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Full Length Article

Comparison of fuel properties of alternative drop-in fuels with standard marine diesel and the effects of their blends

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ABSTRACT

Drop-in fuels are biofuels or synthetic fuels designated to be blended with conventional petroleum-derived hydrocarbons. These alternative fuel blends can be used without major modifications of the engine or the fuel system. Thus, the use of drop-in fuels offers the marine sector a good first opportunity to reduce the carbon footprint and other emissions. This work investigates the miscibility and compatibility of different potential drop-in fuels with standard distillate marine diesel in order to provide an initial outlook on possible use in the maritime sector based on their fuel characteristics. The five drop-in fuels Fatty acid methyl esters (FAME), Oxymethylene ether (OME), Hydrotreated vegetable oils (HVO), Fischer-Tropsch diesel (FTD) and a pyrolysis oil (HDO) were mixed at 10, 30 and 50 % with standard marine distillate diesel and the physical and chemical properties, the distillation curves and the corrosion stability as well as the storability were analysed. All drop-in fuels can be blended with DMA. Due to the chemically different composition of OME, the distillation curve of the blends significantly differs from the distillation curve of DMA, which should be taken into consideration when using these new alternative blends. Furthermore, the blends of OME and FTD show an unexpected corrosion, which is not observed in the pure drop-in fuels. This is expected to have a considerable influence on the engine operation as well as on the storage.

1. Introduction

The finite nature of fossil resources and especially environmental concerns associated with the combustion of fossil fuels are leading to an increasing interest in developing new alternative fuels. The marine transport sector is still highly dependent on fossil fuels and currently responsible for around 2.5–3 % of global CO_2 emissions [1,2]. The common fuels in this sector are heavy fuel oil (HFO), marine diesel oil (MDO) or marine gas oil (MGO) [3]. In order to reduce emissions and global warming, the European Union (EU) implemented the “Fit for 55” plan, which was first published in June 2021 [4]. This initiative focused on expanding sustainable shipping in the EU. The plan aims to reduce CO_2 emissions from shipping in the EU by at least 50 % by 2050 in order to meet the EU’s climate targets. To achieve this goal, the EU has presented a number of measures, including:

1. Encouraging the development and use of alternative fuels, such as bio-based fuels and synthetic fuels.
2. Supporting the development of low-emission ship propulsion systems, such as fuel cells and hybrid propulsion systems.
3. Introduce taxes and levies that penalize the use of fossil fuels in shipping.
4. Promotion of energy efficiency in shipping by introducing minimum standards for the energy efficiency of ships [5].

Furthermore, the International Maritime Organization (IMO) has also set itself the goal to reduce the carbon intensity of shipping by 70 % and the total greenhouse gas emissions (GHG) by at least 50 %, compared to 2008 [6,7]. Both regulations are leading to an increased demand for environmentally friendly propulsion solutions.

The current aim for many stakeholders is to find alternative non-fossil fuels (low-carbon-fuels or carbon-neutral fuels) that have similar properties to the known petrochemical fuels, so that preferably no modifications to the engines, fuel systems and bunkering are required. A first promising medium-term solution to gradually reduce CO_2 emissions are drop-in fuels obtained from different processes [8,9]. Drop-in fuels are similar to conventional fossil fuels such as gasoline, diesel, and

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natural gas. This fact makes drop-in fuels miscible with fossil fuels or they can be used directly as a replacement. They are often produced from renewable or abundant feedstocks and are intended to reduce reliance on fossil fuels and emissions of greenhouse gases. Examples of drop-in fuels include biofuels made from plant material, synthetic fuels produced from carbon dioxide and hydrogen, and renewable natural gas made from organic waste. However, the development of these alternative fuels as well as the expansion of the fuel infrastructure is still in the early stages and studies have shown that shipping companies must expect higher prices [10,11]. The available alternative fuels are not yet mature, therefore there is no clear choice of the 'one fuel' for the entire world fleet [12]. In addition, most of these fuels have not yet been extensively tested in ship engines and standardisation is in an early development stage. Thus, testing the compatibility of these new fuels with marine diesel or heavy fuel oil and analyzing their fuel properties in the laboratory are very important before the fuel is used.

In this study, a standard marine diesel is blended in different proportions with various other drop-in fuels, and the properties of the blends are investigated. The following selected bio and synthetic fuels can be classified as carbon-neutral fuels that do not cause greenhouse gas emissions (GHG) or whose GHGs are neutralized along the value chain [13].

Oxymethylene ethers (OMEs) represent one of the novel synthetic fuels. OMEs, especially OMEs with a chain length of $n = 3–5$, are liquid fuels with a similar viscosity to marine diesel, hence it could be directly used as drop-in fuel and substitute one part of the diesel [14]. Comparing the chemical composition of both fuels, it can be observed that OME contains more oxygen. This leads to a significantly lower soot formation during combustion and also to a lower NOx emission [15,16]. In addition, OME exhibit a high cetane number [17]. OMEs can produced from renewable methanol, therefore the overall CO_2 emissions can be reduced [18,19].

Synthetic fuel can be produced using the gas-to-liquid (GTL) process. In this process, the liquid fuels are obtained from natural gas with the use of the Fischer-Tropsch technology [20,21]. Fischer-Tropsch fuels (FT) have a number of advantageous properties compared to fossil diesel such as virtually no sulphur, very low levels of aromatics, no nitrogen and high cetane number [22]. Furthermore, FT diesel is expected to be an ideal alternative to fossil diesel due to the very similar fuel properties such as viscosity, flash point and cold properties [23].

