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Corrosion study on carbon steel immersed in alternative fuels

Fuels - Alternative & New Fuels

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ABSTRACT

The introduction of alternative fuels in international shipping is the most relevant way to decarbonize the marine sector. In addition, adapting low temperature combustion technologies such as reactivity-controlled compression ignition approach to marine engines, aims to increase the total efficiency from the perspective of combustion phasing control, and near-zero emissions. The use of biofuels, methanol and renewable diesel (RD) in RCCI operation has shown improved performance and reduced emissions. However, corrosion of metallic materials in the presence of alternative fuels has become an important concern in various industries, including automotive and marine applications. The compatibility of alternative fuels, especially RD-methanol blends with different metal alloys used in engine components, is not yet fully clear. This paper aims to study the corrosion propensity of carbon steel immersed in two fuels; methanol and methanol-RD blend stabilized by 1-octanol. The blend share was methanol 71%, RD 7%, and 1-octanol 22% based on energy content. The immersion test was conducted for three weeks. After the test, the surfaces of the carbon steels were analyzed by Scanning Electron Microscopy. In addition, the amount of leached trace elements was analyzed from the fuels. The findings will help to better understand corrosion behavior and material compatibility of alternative fuels.

1 INTRODUCTION

The maritime industry faces major challenges due to tightening emission regulations. Traditional diesel fuels used as marine engine fuels are known to emit sulfur oxides (SO_x), nitrogen oxides (NO_x), black carbon and other greenhouse gases (GHG). Limiting these emissions is particularly of interest in vulnerable Arctic regions that are warming at a rate approximately twice as fast as the global average [1]. The International Maritime Organisation (IMO) has set the target to reduce greenhouse GHG emissions from international shipping by at least 20%, intending for 30%, compared to 2008 levels by the year 2030, reaching net-zero GHG emissions by 2050 [2].

The introduction of alternative fuels in international shipping is the most relevant way to decarbonize the marine sector and achieve emission reduction targets. For example, hydrotreated vegetable oil, HVO, is one of the most technologically feasible low carbon fuel options [3], and coupled with carbon capture, its use could achieve zero, or even negative GHG emission levels [4]. Hydrogen, produced from the electrolysis of water, utilizing renewable electricity as power source [5] can be combined with a source of CO_2 to form synthetic renewable hydrocarbon fuels such as methanol [6].

Methanol is an alternative fuel option that has the feasibility of upholding the IMO 2023 strategy on GHG emissions reduction in the maritime industry. Its renewable form can be produced both as a second-generation biofuel and as an electro-fuel from recaptured carbon dioxide (CO_2) and renewable hydrogen (H_2). Recent studies of the techno-economic environmental assessment of the most sustainable routes for methanol production identified that the biogas reforming to methanol process appears to be the most promising way from the economic perspective [7]. The sustainable mode of methanol production, biodegradability, high combustion performance and low GHG emissions characteristics, make methanol a promising candidate as a maritime fuel [8,9]. Methanol has safety concerns such as its high laminar flame velocity, acute toxicity and vague material compatibility which must be considered when planning to burn it in compression ignition (CI) engines [10,11]. However in recent years, there is more knowlegde on methanol material compatibility [12]. For methanol blends with cetane improver, e.g HVO, in monofuel CI alcohol engines, material compatibility needs to be investigated.

Compared to other carbon neutral fuel options such as hydrogen and ammonia, methanol's advantage is that there is already global supply of methanol available and due to its liquid form, methanol is easy to store and handle on board ships [13]. However, the availability of green methanol is still limited [14]. Methanol produced from fossil resources is not considered sustainable and it can cause even more emissions from well-to-wake perspective than the use of fossil marine diesel [13].

Methanol is a high octane and low cetane fuel and therefore not ideal for CI engines without adaptations. Researchers have proposed dual fuel systems where diesel fuel is used as pilot fuel for ignition assistance [15]. Premixing methanol with intake air and using diesel as pilot fuel in a dual fuel concept is the most common way to combust methanol. Another option is to use cetane improvers added to methanol [16].

