even promote fuel degradation reactions due to their chemical composition.

FAME may degrade some hoses, gaskets, seals, elastomers, glues and plastics after prolonged exposure. FAME may also permeate some types of plastics (polyethylene, polypropylene) over time and they are not recommended for use in storing B100. Natural or nitrile rubber compounds, polypropylene, polyvinyl, and Tygon® materials are particularly sensitive.

Teflon®, Viton®, and Nylon are not sensitive to FAME and are among the materials that can be used to update incompatible materials in equipment.

Most tanks that are designed to store diesel fuel will also be adequate for storing B100. Acceptable storage tank materials include aluminium, steel, fluorinated polyethylene, fluorinated polypropylene, Teflon®, and most fibreglass products.

Brass, bronze, copper, lead, tin, and zinc may catalyze the oxidation of FAME accelerating the formation of insoluble gels and salts. Lead solders and zinc linings should be avoided, as should copper pipes, brass regulators, and copper fittings. Affected equipment should be replaced with stainless steel, carbon steel, or aluminium.

Table 5 provides an overview of materials that are either recommended for use or should be avoided when handling biodiesel (B100). This list is not comprehensive and the quality of the material must be appropriate for the intended application. Suppliers of B100 products and equipment vendors should be consulted to ensure the most recent findings on material compatibility for bio-component applications.

Table 5 Material compatibilities with FAME (B100)

Material	Recommended	Not Recommended
Metals	Carbon steel Stainless steel Aluminium	Brass Bronze Copper Lead Tin Zinc
Elastomers	Fluorocarbon Nylon Teflon® Viton®	Nitrile rubber Neoprene Chloroprene Natural rubber Hypalon Styrene-Butadiene rubber Butadiene rubber
Polymers	Carbon filled acetal	Polyethylene Polypropylene Polyurethane Polyvinylchloride
Others	Fibreglass	

In general, diesel fuels containing much lower FAME concentrations will have a much smaller effect on materials used in the fuel distribution system. At 10% v/v FAME or lower concentrations, the effects are not likely to be appreciable although some sensitivity of nitrile rubbers has been reported [13]. Although this is the case with fuel system materials, the metals indicated above (and in **Table 5**) should still be avoided, even for diesel fuel blends, in order to minimize the potential for metal pick-up.

3.8. HYDROCARBON-ONLY BASESTOCKS FOR FAME BLENDING

If FAME blends are produced outside the refinery by blending FAME into a hydrocarbon-only diesel basestock, the properties of this basestock should be such that the blended diesel fuel meets the EN 590 specification. The required properties will depend on the percentage and quality of the FAME that is to be blended, which can vary considerably depending on the feedstock used to manufacture the FAME. Since FAME is typically purchased without knowledge or analysis of the feedstock used to produce the FAME, extra care must be taken to ensure that the final diesel blend meets the EN 590 specification.

The maximum density and viscosity of the FAME require extra attention. **Table 6** provides an indication of safety margins for blending up to 7% v/v FAME with the maximum allowed density and viscosity values, according to the EN 14214 specification.

Table 6 FAME properties and suggested safety margins for hydrocarbon-only diesel fuel before blending with FAME

Property	Units	FAME	Hydrocarbon-only Basestock
Density	kg/m^3	900 max	5 kg/m^3 below EN 590 max
Viscosity	mm^2/s at 40°C	5.00 max	0.10 mm^2/s below EN 590 max

The picture is more complicated for cold flow properties which depend on season and location as well as the responsiveness of the hydrocarbon-only diesel fuel and FAME to cold flow additives. For this reason, no general guidelines can be provided for cold flow properties.

3.9. FOAM DECAY TIME

While B100 does not foam, FAME/diesel blends can show significant increases in foam decay time compared to the hydrocarbon-only diesel basestock. In addition, diesel blends can entrain more water than hydrocarbon-only diesel fuels which can affect the performance of antifoam additives. For this reason, the antifoam performance of finished diesel fuel formulations should be rechecked before increasing the FAME content to a higher value.

3.10. FUEL ADDITIVE PERFORMANCE

It is recommended that FAME used for blending should not contain any additives other than oxidation-stability improving additives. This helps to avoid problems caused by incompatibility of additives in the FAME with typical diesel cold flow and performance additive packages. Performance additive packages are preferably injected during or after blending FAME into the hydrocarbon-only diesel fuel.