Fatty acid methyl esters (FAME) produced from vegetable oils are also an alternative fuel. It is also possible to use recycled waste vegetable oils such as used cooking oils. FAME offers many advantages such as renewability, reduced exhaust emissions, absence of sulphur and a higher flash point [24]. The higher polarity of FAME leads to improved lubricity, whereby component wear could be reduced. However, FAME can decompose over time and form peroxides, acids or other insoluble components, which also lead to an increased viscosity [25,26].

Hydrotreated vegetable oils (HVO) are a biofuel produced from vegetable oils by complete hydrogenation. The oxygen is completely removed from the triglyceride vegetable oil molecules and by splitting, mixtures of straight chain saturated hydrocarbons are formed [25,27,28]. Due to this chemical structure, they are very similar to fossil-based fuels such as marine diesel. Furthermore, HVOs have a high cetane number, good oxidation stability and are free of sulphur. In blends with marine distillate fuel, the HVO remarkably improve the cold properties [25]. All these properties support the use of HVOs as a drop-in fuel.

Another new innovative bio oil is obtained from sewage sludge by using the Thermo-Catalytic Reforming process. In the final production process, a hydrodeoxygenation (HDO) is carried out to minimize the oxygen as well as the water content. In this way, HDO diesel is generated, which has similar properties to standard diesel [29].

For a better overview, Table 1 once again shows the various production processes or sources of the used drop-in fuels.

All blends as well as the pure fuels are analysed with regard to their physical and chemical properties such as kinematic viscosity, density, flashpoint and pourpoint. In addition, the boiling curve of the fuels and the chemical composition are determined by gas chromatography coupled with a mass spectrometry (GC/MS). Furthermore, the corrosion stability and the storability of the blends were evaluated to give an outlook on the handling of the fuels on board of a ship.

Table 1
Overview of the drop-in fuels and their individual raw material sources or production process.

Drop-in Fuel	Sources/Process
FAME	Vegetable oils
FT diesel	Gas-to-liquid
OME	Power-to-liquid (e-Fuel)
HVO	Hydrotreated vegetable oils
HDO diesel	Pyrolysis oil

2. Materials and methods

2.1. Materials

The marine diesel (DMA) was provided by Hans Rinck GmbH & Co. KG, supplier of Marine Bunker Fuels in Germany. The HDO diesel was provided by the Fraunhofer Institut Umsicht from Sulzbach. The other fuels were provided by ERC Additive GmbH. The HVO is a "care diesel" that has already been pre-additivated.

2.2. Preparation of the blends and analytical methods

The marine diesel was blended at 10 %, 30 % and 50 % with the drop-in fuels fatty acid methyl esters (FAME), Fischer-Tropsch diesel (FTD), Oxymethylene ether (OME), Hydrotreated vegetable oils (HVO) and HDO diesel. The respective quantities were combined gravimetrically.

Marine fuels must comply with the specifications of DIN ISO 8217:2018. All fuel blends to be investigated should also comply with this standard. Consequently, the physical and chemical properties of all samples were analysed according to the corresponding standard specifications as listed in Table 2.

The distillation of the fuels was carried out with a fully automated device OptiDist from PAC – Walter Herzog GmbH. For this propose, 100 mL of each fuel was placed in a round bottom flask and continuously heated to a maximum distillation rate was 5 mL min^{-1}.

The long-term stability of maritime fuels is essential, to be able to keep reserve of fuel on ships. In case of sludge formation during the storage period or due to temperature influences, this could lead to clogging of the fuel pipelines, pumps or filters. To accelerate possible aging effects, the samples were heated to 43 °C for 12 weeks. One week at 43 °C corresponds to one month of storage at a normal temperature of 21 °C [30]. In addition, 1 % water was added to simulate the increased water vapours on board of a ship. The water vapours can condense as a result of temperature decrease and increase the water content in the fuel. Furthermore, seawater ingress through venting pipes is possible.

Corrosion effects are also a problem during storage of the fuels. The corrosion stability was determined in the same way, except that an iron nail was added to the current sample. The X-ray fluorescence spectroscopy (XRF) was performed with the ARL Optim'X from Thermo Fisher. For this purpose, 8 g of the sample were filled into a cuvette, measured

Table 2
Methods.

Property	Method
Flash point	DIN ISO 2719
Density	DIN ISO 3675
Pour point	ASTM D5950
Kinematic viscosity	DIN ISO 3104

under helium atmosphere and evaluated with a stored calibration of the selected elements sulphur and iron.

ATR (attenuated total reflection) measurements were performed using a Thermo Scientific Nicolet iS50 equipped with a Specac Golden Gate Diamond unit.

The composition of the fuels with regard to individual chemical components was analysed by GC/MS (gas chromatography/mass spectrometry). An ISQ 7000 coupled with a Trace 1310 GC instrument (Thermofisher Scientific) was used equipped with a TG-SQC column.

3. Results and discussion

3.1. Miscibility and general fuel properties

Marine diesel was mixed in proportions of 10 %, 30 % and 50 % with the various drop-in fuels. First, a purely visual observation of the mixtures was carried out to evaluate the miscibility. All mixtures were clear and in one phase, thus complete mixing can be expected. In addition, the complete miscibility can be confirmed by measuring the sulphur content using XRF measurements, as shown in Fig. 1. Fig. 1 shows the sulphur content as a function of drop-in content. The marine diesel exhibits the highest sulphur content with 868 ppm (0,087 w.%) as shown in the illustration in the 0 % drop-in fuel point. An increase in the amount of drop-in fuel leads to a decrease in the sulphur content, since the alternative drop-in fuels are sulphur free. For all drop-in fuels FAME, FTD, HVO, OME and HDO the measured sulphur contents are almost on a straight line. The tolerable deviations may have been caused by measurement-specific errors, such as the instrument-specific measurement error of the XRF device, as well as minor weighing errors.

