

The Introduction of Biofuels in Marine Sector

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Abstract: Sulphur and emissions related limits which are imposed on marine fuels drive the maritime industry to look on alternative fuels. The maximum sulphur content of the fuel has already decreased in the ECAs SO_x (Sulphur Emission Control Areas) from 1.5% to 1% from 1 July 2010, and to 0.1% from 1 January 2015. Globally, the highest permitted sulphur content of fuel will be reduced, as from 1 January 2020 to 0.5%. Increasing demand of low sulphur fuel is anticipated, leading to a substantial mitigation of marine fuels from residual to distillate ones.

Biodiesel or else Fatty Acid Methyl Esters (FAME), and mixtures of it with conventional petroleum fuels, constitute alternative energy source for the maritime industry. The International Standard EN ISO 8217 specifies the requirements of petroleum fuels for use in marine diesel engines. According to the previous version of EN ISO 8217:2012 distillate fuels should comply with the “de minimis level” of approximately 0.1% v/v FAME. Nevertheless with the latest revision of EN ISO 8217 standard in 2017, the incorporation of FAME up to 7% v/v is allowed in specific marine distillate grades (DF). Marine distillates can also include hydrocarbons from synthetic or renewable sources, similar to the composition of petroleum distillate fuels.

Keywords: Marine Fuel, Distillate Fuel, SECAs, DF grades

1. Introduction:

The shipping industry is the backbone of global trade and the lifeline for island communities, transporting approximately 90% of the tonnage of all traded goods, as estimated by the International Chamber of Shipping. The energy source for the propulsion of ships has undergone significant transformations over the last 150 years, starting with sails (renewable energy) through the use of coal to heavy fuel oil (HFO) and marine diesel oil (MDO). The consumption of these fuels has been increasing over the years in line with the rising demand for shipping. The International Maritime Organization (IMO) estimates that between 2007 and 2012, on average, the world's marine fleet consumed between 250 and 325 million tons of fuel annually, accounting for approximately 2.8% of annual global greenhouse gas emissions (*The energy efficiency gap in maritime transport*). However, compared to other

modes of transport, shipping produces the lowest emissions of carbon dioxide (CO₂) per ton per kilometer travelled.

Still, emissions are expected to rise with shipping demand and they could triple by 2050 if left unregulated. On 10 October 2008 the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO) adopted the revised MARPOL 73/78 (International Convention for the Prevention of Pollution from Ships) Annex VI on air pollution from ships. The sixth Annex, which came into force on May 19, 2005 concerns the prevention of air pollution from ships and provides the synthesis of specific emission control areas, (*MARPOL 73/78*).

The aim of the IMO is to reduce emissions from ships by a switch from heavy fuel oils to light fuel oils. The most recent regulations place restrictions on nitrogen and sulphur oxides (NO_x and SO_x) emissions from the seagoing ships. The MARPOL is the main international convention covering prevention of pollution of the marine environment from operational or accidental problems of ships. The fuel sulphur content decreases in the ECAs SO_x (Sulphur Emission Control Areas), which is the Baltic Sea, the North Sea and the English Channel, from 1.5% m/m to 1% m / m from July 1, 2010 and 0.10% m/m from 1 January 2015. At a global level, the highest permissible sulphur content of fuel is reduced from January 1, 2012, from 4.5% m/m to 3.5% m/m, and 0.5% m / m from January 1, 2020.

The concentration of sulphur in marine fuel depends both on the degree of the refinement as well as on the original sulphur content of the crude oil processed by the refinery. The requirement for maximum sulphur content of 0.10% m/m in fuel oil used on board ships sailing or operating in the ECAs (Emission Control Areas) from January 1, 2015 means in practice that it is not always effective to mix residual fuel with distillate fuel and still meet this limit in sulphur content. Recently, in an effort to combine the low sulphur content with the more preferable high viscosity of the fuel, a series of new types of fuels have been introduced which are referred to as ULSFOs (Ultra Low Sulphur Fuel Oils). However, these products are not exactly included in the relevant specifications and their availability is currently limited compared to the conventional types, Therefore, practically distillate grades

(DMA, DMB and DMZ) that meet the ECA sulphur requirements remain the most popular option

2. Specifications of Marine Fuels

The International Standard EN ISO 8217 lists the requirements of petroleum fuels for use in marine diesel engines and ship boilers, specifying different distillate grades (DM) and a number of residual grades (RM). The previous editions of EN ISO 8217:2010/12 standard take into account the main issues related to the use of low sulphur distillate fuels and according to it, fuels must be deprived from biofuels except from the “de minimis” levels of fatty acid methyl esters (FAME). The “de minimis” level for distillate fuels was indicated as approximately 0.1 volume % FAME.

