The Effect of Fatty Acid Methyl Esters and Hydrogenated Vegetable Oils on Oxidation Stability, Cold Properties and Lubricity of Marine Distillate Fuels

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Abstract: Shipping plays a vital role in the world economy. Around 90% of the world’s trade is transported by ship in a cost-effective and reliable manner. Global shipping is responsible for 2-3% of the total global CO₂ emissions. In addition, shipping accounts for up to 4-9% of all sulphur, and 10-15% of all nitrous oxide emissions. Without taking any measures, these emissions would more than double as seaborne trade is expected to further grow from 30 billion tonne miles in 2006 to more than 100 billion in 2050. To counter these emissions the international community has developed frameworks for energy efficiency measures, as well as emission reduction targets for SOₓ and NOₓ in appointed ECAs (Emission Control Areas). Biofuels satisfy fully or partially the new emission regulations and sulfur limits without compromising the economy. The goal of this work is to study and evaluate the physicochemical properties of conventional marine distillate fuel and its blends with renewable-alternative fuels (UCOME (Used Cooking Oils Methyl Esters) and HVO (Hydrogenated Vegetable Oils)).

Key words: Marine fuel, distillate fuel, biofuels, ECAs, emission reduction.

1. Introduction

Shipping is the backbone of global trade and the lifeline for island communities, carrying about 90% of the capacity of all traded goods, as estimated by the International Chamber of Shipping. It consists of a relatively pure form of transportation (per pound of material) and is effective simultaneously.

Sustainable transport is recognized as one of the biggest challenges of the 21st century [1]. The maritime industry is currently facing a period of rapid growth in global demand for transport, with corresponding increase in ship fuel consumption and emissions. Maritime transport accounts for over 80% of world trade by volume and for approximately 3% of global greenhouse gas emissions. International shipping uses in majority heavy fuel oil (residual fuel) with a very high sulphur content. The marine fuel currently in use is on average 2,700 times dirtier than the fuel used in the road sector, where strict limits have been applied for many years.

Today, the contribution of shipping industry to sulphur oxide (SOₓ), nitrogen oxide (NOₓ), PM (Particulate Matter) and carbon dioxide (CO₂) emissions, is considerable. These polluting emissions have great negative impact on world environment, affecting not only the populations living near ports and coastlines, but also those living hundreds of miles inland [2]. Due to the poor quality of bunker fuels used in maritime transport, SO₂ shipping emissions are projected to increase and by 2020 exceed SO₂ emissions from all land-based sources such as power plants in the European Union.

Thus the need for reduction of harmful emissions is mandatory. International regulatory bodies such as the IMO (International Maritime Organization) and national environmental agencies of many countries...
have issued rules and regulations that drastically reduce the allowable GHG (Greenhouse Gas) emissions emanating from marine sources. These new rules are impacting ships that engage in international and coastal shipping trade, the cruise industry, ship owners and operators.

The IMO, the legal governing body for International Shipping and subsidiary organ of the United Nations, sets global sulphur limits for marine fuels as per the International Convention Marine Pollution (MARPOL)—Annex VI Regulations for the Prevention of Air Pollution from Ships [3]. MARPOL Annex VI sets limits on NOx and SOx emissions from ship exhausts, and prohibits deliberate emissions of ozone depleting substances. Annex VI of MARPOL was adopted in September 1997 so to address air pollution from shipping. It contains regulations for the prevention of air pollution from ships and addresses the specifications of marine fuels and engines.

The revised Annex VI entered into force on 1st July 2010, setting limits on sulphur oxide and nitrogen oxide emissions from ship exhausts as well as PM and prohibiting deliberate emissions of ozone depleting substances, such as chlorofluorocarbons [4]. In October 2012, the regulations were officially transposed in Europe. Under the current European Union regulations:

From 2015, ship sailing in the sulphur ECAs (SOx) cannot use fuel with more than 0.1% of sulphur. European ECAs currently include the Baltic Sea, the North Sea and the English Channel;

Globally, ships have to cut their fuel’s sulphur content to a maximum of 0.5% in 2020.