Table 3 shows further physical and chemical characteristics of the feedstocks and blends. The flash point is of particular importance for a trouble-free operation as fuel in the marine transport sector. According to standard DIN ISO 8217:2018, the flash point of the fuel used to transport a ship must be at least 60 °C. Where the flash point of the used fuel is below 60 °C, special safety-relevant modifications must be implemented on the ship. With a value of 63 °C OME has the lowest flash point and FAME with a value of 169 °C the highest flash point of the drop-in fuels. Thus, no conversion of the entire fuel system is necessary when using these selected drop-in fuels.

The kinematic viscosity and lubricity of the fuels significantly influences the operating conditions not only of the fuel pumps and the injection system but of the whole fuel system including supply, circulating, transfer and feed pumps. In ISO 8217:2018 the minimum viscosity of distillate fuels is specified as to be no lower than 2 mm^2s^{-1} at a temperature of 40 °C. The measured viscosities are presented in Tables 3 and 4. The standard marine diesel, DMA 100, has a kinematic viscosity of 4.5 mm^2s^{-1}. The drop-in fuels, with the exception of FAME (FAME 100), exhibit lower viscosities in a range of 1.2–2.8 mm^2s^{-1}. Accordingly, all analysed fuel blends show lower viscosities than the reference component DMA 100. Therefore, it should be considered to install, if not already present, a fuel cooler or even a chiller (meaning an active refrigeration cycle) to keep the viscosity of those fuel blends to reach the required minimum viscosity of 2 mm^2s^{-1} at the engine inlet. There are mainly three problems with low viscosity fuel. Firstly, a lack of the hydrodynamic oil film which could lead to failures of pumps and secondly the internal plunger leakage losses in the fuel system will be much higher. This will result in lower fuel flow rates. Combined with the third problem, the inability to build up sufficient pressure for the injection, would effect the engine combustion, especially in low-load performance operations. In cam driven fuel injection systems, injection pressure is a function of engine speed and load. At low load, the pressure drops, resulting in very large fuel droplets that survive until they contact the combustion chamber surfaces. Engines with common-rail injection systems suffer from the same effects and are even more sensitive to low-viscosity fuels. However, within certain margins, variations in viscosity can be compensated by the flexible control system. Engines with a common-rail system are by design more tolerant towards low viscosity fuels. Increased engine and pump wear, however, will influence the tolerance for these fuels [31,32].

The pour point is the lowest temperature at which the fuel will flow under given conditions. The pour point values of the used fuels and prepared blends are listed in Tables 3 and 4. As shown in Table 3, all drop-in fuels have a lower pour point and thus better cooling properties than the standard marine diesel DMA. Accordingly, it is to be expected that the pour points of the blends will decrease as the content of drop-in

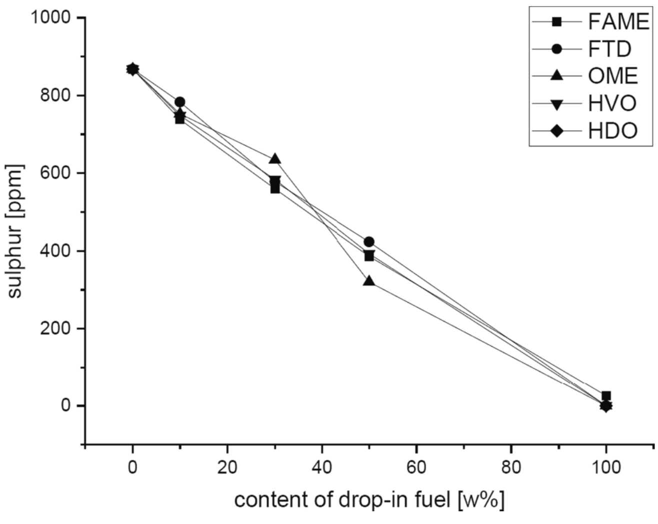

Fig. 1. Sulphur content as function of the drop-in content.

Table 3
Physical properties of the DMA and the potential drop-in fuels.

Sample	Viscosity at 40 °C [mm^2s^{-1}]	Density at 15 °C [$kg\ m^{-3}$]	Flash point [°C]	Pour point [°C]
DMA 100	4,52	864	102	−9
FAME 100	4,55	876	169	−11
FTD 100	2,53	763	71	−29
OME 100	1,18	1071	63	−21
HVO 100	2,88	766	76	−60
HDO 100	2,38	821	99	−16

Table 4
Physical properties of the drop-in blends.

Sample	DMA content [w%]	Drop-in content [w%]	Viscosity at 40 °C [mm^2/s^2]	Pour point [°C]
FAME 10	90	10	4,47	−9
FAME 30	70	30	4,41	−9
FAME 50	50	50	4,39	−9
FTD 10	90	10	4,19	−10
FTD 30	70	30	3,65	−13
FTD 50	50	50	3,23	−16
OME 10	90	10	3,56	−10
OME 30	70	30	2,58	−10
OME 50	50	50	1,95	−7
HVO 10	90	10	4,22	−10
HVO 30	70	30	3,81	−16
HVO 50	50	50	3,46	−20
HDO 10	90	10	4,17	−10
HDO 30	70	30	3,61	−12
HDO 50	50	50	3,19	−17

fuel increases. However, this only applies to the blends with FTD, HVO and HDO. The blends FAME 10, FAME 30 and FAME 50 exhibit the same pour point as DMA 100 in spite of the fact that the pour point of FAME 100 is 3 °C lower. Therefore, this small difference in the pour point between DMA 100 and FAME 100 has no influence on the pour point of the blends.

