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Overcoming the technical barriers of methanol and ammonia fuels using additives

Fuels - Alternative & New Fuels

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ABSTRACT

Methanol and ammonia have emerged as front-runners for alternative fuels in the marine industries decarbonisation strategy. However, both fuels are associated with significant technical challenges, such as the lubricity, corrosivity and combustion. In this paper we demonstrate technical solutions to solve challenges in this area. A carefully selected lubricity additive for methanol (additive A) provides lubricity enhancement in both low and high-water content methanol fuels, comparable to that observed in EN590 compliant diesel (as measured by modified HFRR tests). This observation is consistent across varying levels of a common contaminant, chloride. The result is a methanol fuel composition that performs on par with diesel in marine engines in these areas. Additives were also compared to alternative lubricity improving agents, such as fatty-acid methyl esters (FAME), and found to give superior performance in lubricity, cold temperature stability, water compatibility, and filtration time. In addition, it is shown that additive A contributes to a significant reduction in corrosion of steel in methanol fuels, again at varying chloride concentrations. In ammonia fuels, three additives (B, C and D) were studied for their potential to combat the corrosivity of ammonia with steel. A corrosion test method is described, with results indicating significant improvement over an unadditised baseline with both additives. Finally, a combustion improver, additive E, was deployed in ammonia-diesel fuel mixtures. In the test, exhaust gas emissions, measured by FTIR, showed that depending on the operational point, additive E could provide reductions in NH3 and NOx emissions (up to 22 and 9% respectively). The findings of this paper outline how developments in future fuel additives have solved the technical issues of lubricity, corrosion and combustion associated with methanol and ammonia fuels, accelerating their adoption, and enabling the shipping industry to meet its ambitious decarbonisation goals.

1 INTRODUCTION

The International Maritime Organization (IMO) requires the shipping industry to significantly reduce its greenhouse gas emissions and become net zero by 2050.[1] In order to achieve this target, regulations must be implemented concerning, but not limited to, ship machinery, exhaust aftertreatment, logistics, and digitalization. However, it is projected that the greatest reduction in GHG emissions, up to 60%, will come from the replacement of traditional fuels with low- and zero-carbon alternatives such as green methanol and ammonia.[2] Moreover, the shipping industry's dependence on fossil fuels is unsustainable long term due to their finite nature. Adding to this, geo-political issues of relying on fossil fuels, increasing regulatory pressures, and mounting demand from consumers for green shipping, it is clear that a transition to cleaner, more sustainable energy sources is seemingly inevitable.

In this context, green methanol and ammonia have emerged as promising alternative marine fuels. According to classification society DNV's Energy Transition Outlook, ammonia and e-fuels (like methanol) could account for 30% each of marine fuel by 2050, depending on the scenario for the decarbonisation pathway.[2] However, the adoption of these fuels presents operational challenges, particularly in areas such as lubricity, corrosion, and combustion. This paper explores the role of fuel additives in mitigating these drawbacks and enhancing the operability of marine vessels powered by methanol and ammonia.

1.1 Methanol

Methanol, or methyl alcohol, is the simplest alcohol with chemical formula CH_3OH. It is a colourless, volatile liquid at room temperature, with a sharp odour.[3] First isolated by Robert Boyle in 1661 by the pyrolysis of boxwood,[4] methanol is now one of the most widely used chemicals in the world, used as a cleaning agent, chemical reagent, and fuel. Produced industrially from synthesis gas via the hydrogenation of carbon monoxide,[5] most methanol on the market is of very high purity (>99.8% pure). Production from renewable sources such as biomass, organic waste, or green hydrogen and carbon dioxide are increasing but are still only a small minority.

From 1978-2005, the state of California initiated a field trial to convert gasoline vehicles to operate on 85% methanol. It was ultimately unsuccessful due to technical issues and cost of the fuel when compared to gasoline, but provided valuable insight into methanol as a transportation fuel.[6] Today, methanol is the fuel of choice in many automotive racing disciplines. For instance, drag racing, speedway bikes, IndyCar events, and even monster trucks use methanol due to it's high octane rating of 112 and high power output.[7] In recent years green methanol, which is the exact same chemical simply produced from sustainable feedstocks, has gained a lot of interest from the maritime industry as an alternative fuel. Owing to the decarbonisation targets outlined by the IMO, methanol accounted for 12% of the newbuild orderbook in the last 12 months.[8] Retrofit of existing engines is also possible due to the chemical compatibility of methanol with other materials with only relatively minor modifications required. Being a polar solvent, methanol is fully miscible with water and ethanol, making stable mixtures with both in any proportion. This can improve the performance, reduce the cost of the fuel mixture and despite its toxicity, the high degree of miscibility reduces the environmental damage in the event of a chemical spill compared to conventional fuels. Moreover, methanol's easy handling and versatility makes it suitable for applications outside of shipping such as mining, power generation and construction.

Despite the huge potential for methanol as a fuel, there are several commercial and technical challenges that must be addressed. Firstly, even with large investments in green and biomethanol sites across Europe, the production is still not expected to meet demand. Furthermore, the cost of green methanol relative to conventional fuel is significantly more expensive and volatile, inhibiting widespread adoption.[9] The energy density of the fuel is less than diesel to, meaning 2.3x additional storage capacity is needed for the same energy output. It is also hygroscopic, requiring specialised storage to prevent water ingress from the atmosphere into the fuel. Further technical challenges arise from the low viscosity of methanol (0.545 mPa at 25 ^{o}C), making the inherent lubricity of the fuel poor and very likely to damage the engines fuel delivery system, specifically injectors and pumps.[10] Corrosivity of methanol, particularly with copper and steel, is another area of concern.[11],[12] Corrosion is particularly noticeable when soluble chloride ions are present in the fuel, which can arise from some of the chemical processes involved in bio methanol production, and accelerate the corrosion reaction of the metal surfaces with methanol. Finally, compression ignition engines are not yet capable of burning methanol without the presence of a small amount of pilot fuel as a combustion aid. This retracts some of the environmental benefits one might associate with using pure green methanol.