4. OPERATIONAL AND DESIGN GUIDELINES

4.1. BLENDING FAME AT REFINERIES

Blending FAME with hydrocarbon-only diesel can take place at refineries or at terminal locations. Because refineries are usually better equipped to perform fuel product quality testing and optimise blend composition, they are also the preferred place to carry out blending operations. Terminal blending is also acceptable, however, from a quality assurance point of view as long as proper procedures are followed.

FAME is fully compatible with petroleum diesel so the blending of FAME is not particularly difficult. Regardless of the blending strategy, however, it is important to understand some of the significant characteristics of FAME that can impact blending.

- FAME has a higher density (~0.88 vs. 0.84 kg/l) and viscosity (max ~5 vs. 4 mm^2/s at 40°C) compared to EN 590 diesel fuel. If blend components are added sequentially into a blending tank, FAME should not be the first or the last component to be added in order to avoid the formation of an unmixed bottom layer. Precautions should be taken to ensure a homogeneous blend.
- FAME has a higher cloud point than EN 590 diesel. If different components are added into the blending tank, the temperature of all of the components should be well above the FAME cloud point to ensure easy flow and prevent formation of precipitates that may be difficult to redissolve.

Several blending strategies can be used to achieve proper mixing: in-tank blending, in-line blending to a tank, in-line blending at the loading rack, and splash or sequential blending.

In-tank blending: The required volumes of FAME and diesel fuel are pumped separately into a tank and proper mixing is achieved by in-tank agitators or by circulation of the tank contents. The tank can then be sampled and tested prior to releasing the diesel blend.

In-line blending into a tank: The FAME and other blend components are pumped simultaneously under flow control into a common product line to a product storage tank. The turbulent flow conditions at the injection points and in the line promote mixing but the use of a static mixer is also recommended. In this case, the receiving tank should not require mixing facilities.

In-line blending at the loading rack: FAME is injected continuously into the diesel fuel stream under flow control during truck loading. Alternatively, the FAME can be added in small slugs or in pulsed quantities spread evenly throughout the time that the truck is being loaded. This is similar to the way most additives are blended into diesel fuel at the loading rack.

Splash or sequential blending: This is an operation where the FAME and diesel fuel are sequentially loaded into a truck or other vessel. In this case, relatively little mixing occurs as the fuels are loaded into the vessel. After the fuels are in the truck, driving down the road is sometimes considered to be sufficient agitation to allow the FAME and diesel fuel to be mixed in transit. This blending strategy is not recommended, however, because there is some risk that the product may not be homogeneous when it arrives at the delivery point, particularly when the ambient temperature is low.

Diesel performance additives such as cold flow improvers or cetane boosters should be injected into the diesel fuel stream during blending. The additive dosage in diesel blends will probably be different from hydrocarbon-only diesel fuels in order to achieve the same level of performance; some dosages may be higher and some may be lower. Additive dosages that should be rechecked include cold flow, cetane improvers, lubricity enhancers, conductivity improvers, performance packages, and antifoam additives.

Blending FAME into diesel fuel, even at low concentration, can increase the lubricity of the diesel blend. The amount of FAME required to achieve adequate lubricity will depend on the properties of the hydrocarbon-only diesel. Preliminary evidence suggests that about 2% v/v FAME provides sufficient lubricity to meet the EN 590 lubricity specification in almost all cases.

4.2. BLENDING FAME AT TERMINALS

The recommendations for blending FAME at refineries also apply to blending at terminal locations. The quality of the hydrocarbon-only diesel fuel should be such that the diesel blend after FAME addition meets the EN 590 specification, as discussed earlier. If blending operations are based on volume control, without access to analytical facilities, this should be reflected in the blending procedures and blending margins for critical properties should be included in the diesel fuel properties. Precautions should be taken to ensure a homogeneous blend.

4.3. STORAGE OF FAME IN REFINERIES AND TERMINALS

Storage temperature

FAME (B100) should be stored at temperatures at least 6°C higher than the cloud point. Therefore, most underground storage facilities are adequate, but above ground storage, depending on the climate, should be protected with insulation, agitation, heating systems or other methods. This precaution includes piping, tanks, pumping equipment, and trucks used to transport FAME. Heating can be achieved by any of the common heating methods, but should be designed to minimise hotspots and prolonged exposure of the FAME to high temperatures.