OME 10 and OME 30 exhibit the same pourpoint with a value of −10 °C. For OME 50, a pour point of −7 °C was measured and a phase separation was observed after the analysis. For further characterisation, an ATR spectrum was obtained from each phase, as shown in Fig. 2 and Fig. 3. The upper phase contains DMA and OME, Fig. 3. This fact becomes clear by comparison with the ATR spectrum of DMA and is indicated by the following characteristic bands. The peaks at 2921 cm^{-1} and 2852 cm^{-1} assigned as CH_2 and CH_3 stretching vibrations. At 1456 cm^{-1} and 1376 cm^{-1} are the C–H deformation vibrations of CH_2/CH_3. The presence of both types of vibrations confirms that DMA is present in this phase. In addition, this phase shows broad and strong bands in the range from 1102 cm^{-1} to 915 cm^{-1}. These corresponds to OME and represent the C-O stretching.

The ATR spectrum of the lower phase is shown in Fig. 3 in comparison to OME 100. The typical bands for CH_2 and CH_3 of the aliphatic chains of DMA 100 are not clearly detectable. Instead, the bands of the C-O strechting vibrations in the range from 1102 cm^{-1} to 915 cm^{-1} are definitely more prominent than in the upper phase. This indicates that the proportion of OME is significantly higher in this phase or even that only OME is present. The density of OME 100 is with value of 1071 kg m^{-3} noticeably higher than the density of DMA 100. The difference in density between DMA 100 and OME 100 also suggests that OME is in the lower phase. It seems that this difference in the density becomes more pronounced at lower temperatures and is therefore responsible for the separation of the two fuels. Due to this phase separation, it can be assumed that no exact pour point could be determined and that the value of −7 °C is incorrect. The pour point values of OME 10 and OME 30 should therefore also be evaluated with caution.

The density difference between DMA 100 and the other drop-in fuels is lower and has no influence on the miscibility of the fuels.

3.2. Distillation

The boiling or distillation curve of a fuel describes the proportion of evaporated liquid at different temperatures. On the one hand the measuring of the distillation curve is to ensure the quality of the fuel. Especially in case of new blends, it is necessary to ensure that there are no boiling gaps. On the other hand, the distillation curve provides insights into how the fuel will behave under different temperature conditions. The distillation curve of a fuel is directly related to its combustion characteristics and gives information's about optimizing combustion efficiency. The temperature range in which the fuel vaporizes depends on its chemical composition. Fig. 2 shows the boiling curves of the pure 100 % fuels. The temperature at which the first steam rises at the distillation head is the initial boiling temperature (IBT) of the individual fuel [33]. The temperature difference between 10 % and 90 % can be used to determine the chemical uniformity of the individual fuels. All measured temperature values and the temperature difference described above are summarised in Table 5. The pure DMA sample has an IBT of 217 °C and a finial boiling point (FBP) of 376 °C. The difference between 10 % and 90 % amounts 93 K and the boiling curve rises steadily in this range, Fig. 4.

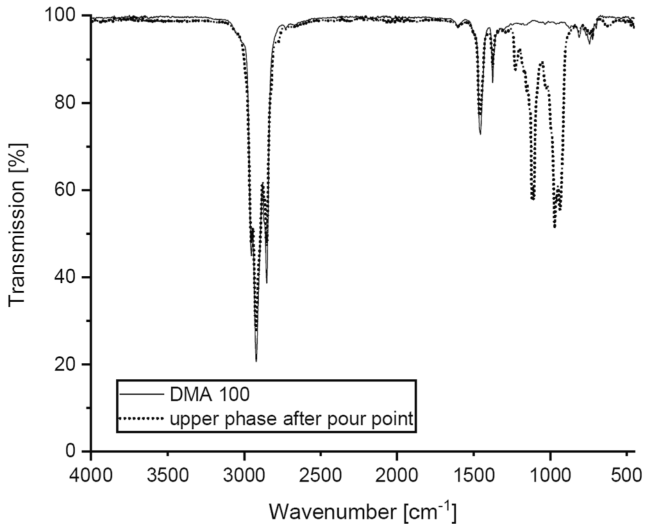

Fig. 2. ATR spectra of DMA 100 and the upper phase of the blend OME 50 after pour point measurement.

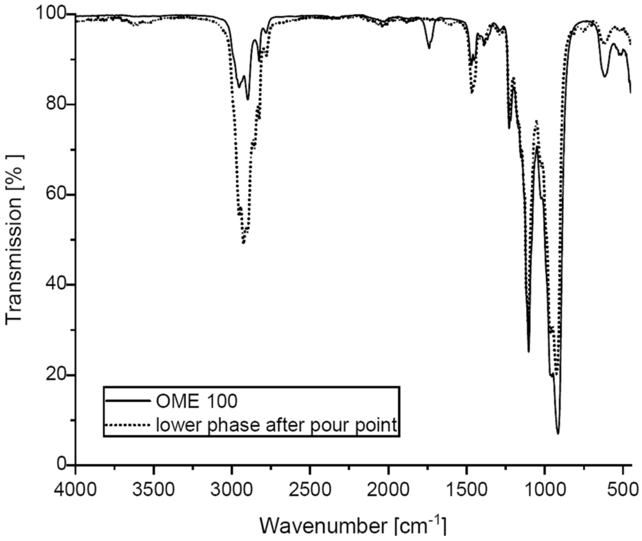

Fig. 3. ATR spectra of DMA 100 and the lower phase of the blend OME 50 after pour point measurement.