Prospective routes for emission control also include the use of advanced combustion concepts for low-carbon fuels like methanol. The success of these concepts depends on the fuel reactivity, ignition timing, air-fuel equivalence ratio, exhaust gas recirculation (EGR) and other parameters. The target is to enable low-temperature combustion (LTC), below the NO_x formation temperature and curb soot formation with a well-homogenized mixture [17]. Various low temperature concepts have been developed with unique approaches. According to the increasing order of local temperature and emissions levels, the most researched LTC concepts include homogeneous charge compression ignition (HCCI), reactivity-controlled compression ignition (RCCI), and partially premixed compression ignition (PPCI) [18]. Figure 1 shows the local equivalence ratio – temperature map, illustrating the area of LTC and the emission profiles. Although HCCI has the simplest setup with very low emissions, its drawbacks are difficult ignition control (especially with methanol) and a limited operating load range [19,20].

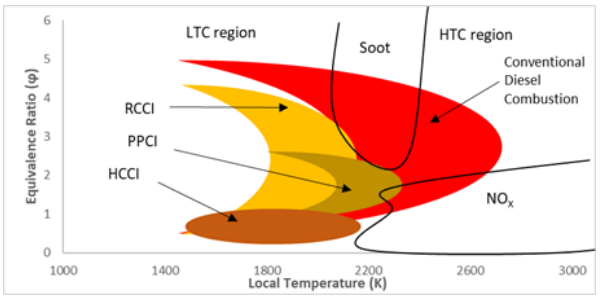


Figure 1. LTC and Conventional CI combustion profile in ϕ – T domain (adapted with emphasis on LTC emission profile from [18]).

The direct mixing of methanol and diesel fuel e.g. renewable diesel (RD), referred to as HVO in the

original publication, is challenging due to their limited solubility [21]. According to [22], methanol-RD blends utilizing 1-octanol as co-solvent are promising options for low temperature combustion concepts based on the blend properties.

The compatibility with metallic surfaces must also be ensured for methanol and its blends. Many surfaces in the engine are in contact with fuel when the engine is running. The fuel system consists of pumps, filters, fuel lines and injectors. When engines are designed for alternative fuels, the possibility of corrosion must be considered by selecting suitable materials. The more homogeneous the metal is, the better it can resist corrosion [23].

Corrosion shortens engine lifespan and may cause various malfunctions and breakage. Malfunction may be avoided by regular maintenance before major engine failure [24]. Corrosion inhibitors are normally used in diesel fuels to prevent corrosion, therefore future fuels may also require these kinds of additives [25,26].

Specifically, methanol is shown to be corrosive in the presence of aluminum and titanium alloys as well as stainless steel, copper, brass and carbon steel [14,27]. The three primary types of corrosion induced by alcohols are general corrosion, dry corrosion, and wet corrosion [27]. Ionic impurities such as water, absorbed atmospheric oxygen, sulfur, chloride ions or acetic acid may affect general corrosion. The hydroxyl groups cause the polarity of the alcohol molecule which again increases conductivity, and this may cause dry corrosion. The strong attraction of methanol to water makes it probable that water will enter to methanol during transportation. The azeotropic formation of alcohol and water produces wet corrosion and this again will activate the acidic corrosion and electrochemical corrosion of metals [27,28].

The study by Wang-Alho et al. [22] revealed that a methanol-RD blend, stabilized with 1-octanol, the blend share being 50:50, did not cause any corrosion in carbon steel. However, pure methanol showed a slight dissolving effect on carbon steel and aluminum [22].

The current study investigated propensity of carbon steel when immersed in two fuels, methanol and methanol-RD blend. All tested fuel batches were intentionally unadditivised to avoid possible variance in results. The blend was stabilized by 1-octanol. The final energy ratio of the blend based on lower heating value (LHV) was methanol 71%, RD 7%, and 1-octanol 22%. The RD content of 7% is considered as ignition enhancer.