If the temperature does drop and crystals begin to form, the crystals should redissolve if the fuel is warmed up although residual mono-glycerides and SGs may be difficult to redissolve. This redissolving process can be slow, however, especially if the fuel only warms marginally or very slowly. Crystals formed in FAME or in diesel blends can also settle to the bottom of the tank and begin to form a gel layer. Slow agitation can prevent crystals from building up on the tank bottom and agitation can also help to redissolve crystals once they are present in the fuel.

If the FAME product has gelled completely, it is advisable to raise the temperature up to 40-60°C in order to melt the most saturated FAME components, especially if the FAME needs to be used right away. Lower warming temperatures can be used for the FAME to reach its equilibrium cloud point if enough time is available.

During colder seasons, B100 is sometimes pre-blended with low cloud point diesel fuel in order to prevent crystallisation. This pre-blend is prepared before it is blended into the diesel fuel.

The recommendations for FAME also apply to diesel blends.

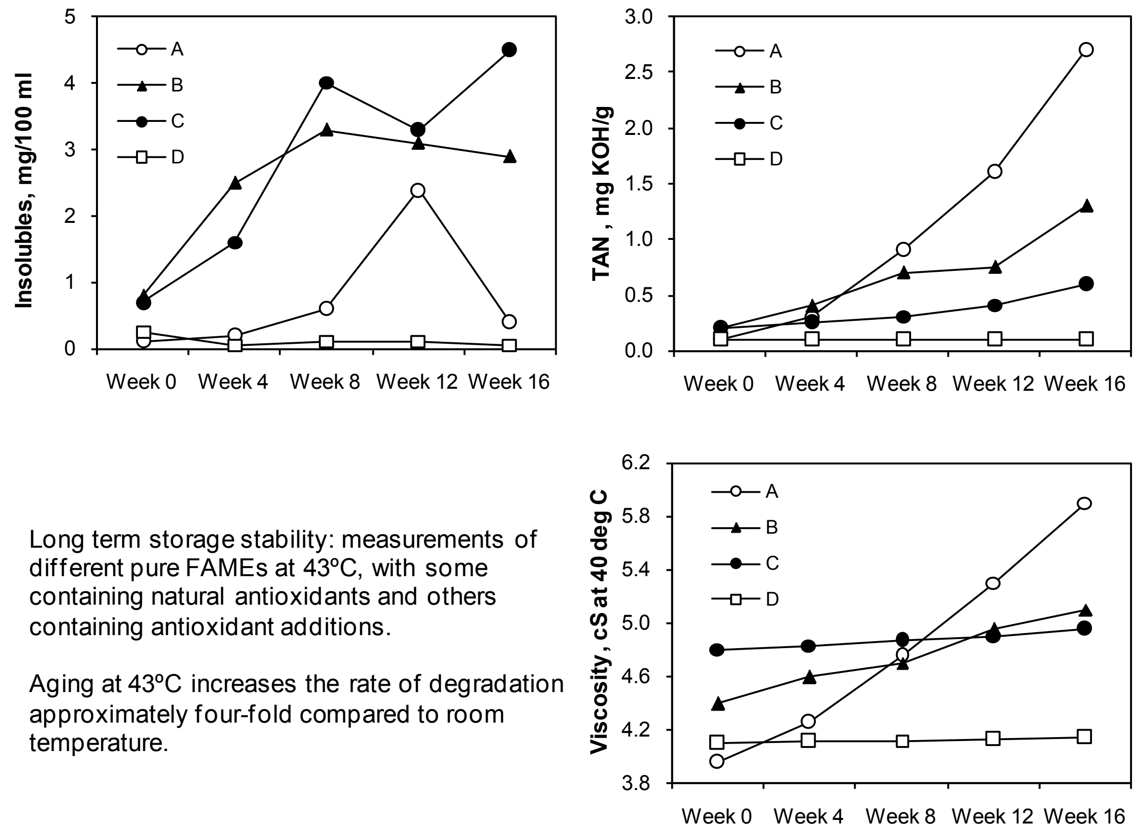
Storage duration

Although some data suggest that more stable FAME types can be stored for a year or more, it is generally recommended to limit FAME storage to no more than about six months. It appears that diesel blends have a longer storage life than B100, depending on the FAME type and additive treat. Even so, it is also recommended to limit the storage of diesel blends to no more than about 6 months. In practice, operators should turnover their FAME stock faster than this.

