



Chapter 22 – Biofuels: Marine Transport, Handling and Storage Issues

The production and use of biofuels as transport fuels has increased significantly in recent years. A number of legislative reforms have mandated the integration of fuels derived from renewable sources into fuel infrastructure. However, the introduction of biofuels has not been without problems and there is considerable research still ongoing into the properties of biofuels and how they behave when blended with conventional fossil fuels.

Generally, the USA and Brazil are the two largest producers of biofuels, mostly ethanol and fatty acid methyl esters (FAME). The EU also has a significant production of hydrotreated vegetable oil (HVO).

22.1 Legislative Targets

Biofuels were originally seen as one answer to the problems of increasing greenhouse gas (GHG) emissions and global warming. Biofuels are produced from renewable sources such as corn, wheat, rapeseed and soya beans, which can be quickly and easily regrown.



Figure 22.1: Potential sources of biofuel.

However, questions were soon raised with regard to the environmental credentials and overall sustainability of commercially available biofuels. Issues included the use of crops that would normally be used for food being put into biofuel production, the questionable CO₂ emissions savings when considering the overall production process, deforestation to make way for biofuel crop plantations and the use of environmentally harmful fertilisers and pesticides employed in growing the crop feedstock.

Amid these growing concerns, as an example of State legislative change, the UK government has amended the targets set out in the *Renewable Transport Fuel Obligation (RTFO)*, a directive aimed at reducing GHG emissions from road transport. This legislation has been periodically amended several times since 2007. As of 1st January 2022, it mandates that 13.5% of fuel oil supplied in the UK must be from renewable energy sources (Reference 33). It also aims for this obligation to reach 21% from 2032 onwards.

Annual figures show that the total volume of all UK sourced biofuels used in the UK in 2020 was 293 million litres/kilograms (biogases such as biomethane and biopropane are reported in kg). This was a 5% increase on the 2019 figure. Of this, the volume of UK sourced biodiesel for UK road transport was at 126 million litres and for bioethanol, the figure was 116 million litres.

22.2 Current Types of Biofuel

There are currently two main classes of biofuels in widespread use; biodiesel (or, more correctly, FAME) and bioethanol. The two are very different in their properties and so there are different associated issues to consider if they are to be safely shipped, handled, stored and used.

22.2.1 FAME/Biodiesel

Biodiesel is a fuel derived from vegetable oils or animal fats, and is more correctly called fatty acid methyl esters (FAME). FAME is the product of reacting a vegetable

oil or animal fat with an alcohol (methanol, a petrochemical that is generally derived from natural gas or coal) in a process known as transesterification. When compared to conventional diesel derived from crude oil, vegetable oils and animal fats generally have higher viscosities (which means they are more difficult to pump and store without heating) and are more unstable (which means they are more likely to degrade during storage, handling and end use). The transesterification process brings the properties of the raw materials closer to those of a conventional diesel, making the product more suitable for use as a road transport fuel. However, while the FAME produced can be used neat as a fuel, it is more commonly blended with conventional petroleum diesel for use in diesel engines.

ASTM International has described a system of nomenclature for naming FAME/diesel blends (see ASTM D6751) (Reference 34). Pure FAME is denoted B100, representing 100% biodiesel (of which there are four sub-grades). Other common blends include B5 (5% biodiesel and 95% conventional diesel), B7 (the EN 590 European diesel standard allows up to 7% by volume FAME in diesel) and B20 (20% biodiesel and 80% conventional diesel).

Raw materials for FAME production

Various raw materials (feedstocks) may be used for the production of FAME, including palm oil, coconut oil, rapeseed oil, soya bean oil, tallow and used cooking oils. A general FAME cargo might be the product of processing any one of these raw materials or may be a mixture of FAMEs produced from different raw materials. Each raw material would produce FAME of a different chemical composition, with correspondingly different characteristics. For example, a FAME derived from palm oil (PME) is likely to be solidified at normal UK winter temperatures, whereas a FAME derived from rapeseed oil (RME) will be a liquid.



Figure 22.2: Examples of FAME.