In Europe only, passenger ships sailing outside ECA SOx will have to respect a limit of 0.5% sulphur fuels, which was set in 2005.

MARPOL Annex VI also includes progressive reductions in NOx emissions from marine diesel engines. NOx emissions are restricted to certain limits (Tier I, II and III) based on the ship’s construction date and the area of operation. Within each of Tier specifications, the NOx emission limit is set based on the ship’s rated engine speed. The Tier I and II limits apply to marine diesel engines installed on ships constructed on or after January 1st 2000 and January 1st 2011 respectively. Replacement engines and additional engines installed on existing ships will be required to meet Tier II standards. These limits apply in all areas not designated as NOx ECAs. The more stringent Tier III emission limit for NOx takes effect for marine diesel engines installed in ships whose keels are laid on or after January 1st 2016 if operating within the North American and United States (US) Caribbean Sea ECA NOx areas. This emission limit is equivalent to approximately an 80% reduction of NOx emissions from marine diesel engines.

2. The International Standard EN ISO 8217 for Marine Fuels

The International Standard ISO 8217 specifies the requirements of residual and distillate fuels for use in diesel engines and boilers of ships. The fifth (previous) edition of EN ISO 8217:2012 takes into consideration the main issues related to the use of low sulphur distillate fuel. Marine fuel must be free of biofuels outside the levels “de minimis” of FAME (Fatty Acid Methyl Esters). “De minimis” is considered the quantity of biofuel that makes the fuel suitable for use in marine applications. The level “de minimis” for fuel oil distillates is indicated to be 0.1% v/v FAME [5].

The demand for use of distillate fuels with extremely low sulphur content in marine engines has led to further research and data collection that allowed the incorporation of FAME in specific marine distillate grades. The sixth edition of EN ISO 8217:2017 is now available and the final draft specifies the requirements of fuels for use in marine diesel engines and boilers, prior to conventional on-board treatment (settling, centrifuging, and filtration) before use. The sixth edition cancels and replaces the previous one, since it has been technically revised [6]. The sixth edition reflects important and
significant changes and includes substantial amendments to the scope and to the general requirements. Changes to the distillate fuels include the following:

Additional grades, DFA (Distillate FAME A), DFB (Distillate FAME B) and DFZ (Distillate FAME Z) have been added with a maximum FAME(s) content of 7% V/V.

The fuel oil distillates are allowed to contain not only “hydrocarbons from petroleum crude oil” but also from oil sands and shale, and hydrocarbons from synthetic or renewable sources. Hydrocarbons from synthetic and renewable sources are similar in composition to and in practice indistinguishable from petroleum hydrocarbons.

The DF (Distillate FAME) grades have been introduced to allow for greater use of automotive diesel in the marine distillates pool, which is expected to improve fuel oil availability in some ports which may otherwise struggle to provide fuels complying with a 0.10% sulphur limit to ships.

3. Biofuels for Use in Marine Waterways

Currently the easiest way of reducing pollutants from ships is by adopting the wide use of low sulphur fuels. Low sulphur fuels can make the ship’s engine run smoother and with less operating problems and maintenance costs. The increasing demand for clean fuel sources in the marine industry has led to the growing demand of alternatives for fuelling the shipping industry. The use of alternative fuels satisfies the new emission regulations and sulphur limits hence without compromising the economy.

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 are carbon-neutral renewable and capable of being cultivated in many different environments. They are flexible, since they can be blended with conventional fossil fuels and burned in conventional internal combustion engines or act as alternative fuels. In the future these are expected to increasingly replace chemicals derived from fossil oil.

3.1 The Transition from the 1st Generation Biofuels to 2nd Generation Ones

The first generation biofuels are made from feedstock that can also be consumed as human food. The first generation biofuels are derived from sources like starch, sugar, animal fats and vegetable oil [7]. The oil is obtained using the conventional techniques of production. Some of the most popular types of first generation biofuels are: biodiesel, vegetable oil, biogas, bioalcohols and syngas.