The demand for use of marine distillate fuels with low sulphur content has led to further research and data collection that eventually permitted the incorporation of FAME to specific grades of distillate marine fuels supplied in the marine market (DF grades). This is incorporated in the latest ISO 8217 edition which was put into force earlier this year. Eventually new types of 0.1% S fuels are entering the market in response to the 0.1% S ECAs SOx limit. The sixth edition on the EN ISO 8217 standard includes additional requirements for distillate fuels to protect against cold operability issues as well. Hence, it offers improved quality control and better protection against operational issues while the introduction of DF grades improves fuel oil availability in some ports.

Fatty acid methyl ester(s), or FAME, has previously been regarded as a contaminant in all marine fuels, but the new grades allow bio-fuel blends containing up to 7% v/v FAME. Marine distillates can also include hydrocarbons from synthetic or renewable sources, similar to the composition of petroleum distillate fuels (*ISO/FDIS 8217:2017*). There is substantial positive experience with these fuels in other transportation sectors.

3. Alternative Fuels in Marine Industry

The incorporation of biofuels in marine distillate fuels is still one of the major options for the transition to a smarter and greener transport system with low carbon footprint. Biofuels have already entered the market, driven amongst other by their potential to improve energy security and to contribute to climate change mitigation.

Biofuels are one of the few technologies currently available that have the potential to substitute oil and provide benefits to the transportation system. Biofuels on their own cannot deliver a sustainable transport system and must be developed as part of an integrated package of measures, which promotes other low carbon options and efficiency, as well as moderating the demand and need for transport (*Alternative Fuels for Marine Applications*).

Biofuels are usually categorized as first, second and third generation, based on the technology and/or the raw materials that are utilized for their production. In first generation biofuels the carbon source comes from sugar, lipid or starch which is directly extracted from a plant. In

this category are included the following: biodiesel, vegetable fats, biogas, bio-alcohols, and synthetic gas. First generation biofuels can offer substantial CO₂ benefits and can help to improve domestic energy security. The production of 1st generation biofuels is commercial today, with almost 50 billion liters produced annually. Nevertheless 1st generation biofuels seem to create great concerns about the environmental impacts and carbon balances - reasons that set remarkable limits in their production. The main disadvantage of first generation biofuels is the food-versus-fuel debate and one of the major reasons for rising food prices is due to the increase in the production of these fuels. Additionally biodiesel is proven to be not a cost efficient emission abatement technology, (*Renewable Energy Options for Shipping*).

Second-generation biofuels can broadly grouped into those produced either biochemically or thermochemically, either route using non-food crops, especially from lignocellulosic feedstocks sourced from crop, forest, or wood process residues, or purpose-grown perennial grasses or trees. Such crops are likely to be more productive than most crops used for 1st generation, in terms of the energy content of the biofuel produced annually per hectare (GJ/ha/yr), (*Sustainable Production of Second Generation Biofuels*). In the second generation biofuels are included the following: methyl esters derived from used cooking oils, bio-oil, butanol, mixed alcohols, lignocellulosic alcohol and Hydrogenated Vegetable Oils (HVO). It is anticipated that 2nd generation biofuels could significantly reduce CO₂ emissions. Moreover they do not compete with food crops and some types of them can offer better engine performance (*From 1st to 2nd Generation Biofuel Technologies*).

Liquid biofuels that are under consideration generally in the marine section and specifically in this work are biodiesel-FAME, Hydrogenation-Derived Renewable Diesel (HDRD or HVO - Hydrotreated Vegetable Oil) and synthetic diesel BTL (Biomass to Liquid). Both HVO and BTL are high quality synthetic renewable diesel fuels.

3.1. Biodiesel or FAME (Fatty Acid Methyl Esters)

Biodiesel, which is defined as the monoalkyl esters, mainly methyl esters (FAME), of long-chain fatty acids derived from renewable biological sources, such as vegetable oils or animal fats or waste cooking oils by transesterification, is considered as a possible substitute or extender of conventional diesel fuel. Biodiesel should comply with the requirements set by EN ISO 14214 which is a standard developed only for fatty acid methyl esters.