One of the most important chemical characteristics of FAME is the structure and composition of the fatty acid methyl ester groups, which will be determined by the fatty acid components of the raw material used in the production process.

FAME types composed of a relatively high proportion of saturated fatty acid methyl esters, such as palm oil derived FAME (denoted PME), will generally be relatively stable

to unwanted degradation reactions, but will have poorer cold temperature performance. FAME types composed of a relatively high proportion of unsaturated fatty acid methyl esters, such as soya bean oil derived FAME (denoted SME), will display markedly different behaviour, with better cold temperature properties in comparison to PME, but less stability to degradation reactions.

The presence and composition of other chemical constituents is also important. For example, FAMEs with high levels of vitamin E are thought to be more stable in terms of unwanted oxidative degradation reactions.

22.2.2 FAME Problems

Water contamination

A major problem with regard to the carriage of FAME by sea is the issue of water contamination. FAME is a hygroscopic material, which means that it will absorb water from its surrounding environment, including the atmosphere. This renders FAME very sensitive to water contamination. The current maximum allowable water content in the European EN 14214 and American ASTM D6751 FAME standards is 500 mg/kg, although selling specifications are often lower (300 mg/kg being a typical maximum water content on a sales specification), reflecting the high potential for water pick-up in this material (References 34 and 35).



Figure 22.3: FAME cargoes are extremely sensitive to water contamination, the source of which can be seawater taken in during heavy weather.

Unlike most conventional diesels, in which any undissolved water present will generally settle out over a period of time, FAME can hold water in suspension up to relatively high levels (above 1,000 mg/kg). Apart from the fact this will render the cargo off-specification for water content, the presence of water can promote unwanted hydrolytic reactions, breaking down the FAME to form free fatty acids. These fatty acids not only affect certain specification parameters for the material, but are also corrosive and may attack exposed metal surfaces. Additionally, once a certain threshold level of water content is reached, water can separate out from the FAME, forming a separate (and potentially corrosive) free water phase. The possibility of phase separation occurring is greater for blends of FAME and conventional diesel.

The presence of a FAME/water interface provides ideal conditions for the promotion of unwanted microbiological growth, which may in turn lead to filter blocking and corrosion problems.

Some publications have referenced the greater degree of biodegradability of FAME as a positive factor when dealing with environmental spillages. While this is correct, it also means that FAME is considerably more prone to microbiological attack than a conventional fossil fuel.

Possible sources of water contamination on board a ship range from the obvious, such as seawater ingress or residues of tank washing operations, to the less obvious, for example, moisture in an inert gas blanket produced from a faulty flue gas generating system, or atmospheric humidity in tank ullage spaces that are not under a positive pressure of dry inert gas. Despite having relatively high flashpoints, FAME cargoes are generally carried under a (dry) nitrogen blanket to avoid the potential increase in water due to absorption of moisture from tank ullage spaces.

Stability problems

FAMEs are generally more prone to issues with regard to their stability than conventional petroleum diesel. FAME can degrade under the influence of air, heat, light and water, and this may occur during transport, storage or even during end use. FAME cargoes may display different levels of stability depending on their composition and the feedstock(s) used in their production.

Potential shipping problems include the promotion of degradation reactions by trace metals, as copper heating coils or zinc-containing tank coatings have the potential to cause deterioration in quality. Thermal stability issues may arise if the FAME cargoes are stored next to heated tanks, for example bunker settling tanks. Issues with the promotion of instability by the presence of trace metals are worse for B100 than for lower biodiesel blends such as B5 or B20. Degradation reactions can form insoluble sediments and gums that may increase the viscosity of the FAME, leading to filter blocking, or they may potentially further decompose to other more corrosive species.

Low temperature behaviour

Certain FAMEs form waxy precipitates at low temperatures, which will then not redissolve when the product is reheated, although this appears to be an uncommon problem. However, there is the potential for FAME cargoes shipped from a warm, humid climate to extremely cold conditions, if the correct measures for heating the cargo are not applied, to form unwanted waxy precipitates that may lead to specification failure or pumping problems. It is, therefore, vital that the correct heating instructions are issued and followed. An understanding of the nature of the FAME will inform the necessary heating instructions.