Because FAME ages in storage, the acid number tends to increase, the viscosity can increase, and gums and varnish can form. To monitor FAME quality during storage, oxidation stability, acid number, viscosity, water, and sediment can all be used as indicators to ensure that the FAME complies with EN 14214.

When oxidised or aged FAME is blended with diesel, data suggest that some of the sediments and gums that are soluble in the B100 become insoluble in the diesel blend and form sediments. For this reason, FAME that does not comply with EN 14214 should never be used for blending. **Figure 7** shows how some FAME properties change during storage at 43°C elevated temperature using the ASTM D4625 long term storage stability test.

Figure 7 Changes in FAME properties during long-term storage [3]



Long term storage stability: measurements of different pure FAMEs at 43°C, with some containing natural antioxidants and others containing antioxidant additions.

Aging at 43°C increases the rate of degradation approximately four-fold compared to room temperature.

Good fuel stock management practices (first-in, first-out) and frequent product turnover should minimise stability concerns for most applications.

Minimum Headspace

As a fuel tank is emptied, air will enter through the vent pipes to displace the fuel that was in the tank. The extra air drawn into the tank may lead to more oxidation, particulate contamination, and increased water levels. These contaminants will affect the quality of the FAME. In order to limit the effects of air in the tanks, it is recommended that FAME and diesel blends are not stored for long periods of time in partially empty tanks without the use of oxidation stabilising additives.

Water Contamination

Biodiesel is susceptible to water-related problems. Desiccant filters on breathing vents will greatly reduce water condensation in the storage tank and are highly recommended. Sump drains are also recommended where they are practical. Both free and dissolved water accelerate corrosion and fuel degradation. Free water may enter bulk fuel tanks by condensation, by carry-over from the fuel distribution system, or by leakage through the fill cap, spill containment valve or piping.

In addition to accelerating the degradation of the fuel product, water also provides a suitable environment for microbial growth. Microbial activity, surfactants, alcohols, particulates, and poorly designed additives may be the cause of water problems. Poor tank design can make it almost impossible to completely remove free water once it is present so it is important to take steps to prevent water from entering the fuel storage vessel.

Biocides

The preferred approach to prevent microbiological contamination is a good tank housekeeping program. If microbiological problems are encountered, however, a biocide shock treatment can be used as a temporary measure, after removing all water and contamination. Following such an incident, the details of the housekeeping practices should be reviewed and adjusted as necessary in order to avoid another occurrence.

The continuous application of biocide does not prevent the introduction of water and is therefore not a suitable preventative measure against water related problems. The regular use of biocides may even increase the resistance of micro-organisms to treatment.

The regular use of biocides also has some drawbacks that can and must be properly managed. For example, biocides are toxic chemicals and produce bio-sludges that must be removed immediately. Regulations frequently restrict the use of biocides while water from tanks treated with biocides must be disposed as chemical waste. Biocide treatments should therefore be executed by specialists who can also advise on the selection of the most appropriate biocide for the type of fouling problem that has been encountered.

4.4. DRAIN OR WASTE WATER HANDLING

FAME is only slightly soluble in water and existing facilities for handling drain and waste water from conventional diesel fuels will generally be adequate. Since FAME degrades more easily than hydrocarbon-only diesel fuel, biological effluent treatment should pose no special problems, provided that the FAME quality is in line with EN 14214. If the free fatty acid or glycerol contents are especially high, however, these could result in a higher than expected Biological Oxidation Demand (BOD) for drains and waste water. This could disrupt effluent treatment operations, depending upon the degree of dilution with other streams.

For installations that do not have their own biological treatment facilities and instead send their waste water to a municipal treatment plant, it would be prudent to review the likelihood of such a disruption and, if appropriate, discuss this with the treatment plant operators. In any case, the disposal of drain or waste water must be done in accordance with all local regulations and permits. When biocides are used, waste water should be handled and treated appropriately.