In the near future, ships are friendlier to the environment with reduced emissions, greater durability requirements and with cleaner fuel than today. Moreover, they must be able to operate in all weather conditions, even at very low temperatures in some markets.

First generation biofuels manufacturing faces important implications. They are limited in their ability to achieve targets for oil-product substitution, climate change mitigation and economic growth. The cumulative impacts of these concerns have increased the interest in developing biofuels produced from non-food biomass. Unlike first generation biofuels, second generation biofuels (or else advanced biofuels), are different from the first-generation ones to the fact that the raw materials that are used to produce them are not food crops. They are made from lignocellulosic biomass or woody crops, agricultural residues or waste. The main second-generation routes are the thermochemical routes (gasification, pyrolysis, torrefaction) and the biochemical routes (biochemistry). In second generation biofuels included the following: methyl esters derived from UCO (Used Cooking Oils), biomethanol, bio-hydrogen, bio-methane, butanol, mixed alcohols, lignocellulosic alcohol, HVO (Hydrotreated Vegetable Oil).

By 2030, biofuels are expected to play an important
role in the energy sector and provided that significant quantities of these can be produced in a sustainable manner and at an attractive price, at least 10% of the maritime fleet in the world could be powered by biofuels.

3.2 Evaluation of FAME and HVO Technologies

The liquid biofuels that are of great concern in the Marine Industry and in this study are 2nd generation biodiesel derived from UCO and hydrogenated vegetable oil (HDRD: Hydrogenation Derived Renewable Diesel) or HVO.

Biodiesel, chemically known as FAME is the most common type of biofuel used in the European countries. It is obtained by transesterification from fatty acids based on triglycerides. Biodiesel can be used for various diesel engines after mixing up with mineral diesel [8]. It provides significantly reduced emissions of CO, PM, unburned hydrocarbons, and sulphates compared to petroleum diesel fuel. Biodiesel provides excellent lubricity to the fuel injection system. By blending biodiesel in amounts as little as 2%, the lubricity of the conventional marine fuel can be dramatically improved, and the life of an engine’s fuel injection system is extended. Nevertheless it faces a number of challenges as its concentration increases in terms of: (a) storage stability, (b) formation of deposits in vehicle’s fuel, (c) engine oil compatibility and (d) lifetime of exhaust after treatment systems.

HVO is a renewable, paraffinic fuel produced from either vegetable or animal sources. In the HVO production process, hydrogen is used to remove the oxygen from the triglyceride (vegetable oil) and integration to an existing oil refinery is preferred for small plants. It can be mixed with conventional marine fuel at any blend without any problem as they have similar properties. The HVO is an alternative method for production of renewable fuels for use in maritime engines and due to the very low CFPP (Cold Filter Plugging Point), it can be properly used during winter months at fairly low temperatures. It has a superior quality that helps lower NOx and HC (Hydro-Carbon) emissions and it is more stable than biodiesel during long-term storage.

Hydrotreating is a more advantageous procedure over transesterification in terms of lower processing cost, compatibility with infrastructure, existing engines and fuel standards, and flexibility in terms of feedstock. Nevertheless there are few companies that have invested to produce HDRD, so eventually its current availability is still low.

4. Experimental Measurements and Discussion

The base fuels that are used are the following:

Distillate Marine Fuel grade A-DMA: Fuel properties comply with EN ISO 8217:2017 (as shown in Table 1).

Biofuel 1: Biodiesel/FAME derived from used cooking oils (UCOME: Used Cooking Oils Methyl Esters). Biodiesel complies with the European Standard EN ISO 14214:2012 (as shown in Table 2).

Biofuel 2: HVO-NEXBTL or Neste Renewable Diesel. HVO is specified in the CEN (European Committee for Standardization) standard EN 15940:2016 for paraffinic fuels made from synthesis or hydrotreatment and it is a high cetane paraffinic diesel fuel (as shown in Table 3).