DMA consists of a large number of different hydrocarbons, which can mainly be classified as different paraffins with a low aromatic content (Fig. 5). The GC measurement provides additional information of the chemical composition (Fig. 6). The paraffinic chain is growing as the retention time increases up to a time of about 24 min. At this point the molecular weight is the highest, which also results in the highest FBP compared to the other fuels. In summary, the sample DMA 100 has components with the highest molecular weight compared to the other alternative drop-in fuels.

The distillation curve of the pure FAME (sample FAME 100) is shifted to higher temperatures compared to the DMA 100 sample (Fig. 4). The temperature difference between 10 % and 90 % distillation volume

Table 5
Results of distillation.

Sample	Initial boiling point [°C]	Final boiling point [°C]	Temperature difference between 10 and 90 % [K180]
DMA 100	217	376	93
FAME 100	257	350	11
FTD 100	174	340	124
OME 100	146	249	72
HVO 100	188	293	32
HDO 100	227	293	46

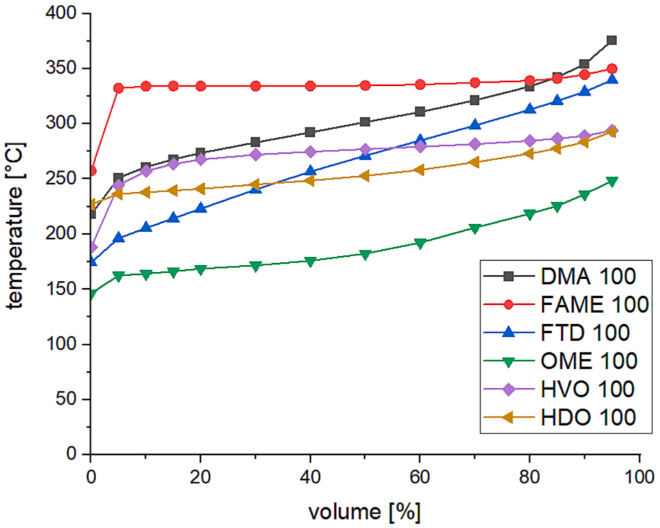

Fig. 4. Distillation curves of the pure fuel samples.

amounts only 11 K. Therefore, the boiling curve shows only a short increase up to 5 % distillation volume and then remains almost horizontal on a straight line. The linearity of the curve is the result of the fact that FAME consists of very few chemical components. Accordingly, the chromatogram of FAME 100 shows a main peak at a retention time of 18.8 – 19.2 min (Fig. 6). The peak belongs to different derivatives of a fatty acid methyl ester with a chain length of C$_{19}$. Thus, the pure FAME 100 has an almost constant boiling point and the chemical composition changes only insignificantly with increasing distillation volume. This boiling curve is disadvantageous for good fuel ignition and combustion in the cylinder [34]. The problem of a flat boiling curve during combustion is due to the fact that after reaching the initial boiling point almost the entire fuel evaporates and ignites abruptly. Consequently, the permissible ignition peak pressure may be exceeded. This leads to increased engine wear or can even cause the total failure of a cylinder. In addition, sound and NOx emission would increase while soot emissions would be lower.

The distillation curves of the blends with FAME show that the starting temperature as well as the further temperatures are higher up to a distillation volume of 85 % than for the pure DMA sample (Fig. 7). Above 85 %, the components of the DMA dominate again the course of the curve. Accordingly, the disadvantages described above for FAME100 with a flat distillation curve are reduced in the blends with DMA.

Fischer Tropsch diesel is a synthetic fuel with a uniform linear paraffinic composition. The chromatogram of the GC/MS measurement shows main peaks at regular intervals of 1.5 min with smaller peaks in between (Fig. 6). These peaks represent the main fraction in which the chain length increases by one CH$_2$ group with each peak. Branched hydrocarbon chains are located in between. The uniform structure is responsible for the straight-line rising course of the distillation curve, Fig. 7. The boiling points of the individual paraffinic chains rise continuously and uniformly as the molecular size increases. For this reason, the temperature difference between 10 % and 90 % distillation volume is with a value of 124 K the highest difference compared to the other drop-in fuels, Table 3. The total distillation curve is lower than the curve of DMA 100. This shows that FT diesel is easier to vaporise and forms a combustible air-fuel mixture more quickly. This results in distillation curves of the mixtures are below those of the pure DMA, however, they show similarly increasing course (Fig. 7, right).

OME has the lowest initial and end boiling temperature of all drop-in fuels (Table 3). The chromatogram shows that this drop-in fuel has a completely different chemical structure than DMA. OMEs are oxygenated compounds with different chain lengths (Fig. 3). According to the GC/MS measurement, the used OME sample has a maximum chain length of 5. Due to the significantly lower molecular weight, the distillation curve is much smoother compared to DMA 100, Fig. 8. The mixture OME 10 has an low IBP and at the end the curve behaves like that of DMA 100. In contrast, the OME 30 and 50 blends exhibit non-azeotropic behaviour. At about 40 to 50 % distillation volume, all OME is distilled out and the curve slope increases. The lower boiling temperature of OME can lead to a better fuels atomisation and a better air mixing, resulting in more efficient combustion and lower emissions. On the other hand, the lower boiling temperature can also lead to higher fuel consumption in order to achieve the same performance compared to a fuel with a higher boiling temperature. The reason for this is that the lower distillation curve also leads to a lower energy density. Accordingly, a larger tank would have to be installed to be able to achieve the same distance as with DMA.