FOSFA (The Federation of Oils, Seeds and Fats Associations Ltd) has now included FAME products in its published heating recommendations (Reference 36):

Oil type	Temperature during voyage		Temperature at discharge	
	Min (°C)	Max (°C)	Min (°C)	Max (°C)
FAME from maize/rapeseed/soya/sunflower	Ambient		Ambient	
FAME from coconut/palm/palm kernel/tallow	25	30	30	40

Table 22.1: FOSFA heating recommendations for FAME products.

FAME contamination of jet fuel

FAME is a surface active material and can adsorb onto the walls of tanks or pipelines and de-adsorb into subsequently carried products. This may be an issue where multiproduct pipelines or storage tanks are utilised, or where ships carry jet fuel cargoes after carrying FAME/diesel blends.

In May 2008, a number of jet fuel storage tanks at Kingsbury supply terminal and Birmingham Airport were quarantined after it was discovered that samples of the jet fuel in question contained up to 20 ppm of FAME. The cause of the contamination is thought to have been as a result of mixing of jet fuel with B5 diesel in the distillate manifold at Kingsbury terminal. As an indication of the very small quantities needed to cause such contamination, the 5 ppm specification limit would be equivalent to just 1 litre of B5 diesel in 10,000 litres of jet fuel.

When ships may potentially carry jet fuel cargoes following on from FAME or FAME/diesel blends, care must be taken with tank cleaning and flushing and draining of common lines, including sea or jetty loading lines. Switching from a B5 to jet fuel requires at least a hot water tank wash (but preferably also an intermediate FAME-free cargo) to remove FAME residue. Switching from neat FAME to jet fuel requires particular care and some advocate at least three intermediate (FAME free) cargoes plus a hot water wash before loading jet fuel. Jet fuels from a marine terminal storage tank do not require testing for FAME contamination where it can be confirmed that there is no FAME in the marine supply system. Where there is direct knowledge that any diesel on board, or any diesel having any interface with the jet fuel, is B0, and the ship has not carried biodiesel within the last three loads, then the jet fuel may be exempted from testing.

The industry guidelines for the prevention of FAME contamination of aviation jet fuel are as follows¹:

- I. Three intermediate cargoes with a no FAME content between a FAME B100 (100%) cargo or any cargo with a FAME content greater than 15% (above B15) and a subsequent aviation jet fuel cargo.

¹ Source: *The Energy Institute Guidelines for the cleaning of tanks and lines for marine tank vessels carrying petroleum and refined products (HM 50) – Section 2.12.7* (Reference 39). While not a legal requirement, these guidelines are based on sensible practice and owners should give serious consideration to adopting such advice.

- II. When following cargo with a FAME content of 5% or less (B5 or below), a hot water wash, including flushing of pumps and lines, followed by draining is recommended as a minimum.
- III. When following cargo with a FAME content of 15% (B15) or less but above B5, a hot water wash, including flushing of pumps and lines, followed by draining is recommended as a minimum. Tanks must be in good condition and washing needs to be particularly stringent. A single intermediate cargo with no FAME content is suggested as an alternative, followed by a hot water wash, including flushing of pumps and lines, and by draining.

The UK Ministry of Defence Standard 91-91 (Reference 37) states that the maximum permitted level of FAME is 50 mg/kg. It is also suggested that the currently specified method of flushing sample containers three times for jet fuel samples may not be sufficient to remove traces of FAME, which may even be transferred from contaminated gloves. This could potentially lead to false positive detection of FAME in actually on-specification material, resulting in erroneous claims being made. It is therefore recommended that new sample containers and new gloves are used when sampling jet fuel cargoes.