The goal of this study is the addition of renewable-alternative fuels: a. 2nd generation biodiesel-UCOME and b. hydrogenated vegetable oil-HVO in conventional marine fuel DMA grade (Tables 4, 5), in order to measure and evaluate the physicochemical properties of both base fuels and their blends.

Three different types of blends are studied:

- DMA-UCOME (2%v/v, 5%v/v, 7%v/v);
- DMA-HVO (5%v/v, 10%v/v, 15%v/v, 20%v/v, 25%v/v);
- DMA-20%v/v Blend of the two biofuels (UCOME2%v/v-HVO18%v/v, UCOME5%v/v-HVO15%v/v, UCOME7%v/v-HVO13%v/v).
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. UCOME when blended with marine distillate fuel at predetermined percentages, reduces considerably fuel’s sulphur content, as indicated in Table 4. The increasing addition of biodiesel in marine distillate fuel brings significant improvement in the CI of blends. The cold flow properties of the blends (CP, PP and CFPP) are slightly comprised by the addition of increasing quantity of UCOME.
A small increase in cloud point, pour point and CFPP values is recorded. Density and viscosity of the blends increase gradually as the mixing rate of UCOME rises. In biodiesel, those two properties are higher than diesel fuel, therefore the mixture of the conventional marine fuel and biodiesel will be slightly more viscous and denser. EN ISO 12156-1 specifies the HFRR (High-Frequency Reciprocating Rig) method, for assessing the lubricating property of diesel fuels, including those fuels which may contain a lubricity-enhancing additive. It applies to fuels used in diesel engines.

After extensive research on the lubricity of diesel fuel, global specifications for automotive fuels introduced the HFRR method. The ship fuel pumps (as also the car fuel pumps) rely on the fuel as a lubricating agent. The lubricity of blends improves with the gradual mixing of UCOME with DMA. When plugging in UCOME in DMA fuel we observe significant influence on fuel’s lubricity even by adding minor amount such as 2% v/v. The average wear scar diameter (WSD 1.4 corrected to 1.4 kPa pressure) of blend UCOME2 (98% DMA-2% UCOME) is 141 μm less than that of DMA fuel. The repeatability (R) of EN ISO 12156-1 (±70 mm) method is based on the technique of visual observation. In all the lubricity measurements, their standard deviation has been taken into account (Figs. 1-3).

In Table 5, it is sighted that the viscosity of the conventional marine fuel and HVO blends gradually decreases, as well as their density (as the mixing rate with HVO increases). With the percentage addition of HVO in DMA we observe a sizeable increase in fuel’s Cl. The sulphur content of blends decreases as the percent admixture of HVO increases. The HVO is an almost zero sulphur fuel, free from aromatics and oxygen. In the supreme blend HVO25 (75% DMA-25% HVO) there is a significant decrease in fuel’s sulphur content (sulphur decreases in 740 ppm). The cold flow properties in the case of DMA-HVO blends are remarkably improved, since the gradual mixing of the marine distillate fuel with hydrogenated vegetable oil, offers to the fuel lower values in cloud point, pour point and CFPP. With improved cold
properties, marine distillate fuel can be used in severe weather conditions with very low temperatures. Unlike the even declining WSD 1.4 with the percentage addition of biodiesel in conventional DMA, the gradual addition of HVO in DMA aggravates fuel’s lubricity. The WSD 1.4 of HVO25 blend is 551 μm. By taking into account the bias of the measurement (±35 mm) the average wear diameter [516 < WSD 1.4 < 586] based on the lower assessment (516 μm) is within the limit of EN 12156-1 method and based on the upper assessment is outside the permissible limit.

The oxidation stability of fuels was estimated in accordance with ASTM D7545. The patented RSSOT (Rapid Small-Scale Oxidation Test) provides a complete oxidation stability analysis of petroleum products automatically in a very short test time. The temperature was determined at 160 °C.