1.2 Ammonia

The absence of carbon enables ammonia (NH_3) to seamlessly align with decarbonisation strategies.

Complete combustion of NH_3 produces only nitrogen (N_2) and hydrogen (H_2) with no CO_2, sulphur or particulate emissions. Whilst gaseous at room-temperature, it can be condensed below -35 °C and easily stored in pressurised or refrigerated vessels. There are several examples of successful implementations of NH_3 fuel. During World War II, due to fossil fuel shortages, Belgium powered buses using NH_3/coal gas hybrid motors and in 1960, the XLR99 engine propelled the "record breaking" North American X-15 rocket using an anhydrous NH_3 and liquid O_2 mixture.[13,14] More recently, the maritime industries are investigating the use of NH_3 as a fuel due to its high energy density relative to H_2 (12.7 vs 8.5 GJ m^{-3}), decarbonisation potential and well-established infrastructure.[15,16]

NH_3 production is a highly energy intensive process, accounting for 2% of global energy consumption.[17] Therefore, any meaningful reduction in anthropogenic GHG emissions by establishing NH_3 as a fuel will require an equivalently ambitious decarbonisation of the global energy grid such as those set out by the European Commission.[18] Predominantly manufactured by the Haber-Bosch process, it was estimated that in 2023, 150 MMT of NH_3 was produced, of which 70% was deployed to the fertiliser industry. [17] Recent forecasts suggest that up to 182 MMT could be utilized as shipping fuel in 2050, accounting for 39% of the global NH_3 market share, underpinning the scientific and financial incentives to develop cleaner routes to ammonia production.[19]

The expected transition to NH_3 fuel will not be without its challenges. Classified as extremely dangerous to humans, associated health hazards rightfully remain a primary concern.[20] Lessons from pre-existing NH_3 sectors, such as agriculture, plastics, and synthetic fibres must be implemented to fully achieve its safe transportation, storage, and application.[21] Compared to conventional carbonaceous fuels such as diesel, NH_3 requires higher ignition temperatures (651 °C vs 210 °C of ammonia vs diesel) and larger fuel tanks (~3x volume per energy return compared to diesel), in addition to possessing a reduced lower heating value.[23] Solutions will accordingly require a combination of engine design and additive development for the efficient and safe use of NH_3.

All the components of a prospective fuel-system must also be considered: NH_3 is extremely basic and corrosive to soft metals such as copper, copper-alloys and nickel-alloys, as well as certain plastics, making diligent engineering mandatory.[24] Materials such as carbon steel and aluminium demonstrate greater corrosion resistance,[25] however, where these materials are unsuitable, corrosion inhibitors may present an attractive mitigation solution.[24] The lubricity of ammonia and other gases has become of recent academic interest. One study reported that a dry ammonia environment at atmospheric pressure has reduced friction compared to other gases, such as dry air or oxygen, suggesting ammonia has some inherent lubricating properties.[26] In addition, further studies demonstrated that ammonia could be used to decrease wear when present at concentrations of 1000 ppm (parts per million) in hydrogen, indicating that it is a reasonably lubricating material.[27] Despite these seminal reports, there are still concerns regarding the service lifetime of an ammonia fuel system. The effects of wear and corrosion, both synergistically and independently are inadequately understood, warranting in-depth investigations. Finally, the environmental effects of ammonia combustion must be considered. Post-fuel injection, the incomplete combustion of NH_3 can result in undesirable nitrogen (di)oxide (NO_x) and nitrous oxide (N_2O) emissions.[28] As examples, NO_2 can be fatal if inhaled at concentrations of 1000 ppm and N_2O emissions are ~300x more potent to ozone layer depletion than CO_2.[30] Thus, design of combustion improvers and catalytic convertors will be critical to eliminating residual pollutants, greenhouse gases and stabilise ammonia combustion.

In conventional fuels, such as diesel, the problems of wear, corrosion and combustion have been somewhat solved by the use additives. Therefore, we hypothesised that additives could be used to improve alternative fuels like methanol and ammonia. Herein, this report systematically investigates selected additives to successfully overcome the technical barriers of these fuels and improve overall performance.

2 METHODS

2.1 Lubricity Test Methods

A test method to determine the lubricity of methanolic fuels was developed based on ISO12156-1:2023,[31] which assesses the lubricity of diesel fuels, by examining the resulting wear on reciprocating metal specimens, using a High Frequency Reciprocating Rig (HFRR). Modifications were made for use with methanol fuels due to its toxicity, volatility and flash point. A gasoline conversion kit was needed to reduce evaporation, and the rig was moved into a wellventilated area. The test parameters are shown in Table 1, and the apparatus schematic in Figure 1.

Table 1. Parameter Table for the modified HFRR lubricity test for methanol.