Corrosion of carbon steel discs was investigated in response to time. The experiment lasted for 20 days. Carbon steel discs and fuel trace elements were sampled every 5 days during that period. Discs were investigated in a scanning electron microscope, and trace element concentrations were determined in the fuel samples. Basic fuel properties (kinematic viscosity, density, distillation) were analyzed for the methanol (MeOH) and the MeOH-RD-1-octanol stabilized blend in the beginning and in the end of the experiment after carbon steel immersion for 20 days.

2 MATERIAL AND METHODS

The present study was conducted as a laboratory experiment.

2.1 Material

2.1.1 Chemicals and fuel

Methanol was of analysis grade. The renewable diesel was intentionally unadditivised. Properties of the three chemicals are shown in Table 1.

Table 1. Properties of the chemicals and fuel.

Properties	Methanol[1]	RD[2]	1-octanol[1]
Density at 15 °C (kg/m^3)	790 (at 20 °C)	781	828
Kinematic viscosity at 40 °C (mm^2/s)	0.54 – 0.59	3.14	5.58
Boiling point (°C)	64.7	223	196

[1]data from the manufacturer; [2]data according to laboratory measurements [22]

2.1.2 Metal samples

The carbon steel had been cut into discs 2 mm thick and 25 mm in diameter, with a hole in the centre with 8 mm diameter. The material was uncoated. The carbon steel elemental composition as per manufacturer's information is shown in Table 2.

Table 2. Chemical composition of the carbon steel according to the manufacturer's information.

Element	Concentration (%)
C	0.743
Si	0.2560
Mn	0.670
P	0.014
S	0.023
Cr	0.216
Al	0.010
Mo	0.026
Ni	0.047

2.2 Methods

Pure methanol (referred to as MeOH in the following) and one blend of methanol and RD stabilized with co-solvent 1-octanol (referred to as Blend in the following) were investigated. The blend share for methanol and RD was first calculated on energy basis as 90:10 according to their lower heating values (LHV), amounting to a 95:5 vol-% ratio. Then, co-solvent 1-octanol was added until a homogeneous stable mixture of methanol and RD was achieved. This changed the initial volume ratio of methanol to RD. In the end, the volume ratio of the Blend was methanol 83 vol-%, RD 4 vol-%, and 1-octanol 13 vol-%; and the energy ratio based on the LHV was methanol 71%, RD 7%, 1-octanol 22%. The LHVs were 20 MJ/kg for methanol [29], 44 MJ/kg for RD [30], and 37.6 MJ/kg for 1-octanol (measured value). The Blend's LHV was 23.3 MJ/kg. One batch of Blend was prepared and filled into the experimental units.

For both experimental fuels, the pure MeOH and the Blend, multiple 70 mL samples were poured into 100 mL borosilicate bottles. Carbon steel discs were cleaned by rinsing in 2-propanol and removing loose material with a cotton bud, and let to dry. One disc of carbon steel was immersed in each bottle. Additional fuel samples without discs served as control for the 20 d treatment. The bottles were closed with a PE screw cap. The samples were stored in a dark heating cabinet at 23 ºC (MMM Group Venticell Eco line heating cabinet). Every five days, one sample (bottle) per experimental fuel was taken from the cabinet, the carbon steel disc removed from the fuel and the fuel stored in a refrigerator at 8 ºC until further analysis of trace elements. The carbon steel discs were let to dry and stored at room temperature until examination for signs of corrosion in a Scanning Electron Microscope.

Basic fuel properties (kinematic viscosity, density, and distillation) were analysed for the MeOH and the Blend in the beginning of the experiment prior carbon steel immersion, and in the end of the experiment after carbon steel immersion for 20 days.

Two replicate measurements were performed for each experimental fuel and their arithmetic means are presented for density, kinematic viscosity, boiling points, and trace element concentration.

2.2.1 Density and kinematic viscosity

Density at 15 ºC and kinematic viscosity at 40 ºC were determined with a Stabinger SVM 3000 rotational viscometer (Anton Paar GmbH, Austria). The measurements are according to standards EN ISO 12185 for density and standard EN ISO 3104 for kinematic viscosity. The relative standard deviation (RSD) for both methods is <1%.