The percentage addition of biodiesel in the marine conventional fuel reduces oxidation stability of blends, as shown in Table 6. On the contrary, the percentage addition of HVO does not affect significantly the oxidation stability of blends. Oxidation stability of blends is close to the initial value of the base fuel DMA. The addition of HVO at any rate does not have remarkable influence on fuel’s oxidative stability (Table 7). Finally, based on the fact that HVO tends to worsen fuel lubricity when increasing the rate of blending and due to its limited availability yet, great interest lies on blending DMA with specific proportions of both biofuels: UCOME and HVO. Due to the limitation that EN ISO 8217:2017 imposes on biodiesel addition (7% v/v), the three new blends that are examined are the following: DMA (80%)-FAME (2%)-UCOME (18%), DMA (80%)-FAME (5%)-UCOME (15%), DMA (80%)-FAME (7%)-UCOME (13%).

The values of kinematic viscosity and density of blends are lower than those of base fuel, but still as the blending proportion of biodiesel rises, so does the viscosity and density of blends (Table 8). The CI of blends has an ascending march and as the percent addition of HVO rises, so does the CI of the blend. DMA-UCOME2-HVO18 has the same CI as HVO20 blend and DMA-UCOME5-HVO15 has the same CI as HVO15 blend. The sulphur content of the fuel is substantially reduced, compared to the sulphur content of the initial base fuel DMA. All three blends have almost the same content in sulphur. The conventional fuel’s lubricity, due to the addition of biodiesel, is gradually improving.

The oxidation stability of the blends is considerably reduced compared to the corresponding value of DMA base fuel (Table 9).

In these blends the oxidation stability of the most oxidative unstable is outweighed (UCOME). Therefore, the blends with higher percent of biodiesel are less oxidative stable.

### Table 6 Oxidation stability of DMA-UCOME blends.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA</td>
<td>1:42:20</td>
</tr>
<tr>
<td>UCOME2</td>
<td>1:15:20</td>
</tr>
<tr>
<td>UCOME5</td>
<td>1:01:11</td>
</tr>
<tr>
<td>UCOME7</td>
<td>0:50:32</td>
</tr>
</tbody>
</table>

### Table 7 Oxidation stability of DMA-HVO blends.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA</td>
<td>1:42:20</td>
</tr>
<tr>
<td>HVO5</td>
<td>1:34:03</td>
</tr>
<tr>
<td>HVO10</td>
<td>1:48:41</td>
</tr>
<tr>
<td>HVO15</td>
<td>1:44:37</td>
</tr>
<tr>
<td>HVO20</td>
<td>1:34:41</td>
</tr>
<tr>
<td>HVO25</td>
<td>1:44:33</td>
</tr>
</tbody>
</table>
Table 8  Properties of DMA-UCOME-HVO blends.

<table>
<thead>
<tr>
<th>Fuel type properties</th>
<th>Unit</th>
<th>UCOME2-HVO18</th>
<th>UCOME5-HVO15</th>
<th>UCOME7-HVO13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity at 40 °C</td>
<td>mm²/s</td>
<td>3.5555</td>
<td>3.5691</td>
<td>3.6844</td>
</tr>
<tr>
<td>Density at 15 °C</td>
<td>kg/m³</td>
<td>845.2</td>
<td>848.3</td>
<td>851.2</td>
</tr>
<tr>
<td>CI</td>
<td>-</td>
<td>55</td>
<td>54</td>
<td>53</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>Mass%</td>
<td>0.0810</td>
<td>0.0800</td>
<td>0.0790</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Pour point</td>
<td>°C</td>
<td>-11</td>
<td>-10</td>
<td>-10</td>
</tr>
<tr>
<td>CFPP</td>
<td>°C</td>
<td>-4</td>
<td>-5</td>
<td>-5</td>
</tr>
<tr>
<td>Lubricity, WSD 1.4 at 60 °C</td>
<td>μm</td>
<td>485</td>
<td>402</td>
<td>352</td>
</tr>
</tbody>
</table>

