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Influence of combustion gas temperature on piston deposits for diesel and NH3 dual-fuel combustion

Lubricants

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ABSTRACT

As new fuels are adopted for marine engines, it is necessary to understand their impact on lubricant performance. In order to evaluate the performance of existing lubricants and inform the development of new ones, a deposit control test protocol has been developed using the ExxonMobil Enterprise two-stroke marine diesel research engine. Repeated tests at the target speed/load operating condition but different thermal conditions show that the temperature of the combustion gases is a key driver in the formation of deposits on piston surfaces, impacting both the quantity of deposits and whether they are hard or gummy. These impacts are examined for diesel combustion as well as ammonia dual-fuel combustion. Among alternative marine fuels, ammonia has perhaps the most unanswered questions regarding interactions with cylinder lubricants. The influence of ammonia dual-fuel combustion on the thermal conditions experienced by the lubricant are discussed. Scrape down oil samples were collected after operation with ammonia for analysis and comparison with fresh oil. Chemical analysis using a GC/MS instrument did not show significant permanent chemical changes in the lubricant due to ammonia exposure.

1 INTRODUCTION

The primary purpose of cylinder lubricating oils for two-stroke marine engines is to protect the liner, piston, and rings from various types of wear to ensure reliable engine operation. In addition to the primary function of lubricating the piston and liner to reduce friction and wear, lubricants must also neutralize acids formed in combustion and keep the piston and ring pack clean to ensure free movement and avoid sticking and premature wear and seizures. Advances in lubricant formulations have yielded some oils that are highly effective at protecting modern engines. Original equipment manufacturers (OEMs) have various means of evaluating the performance of cylinder oils for protecting their engines, with MAN-ES, in particular, having developed Category I and Category II cylinder oil certifications, with Category II oils being noted for their "excellent overall performance with a special focus on cleaning ability." [1,2].

As new fuels are introduced to the market in order to improve emissions from marine engines and meet targets set by the International Maritime Organization (IMO) for greenhouse gas (GHG) reduction [3], it becomes necessary for providers of lubricating oil to develop new formulations that will protect the engines against the different operating environment encountered and continue to ensure safe and reliable operation. Some of these changes will be in response to fuel chemistry (e.g. lower base number (BN) oils for use with very low sulfur fuel oils (VLSFO)), and some will be in response to changing thermal operating conditions and similar trends (e.g. slow steaming, etc.).

Thermal operating conditions have previously been shown to be a key factor in piston deposit formation [4]. In one of the earliest studies of piston deposits and ring sticking in a diesel engine, Rosen [5] observed that piston temperatures were a key driver, with increased temperatures leading to reduced deposits, and that the deposits changed from "gummy" to "carbonaceous" products as temperature increased. In this case, "normal" ring groove temperatures ranged from 210°–260°C, and a piston designed to have temperatures 25°–40°C higher than normal showed significantly improved performance, with reduced deposits and no ring sticking. Rosen also noted a significant impact of lubricant chemistry and formulation, with additives showing significant potential for avoiding ring sticking problems.

McGeehan, Fontana, and Kramer [5] showed in a turbocharged, four-stroke diesel engine that in the 200°–260°C range, increasing piston temperature was the primary factor in top groove deposits, with deposits doubling for every 30°C rise in temperature. Crankcase oil oxidation was also observed to correlate with piston temperature. Kim *et al.* [7], in a diesel engine with high soot production, showed that top groove deposit formation was most sensitive to soot content below 260°C, but that piston temperature became dominant above 260°C, with increased temperature leading to increased deposits.

In addition to thermal conditions, the chemistry impact of new fuels is also of interest. While the impact of some proposed fuels will be minor or is already well-understood, many questions remain about others which have not been commonly used as fuels in diesel engines in the past—particularly ammonia. Limited studies on lubricant interactions with ammonia have been conducted to date. Peck [8] showed that lubricant films are able to protect copper coupons from ammonia vapor corrosion, and that there was some uptake of ammonia into the lubricating oils (with one lubricant becoming visually hazy). Obrecht [9] showed impacts of ammonia exposure on viscosity, total base number (TBN), deposit control, and/or load-carrying capability that varied with oil formulation, with Obrecht, Griffaton, and Rappo [10] noting that the TBN sometimes increased after exposure to ammonia. Griffaton *et al.* [11] observed differences in the impact of dual-fuel ammonia operation on anti-wear and detergent additives with two different oil formulations in a 250-hour durability test on a diesel engine. From these studies, it does appear that formulation will influence lubricating oil performance for ammonia-fueled engines, but many details of the fuel-lubricant interactions and resulting lubricant performance remain poorly understood.