2.2.2 Distillation

The distillation properties were assessed with an OptiPMD automatic distillation analyzer (PAC L.P., USA). The measurement follows standard ASTM D7345. The RSD for the method is <1.2%.

2.2.3 Trace elements

The trace element concentrations in the fuel samples were analysed with the help of an Inductively Coupled Plasma Optical Emission Spectroscope (ICP-OES). The analysed elements comprised those elements that were the ingredients of the carbon steel, aluminum (Al), manganese (Mn), silicon (Si), sulfur (S), chromium (Cr), molybdenum (Mo), nickel (Ni), and phosphorus (P). In addition, concentrations of copper (Cu), iron (Fe), lead (Pb), vanadium (V), and zinc (Zn) were determined.

Fuel samples were pre-treated in acid digestion. Samples were digested with nitric acid in a microwave oven (MARS 6 iWave by CEM) to decompose all inorganic particles of less than approximately 8 µm size and to destroy remains of organic matrix. The samples were then diluted and analysed in an ICP-OES PerkinElmer Avio 500 (Waltham MA, USA) following an in-house method.

2.2.4 SEM imaging

Scanning electron microscopy was performed on selected carbon steel disc samples. The samples did not need to be pre-treated. The imaging was done with a Zeiss Ultra plus FESEM microscope. Pictures were taken from two places per sample at 200 x, 500 x and 1000 x magnifications.

3 RESULTS

3.1 Density, kinematic viscosity, boiling point

Table 3 presents the density, kinematic viscosity, and initial and final boiling points for the studied experimental fuel samples at the start and at the end of the test. Density of pure MeOH hardly changed during the test. At the beginning of the test density for MeOH was 795 kg/m^3 and after the test density was 796 kg/m^3 for both fuel samples with and without carbon steel discs. Kinematic viscosity of the MeOH fuel sample increased slightly from 0.54 mm^2/s at the beginning of the test to 0.58 mm^2/s at the end of the test in the fuel not containing any disc. The fuel Blend showed some small variation in density and kinematic

viscosity. Density varied more after the test, when density of the Blend without the steel disc was 797 kg/m^3 but with the disc it was 801 kg/m^3. Kinematic viscosity of the Blend increased from the starting value of 0.71 mm^2/s to 0.76 mm^2/s in the sample without the disc after 20 d in the heating cabinet.

Table 3. Density, kinematic viscosity, initial boiling point and final boiling point in the start and at the end of the experiment. MeOH / control and Blend / control refer to fuel samples without carbon steel discs kept for 20 d in the heating cabinet.

Sample	Density at 15 °C (kg/m^3)	Kinematic viscosity at 40 °C (mm^2/s)	Initial boiling point (°C)	Final boiling point (°C)
MeOH / start	795	0.54	64.6	72.0
MeOH / 20 d	796	0.55	64.6	72.6
MeOH / control	796	0.58	64.8	73.7
Blend / start	798	0.71	65.7	266.9
Blend / 20 d	801	0.75	65.8	263.1
Blend / control	797	0.76	66.2	250.2

The initial boiling points did not vary in the MeOH fuel samples nor the Blend samples after 20 days of experiment. The final boiling point showed more variation, which is visualized in Figure 2. The pure MeOH sample showed a final boiling point of 72.0 °C in the beginning of the test. After 20 days in the heating cabinet, the MeOH control sample without carbon steel disc showed a final boiling point of 73.6 °C, that is a 1.7 °C higher value than in the start. The fuel Blend control sample without the carbon steel disc had a final boiling point of 250.2 °C, which is 16.7 °C lower than the final boiling point at the beginning of the test (266.9 °C).