5. TRANSPORT AND DELIVERY OF DIESEL BLENDS TO TERMINALS AND FILLING STATIONS

Existing supply and distribution facilities designed for use with hydrocarbon-only diesel fuels will in general be adequate for handling diesel fuels containing FAME. It is recommended to review the need for hardware modifications throughout the supply chain with consideration of potential material incompatibilities and the increased risk of deposit formation [5,14]. The following points should be specifically considered:

- Dedicated lines may be needed for imports and exports (at terminals) in order to avoid water contamination.
- Gaskets should be compatible with B100 including those fitted in flanges and swivel joints.
- Lagged or heat traced pipelines may be appropriate depending on the ambient temperatures and the cold flow properties of the diesel blend.
- The design of product filters should be considered as well as the frequency of change out.

Throughout the supply chain, good housekeeping practices that apply to diesel fuel handling should also be used for diesel blends [15]. These practices are even more important for diesel blends in view of the more hygroscopic nature of FAME.

The presence of FAME requires that adequate measures are taken to prevent cross-contamination in the supply chain [16] between diesel and other fuels that may not be permitted to contain more than trace amounts of FAME [17]. Currently, this specifically applies to Jet A-1 fuels where a 5 ppm maximum limit of FAME is defined by DEFSTAN 91-91[4]. Supply chains for Jet A-1 should be carefully reviewed and potential contamination of Jet A-1 with diesel containing FAME should be avoided. Other fuels, such as heating oil and marine gasoil, may be similarly restricted and should also be protected from potential FAME contamination.

5.1. TRANSPORT VIA MULTI-PRODUCT PIPELINES

Some pipeline companies allow the transport of diesel blends containing up to 7% v/v FAME while other companies do not. The main concern is the potential cross-contamination of Jet A-1 with diesel fuel containing FAME [17,18]. This may be caused by the adsorption of FAME on the pipeline wall during transport of a diesel blend batch and the later desorption of FAME into trailing products. Contamination may also be caused by inadequate operation of pipeline feeder and take-off systems, resulting in the entrainment of small amounts of biodiesel left behind in manifolds, pump stations, dead legs or meter bays during the changeover to other products. Insufficient buffer volumes and small batch sizes are another potential source of contamination. These issues should be reviewed before considering pipeline shipment of diesel blends and acceptability should be confirmed by large scale trials [19].

If diesel blends are transported through a pipeline system, more frequent cleaning and inspection may be required due to the potential for diesel blends to pick up dirt

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[4] A test programme, coordinated by the UK's Energy Institute, is in progress to allow a higher (100ppm) FAME concentration in Jet A-1. The results of this programme are expected in 2010.

throughout the system. It is also important to note that biocides cannot be used to treat Jet A-1.

5.2. TRANSPORT BY BARGE, ROAD AND RAIL

In principle, the transport and distribution of diesel blends by barge, road truck and rail should be done in the same way as hydrocarbon-only diesel fuel. Transport vessels should be clean and should not contain residuals from a previous load that may not be compatible. Precautions should be taken to avoid contamination with water, dirt and rust.

5.3. HANDLING OF DIESEL BLENDS AT FILLING STATIONS

Existing facilities and procedures at filling stations for handling hydrocarbon-only diesel fuel are in principle adequate for handling diesel blends containing FAME. Except for a review of material compatibilities, the following points are particularly important:

- Water bottom measurements should be made on an appropriate frequency. This can be done by automatic gauging, regular tank dipping with water finding paste that is compatible with diesel blends, or by taking tank bottom samples. Water should be removed when necessary. This is particularly important since any water and sediment can be stirred up when the tank is refilled. Procedures should allow for local conditions, e.g. rain fall, tank breathing through temperature fluctuations etc. Attention should be paid to inspection pits to avoid water entry.
- The best practice is to implement automatic fuel level recording and water bottom measurements and these should ideally be fitted to all new facilities. Frequent tank dipping via gauging or with water finding paste, preferably prior to every delivery, is recommended. This may however not always detect water and it is therefore recommended to take liquid samples from the bottom of fuel tanks on a regular basis as well, e.g. once per month.
- All transfer hoses and connectors should be maintained in a clean and dry condition before use.
- Tank condition should be periodically checked to avoid the build up of dirt, rust etc., consistent with local Underground Storage Tank (UST) regulations.
- Diesel blends can increase the risk of filter plugging at the fuel dispenser. This could be due to fuel oxidation and microbiological growth that may foul and eventually plug dispenser filters. These filters are the last line of defence for ensuring delivery of fit for purpose fuel to the customer’s vehicle. For this reason, filters should be in good condition and replaced when plugged before resuming product deliveries.