Parameter	Value
Fluid Volume, mL	15 ± 0.2
Stroke Length, mm	1 ± 0.02
Frequency, Hz	50 ± 1
Fluid Temperature, ºC	25 ± 2
Test Mass, g	500 ± 1
Test Duration, min	30 ± 0.1
Reservoir Surface Area, mm^2	1470 ± 100

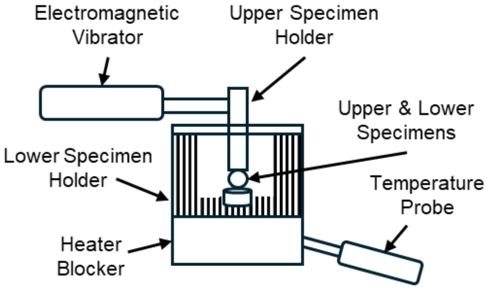

Figure 1. Methanol HFRR test schematic

Further information on the lab air conditions, apparatus, sampling, preparation and calibration can be found within the energy institute publication, IP PM FK: Methanol fuel – Assessment of lubricity using the high-frequency reciprocating rig (HFRR).[32] Samples were prepared and measured in accordance with this method. The method used herein this paper differs from IP PM FK only by the Test Mass and Duration parameters in the method. IP PM FK uses 200 ± 1 g mass, and 75 ± 0.1 min duration, as this is consistent with the original well-established diesel test method ISO12156.

As an overview of the test, A sample of the fuel under investigation was placed in a reservoir maintained at a constant temperature of 25 °C. A steel ball, fixed within a vertically mounted chuck, was pressed against a horizontally mounted stationary steel plate using a predetermined load. The steel ball was subjected to oscillatory motion at a fixed frequency and stroke length, ensuring that the interface between the ball and the plate remained fully immersed in the test fluid throughout the experiment. The metallurgies of the ball and plate, test fluid temperature, load, frequency, stroke length, and the ambient air conditions during the test are specified. The wear scar generated on the test ball was measured digitally using a microscope post-experiment and used as an indicator of the lubricity of the fuel sample. One instance of this test will record the wear scar components in the X and Y direction on the ball bearing, then average them to get one result. The values in this paper are averages of at least 2 instances of the test.

As a benchmark for the fuels tested, the lubricity characteristics of an on-spec diesel in the modified test (mHFFR) was determined to be 292 µm. The diesel fuel used was Swedish Class 1 containing a known amount of lubricity improver and was compliant with EN590 lubricity specification.

2.2 Stability Test Method

The material to be evaluated is stored at selected temperatures over the described time and examined at prescribed intervals for signs of product instability. Measurements are a visual assessment of the sample. Volumetrically graduated glass centrifuge tubes of 100 mL capacity are used, with the first graduation not exceeding 0.05% vol. The centrifuge tube must be of such quality that the graduations are distinguishable enough to be read (the most important graduations being at the bottom of the tube) and the tube is in a clean condition with no deposits. Stoppers of cork or rubber are used to prevent water ingress from condensation. Test temperatures differed between the 3 fuels, however they ranged from 10 ºC down to –30 ºC using calibrated refrigerator(s) or freezer(s) capable of maintaining the selected temperatures to ± 5 °C throughout the 28-day test period. 100 mL of the prepared sample for testing is poured into a glass stability tube and placed in the refrigerator at the desired temperature. Observations of the conditions of the sample were taken after 24 hours, 7 days, 14 days, 21 days, and 28 days at the specified temperature. If a sample is observed as “CB”, this denotes “Clear and Bright” meaning the markings on the opposite side of the stability tube are clearly visible under natural light. “Sed” or “Sediment” refers to hard, solid particles which have collected at the very bottom of the stability tube.

2.3 Filtration Test Method (SEDAB)

The filtration times of the fuels can be compared using a filter blocking tendency test method. 500 mL of a fuel sample is sucked through a glass fibre filter of 47 mm diameter, with a 0.7 µm pore diameter. The time in seconds, which is needed in order to filter this volume at a temperature of 20 ± 2 ºC and at 20 kPa (equals 80 kPa differential pressure) is determined. If this should be more than 120 seconds, it is considered a fail. The fuel is homogenised by shaking vertically 10 times just before testing. The glass fibre filters are conditioned in a drying cabinet at 90 ± 3 ºC for 30 minutes and then stored in a closed Petri dish until use, with a fresh GF (Glass Fibre) filter being used for each test instance. The prepared filter is fitted in the filtration apparatus (shown in Figure 2). An earthing cable is connected to the funnel during filtration. A cooling trap is fitted between the Büchner flask and the vacuum pump to stop any methanol from entering the pump system. The funnel is filled with the 500 mL fuel sample and a pressure of 200 hPa is immediately applied. The time it takes for the entire fuel sample to pass through the filter is recorded using a stopwatch. If the filtration time exceeds two minutes without the whole sample passing through the filter, the test is stopped, and a fail is recorded. The funnel and the sintered filter are rinsed with heptane, then acetone between each test to clean the equipment of fuel. The test is repeated twice and the results recorded in this paper are the averages of the 2 results.

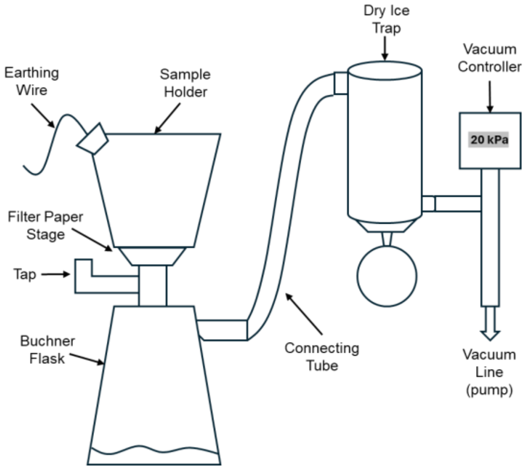

Figure 2. Schematic of filtration apparatus.