This paper presents results from lubricant deposit formation studies on the ExxonMobil Enterprise single-cylinder two-stroke marine diesel research engine. The paper will explore potential reasons for the discrepancies between various studies on thermal effects, where some showed better deposit control performance at increased piston temperatures while others showed degradation. Observations on lubricant performance in initial ammonia dual-fuel operation will also be presented.

2 EXPERIMENTAL SETUP & PROCEDURE

This study was conducted using the Enterprise single-cylinder research engine, a reduced-scale two-stroke crosshead engine designed to replicate the boundary conditions of cylinder lubricants in full-scale low-speed two-stroke marine diesel engines. The engine is well-instrumented for relevant pressures and temperatures, including a telemetry piston temperature measurement system. Details of the engine setup can be found in previous papers by the authors [12,13]. The engine was also recently upgraded with a low-pressure ammonia injection system to enable dual-fuel ammonia operation, as described in detail in Marion *et al.* [14].

The engine was operated using an 18-hour test protocol previously developed by the authors for evaluating lubricant deposit control performance [13]. This protocol consists of 18 total hours of steady-state operation at a mid-speed/mid-load operating condition nominally representative of slow steaming operation, over the course of three days of engine operation. This engine operating condition was specifically chosen to avoid significant levels of fuel impingement on the cylinder liner and focus on lubricant-sourced deposits. Two different engine oils were used during the operation described in this paper: Oil A, a commercial MAN-ES Category-II 40 BN product, and Oil B, a test formulation being evaluated for deposit control performance. Oil A was tested using this test protocol with three repeats using ultra-low sulfur diesel (ULSD) as a surrogate for marine gasoil (MGO). Oil B was tested using this test protocol for dual-fuel operation with ammonia with ULSD as the pilot fuel. The piston was also evaluated after initial commissioning of the engine for dual-fuel ammonia operation, which comprised approximately 65 hours of operation at various speed-load conditions and air/fuel ratios with Oil A as the cylinder lubricant.

As the deposit control protocol tests were conducted, inconsistent results were noted for the repeated ULSD tests with Oil A. It was determined that the air/fuel ratio and exhaust temperature were varying significantly from test to test despite being nominally at the same operating condition. This was determined to be caused by fouled pressure snubbers at the measurement points for intake and exhaust pressures. The engine control scheme utilizes closed-loop control of intake and exhaust pressures to maintain proper boost and exhaust backpressure and thus air/fuel ratio and scavenging performance. The fouled pressure snubbers introduced error into these measurements and resulted in variation in both boost pressure and exhaust backpressure, and thus in the air/fuel ratio and the thermal conditions in the combustion and exhaust gases. Operating and maintenance procedures were adjusted to avoid future variations due to pressure snubber fouling, but this data set allows for examination of the influence of the thermal boundary conditions—particularly of the combustion gases—on piston deposit formation.

Scrape down oil samples from ammonia dual-fuel operation were also analyzed with a GC/MS instrument in order to evaluate whether any chemical changes occurred due to exposure to ammonia in the engine. The GC/MS instrument employed an Agilent 6890N GC system and an Agilent 5975 mass spectrometer. The carrier gas was helium (99.999% purity) at a 1.0 mL/min flow rate. The gas chromatograph inlet temperature was 300°C. The GC oven temperature was programmed from 45°C and held for 3 min, subsequently ramped at 3°C/min to 300°C, and then held at the maximum temperature for 17 min. The transfer line was kept at 300°C. A DB-5MS GC column (30 m long, 250 µm ID, 0.25 µm film thickness) from Agilent Technologies was used for chromatographic separation. The ion source was held at 230°C. Electron ionization (EI) mass spectra were recorded in the range of m/z 15-700.

3 RESULTS

3.1 Deposit Protocol Test Repeats with ULSD Fuel: Operating Condition Effects

Three repeated cases of operation on the deposit control protocol were conducted with Oil A on ULSD fuel. The piston was then removed for deposit analysis. Figure 1 shows photographs of the piston after each of these experiments. All three experiments used the same fuel and lubricant and were at the same engine speed/load condition. However, due to the pressure snubber fouling issue mentioned previously, the thermal conditions varied. For the first case, shown in Figure 1a, which was typical of other operation using this test protocol, the piston had hard top land deposits all the way around the circumference, and the lower portion of the piston was very clean. For the cases shown in Figure 1b and Figure 1c, top land deposits were reduced and only covered portions of the circumference of the piston, while deposits on the lower portions of the piston were significant and gummy rather than hard.