Due to its polar nature, biodiesel is considered to be a lubricity improver and so it can enhance the lubricating efficiency of low sulfur marine fuels improve the lubricity property and therefore, reduce the wear in the component of the fuel delivery systems. On the other hand it can degrade over time forming contaminants in the form of peroxides, acids, and other insoluble particles. Biodiesel, especially in higher concentrations, can dissolve certain nonmetallic materials such as seals, rubber hoses, and gaskets. It can also interact with certain metallic materials,

such as copper and brass. For an existing ship, the fuel system and engines may have to be modified by changing out susceptible parts with biodiesel-compatible components for an untroubled operation.

3.2. Synthetic Biofuels

Synthetic biofuels are defined as fuels that are synthesized predominantly from synthesis gas produced by cleaned and modified gas from thermal gasification (such as partial oxidation) of biomass. Synthetic fuels have several advantages because they can be used without modification in the existing engines and fuel supply. In addition synthetic biofuels are considered cleaner than traditional fuels due to the removal of all contaminants so to avoid poisoning the catalysts used in the processing, (*Synthetic Fuels for Global Shipping*).

There are several thermal and chemical processes that can be used to produce synthetic hydrocarbons. The main routes are the following:

- Thermal gasification to syngas (a mixture of hydrogen and carbon monoxide) followed by upgrading by Fischer-Tropsch (FT) synthesis.
- Thermal gasification followed by methanol synthesis followed by upgrading with methanol to gasoline (MTG) or methanol to olefins, gasoline and diesel (MOGD) processes.
- Fast Pyrolysis for gasification and subsequent upgrading of the syngas.
- Fast Pyrolysis followed by upgrading by hydro-processing or zeolites.
- Hydro-processing, which uses hydrogen to remove oxygen and other contaminants such as sulphur and nitrogen from vegetable oil.

3.2.1. HVO (Hydrotreated Vegetable Oil)

Hydrotreating of vegetable oils is a modern way to produce high-quality biobased diesel fuels without compromising fuel logistics, engines, exhaust aftertreatment devices, or exhaust emissions. Hydrotreating of vegetable oils as well as suitable waste and residue fat fractions to produce HVO, is a quite new but already mature commercial scale manufacturing process. In this process, hydrogen is used to remove oxygen from the triglyceride vegetable oil molecules and split the triglyceride into three separate chains, creating hydrocarbons which are similar to petroleum diesel fuel components. This allows blending in any desired ratio without any concerns regarding the fuel properties.

Figures published by the Renewable Energy Directive 2009/28/EC (“RED”) show that life cycle greenhouse gas emissions of HVO are slightly lower than those of FAME if both are made from the same feedstock.

Chemically Hydrotreated vegetable oils (HVOs) are mixtures of paraffinic hydrocarbons and are free of sulphur and aromatics with considerably high cetane number and good oxidation stability, (*Neste Renewable Diesel Handbook*). It has the highest heating value of the existing biofuels and low tendency to form deposits in the fuel injection system. In those cases that an isomerization stage is included. HVO has no cold operability issues with severe winter grades.

On the other hand compared to FAME, there are few companies that have invested to produce hydrogenation derived renewable diesel, so eventually its current availability is still low. HVO as well as BTL should meet the specifications contained in EN 15940 for paraffinic diesel fuels.

3.2.2. BTL (Biomass to Liquid)

Biomass-to-liquid or BTL is a process that transforms biomass to a usable form of biofuel. The production process is based on Fischer-Tropsch synthesis for converting lignocellulosic biomass into synthetic liquid hydrocarbons

A great advantage of BTL is the fact that when burned, it does not produce non-renewable carbon dioxide. Therefore BTL is carbon dioxide neutral and has no impact on the enhanced greenhouse effect. BTL can be blended with marine distillate fuel, according to EN ISO 8217-2017 but there is more experimental research to be done concerning the optimum ratio of biofuel and marine distillate fuel that will be aligned with the requirements of EN ISO 8217.

4. The Use of FAME, HVO and BTL in Marine Distillates

The percent of ester-type biodiesel fuel (e.g. FAME derived from used cooking oil) that can be added to a marine distillate fuel is up to 7% v/v. Neat biodiesel contains almost no sulphur, so SO_x (sulphur oxide) exhaust emissions are practically zero. Biodiesel when blended with marine distillate fuel at a predetermined percentage (up to 7% v/v) leads to remarkable improvement of the conventional marine fuels’ lubricity. The increasing addition of biodiesel in marine distillate fuel brings significant improvement in the cetane index of the resulting blends and in their ignition point. With the percentage increase of biodiesel mixed with the conventional marine fuel, the sulphur content of the mixture is considerably reduced. The cold flow properties of the blends (Cloud Point, Pour Point, and Cold Filter Plugging Point - CFPP) are slightly comprised by the addition of increasingly quantity of biodiesel, since a slight increase in these properties is observed (*T. Tyrovolá et al.*).