2.4 Corrosion Test Methods

Methanol: A test method to investigate the corrosion of methanol fuel mixtures with steel was developed as part of this study. A standardised steel rod, as used in the ASTM D665A[33] corrosion procedure, was used placed in a round bottomed flask and submerged in the test fluid. The flask was then heated under reflux at 60 ºC for 72 hours. The steel rod is then removed from the flask and dried using compressed air. High resolution images are then taken of the front and back of the rod under standard conditions. The masses of the rods are also measured.

In developing this test, it became obvious that methanol corrosion with steel in a lab needed to be accelerated as the rate was too slow to notice. Therefore, elevated temperatures and reflux conditions were used as well as the inclusion of water, in order to obtain noticeable corrosion.

Ammonia: A test method to investigate the corrosion of ammonia fuel mixtures with steel was developed as part of this study. A steel rod (BRITISH BS 970:1991) with a threaded top was attached to a PEEK plastic holder and placed into a 250 mL Schlenk. The Schlenk was charged with a 1:1 Air:NH_3 atmosphere and 1 vol% water and sealed. The Schlenk was heated to 60 ºC for 72 hours after which the steel rod was removed from the flask and dried using compressed air. High-resolution images were then taken of the front and back of the rod and imaging software used to quantify the level of corrosion. The masses of the rods were also measured.

2.5 Combustion Data

Combustion data was measured using a 4-stroke DUETZ dual-fuelled single cylinder research engine with a 1.29 L engine displacement volume. Gaseous ammonia was introduced by port fuel injection between 3-6 bar. Diesel (with or without additive) was introduced by direct injection between 600-1600 bar. Five operational points were investigated, low load/low speed (LL/LS), medium load/ low speed (ML/LS), low load/medium speed (LL/MS), medium load/medium speed (ML/MS) and high load/high speed (HL/HS) with variable quantities of ammonia energy share as described in Table 2. Charge air pressure and charge air temperature for each operational point was kept constant. The concentration of additive in diesel remained constant despite changing diesel energy share. The injection timing was not altered. To maintain the same IMEP at each operational point the functional injection duration of ammonia and diesel was adjusted as necessary. Exhaust gas was measured using fourier transfom infrared spectroscopy (FTIR)

Table 2: Operational points used in Engine test data

Load Point	NH_3:Diesel Energy Share	IMEP (bar)	Speed (rpm)	Charge Air Temperature (°C)
LL/LS	30:70	5	1000	50
ML/LS	60:40	10	1500	55
LL/MS	30:70	5	1000	55
ML/MS	60:40	10	1500	55
HL/HS	80:20	18	2000	55

3 RESULTS

3.1 Lubricity

3.1.1 Methanol Lubricity

Comparisons of various methanol-based fuels were evaluated to determine the resulting mixtures lubricating qualities. In this paper the influence of water, fatty acid methyl esters (FAME), chloride and lubricity additives on the lubricating characteristics of the methanol are investigated.

Table 3 presents the composition of the methanol fuels used to study the influence of water, as well as the wear scar results obtained from the mHFRR test.

Table 3. Compositions of Fuels **1**-**3** and corresponding mHFRR wear scar measurements compared to EN590 diesel and deionised water.

Fuel No.	Methanol %(vol)	Water %(vol)	Cl$^-$ (ppm)	mHFRR (µm)
1	>99.85	<0.15	<0.1	566
2	90	10	<0.1	506
3	75	25	<0.1	411
Diesel[a]	-	-	-	292
Water[b]	-	-	-	392

[a]EN590 Grade Diesel; [b]Deionised Water.

The lubricity results in Table 3 above show the lubricity of methanol fuel improving as more water is added to the fuel (from ~0 to 25%). High purity (IMPCA grade, >99.85%) methanol results in the most severe wear scar (566 µm), with M75 having a much smaller wear scar (411 µm). This has been attributed to the increased viscosity of the mixture which can be higher than that of methanol and water separately due to the stronger intermolecular interactions in the mixture preventing the molecules from sliding past one another,[34] hence the mixture can absorb more force from the reciprocating ball bearing on the disc. Despite this improvement, the fuels still do not possess the same lubricating quality as EN590 diesel in the same mHFFR test (determined to be approximately 300 µm – see section 2.1). In another study, the lubricity of 100% deionised water was found to be 392 µm.

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Table 4. Static stability test results for fuels 1-3

Fuel No.	Additive **A** Treat Rate (ppm)	Temp. (°C)	Day 1 (mL sep)	Day 7 (mL sep)	Day 14 (mL sep)	Day 21 (mL sep)	Day 28 (mL sep)
1	1000	-15	CB[a]	CB	CB	CB	CB
1	1000	-30	CB	CB	CB	CB	CB
2	500	-10	CB	CB	CB	CB	CB
2	500	-15	CB	CB	CB	CB	CB
2	500	-30	CB	CB	CB	CB	CB
3	500	10	0.05[b]	0.05	0.05	0.05	0.05
3	1000	10	CB	CB	CB	0.05	0.05
3	500	0	0.05	0.05	0.05	0.05	0.05
3	1000	0	CB	CB	0.05	0.05	0.05

[a]'CB' denotes the sample is 'Clear & Bright' in appearance with no separation or sedimentation; [b]Separation volumes are from a 100 mL stability tube.