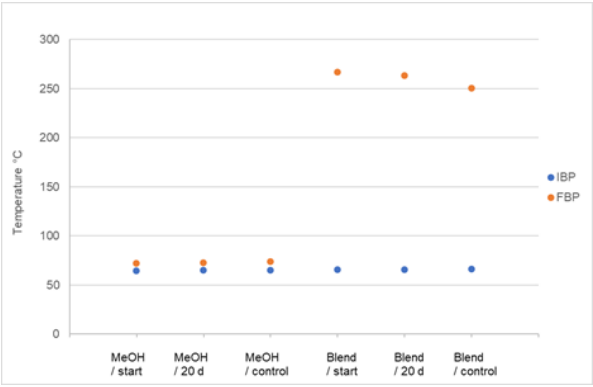


Figure 2. Initial boiling point (IBP) and final boiling point (FBP) in the start and at the end of the experiment. MeOH / control and Blend / control refer to fuel samples without carbon steel discs kept for 20 d in the heating cabinet.

3.2 Trace element concentrations

The concentrations of trace elements Al, Mn, Si, S, Cr, Mo, Ni, and P in the MeOH fuel samples (5 d, 10 d, 15 d and 20 d) and the fuel Blend samples (5 d, 10 d, 15 d, 20 d) were all below the determination limit of the ICP-OES method used (Table 4). In other words, no leaking of elements from the carbon steel discs could be detected over the period of 20 days.

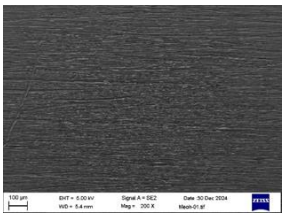
In addition, elements Cu, Fe, Pb, V, Zn were also below the determination limits which were 1 ppm for Cu, Fe, V and Zn, and 4 ppm for Pb. These elements were not expected to be found unless contamination of the carbon steel or fuel components had occurred.

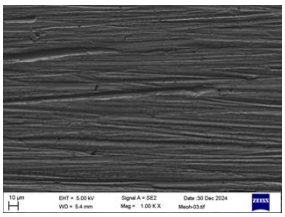
Table 4. Trace element concentrations in the MeOH and Blend samples at the start, after 5 d, 10 d, 15 d and 20 d of carbon steel disc immersion. Control refers to the liquid samples without carbon steel discs.

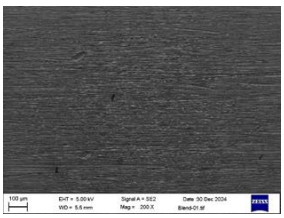
Element (mg/kg) Sample	Al	Mn	Si	S	Cr	Mo	Ni	P
MeOH / start	<1	<2	<1	<4	<1	<1	<1	<4
MeOH / 5 d	<1	<2	<1	<4	<1	<1	<1	<4
MeOH / 10 d	<1	<2	<1	<4	<1	<1	<1	<4
MeOH / 15 d	<1	<2	<1	<4	<1	<1	<1	<4
MeOH / 20 d	<1	<2	<1	<4	<1	<1	<1	<4
MeOH / control	<1	<2	<1	<4	<1	<1	<1	<4
Blend / start	<1	<2	<1	<4	<1	<1	<1	<4
Blend / 5 d	<1	<2	<1	<4	<1	<1	<1	<4
Blend / 10 d	<1	<2	<1	<4	<1	<1	<1	<4
Blend / 15 d	<1	<2	<1	<4	<1	<1	<1	<4
Blend / 20 d	<1	<2	<1	<4	<1	<1	<1	<4
Blend / control	<1	<2	<1	<4	<1	<1	<1	<4

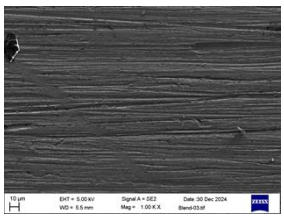
3.3 SEM imaging of carbon steel surface

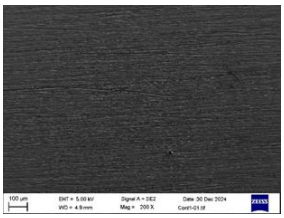
Images of the carbon steel discs after immersion in MeOH and in the Blend for 20 days, and of a carbon steel disc that had not been immersed in any experimental fuel are shown in Figure 3. The SEM imaging did not reveal any signs of corrosion on the disc surfaces from the MeOH and the Blend. They did not appear any different from the control disc either.