The distillation curve of HVO shows a rapid increase at the beginning up to about 240 °C and then runs on a straight line with a slight slope up to the FBP of 293 °C, which is significantly lower than for DMA 100. The IBP, with a temperature of 188 °C, is also significantly lower than for DMA. This results from the higher content of short-chain paraffinic components, which range between retention times of about 4 to 8 min in the chromatogram (Fig. 6). The difference between 10 % and 90 % distillation volume amounts only 32 K. The last peak in the chromatogram is at a retention time of 15.88 min and most likely corresponds to a C$_{18}$ or C$_{19}$ compound according to the mass spectrum. Therefore, the curve is smoother compared to standard marine diesel, which contains significantly higher molecular weight components with higher boiling points. The three blends, HVO 10, 30 and 50, show a similar course to DMA 100 at lower temperatures (Fig. 8).

HDO 100 and DMA 100 exhibit almost the same IBP. However, the FBP of HDO 100 is with a temperature of 293 °C significantly lower than the FBP of DMA 100. Accordingly, the boiling curves of the blends also proceed at a lower temperature, Fig. 9. The temperature difference

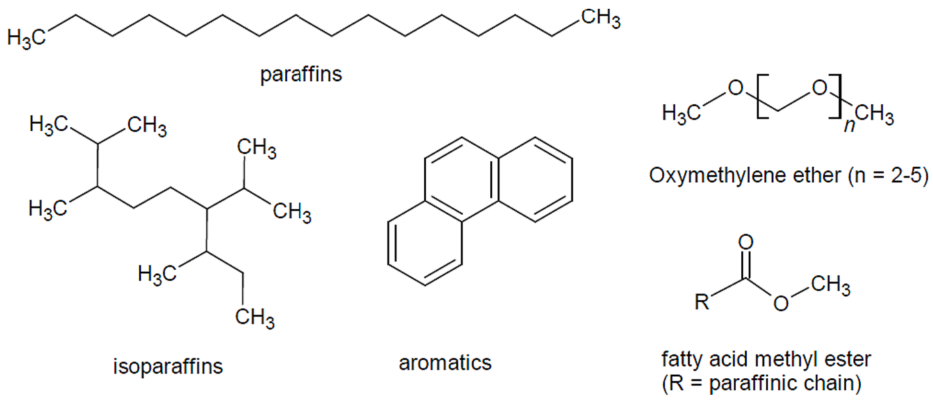

Fig. 5. Different components of the fuels.

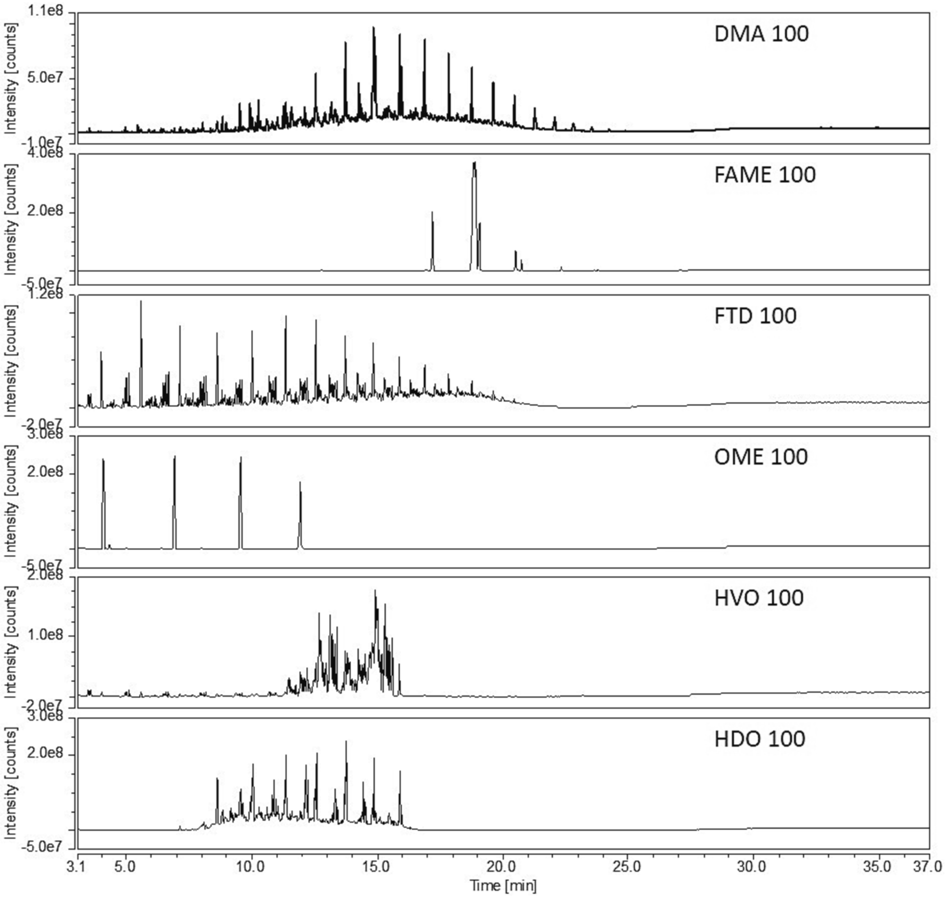

Fig. 6. Chromatograms of the drop-in fuels.