In a second stage of testing, a lubricity additive (additive **A**) was mixed into fuels **1**-**3** at concentrations up to 1000 ppm. The storage stability and mHFRR performance of the additised fuel mixtures were evaluated, Table 4. In Fuel **1**, the lubricity additive was fully soluble and dispersed easily into the fuel with minor agitation to the sample. Weekly observations were made to the samples throughout 28-days at -15 °C and -30 °C, and in each case a clear and bright mixture was observed. In fuel **2**, the additive was also easily dispersed with little agitation needed. Samples of the mixture containing 500 ppm of the additive were stored from -10 °C to -30 °C and observed weekly for 28 days. In each case the samples were clear and bright. In fuel **3**, the additive again easily dispersed into the fuel with little agitation required. Samples containing 500 ppm and 1000 ppm of additive were prepared and stored for 28 days at 10 °C and 0 °C. The sample with a higher treat rate of 1000 ppm showed a small amount of crystallisation (<0.1 mL) at both temperatures within 21 days, the colder temperature producing the small, white crystalline precipitate within 14 days. The same phenomenon was also observed for the lower treat rate sample containing 500 ppm additive at both temperatures within 1 day. The results show that the additive blends easily and is compatible with methanol and methanol/ water mixtures at room temperature and below, with no issues observed at very low temperatures of -30 ºC, even with water content as high as 10%. In fuels with water content of 25%, the additive was still fully miscible and blended into the mixture easily at room temperature, but crystallisation and drop out is observed within days at 10 ºC or lower.

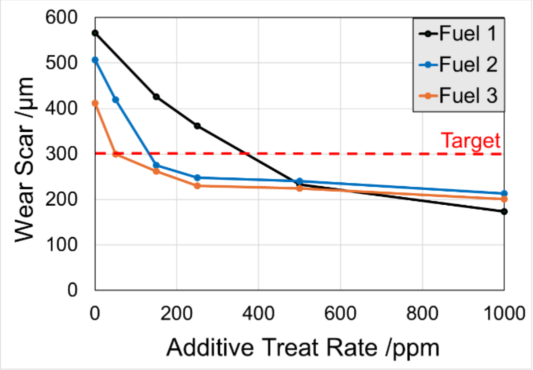

Figure 3. Wear scar results versus lubricity additive (**A**) concentration for fuels **1**-**3**. Reports are averages from least 2 instances of test in each case.

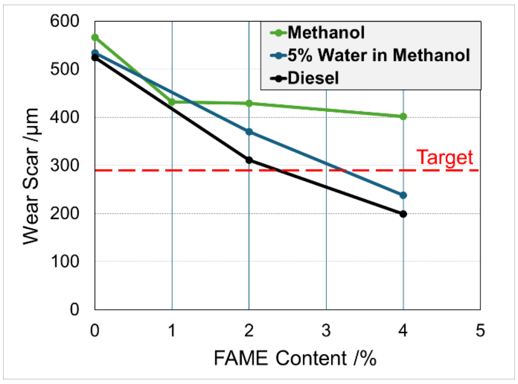

Figure 4. Lubricity results of Fuels 4-8, showing the effect of increasing FAME content in low-sulfur diesel (black), methanol (green) and methanol with 5% water content (blue) fuels

The lubricity of fuels **1-3** were examined with varying amounts of lubricity additive using the mHFRR method described previously. Figure 3 shows that in each of the three fuels, the lubricity additive is able to reduce the wear scar considerably, surpassing the 300 µm target indicating the equivalent wear to EN590 compliant diesel fuel. The impact is most pronounced in the higher water content fuels, where only 250 ppm of additive was needed to ensure the lubricity target was met. In Fuel **1** however, a slightly higher treat rate of 500 ppm of additive is necessary to achieve the same target

FAME is known to improve the lubricity of diesel when used as a drop-in fuel therefore we investigated lubricity performance of FAME in methanol. The quantity of FAME used in diesel varies but is typically around 4% vol. This was used as a guide for mixing with methanol. Table 5 shows the composition of methanol and FAME containing fuels used for this study. Figure 4 shows a graphical representation of the FAME content versus mHFRR result for fuels **4**–**8**, as well as a typical diesel with FAME.

Table 5. Composition of the FAME-containing fuels in this study, and the mHFRR wear scar result.

Fuel No.	Methanol %(vol)	FAME %(vol)	Water %(vol)	mHFRR /µm
4	99	1.0	-	432
5	98	2.0	-	429
6	96	4.0	-	402
7	93	2.0	5.0	370
8	91	4.0	5.0	238

The FAME was used throughout this study was sourced from Europe and is considered representative of FAME used within the market. The diesel fuel is a low-sulfur diesel fuel containing no other lubricity improvers, and is therefore not compliant with the EN590 diesel specification. When the two are mixed, the FAME reduces the wear scar as expected, enabling this diesel to meet the target lubricity specification with between 2 and 4% FAME content, Figure 4. This is not the case in Methanol and FAME fuel blends. Initially the FAME has a strong impact on the lubricity of the methanol, reducing the wear scar by 134 µm with 1% FAME content. However, increasing FAME content to 4% has negligible effect on the lubricity, only reducing the wear scar to 402 µm, which is still over 100 µm away from meeting the target wear scar. Fuels **7** and **8** which contain methanol, FAME and water did show better performance in this test than fuels **4**–**6**. The addition of water to methanol and FAME blends improves the lubricity similarly to the improvement observed in the absence of FAME, Table 2. Furthermore, when 5% water is present in the fuel, FAME continues to improve the lubricity performance, Figure 4. From a baseline of 534 µm without FAME, to 370 µm at 2%, and finally 238 µm at 4% FAME content. This result shows that mixing just methanol and FAME will not improve the lubricity of the fuel significantly enough to prevent a sizeable wear scar, however, the addition of 5% water creates a synergy where the FAME can further improve the lubricity of the fuel mixture, surpassing the target at 4% FAME.

Table 6. Static stability of FAME-containing fuels 4-8, row sections are split by temperature.