For product tankers carrying multiple products, the danger of inadvertently contaminating a cargo of jet fuel with traces of FAME is a very real risk, even if it does not initially appear that there is any potential for cross contamination to occur. For example, ultra-low sulphur diesel meeting the EN 590 specification may appear in the shipping documents as ULSD, which would not immediately indicate that the product contained any FAME. However, the EN 590 diesel specification allows up to 7% by volume FAME content (Reference 38). If the ship's tanks and lines are not completely stripped of all the ULSD prior to loading a cargo of jet fuel, the quantity of ULSD containing 7% FAME needed to render the jet fuel cargo off-specification would be very small.

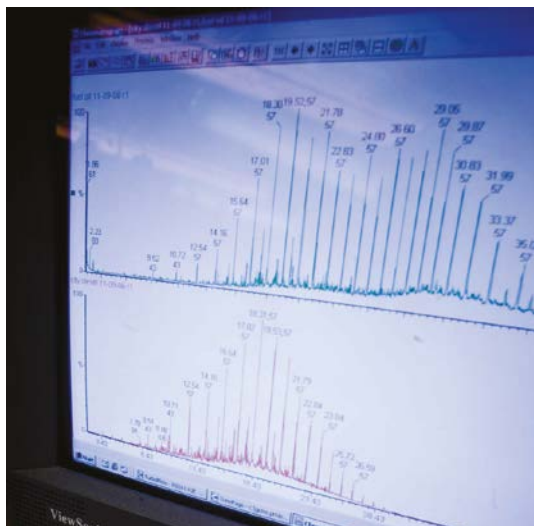


Figure 22.4: Chromatogram showing the components of a fuel cargo.

Solvent behaviour

FAME has the ability to act as a solvent, taking up any organic residue, dirt or scale that may have accumulated on the surfaces of tanks or pipelines. This may have the effect of cleaning out the dirty storage or pumping systems, but it will contaminate the FAME itself and may lead to subsequent fouling of filters or pump blockages.

FAME is known to attack and quicken the ageing process of certain materials, including elastomers (elastic materials that may be used as seals, valves, gaskets, etc). Materials should be checked for compatibility with FAME and FAME/diesel blends by consultation with the equipment manufacturer.

Biodiesel in bunkers

In 2017, the sixth edition of the marine fuels international standard, ISO 8217:2017 (Reference 40), was issued. The third edition of the marine fuels standard, ISO 8217:2005, required under point 5.1 of Section 5 that the fuels to be classified in accordance with the standard should be “*homogeneous blends of hydrocarbons derived from petroleum refining*”. This was interpreted as precluding fuel from containing any bio-derived components. During preparation of the fourth edition of the standard, the working group committee considered the topic of biodiesel and the potential for the material to find its way into the marine fuel supply chain. It concluded that it was almost inevitable that, as a result of blending FAME into automotive diesel, some marine distillates and possibly even marine residual fuels would contain a proportion of FAME as a result of cross contamination within the distribution system.

As such, ISO 8217:2012 required, under point 5.4 of Section 5, that “*The fuel shall be free from bio-derived materials other than ‘de minimis’ levels of FAME (FAME shall be in accordance with the requirements of EN 14214 or ASTM D6751). In the context of this International Standard, ‘de minimis’ means an amount that does not render the fuel unacceptable for use in marine applications. The blending of FAME shall not be allowed.*”

The current standard, ISO 8217:2017, retains this *de minimis* level requirement but with a wider tolerance to a level of approximately 0.5 volume % FAME and with additional specifications (DF grades) for distillate marine fuels (Reference 40).



Figure 22.5: Bunkering vessel supplying fuel to a cruise ship.

Annex A of the current standard (Reference 40), considers the issue of bio-derived products and FAMEs finding their way into marine fuels in more detail. It states that, notwithstanding the fact that FAME has *“good ignition and lubricity properties together with perceived environmental benefits, there are potentially specific complications with respect to the storage and handling of distillates with a FAME component in a marine environment, such as:*

- *A tendency to oxidation and long-term storage issues*
- *an affinity to water and risk of microbial growth*
- *degraded low-temperature flow properties, and*
- *FAME material deposition on exposed surfaces, including filter elements.”*

It is recognised that there are a number of differently sourced FAME products, each with their own particular characteristics, which may impact upon storage, handling, treatment, engine operations and emissions.