The great concern with biodiesel lies between the variant quality of the biofuel; the impact of the fuel system components; the possible loss of the engine manufacturer’s

warranties; the unfavorable hydroscopic properties; the impact on the cold flow parameters and the limited long term storage stability, (*Potential of biofuels for shipping - Final Report*).

By blending 10% of HVO into marine distillate fuel quality is not compromised while it reduces exhaust emissions and enhances engine operation. In fact, the fuel blends are proven to be of premium grade since their cetane number is increased and the aromatic content is decreased, resulting in reduced exhaust emissions and satisfactory cold-start performance. HVO fuel also contains almost no sulphur so the SO_x exhaust emissions are practically zero. When blended with marine distillate fuel in increasing proportions it lowers the sulphur content of the mixtures. HVO fuel meets the diesel fuel specification and is as safe as the diesel fuel. The cold flow properties in the case of mixtures of marine distillate fuel with HVO are remarkably improved since by gradually mixing marine distillate fuel with hydrogenated vegetable oil, the resulting mixtures exhibit better cold properties and they can be used in more severe conditions.

The lubricity of neat HVO corresponds to that of sulfur-free fossil diesel and GTL diesel fuels. Without any lubricity additives the HVO doesn't meet the HFRR (High Frequency reciprocating Ring) - ISO 8217 requirement of < 520µm for protecting fuel injection equipment against wear. So when blended with marine distillate fuels it cannot enhance the lubricity of the resulting mixtures, As it is already mentioned FAME addition is proven to amend lubricity properties in ultra low sulphur marine distillate fuels. This trade-off in marine distillate's properties for blends with FAME and renewable diesel is indicative that both fuels could be used simultaneously and complement each other in marine diesel fuel blends. .

Both HVO and BTL are paraffinic diesel fuels with several fuel advantages over transesterified lipids. HVO and BTL have higher cetane number, implying easier ignition and more efficient combustion, better storage stability, better cold properties and less tailpipe NO_x emissions. They also have higher renewability fraction of the fuel (97%–98% and renewable mass inputs versus 90% renewable mass inputs of transesterified lipids). In case HVO is produced from waste feedstock with low upstream impacts, the high conversion efficiency of the HVO production process will make HVO the preferred fuel to BTL from any woody feedstock, even woody waste.

5. Conclusion – Acknowledgments

Strict regulations on emissions and reports on harmful effects associated with the use of traditional marine fuels are driving the marine industry to adopt alternative fuels. Many ship operators, with present-day propulsion plants and marine fuels, cannot meet the new regulations without installing expensive exhaust after treatment equipment or switching to low-sulfur diesel, ultra-low-sulfur residual, or alternative fuels. All of them contain properties that reduce engine emissions below mandated limits but impact bottom-line profits.

Thus the search for alternative fuels which will satisfy fully or partially the new emission regulations and sulfur

limits without compromising the economy, has been brought to limelight worldwide.

The shipping industry is starting to understand the potential of truly sustainable biofuels as an emerging solution. Driven by both regulatory and market factors, biofuels could make up 5-10% of the total global marine fuel mix by 2030. For the market to properly embrace marine biofuels as a viable long-term solution, they must be comparable and compatible with current shipping fuels. They must also be truly sustainable; adhering to principles concerning all aspects of the biofuel chain, including the environmental, social, legal, local and global effect of biofuel extraction, production and delivery.

The commercial marine use of biodiesel involves compression ignition engines, boilers and gas turbines. Biofuels are sulphur-free, thus their uses can reduce the SO_x problem from shipping. The emissions of particulate matter will be also significantly reduced resulting in a reduced health risk and finally only renewable CO₂ will be emitted during combustion.

The increased awareness of human induced environmental crisis has created an interest in using cleaner renewable energy instead of fossil fuels. Marine transport is one of the sectors with the fewest available alternatives to fossil fuels, (*Overview of Alternative Fuels and Their Drivers to Reduce Emissions in the Shipping Industry*). On a technical level, the introduction of alternative fuels is accompanied by additional complexity, in the areas of fuel supply infrastructure, rules for safe use of fuels on board, and operation of new systems. Over the last years, barriers for biofuels deployment have moved from the biofuels technology to policy and financing. Commercialization depends on political leadership and adequate policies, as it is recognized that innovative energy technologies are not yet cost-competitive against conventional biofuels and fossil fuels they aim at displacing.

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