Fuel No.	FAME Content (%vol)	Water Content (%vol)	Temp (°C)	Day 0 (mL sep)	Day 7 (mL sep)	Day 16 (mL sep)	Day 21 (mL sep)	Day 28 (mL sep)
4	1.0	-	**5**	CB[a]	CB	<0.05	<0.05	<0.05
5	2.0	-	**5**	CB	H	0.1[b]	0.15	0.15
6	4.0	-	**5**	CB	0.5	0.6	0.5	0.6
7	2.0	5.0	**5**	CB	H[c]	0.1	0.15	0.15
8	4.0	5.0	**5**	CB	<0.05 + H	0.6	0.6	0.7
4	1.0	-	**0**	CB	CB	0.1	0.15	0.15
5	2.0	-	**0**	CB	0.15	0.25	0.25	0.25
6	4.0	-	**0**	CB	0.15	0.5	0.5	0.7
7	2.0	5.0	**0**	CB	1.0	1.0	1.0	0.8
8	4.0	5.0	**0**	CB	3.0	3.0	3.0	2.8

[a]'CB' denotes 'good' stability, the sample is 'Clear & Bright' in appearance with no separation or sedimentation; [b]Separation volumes are from a 100 mL stability tube; [c]'H' indicates the sample was 'Hazy' and not clear

Once the lubricity of the fuels **4-8** were determined, the static stability of the fuels was investigated for 28 days at 0 °C and 5 °C. The full results for this study can be found in Table 5 and are described herein. Fuel **4** with 1% FAME content was the only fuel mixture to remain stable for 7 days. All the other fuels showed cloudiness, separation or both before 7 days at both test temperatures. After the 28-day period of testing all samples showed cloudiness and some degree of sedimentation or phase separation. In fuels **4**–**6** the separation increased with FAME content at both temperatures, the highest being fuel **6** with 0.7 mL (0.7 %) separation observed at 0 °C. More significant phase separation was observed for the water containing fuels **7-8**, which is unsurprising given FAME is known to cause emulsification issues with water in diesel and FAME blends. At 0 °C, the stability of fuel **8** was most severe with 3.0 mL (3.0 %) separation within 7 days. The results show FAME and methanol blends have poor compatibility. Even at 5 °C, cloudiness and dropout is observed within days for samples with 2% FAME or higher. Whilst water does improve the lubricity of methanol and FAME blends, it causes very poor stability results, increasing the observed dropout in testing.

A further consideration of using FAME in methanol is the impact on filtration times of the fuels. It is understood that FAME-containing diesel fuels have a longer filtration time than regular diesel fuels and this is important when evaluating the impact of the fuel on the delivery system in the engine. To evaluate this a filtration study was conducted on non-additised fuels **1**, **2**, **5**, **6** and fuel **1** blended with 500 ppm of lubricity additive **A**, referred to as **1a**. Table 6 below shows the fuels average SEDAB filtration time from 2 filtration tests, as well as the percentage change compared to the methanol (fuel **1**) base result.

Table 6. SEDAB filtration time and % change versus high purity methanol (fuel **1**)

Fuel No.	Filtration Time (s)[a]	% change (Δ) vs 1
1	15.1	-
2	>120	>700
5	15.7	+4.0
6	16.3	+8.0
1a	15.0	-0.7

[a]Average filtration time from 2 instances of test.

The results above show that FAME has an adverse effect on the filtration time of methanol. The percentage increase in the SEDAB filtration time was exactly twice the FAME content of the fuels. When compared to the methanol fuel containing the lubricity additive (fuel **1a**) the filtration time was a lot quicker and slightly lower than the corresponding base fuel measurement. Also, it should be noted that methanol with 10% water content had drastically different filtration time to all the other fuels studied. This is a result of several factors, firstly the viscosity of the fuel mixture is higher than methanol which will cause the filtration to take longer. Secondly, the filtration used glass fibre filter paper which may have a higher affinity for water than methanol and therefore hinder the filtration of the sample.

3.2 Corrosion

3.2.1 Methanol Corrosion

An investigation into the effect of chloride ions on the corrosion of steel in methanol fuel was undertaken using the corrosion test method described in section 2.4. To accelerate the rate of corrosion in this test, 20% volume of the test fluid used was distilled water. In each case the distilled water and methanol mixtures were tested in combination with a known amount of chloride and lubricity additive. Table 7 below shows the composition of the 6 fuels used in this corrosion study.

Table 7. Composition of fuels **1-3a** varying in chloride and additive content, 'a' denotes additised fuel.

Fuel No.	Methanol %(vol)	Water %(vol)	Cl^- content /ppm	Additive A /ppm
1	80	20	2	-
1a	80	20	2	450
2	80	20	4	-
2a	80	20	4	450
3	80	20	10	-
3a	80	20	10	450

Images of the steel test rods at the end of each test and are shown in Figure 3 below.

The results from the tests show corrosion of steel occurs in fuel **1** with concentrations as low as 2 ppm chloride. The visual assessment of the steel rod for this fuel showed many brown spotted patches covering both the front and back surfaces of the rod. Comparing this result with additised fuel **1a**, the corrosion is significantly reduced with brown colouration being almost completely removed, however some small faint spots and markings are still present on both sides of the steel test rod. In fuel **2**, the corrosion is more severe with a higher number of spots, that are also larger in appearance, again covering the surface on both sides. The additised fuel **2a**, demonstrated significantly reduced corrosion, however more corrosion was present than with the steel test rod from fuel **1a**. Evidently the increase in chloride concentration still has a strong impact on both base fuel and non-nadditised fuel systems. Finally, fuel **3** with 10 ppm chloride content showed many large areas of visible brown corrosion across the majority of the surface. The additive in fuel **3a** did manage to reduce the visible corrosion, however there were still many small brown spots across the front and back of the steel test rod, although to a much-reduced extent.