MeOH / 20 d, 200 x


MeOH / 20 d, 1000 x


Blend / 20 d, 200 x


Blend / 20 d, 1000 x


Control disc, 200 x

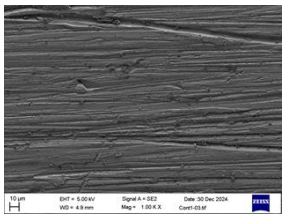

Control disc, 1000 x

Figure 3. Images of carbon steel discs after immersion in MeOH and in the Blend for 20 d, and a control disc that had not been immersed in the experimental fuels. Shown one site per disc at magnification of 200 x and 1000 x.

4 DISCUSSION

The present study investigated whether blending methanol with RD and 1-octanol could produce a fuel mixture with acceptable properties for use in CI engines. There is vast knowledge of methanol compatibility with various metal materials [31,12], but less knowledge of the material compatibility of fuel blends. Since the availability of renewably produced methanol is still limited [14], blending could also help achieving goals of a higher proportion of renewable fuels in the marine sector.

Fuel samples of MeOH and Blend were stored in a heating cabinet over the period of 20 days. The samples also contained carbon steel discs to investigate possible corrosion in the contact of the experimental fuels with metal material used in the engine's fuel supply systems. Based on the results from the present study, there were no changes noticed in the fuel samples nor in the carbon steel samples in this time.

The density, kinematic viscosity, and IBP of the Blend were only slightly higher due to the presence of RD and 1-octanol than the density and kinematic viscosity of the pure MeOH. The study by Wang-Alho et al. [22] tested a fuel blend of methanol and RD based on 50:50% energy density stabilized with 1-octanol. The measured density was 798 kg/m^3, and the kinematic viscosity was 1.33 mm^2/s [22]. In other words, density was the same, but kinematic viscosity was almost twice the value as in the present study. The IBP and FBP of the 50:50 methanol-RD blend were 68 °C and 259 °C, respectively. The initial boiling point is 2 °C higher and the final boiling point almost 8 °C lower than in the present study. Thus, the different blend share was reflected in kinematic viscosity and in the boiling points.

Density, volatility and viscosity are dependent on each other [32]. Slight changes in kinematic viscosity may have been caused by the evaporation of methanol from the Blend and the pure MeOH even though the bottles were closed. The blend consisted mostly of methanol, but the second highest volume ratio was for 1-octanol. Methanol has the lowest boiling point, so its evaporation at 23 °C is more likely than evaporation of the other components. If methanol evaporates, its volume ratio decreases and the ratios of other components increase. Thus, it can be assumed that the properties of the fuel blend change to the direction of the remaining components. Because 1-octanol had the second highest volume ratio in the original blend, blend properties could change towards 1-octanol's properties. According to the results, this would mean an increase in kinematic viscosity. The increase in kinematic viscosity when methanol content decreases is also supported by the study of [22]. The fuel blend containing the same components as in the present study but less methanol had higher kinematic viscosity (1.33 mm^2/s).

For the tested carbon steel quality, no leaching was noticed of elements from the steel discs into the experimental fuels. This observation was corroborated by the SEM images that did not show any noticeable signs of corrosion. Wang-Alho et al. [22] investigated three different steels and one aluminum in immersion tests with methanol-RD (without additives)-co-solvent. No dissolving of elements was noticed. However, in pure methanol, zinc traces were detected after carbon steel immersion. The tested carbon steel had a different composition than the one tested in the present study.

In diesel engines fuel pump and injectors deliver fuel based on volume, and an important parameter for combustion is air-fuel mass ratio [32]. For that reason, density of diesel fuel plays an important role [32]. The viscosity of diesel fuel also has an effect on combustion [32]. Too viscous fuel causes pumping losses, which affects

the injection pressure and deteriorates atomization. On the other hand, too low viscosity causes leakage at the injection pump and if the fuel viscosity is insufficient, the injection pump can seize [32]. The fuel blend studied here should be used with a fuel system designed for methanol. The densities of pure methanol and MeOH-RD-1octanol fuel blend at the beginning of the test vary only by 3 kg/m^3, and the difference in kinematic viscosity was 0.17 mm^2/s.