The standard states that in *“... those instances where the use of fuels containing FAME is being contemplated, it should be ensured that the ship’s storage, handling, treatment, service and machinery systems, together with any other machinery components (such as oily-water separator systems), are in terms of materials and operational performance*

compatible with such a product. Contact of materials such as bronze, brass, copper, lead, tin and zinc with FAME should be avoided as these may oxidize FAME thereby creating sediments."



Figure 22.6: Ethanol biorefinery.

22.2.3 Bioethanol

Bioethanol is ethanol produced by the fermentation of renewable sources of sugar or starch crops. Unlike FAME, bioethanol is a single chemical compound, the properties of which are well documented and understood. It is a volatile, colourless liquid that is miscible with water and is hygroscopic. Ethanol is the alcohol found in alcoholic beverages and is also commonly used as a solvent in perfumes, medicines and paints. However, the most common use for ethanol is as a fuel or fuel-additive. Ethanol for use as a fuel is generally dosed with a 'denaturant' to render it unsuitable for human consumption.

There is significant experience worldwide in the use of ethanol as a fuel or fuel-additive. In the USA, there has been over 10 years' successful use of gasoline containing up to 10% ethanol (E10) and in Brazil blends containing up to 85 to 100% ethanol (E85 and E100) are commonly used in flexible-fuel vehicles. The current European gasoline specification, EN 228, allows up to 10% ethanol by volume (E10) (Reference 41). However, in practice, many EU States continue to use up to 5% (E5).

Bioethanol can be produced from a number of raw materials, but they do not impart the same variation in the properties of the end product fuel as is the case with FAME. However, there are still a number of potential hazards for consideration.

22.2.4 Bioethanol Problems

Water contamination

An issue during the carriage of bioethanol and bioethanol-gasoline blends is the potential for water contamination, because ethanol is hygroscopic and highly soluble

in water. Small quantities of water can be dissolved in gasoline/bioethanol blends but, depending on temperature and the gasoline/bioethanol blend ratio, there is a critical threshold level of water that can be dissolved. Once this threshold level has been exceeded, irreversible phase separation will occur where the water causes the ethanol to separate from the gasoline, forming an alcohol rich water/ethanol aqueous phase and an alcohol poor gasoline phase. The alcohol rich aqueous phase will collect at the bottom of the ship's tank or storage tank.

This phase is likely to be highly corrosive and it will not be able to be used as fuel. In addition, if such phase separation does occur, it is possible that the gasoline phase will be classed as *Pollution Category Z*, which means that it is considered to present a "minor hazard to either marine resources or human health" if discharged into the sea from tank cleaning or deballasting operations and therefore "justifies less stringent restrictions on the quality and quantity of the discharge into the marine environment" (Reference 30). While the regulations do not require ethanol to be carried on a chemical tanker, ethanol is generally shipped on chemical tankers to maintain the integrity of the product.

It should be noted that the terms biodiesel and bioethanol do not appear in the IBC Code (Reference 42). As it is a requirement that the proper shipping name is used to describe any product to be carried that appears in the IBC Code, these terms cannot be used to describe the products being carried.

The situation becomes more confusing when considering how blends of conventional fossil fuels and biofuels are shipped and which Annex of MARPOL they fall under. MARPOL Annex I covers the prevention of pollution by oil and MARPOL Annex II covers the control of pollution by noxious liquid substances carried in bulk (Reference 30). Blends of biofuels and conventional fuels are essentially mixtures of mineral oil based hydrocarbons and noxious liquid substances. The IMO has issued guidelines on biofuels. MSC-MEPC.2/Circ.17 contains *Guidelines for the Carriage of Blends of Biofuels and MARPOL Annex I Cargoes* and was approved in June 2019 (Reference 43). It replaced and revoked an earlier circular (MEPC.1/Circ.761/Rev.1) regarding blends of biofuels and petroleum fuels.