Figure 3. Images of the steel test rods comparing base fuels **1-3** to the additised versions at end of each test.

Assessing the additised rods compared to the corresponding base fuels, it is clear that the lubricity additive also protects steel from visible corrosion in methanol. It is also evident that steel is very sensitive to chloride ions in the fuel system, with corrosion observed in each instance of the 72-hour test, and further increased dramatically as the chloride content increases up to 10 ppm. It is hypothesised that the lubricity additives ability to act as a surfactant and preferentially adhere to the metal surfaces protects the metal from reacting with corrosive species in the fuel mixtures. As the chloride content increases, the ability of the additive to coat the entire surface is reduced as it competes with the chloride and methoxide species for sites on the surface.

3.2.2 Ammonia Corrosion

The corrosion of steel by ammonia was investigated as described in Section 2.4. Additives were sprayed onto steel rods and the rods exposed to a 1:1 atmosphere of Air:NH_3 with 1% water by volume, at 60 °C, for 72 h in a sealed system. The number of deposits on the rod and the percentage of surface rusted was calculated using ImageJ processing software, Table 8 and Figure 5.

Table 8: Corrosion Rod Analysis of different additives in Ammonia

Additive	Number of Deposits on Rod	Average Area of Rust Deposits (mm^2)	Total surface rusted (%)
None	1724	0.041	11.7
B	536	0.135	9.4
C	353	0.041	1.9
D	40	0.060	0.2

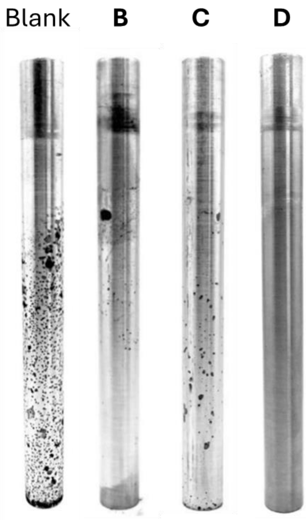

Figure 5. Image of steel rods after exposure to a 1:1 Air:NH_3 atmosphere, 1% water at 60 °C for 72 h. Additives at a concentration 120 ppm. From left to right, no additive, Additive **B**, Additive **C** and Additive **D**.

Initially, a steel rod with no additive was exposed to ammonia to serve as a benchmark. Under these conditions, the rod was calculated to have 1724 individual rust deposits, with an average surface area of 0.041 mm^2 and the total surface area rusted was 11.7%. Next, rods pre-coated with 120 ppm of additives **B**-**D** were investigated. After the corrosion process, it was calculated that all additives reduced the number of unique deposits on the rod compared to the benchmark (**B** = 536, **C** = 353 and **D** = 40). However, in the case of **B**, the measured average area of the rust deposits was triple compared to the benchmark rod whereas no difference was observed for additive **C** and a slight increase was observed for **D** (**B** = 0.135 mm^2, **C** = 0.041 mm^2 and **D** = 0.060 mm^2). Finally, the total surface rusted of each rod was calculated. additives **C** and **D** demonstrated remarkable improvement compared to the benchmark rod, with only 1.9 and 0.2%, respectively, of the total surface rusted. On the other hand, the large surface area of the deposits on the rod coated with additive **B** translated to 9.4 % of the total surface area rusted. In order of effectiveness, the additives can be arranged as **D** > **C** > **B** > no additiveTo determine the difference in corrosion inhibition, the stability of the additives in ammonia was investigated. Control experiments, which treated each additive with ammonia for 72 h demonstrated that no reaction occurred between ammonia and additives **C** and **D**, observed by ^1H NMR and IR spectroscopy. However, after analysis, it was observed that additive **B** was completely converted into a new product(s). This result suggests that the inferior performance of additive **B** compared to **C** and **D** is due to the formation of compounds which are not adequate corrosion inhibitors. Therefore, owing to the reactive nature of ammonia it is recommended that all fuel additives proposed for ammonia fuel systems are investigated for compatibility as well as operational improvements

3.2.3 Ammonia Combustion Testing

The NH_3-diesel blends with additive **E** were investigated against an analogous baseline fuel without additive to determine the impact on NH_3 and NO_x emissions. A single concentration of additive **E** in the diesel pilot fuel was used despite the varying ratios of NH_3-to-diesel to simulate real world practice. Five load points were investigated, with variable quantities of ammonia energy share as described in Table 9.

Table 9: Difference in NH_3 and NO_x based gas exhaust emissions of non-additised and additised ammonia-diesel dual fuel mixture.

	Emission difference between non-additised and additsed ammonia-diesel dual fuel	
Load Point	NH_3 (%)	NO_x (%)
LL/LS	-4.5	-1.4
LL/MS	+6.1	-7.5
ML/LS	-22.1	-8.7
ML/MS	+8.2	-6.4
HL/HS	-11.4	+4.2

Initially, LL/LS was investigated, Table 9. Compared against the baseline engine test, both nitrogen-based emissions decreased when additive **E** was used at this operational mode. Next, it was observed that NH_3 slip was reduced at low and high speeds but increased at medium speeds. On the other hand, NO_x emissions decreased at all low and medium loads but increased at HL/HS. It is rationalised that at low speeds, additive **E** facilitates a higher proportion of NH_3 combustion (to N_2), minimising both NH_3 and NO_x emissions. At medium speeds the effect of additive **E** is more complicated. In these tests, NH_3 emissions increase by 6-8%, while the NO_x emissions decrease by a similar margin. It is possible that it is a combination of the engine mode and the effective decrease in additive concentration is contributing to these results. At HL/HS the additive clearly improves NH_3 combustion but not cleanly, as observed with the increase of NO_x emissions.