Table 9  Oxidation stability of DMA-UCOME-HVO.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA</td>
<td>1:42:20</td>
</tr>
<tr>
<td>DMA-UCOME2-HVO18</td>
<td>0:38:36</td>
</tr>
<tr>
<td>DMA-UCOME5-HVO15</td>
<td>0:22:03</td>
</tr>
<tr>
<td>DMA-UCOME7-HVO13</td>
<td>0:17:56</td>
</tr>
</tbody>
</table>

![Fig. 1](image)

Fig. 1  The effect of percent addition of biodiesel on marine distillate fuel’s lubricity.
The Effect of Fatty Acid Methyl Esters and Hydrogenated Vegetable Oils on Oxidation Stability, Cold Properties and Lubricity of Marine Distillate Fuels

Fig. 2  The effect of percent addition of HVO on marine distillate fuel’s lubricity.

Fig. 3  The effect of addition of biodiesel and HVO on marine distillate fuels’ lubricity.
5. Conclusion

The percentage mixing of biodiesel derived from used cooking oils with marine distillate fuel has a significant impact on oxidation stability and lubricity of the fuel. Sulphur content is considerably limited and the impact on mechanical engine parts is minimized. HVO has better functionality and efficiency at low temperatures over biodiesel. 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, without clogging fuel filters [9]. Without any lubricity additives the HVO does not meet the HFRR requirement of \( \leq 460 \, \mu m \) for protecting fuel injection equipment against wear; when blended with marine distillate fuels it cannot enhance the lubricity of the resulting mixtures. As soon as HVO is blended with biodiesel (up to 7% v/v), the resulting mixture biofuel can be added to the conventional marine distillate fuel. Thus, the lubricity of fuel is improved as well as the CI. The sulphur content is also positively affected.

The market has moved to the point where sustainable marine biofuels are no longer at an experimental stage—they are already proving a commercially viable solution and increasing numbers of ship owners are open to the idea of exploring their potential. Biofuels are clearly in a strong position to provide solutions. They can already offer ship operators a way to reduce a vessel’s CO\(_2\) emissions by 80-90%. They eliminate SO\(_x\) emissions, cut NO\(_x\) emissions by 10% and cut PM expelled in a ship’s exhaust plume by 50%.

The product can be either delivered by truck or barge as a pre-blended finished grade or alternatively as “drop-in” fuel whereby the biofuel is almost instantly mixed with gasoil on board, as the compatibility of both products in most locations is high. Drop-in biofuels are liquid hydrocarbons that are functionally equivalent to petroleum-derived fuels, meaning that they can be effectively “dropped in” to existing infrastructure on board vessels. That means biofuels can be used with little or no change to existing infrastructure. They are comparable and compatible with current shipping fuels and can be delivered using existing logistics.

The supply chain for biofuels is rapidly maturing, resulting in greater efficiency and leading to more competitive pricing. HVO has a shelf life which is much longer than normal petro-carbons, has virtually no contaminants and, of course, generates no sulphur emissions. It generally emits lower levels of NO\(_x\) and meets Tier II standards, although like traditional fuels, an SRC (Selective Catalytic Reduction) system is needed for Tier III compliance [10]. Second generation biodiesel can play a vital role in meeting the energy demands of marine industry. It can be generated from the marginal and waste lands which require less maintenance, less soil fertility and less water. The waste cooking oil (used cooking oil) is a valuable feedstock for biodiesel production, as its price is 2-3 times cheaper than the virgin vegetable oils in most of the countries of the world except the EU [11]. However, it is noted that in the EU the cost of waste cooking oil is higher than that of the fresh vegetable oil because of the double counting in the Renewable Energy Directive 2009/28/EC (RED) policy.

Despite the great advantages, significant barriers, which have moved from the biofuels technology to the policy and financing, arise. 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. The stricter regulations on emissions have forced the shipping industry to look for alternatives to conventional fuels. In any case, ship operators are alive to the idea that “drop-in” biofuels can really cut emissions and offer operational and financial advantages in the near future.
References