When examining the differences between the operating conditions for these cases, the exhaust temperature was found to have the strongest correlation with the results—in particular, exhaust

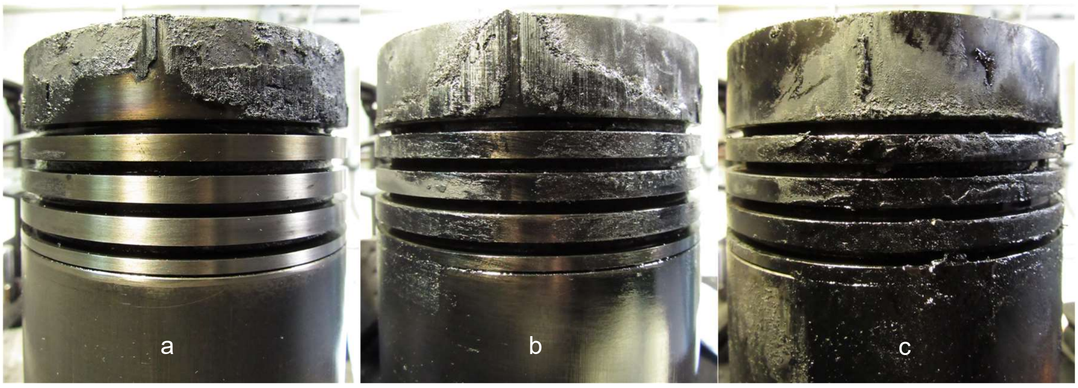

Figure 1. Piston deposits after 18-h operation on deposit control test protocol with Oil A and ULSD. Average exhaust temperature for subfigures: a, 515°C; b, 453°C; c, 491°C.

temperatures above 500°C are correlated with hardened top land deposits, while exhaust temperatures below 500°C are correlated with a lack of hard top land deposits and increased gummy deposits on the lower portions of the piston. Note that this effect is a threshold rather than a proportional relationship. This correlation was also observed to hold true across various other fuels and oils not presented in this paper. Exhaust temperatures here are a marker of the temperature of the combustion gases to which the lubricant in the top crevice region is exposed.

Piston temperatures, shown along with exhaust temperatures in Figure 2, did not strongly correlate with deposit type: piston temperatures for case *b* (which had gummy deposits) are slightly higher than for case *a* (which had hard top land deposits), while those for case *c* (which had gummy deposits) are slightly lower. The exhaust temperatures in both cases were substantially reduced, with case *a* having exhaust temperatures of approximately 515°C while cases *b* and *c* had exhaust temperatures of 453° and 491°C.

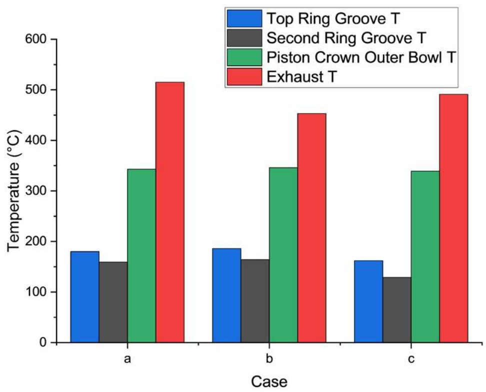

Figure 2. Piston and exhaust temperatures at 18 hours of operation

While piston temperatures certainly have a role to play in deposit formation on surfaces of the ring grooves and lands, the top land deposits, which are directly exposed to combustion gases in the crevice region, are more strongly influenced by the gas temperature. In this case, in line with initial observations by Rosen [5], lower temperatures lead to gummy deposits, where the viscous, sticky products of oil decomposition collect soot and accumulate in the ring grooves, while the formation of hard deposits requires higher temperatures to eliminate the volatile organic components.