In diesel engines “the distillation curve of the fuel directly affects the evolution of combustion” [32]. The evolution of combustion is also affected by the atomization of the fuel, which in turn is affected by the fraction portion of the fuel [32]. Therefore, in diesel fuels the proportion of heavy-fraction cannot be too large [32]. In this study the initial boiling points do not differ much from each other both within the same sample and when compared to each other. Correspondingly, with pure methanol the final boiling points are of the same range. The final boiling points of the MeOH-RD-1 octanol fuel blends differ from the values of the pure methanol. This is due to the fact that the blend in part consists of substances with higher boiling points, which distill later in the distillation.

Methanol is seen as a potential fuel for decarbonizing shipping. Safety guidelines and regulations for its use onboard ships have been developed [14]. The IGF Code [33] provides an international standard for ships using low-flashpoint fuels, and the IMO has issued interim guidelines for ships using methyl or ethyl alcohol as fuel [34].

Some of methanol’s properties set higher requirements for safety measures. Methanol has a low flashpoint of only 12 °C, and the flammability range of methanol vapor to air is 6%....36.5%, thus wider than those of ethanol or MGO [31]. In addition, because of its low boiling point and low vapor pressure, methanol evaporates readily at room temperature [35]. In the present study, kinematic viscosity in the end of the experiment after 20 days was slightly higher for the MeOH and Blend samples and their controls as compared to the starting point. It is possible that methanol had evaporated from the glass bottles although the screw caps had been tightly closed, and thus the kinematic viscosity changed slightly.

Based on the results of this study, a longer test period should be considered. Also, a small increase in the test temperature could be justified. Future research should investigate the chemical composition of the fuel blend after some storage time to ascertain whether methanol is evaporating from the blend and to which extend. Additionally, it might be interesting to investigate whether changes in the blend compounds might occur.

5 CONCLUSIONS

This study investigated corrosion propensity of carbon steel discs immersed in pure methanol (MeOH) and in a methanol-RD-1 octanol blend (Blend). The experiment lasted for 20 days. Based on the obtained results, the following conclusions could be drawn.

- Density, kinematic viscosity and IBP were slightly higher in the Blend than in the pure MeOH.
- Density of MeOH or the Blend was not affected in contact with the carbon steel discs over the period of 20 days.
- Kinematic viscosity rose slightly in both experimental fuels over the 20 days. This might have been caused by evaporation of methanol from the bottles.
- Adding RD and 1-octanol to methanol provides a wider boiling range which can be seen from the results when the final boiling points of MeOH and the Blend are compared.
- No trace elements were released from the carbon steel discs into the MeOH nor the Blend over the period of 20 days.
- There were no visual signs of corrosion on the carbon steel discs after 20 days of immersion in the experimental fuels.

In the present study, only minor changes in physical-chemical properties were noticed and no signs of corrosion on the tested carbon steel quality. Overall, this is an encouraging outcome for the perspective for using methanol-RD-1-octanol blends in engines. Further research is still required on combustion.

6 DEFINITIONS, ACRONYMS, ABBREVIATIONS

ϕ: Equivalence ratio

CA: Crank angle

CI: Compression Ignition

CO_2: Carbon dioxide

EGR: Exhaust gas recirculation

FBP: Final boiling point

GHG: Greenhouse gas

HCCI: Homogeneous charge compression ignition

HVO: Hydrotreated vegetable oil

IBP: Initial boiling point

ICP-OES: Inductively coupled plasma optical emission spectrometry

LTC: Low-temperature combustion

MeOH: Methanol

NO_x: Nitrogen oxide

PPCI: Partially premixed compression ignition

RD: Renewable diesel

RCCI: Reactivity controlled compression ignition

SO_x: Sulphur oxide

T: Temperature

TDC: Top dead center

7 ACKNOWLEDGMENTS

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