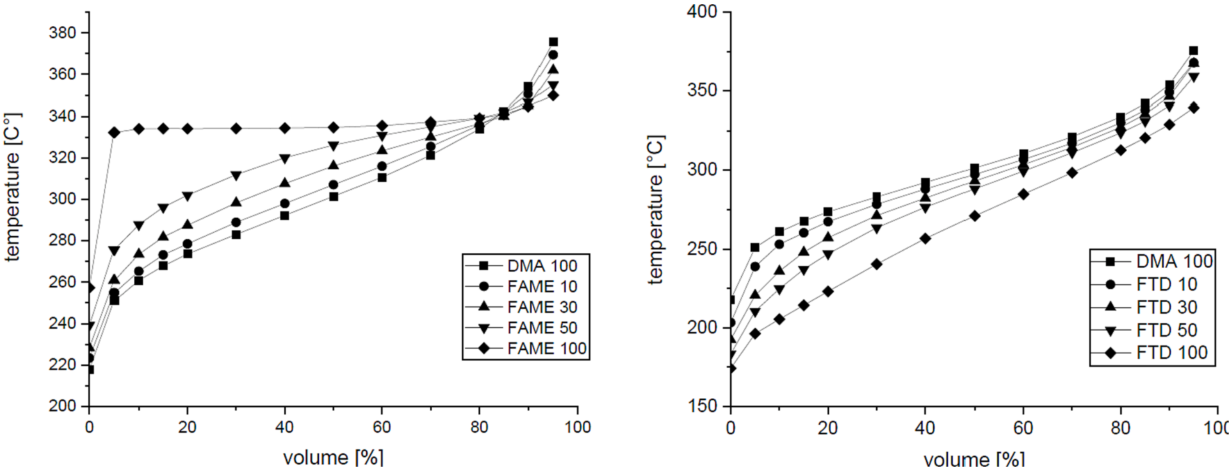

Fig. 7. Distillation curves of the blends with FAME (left) and the blends with FTD (right).

between 10 % and 90 % distillation volume amounts for the pure HDO diesel 46 K, Table 5. The reason for this is the same as for HVO. The HDO diesel also contains fewer high molecular weight compounds.

3.3. Storage and corrosion stability

The storage stability and corrosion resistance were also tested. After 12 weeks, the samples were visually inspected to see if any compounds had precipitated. The kinematic viscosity was measured again with the result that the long thermal stress showed no effect on the viscosity. The blends with FAME, FTD, OME and HVO as well as their pure starting fuels show good aging resistance at the selected conditions. In contrast, the HDO-diesel and the blends thereof show significant precipitation already after the first week, which increased over time. Fig. 10 shows the sludge formation (brown sediment) at the bottom of the sample bottle after 12 weeks. Thus, with the HDO diesel, there is a greater risk that aging effects will cause problems on board of the ship.

Furthermore, an iron nail was added to each sample and thermally stored under the same conditions. This experiment is intended to simulate a possible corrosion attack on the tank material or other

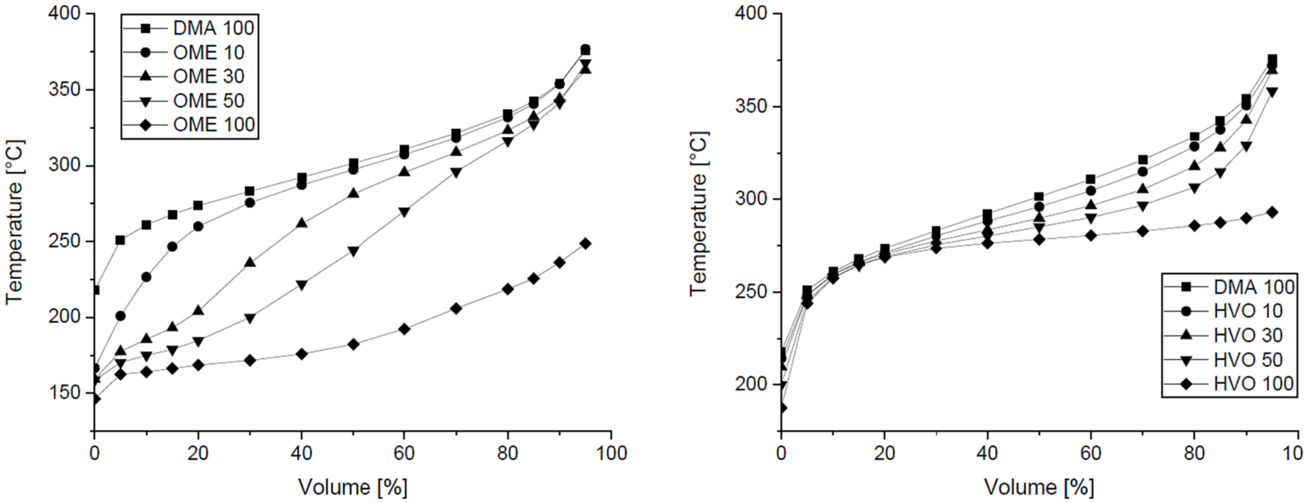

Fig. 8. Distillation curves of the blends with ome (left) and the blends with hvo (right).