A study by Ra *et al.* [15] indicates that crevice flows and temperatures play an important role on deposit formation on crevice surfaces. In this case, it is possible that formation of a layer of hardened deposits on the top land may also impede the transport of hot gases to lower regions of the piston, avoiding the formation of gummy deposits on the lower land and ring groove surfaces. The deposit thickness profile on the surface of the piston was measured for each case with a laser profilometer, using the method described in Kaul *et al.* [16]. The mean and maximum deposit thickness along the midline height of the top land is shown in Figure 3. Note that while the maximum deposit thickness is only marginally lower for case *b* than case *a*, the mean thickness of deposits around the periphery of the top land drops substantially for cases *b* and *c*—which had gummy deposits—relative to case *a*—which had hard deposits on the top land and was largely clean below. This correlation supports the hypothesis that the top land deposit layer is influencing the formation of deposits on the lower sections of the piston by impeding the flow of hot combustion gases past the top land through the crevice region.

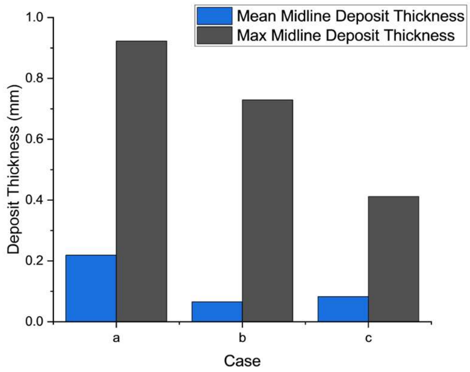

Figure 3. Mean and maximum of deposit thickness along the midline height of the top land

While suppression of gummy deposits lower on the piston is beneficial, excessive top land deposits can cause cylinder bore polishing and accelerate wear [17,18]. Piston cleaning rings (PCR) are commonly used to prevent these deposits from growing to the point that they can polish the liner bore. While the Enterprise engine is not currently fitted with a PCR, the authors hypothesize that to the extent that top land deposits impeding the flow of combustion gases into the crevice is a contributing factor, the growth of these deposits to the steady state thickness where they would be filling the space between the top land and the PCR is likely to similarly restrict the flow of hot gases to lower regions of the piston and have a similar effect on ring groove and lower land deposits.

3.2 Ammonia Dual-Fuel Operation

3.2.1 Piston Deposits

The influence of ammonia dual-fuel combustion on lubricant performance is likely to include both thermal and chemical effects. Piston deposits in initial operation with ammonia dual-fuel combustion follow the same trends with respect to exhaust temperature. Figure 4 shows the piston after approximately 65 hours of ammonia dual-fuel operation at a variety of speeds and loads during initial commissioning operations. Exhaust temperatures varied but were mostly between 400°C and 500°C and averaged approximately 450°C; while there were some excursions to higher temperatures, most of the engine operation fell within this range. In this case, the piston lacked significant top land deposits and had excessive gummy deposits over all land and groove surfaces. While the top ring remained free, the second ring was fully stuck, and the third and fourth rings were “sticky” and nearing a stuck condition.

Figure 4. Piston deposits after 65h of ammonia dual-fuel operation at various speed/load conditions. Average exhaust temperatures were approximately 450°C.

Figure 5, on the other hand, shows the piston after ammonia dual-fuel operation on the 18-hour deposit control protocol with Oil B with ammonia substitution of 63% on a fuel energy basis. For this initial operation, ammonia substitution at this speed/load condition was limited by minimum diesel fuel injection quantity with the current diesel fuel injectors. Future work will include examination of higher ammonia energy fractions. In this case, the air/fuel ratio and diesel injection timings were selected to yield exhaust temperatures with an average of 535°C, and there are some hard deposits on the top land, but the lower regions of the piston are entirely clean. Ring groove temperatures were comparable to case *a* above, with average temperatures of 185°C in the top groove and 155°C in the second groove.

Figure 5. Piston deposits after 18h of ammonia dual-fuel operation on deposit control protocol with average exhaust temperature of 535°C

The temperature of the combustion gases was, in this case, intentionally selected via engine calibration. In practice, additional aspects of ammonia dual-fuel combustion may influence this. For premixed ammonia-air mixtures, the ratio of specific heats, γ, will be reduced, as ammonia has a lower γ than air. This will lead to lower compression temperatures, as illustrated in Figure

6 for ammonia dual-fuel and diesel operation on the deposit control protocol. This will drive in the direction of reduced gas temperatures at a given air/fuel equivalence ratio.