6. HEALTH, SAFETY AND ENVIRONMENT

6.1. SAFE HANDLING

FAME contains no hazardous materials and is generally regarded as safe to use. Inhalation effects are negligible unless heated to produce vapours. Vapours or finely misted materials may irritate the mucous membranes and cause irritation, dizziness, and nausea and may also cause eye irritation. Prolonged or repeated contact is not likely to cause significant skin irritation and no hazards are anticipated from incidental ingestion through industrial exposure.

Safety precautions and equipment for storing and handling FAME and diesel blends are similar to those used for hydrocarbon-only diesel fuels [3,4,5]. Protective equipment including gloves should always be worn and skin that is inadvertently exposed to fuel should be washed with soapy water. The relevant Safety Data Sheet (SDS or MSDS) should also be reviewed for recommendations on safe handling, type of gloves, and related procedures before beginning work with FAME and biodiesel blends.

6.2. SURFACE SPILLS AND LEAKS, AUTO-IGNITION

If FAME is released to the environment [20], the following can occur:

- Release in soil: Biodegradation of the FAME product will occur, with faster rates under aerobic conditions than under anaerobic conditions.
- Release in water: Although FAME is only slightly soluble in water, it will degrade rapidly and fairly extensively in aquatic environments at a rate that is approximately four times faster than that of hydrocarbon-only diesel fuel. Spills and underground leaks of FAME or diesel blends should be treated in the same manner as conventional diesel fuel spills and leaks, including notification of the proper authorities. The FAME supplier's SDS should also be reviewed for recommendations on clean-up procedures for spills.

FAME having high iodine values can oxidise rapidly when exposed to air. Cloths and rags that have been used to clean up neat FAME may exhibit spontaneous combustion due to oxidation of the FAME (two incidents were reported in 2007 [21]). This oxidation reaction can generate a significant amount of heat and, if conditions are favourable, temperatures can rise above the auto-ignition temperature of the fuel soaked rags, resulting in spontaneous combustion.

It is recommended that rags and cloths saturated with FAME are put into a dedicated storage and disposal drum or a can filled with enough water to completely immerse the contents. Facility operators should know where neat FAME is handled and where storage/disposal containers are located. Appropriate warning signs should also be placed in the areas where FAME is handled. While there have been no similar reports for diesel blends, it would be prudent to treat rags saturated with diesel blends in the same way.

6.3. FIRE PROTECTION AND FIRE-FIGHTING AGENTS

Personnel should approach a FAME or diesel blend fire with the same caution as they would use in approaching a conventional diesel fire and similar fire-fighting techniques should be used. Suitable extinguishing media include dry chemical foam, halon, carbon dioxide, and water spray (fog).

6.4. STATIC ELECTRICITY HAZARDS

While neat FAME has a higher electrical conductivity than conventional diesel fuel, introducing up to 7% v/v FAME into diesel fuel has only a small impact on the conductivity of the blended fuel. In some cases, however, large reductions in conductivity have been observed upon blending 7% v/v FAME into diesel fuel that already contains conductivity additive. Hence, when conductivity additives are used, the conductivity should be verified on a case-by-case basis.

7. COMPARISON OF FAME AND FAEE

7.1. PHYSICAL AND CHEMICAL PROPERTIES OF FAEE

The chemical and physical properties of Fatty Acid Ethyl Esters (FAEE) are similar to those of the corresponding FAME products [22]. The main differences due to esterification with ethanol instead of methanol are:

- Viscosity at 40°C of FAEE is typically about 1 mm^2/s higher compared to FAME manufactured from the same feedstock;
- Flash Point is expected to be somewhat higher for FAEE compared to FAME but will typically depend on residual ethanol and the process technology used to remove the ethanol;
- Distillation characteristics of FAEE will differ from FAME due to the higher boiling points of ethyl esters;
- Oxidation stability of FAEE may be comparable or even slightly better than that of FAME although data on commercial samples of FAEE are very limited;
- Cold flow properties of FAEE are expected to be marginally better than those of FAME.