MSC-MEPC.2/Circ.17 contains consequential amendments that reflect the new Annex 12 on energy-rich fuels in the MEPC.2/Circular on Provisional categorization of liquid substances in accordance with MARPOL Annex II and the IBC Code, as well as making reference to SOLAS Regulation VI/5.2. Specifically, the physical blending on board of biofuels and MARPOL Annex I cargoes during a sea voyage to create new products is now prohibited. Circ.17 also defines the following cargo bands:

Band 1: When the biofuel blend contains 75% or more petroleum oil (ie 25% or less biofuel) – the product is carried as a MARPOL Annex I cargo. Oil discharge monitoring equipment (ODME) should be approved/certified for the mixture carried or tank residues and alcohol resistant fire-fighting foams should be used when more than 5% ethyl alcohol blends are used.

Band 2: When the biofuel blends contain more than 1% but less than 75% petroleum oil (ie more than 25% and less than 99% biofuel) – the product is carried as a MARPOL Annex II cargo. A list of existing blends and corresponding IMO IBC carriage requirements is set out in Chapter 17 of the IBC Code. Carriage requirements for new

blends of biofuels identified as falling under the scope of MARPOL Annex II will be incorporated into List 1 of the MEPC.2/Circular, as appropriate.

Band 3: Biofuels blended with 1% or less petroleum oil – the products are not considered as blends and are therefore to be shipped in accordance with MARPOL Annex II, under the appropriate product entry in the IBC Code.

22.2.5 Handing and Usage on Board

For use on board as a fuel, separation and purification is still required. The separation temperature will be determined based on the analysis report, which is the same as for Very Low Sulphur Fuel Oil (VLSFO). Difficulty may be experienced in managing the temperature so that it is neither too cold (causing undesirable cold flow properties) nor too warm (causing ageing of the fuel and low viscosity for the engine). This level will be different for every individual fuel, which may increase the level of difficulty for engineers. However, it is also worth noting that VLSFO may still have aluminium/silicon/water present, therefore purification remains essential.

While biofuel is compatible with low sulphur fuel oil, it should never be mixed on board. Instead it must come from a reputable bunker supplier who will supply a stable blend to the ship.

To manage the issue of waxing, it is recommended to keep the temperature in the tank above the waxing point. If this is not possible a purifier can be used to circulate, provided that it has a heater. Again, depending on storage time and temperature, the fuel might age.

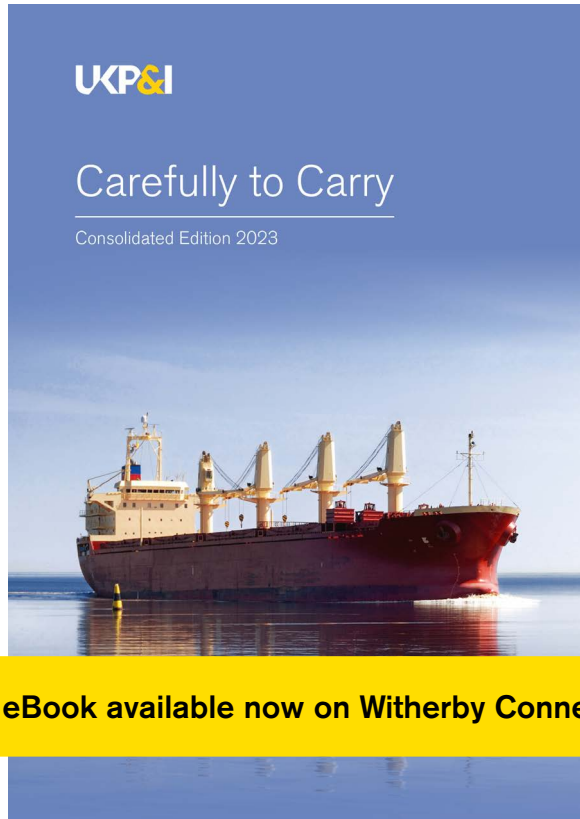
Biofuel should always be used as soon as possible. It is also recommended to dewater the bunker tanks, as water contributes to bacterial growth.

Additives

The use of additives is not typically recommended with biofuels since the effect can be unpredictable. Antioxidants and middle distillate flow improvers may be an option, but these should not be blended routinely on board.



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