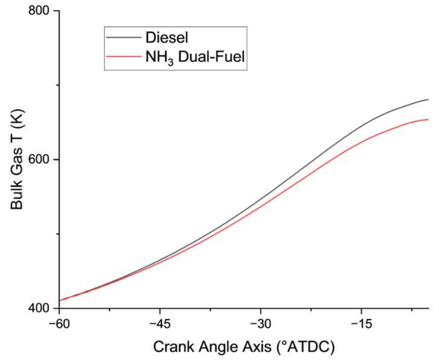

Figure 6. Bulk gas temperature for compression stroke of diesel and ammonia dual-fuel operation at matched intake air temperature and pressure

On the other hand, ammonia can be burned more cleanly and efficiently at richer air/fuel ratios, which would tend to elevate combustion temperatures, and local temperatures near the crevices could be expected to increase for premixed combustion. Ammonia dual-fuel combustion also results in reduced heat transfer, as illustrated in Figure 7. This is likely in large part due to a reduction in radiative heat transfer to combustion chamber surfaces from soot in the diesel flame.

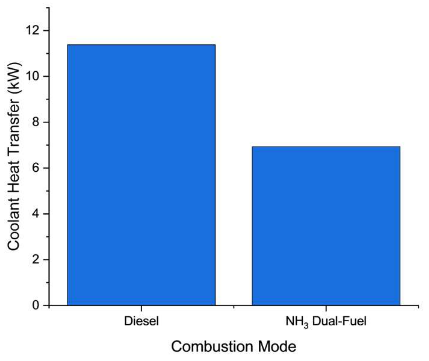

Figure 7. Heat transfer to engine coolant for diesel and ammonia dual-fuel combustion at deposit control protocol operating condition

For this operating condition, with 63% ammonia fueling by energy, the heat transfer to the engine coolant was reduced by 40%. Heat transfer to the piston can be assumed to be reduced in similar proportion, so with the same oil cooling configuration, piston temperatures might also be expected to drop somewhat. In this study, the measured piston ring groove temperatures for the ammonia dual-fuel operation were comparable to the case *a* diesel operation which had similarly hardened top land deposits with the rest of the piston being clean, though the exhaust temperatures were approximately 20°C higher.

3.2.2 Chemical Analysis of Scrape Down Oil

Scrape down oil samples were also collected after ammonia dual-fuel operation. The oil initially had a noticeable ammonia odor, in line with the ammonia uptake observed by Peck [8]. However, this odor dissipated with time, as the ammonia apparently came out of solution with the oil. GC/MS analysis was conducted on the scrape down oil sample to identify whether significant changes in the composition due to reactions with ammonia were occurring (particularly focusing on looking for N-containing species). The GC/MS spectra for the scrape down sample contained peaks for diesel fuel and biodiesel (methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate) that were absent in the fresh oil, but no peaks were identified that would indicate significant chemical changes due to the exposure to ammonia.

The analysis conducted here does not show whether the ammonia would impact the lubricating performance of the oil while it remained in solution, or whether there might be chemical interactions between the ammonia and additive packages in other formulations, but there does not appear to be any permanent chemical interaction between the ammonia and the base oil.

4 CONCLUSIONS

Analysis of the piston deposits formed during operation using a deposit control test protocol was conducted for multiple repeats of diesel operation with varying temperature conditions in the Enterprise research engine. An initial dual-fuel ammonia case was also examined. Key findings include:

1. Piston deposit formation is strongly influenced by the temperature of the combustion gases.
2. Higher combustion gas temperatures (indicated by exhaust T > 500°C) led to the formation of hard deposits on the top land while lower sections of the piston remained clean. Lower temperatures led to reduced top land deposits and significant gummy deposits on piston ring groove and land surfaces.

3. These combustion gas temperature trends hold for ammonia dual-fuel combustion as well.

4. Initial lubricant deposit control performance with ammonia dual-fuel operation is promising; future studies will elucidate the impacts of different lubricant formulations.

5. Ammonia dual-fuel combustion is likely to influence combustion temperatures in practice through a combination of gas properties (γ), air/fuel ratio changes, local temperature distribution changes, and reduced heat transfer.

6. Scrape down oil samples initially had a noticeable ammonia odor, indicating some ammonia dissolved in the oil.

7. No significant chemical changes from ammonia exposure were detected by GC/MS analysis of the scrape down oil sample.

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

γ: Specific Heat Ratio
BN: Base Number
GHG: Greenhouse Gas
IMO: International Maritime Organization
OEM: Original Equipment Manufacturer
MGO: Marine Gasoil
PCR: Piston Cleaning Ring
TBN: Total Base Number
VLSFO: Very Low Sulfur Fuel Oil

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7 CONTACT

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