7.2. OUTLOOK FOR FAEE PRODUCTION

Other than potential performance benefits which are still being explored, the main benefit for FAEE compared to FAME for diesel blends is that it would increase the contribution of renewable components in diesel fuel. This in turn would reduce Greenhouse Gas (GHG) emissions from diesel blends and reduce the demand for fossil diesel. While the GHG emission reduction of FAEE compared to FAME is modest (4-10%), it may in some cases be sufficient for diesel blends to meet future minimum GHG reduction requirements in the EU. There are no data available for FAME produced with methanol from renewable sources, which would be an alternative route to achieve the same benefits.

Both technically and chemically, FAEE production is similar to FAME production. Therefore, existing FAME manufacturing plants should have the technical capability to produce FAEE without major retrofitting. Additional equipment investments would probably be required in order to enable the more difficult phase separation of FAEE from glycerol and the purification of ethanol before recycling.

FAEE is currently not allowed in EN 590 as a diesel blending component and there is no quality standard for this product. Work is underway, however, to extend the test methods and specifications in EN 14214 to include FAEE and to investigate the performance of FAEE-containing blends in engines and vehicles. The successful completion of this work is a prerequisite for accepting FAEE as a diesel fuel blending component.

Since FAEE is not currently allowed as a blending component for EN 590 diesel fuel, it is also not certified by the aviation engine and airframe OEMs to be present in Jet A-1 according to DEFSTAN 91-91. Certification would require an extensive test programme to demonstrate no-harm performance of FAEE in jet fuel as well as a suitable test method for routinely detecting low levels of FAEE in Jet A-1. For this reason, FAEE should not be used in common distribution systems where cross-contamination with jet fuel is possible (see **Section 5.1**) until these issues have been addressed.

Although there are some demonstration plants currently in operation, there is no large-scale commercial production of FAEE at the moment. Commercial developments have been slowed by the higher price of ethanol compared to methanol and the limited economic value that is associated with the favourable GHG emission reduction. If methanol prices were to increase relative to ethanol and if GHG emission reduction become a critical factor for legal compliance, then FAEE production could become an economically attractive alternative to FAME.

Considering the uncertainties in these factors, the outlook for significant commercial production of FAEE in the near term is not especially positive.

7.3. FUTURE USE OF FAEE

Given the similarities in the chemical and physical properties of FAME and FAEE, the guidance that has been provided for handling and blending FAME would be expected to apply as well for FAEE.

8. CONCLUSIONS

FAME can be blended into hydrocarbon-only diesel fuel and handled successfully by implementing where applicable the guidance provided in this report. The main points are summarised below.

- Only FAME fully meeting the requirements of EN 14214 should be used. When FAME is stored for a prolonged period of time before being blended, its quality should be monitored. FAME that is off-specification should never be used for fuel blending.
- Equipment and transport media that are routinely exposed to B100 and used throughout the supply chain (tanks, vessels, pumps, filters, piping, fittings, instruments, gaskets, hoses, etc.) should be made of materials that are compatible with FAME. Where existing materials are not compatible, they should be replaced.
- Material compatibility problems are substantially reduced for diesel fuels containing low FAME concentrations.
- Applying good housekeeping practices to prevent water and sediment contamination is very important for FAME and for diesel blends containing FAME.
- The temperature of FAME and diesel blends should be kept above the cloud point of the FAME during blending, storage and transport in order to minimize drop-out of saturated mono-glycerides.
- The composition and dosage rate of diesel performance additives should be optimised for the diesel blend composition.
- Recommended measures to prevent or minimise the ageing of FAME and diesel blends include good stock and storage tank management and the use of antioxidant additives.
- The size and location of product filters should be reviewed as well as the frequency of filter change out, because FAME can redissolve sediments and facilitate the formation of chemical or microbial deposits.
- The presence of FAME in diesel fuel requires that adequate measures are taken to prevent cross-contamination in the supply chain between diesel and other fuels, especially Jet A-1.

Although there are not expected to be significant differences in the handling and blending of FAEE in diesel fuel compared to FAME, the outlook for significant commercial production of FAEE in the near term is not especially positive. However, the introduction of diesel fuel containing FAEE into common distribution systems should anticipate the potential for cross-contamination with other products, especially Jet A-1.