In conclusion, combustion additives can have a positive effect on emissions, especially at LL/LS. Further studies should look at the effect of additive concentration to optimise their propensity at varying loads, in this example, the additive concentration was constant with regards to diesel, therefore, as the energy share of ammonia increased, the effective additive concentration decreased. It is also likely that this is not the optimised additive; further additives should be investigated to fully understand their role in controlling unwanted emissions.

4 CONCLUSIONS

4.1 Methanol

Lubricity studies of methanol fuels showed that adding up to 25% water to the fuel increases its viscosity, therefore improving the lubricity of the fuel, leading to a reduced wear scar. However, the improvement on its own is not significant enough to achieve the same lubricating performance as EN590 diesel, which is necessary to protect an engine from wear. To do this, lubricity additives must be included in the fuel. This paper further demonstrates that one such additive is fully miscible with methanol and methanol/water blends with high water contents, even down to low temperatures of -30 ºC, the fuel samples remained clear in their appearance. The only cases where the additive caused white precipitation to drop out of the fuel was when the water content was further increased to 25% at 10 ºC and below. In each of the fuels assessed, the additive significantly improved the lubricity of the system. The impact is most pronounced in the higher water content fuels, where only 250 ppm of additive was needed to ensure the lubricity target was met. In >99% methanol fuel however, a slightly higher treat rate of 500 ppm of additive is necessary to achieve the same target lubricity, however in pure methanol the additive is most effective as it is capable of reducing the wear scar below 200 µm, at 1000 ppm additive treat rate, which was not possible in the methanol/water fuel blends. When investigating the effectiveness of FAME to improve the lubricity of methanol fuels, both with and without water, it was found that the resulting fuel mixtures were not stable at temperatures below 5 ºC for more than 7 days, with the exception of 1% FAME in pure methanol, which showed separation between 7 to 14 days at 5 ºC. This was considerably worse for fuels containing water as the fuel mixtures had a much higher degree of separation. Incompatibility issues with methanol aside, FAME also did not show a significant improvement in lubricity, failing to reach values near the target mHFRR result. At least 5% water was needed in the blend to achieve a good lubricity result, however, given FAMEs inherent incompatibility with water, this causes other issues for the fuel mixture, suggesting FAME is not a good option to improve the lubricity of methanol fuels. The filtration time of the fuel mixtures also increased as the FAME content increased. When comparing FAME to the lubricity additive, FAME had performance issues in all areas, lubricity, stability and filtration studies, whereas the lubricity additive demonstrated very good performance in all of these areas.

Studies of steel corrosion in methanol fuels showed that chloride content has a direct impact on the observed corrosion. At 2ppm chloride content, corrosion was observed as many brown spots covering the surfaces of the rod in the 72-hour test. As Chloride content increased to 4 ppm and 10 ppm, the severity of the corrosion increased each time, with increasing numbers of brown spots of larger size. Adding the lubricity additive to these fuels caused a strong reduction in corrosion. In each case, the brown spots were a lot smaller in size and the colours were a lot less prominent across the surface of the test rods. Some brown colouration and surface markings were still present, however these were to a much smaller extent. This phenomenon is due to the lubricity additive coating the metal surface making a protective layer, hence stopping oxidative species from reacting with the metal, reducing corrosion.

4.2 Ammonia

In regard to ammonia fuel, we have shown that corrosion inhibitors can effectively reduce the total surface area of rust on a steel rod exposed to an ammonia atmosphere from 12% to 0.2%. It is anticipated that ammonia fuel systems will require high levels of durability to mitigate harm to human life and minimise maintenance costs that could render a vessel inactive for extended periods of time. This report shows that corrosion inhibitors are a potential solution to this problem.

Furthermore, we have shown that additives present a valuable opportunity to modify emission output from a diesel-ammonia dual fuel mixture. The process should still be optimised, for instance in this example we chose a single additive at a single concentration in relation to the diesel energy share. Ultimately this could prove a cost-effective method of reducing unwanted emissions.

Overall, the scientific findings in this paper demonstrate several key areas where additives can provide cost-effective solutions to technical issues in alternative fuels of the future. In each case, low treat rates of 1000 ppm or less (and significantly lower in the case of corrosion inhibition) were sufficient to overcome performance issues in both methanol and ammonia fuels. The addition of inexpensive additives in these fuels can mitigate hardware complications arising from poor lubricity or material compatibility between the fuel and the fuel delivery system. Furthermore, in the case of methanol, additive **A** was able to consistently perform under extreme low temperature conditions, high water content, and high chloride contamination levels. Investigations into ammonia fuel led to the development of a sophisticated corrosion test in ammonia and results proving additives can work effectively at reducing the fuels corrosivity. Further work will continue in these areas, with the intent to support key members of the industry in overcoming the challenges they face on the path to decarbonisation, using advanced additive solutions.

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

IMO: International Maritime Organisation
GHG: Green House Gas
HFRR: High Frequency Reciprocating Rig
mHFRR: modified High Frequency Reciprocating Rig
GF: Glass Fibre
IMPCA: International Methanol Producers and Consumers Association
IR: Infrared
M75: Methanol and water fuel blend with 75% methanol by volume
FAME: Fatty Acid Methyl Ester
NMR: Nuclear Magnetic Resonance
ppm: parts per million (by mass if not stated otherwise)

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