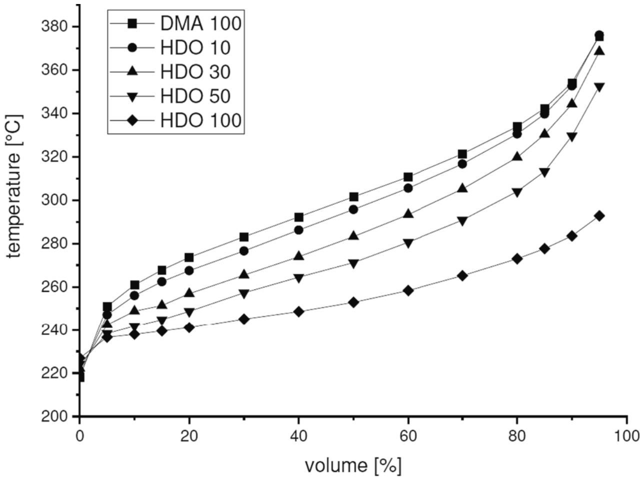

Fig. 9. Distillation curves of the blends with HDO.

Fig. 10. Aging effects of the HDO samples after 12 weeks at 43 °C.

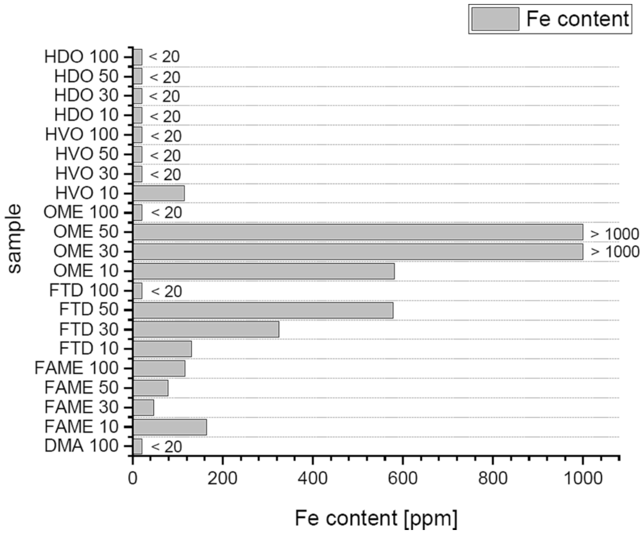

Fig. 11. Fe content after 12 weeks stored with an iron nail.

components. After 12 weeks, the iron nail was removed and the iron content in the liquid fuel samples was determined by X-ray fluorescence. For this purpose, the samples were shaken to achieve a uniform distribution of the iron in the sample.

The result of the measurement is shown in Fig. 11. As expected, the sample DMA 100 shows only a very low iron content after the 12 weeks. In contrast, the blends with FAME as well as the pure FAME sample exhibit higher iron contents. The sample with 10 % biodiesel shows an value with about 160 ppm iron. In comparison with the other biodiesel blends, 30 % and 50 %, no trend is discernible. Whereas for the Fischer Tropsch diesel, a clear increasing trend can be observed with an increase in the proportion of FTD. From 130 ppm iron at 10 % FTD, the iron content increases up to 580 ppm at 50 % FTD. In contrast the pure FTD 100 alone shows no corrosive influence on the nail. The same behaviour and even more clearly can be observed for the blend with OME. In this case, the iron content increases significantly to over 1000 ppm. The tests were repeated again with the same results. The corrosion process in fuels is complex and depends on the one hand on the solubility of water and on the other hand on the solubility of oxygen in the individual fuels. The oxygen solubility decreases with the increase of density, molecular weight and boiling point of hydrocarbons [35]. It can be assumed that these ratios are particularly favourable to each other in the fuel blends and accelerate corrosion. However, this complex phenomenon requires further investigation. In the case of FAME, the addition of water causes hydrolysis of the esters and possible formation of free fatty acids, which accelerates the corrosion process [36,37].

The samples with HVO as well as with HDO diesel exhibit only a low iron content and therefore these fuel blends do not lead to corrosion.

4. Conclusion

The potential of five different drop-in fuels for standard distillate marine diesel was investigated by measuring the fuel properties to provide an outlook on the possible usage of these fuels. For this purpose, the five selected drop-in fuels with different chemical origin, were successfully blended with a standard marine diesel in various proportions. The complete mixing could be verified by measuring the sulphur content.

FAME, FTD, HVO and the HDO diesel shows similar distillation curves as marine diesel. This suggests that these fuels can be used as drop-in fuels in marine diesel at least up to a content 50 %. Within the test series with OME, only the blend with 10 % OME shows a similar distillation curve as the marine diesel. Probably, the motor settings must be adjusted when using OME as drop-in with contents higher than 10 %.

During storage of the samples with HDO diesel at 43 °C, insolubles were formed. Accordingly, the storage stability still needs to be improved. Furthermore, an increased corrosiveness to iron was observed, especially in the blends with FT diesel and OME. It should be noted that the pure drop-in fuels behaved differently from their blends with marine diesel. One possible solution to improve the storage stability and the corrosion stability that is now being investigated is the usage of fuel additives.

As required by regulations the usage of blends with new alternative fuels will increase significantly. As shown in this work it is essential to analyse these new blends as it cannot be assumed that a new fuel, that does not cause problems on its own, can also be used without problems in a blend. Thus, there is need for further research of drop-in fuel blends to achieve a level of operational safety that satisfies all stakeholders in the marine industry.

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CRediT authorship contribution statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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