9. GLOSSARY

B100	100% v/v FAME (also called biodiesel)
BHT	Butylated Hydroxytoluene
Biodiesel	100% v/v FAME or FAEE
BOD	Biological Oxygen Demand
BXX	Diesel blend containing XX% v/v FAME
CEN	European Committee for Standardisation
CFPP	Cold Filter Plugging Point
CI	Cetane Index
CN	Cetane Number
DG	Di-Glyceride
EN 14214	CEN European standard for FAME
EN 590	CEN European standard for regular diesel fuel
EU	European Union
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FBTI	Filter Blocking Tendency Index (IP387)
GHG	Greenhouse Gas
HC	Hydrocarbon
HFRR	High Frequency Reciprocating Rig
MSDS	Material Safety Data Sheet (see also SDS)
MG	Mono-Glyceride
OEM	Original Equipment Manufacturer
PAH	Polycyclic Aromatic Hydrocarbons
PM	Particulate Matter
SDS	Safety Data Sheet (see also MSDS)
SG	Sterol glucoside
TG	Tri-Glyceride
UST	Underground Storage Tank
VOC	Volatile Organic Compound
WSD	Wear Scar Diameter

10. ACKNOWLEDGEMENTS

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APPENDIX 1 EN 590 AND EN 14214 SPECIFICATIONS

Property	EN 590 Test Method	EN 590	EN 14214 Test Method[5]	EN 14214
Flash point, min	EN ISO 2719	55°C	EN ISO 3679	101°C
Water content, max	EN ISO 12937	200 mg/kg		500 mg/kg
Total contamination, max	EN 12662	24 mg/kg		24 mg/kg
Distillation:	EN ISO 3405			
+ % v/v recovered at 250^{o}C		< 65%		
+ % v/v recovered at 350^{o}C		> 85%		
+ 95% v/v recovered at:		< 360 ^{o}C		
Kinematic viscosity	EN ISO 3104	2.0-4.5 mm^2/s		3.5-5.0 mm^2/s
Density	EN ISO 3675 EN ISO 12185	820-845 kg/m^3		860-900 kg/m^3
FAME content	EN 14078	< 7% v/v	EN 14103	> 96.5%
Ash content, max	EN ISO 6245	0.01% m/m		
Sulfated ash content, max			ISO 3987	0.02% m/m
Sulphur content, max (by weight)	EN ISO 20846 EN ISO 20884 EN ISO 20847	10 mg/kg	EN ISO 20846 EN ISO 20884	10 mg/kg
Copper strip corrosion	EN ISO 2160	Class 1		Class 1
Cetane number, min	EN ISO 5165 EN15195	51.0	EN ISO 5165	51.0
Cetane index, min	EN ISO 4264	46.0		
Polycyclic Aromatic Hydrocarbons (PAH), max	EN12916	11% wm/m		
Cold Filter Plugging Point (CFPP)	EN 116	Location & season dependent		Location & season dependent
Carbon residue, max	EN ISO 10370	0.30% m/m		0.30% m/m
Acid value, max			EN 14104	0.50 mg KOH/g
Oxidation stability	EN ISO 12205 EN 15751	< 25 g/m^3 > 20 hrs	EN 14112	> 6.0 hrs
Iodine value			EN 14111	< 120
Linolenic acid methyl ester			EN 14103	< 12.0% m/m
Polyunstatured methyl esters				< 1% m/m
Methanol content			EN 14110	< 0.20% m/m
Monoglycerides content			EN 14105	MG <0.8% m/m
Diglycerides content				DG <0.2% m/m
Triglycerides content				TG <0.2% m/m
Group I metals (Na + K)			EN 14108 EN 14109	< 5.0 mg/kg
Group II metals (Ca + Mg)			EN 14538	< 5.0 mg/kg
Free glycerol content, max			EN 14105 EN 14106	0.02% m/m
Total glycerol content, max			EN 14105	0.25% m/m
Phosphorous content, max			EN 14107	4 mg/kg
Lubricity (HFRR)	ISO 12156-1	<460µm WSD		

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[5] If the test method specified for EN 14214 is different from the test method specified for EN 590

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