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An Experimental Investigation of the Corrosive Influence of SO₂ relative to H₂SO₄ of Marine Engine Cylinder Liners

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ABSTRACT

The present study investigates the corrosive influence of SO₂ on cylinder liner wear relative to H₂SO₄. Several charge gasses with different concentrations of SO₂, H₂SO₄ and H₂O in air are fed to a motored light duty test engine that operates at 98 rpm, in order to resemble the corrosive combustion gas and cycle speed of large low speed two-stroke marine engines. When the trapped cylinder gas is compressed the H₂SO₄ and H₂O vapors can condense on the oil wetted liner surface, and the SO₂ can be absorbed in the oil film. Hereby the liner surface may be exposed to a corrosive attack. A blend of a base oil and a commercial marine engine cylinder lubrication oil is used in the experiments. During testing, oil samples are extracted from the engine and subsequently analyzed for iron and sulfur accumulation (using an Energy Dispersive X-Ray Fluorescence Spectrometer) in order to couple cylinder liner wear with the amount of SO₂, H₂SO₄, and H₂O in the charge gas. In contrast to H₂SO₄, the wear of SO₂ is weak (if any), although the SO₂ accumulates/reacts considerably in the lube oil. The highest wear rates are found at elevated H₂O concentrations.

1. INTRODUCTION

During the last decades, large two-stroke marine diesel engines have been subject to improvements in terms of fuel efficiency and unwanted gas emissions. Increased cylinder gas pressures have negatively affected the cylinder liner wear/corrosion rates. Especially in “slow steaming” operation when Heavy Fuel Oil (HFO) with sulfur (sulfur mass fraction normally up to 5 %) is combusted.

Corrosion of cylinder liners can be coupled to the fuel bound sulfur¹⁻⁴. Moreover, the use of Exhaust Gas Recirculation (EGR) can promote engine wear when sulfur is present^{5,6}. The cylinder liner wear in marine engines is normally stated in units of mm/1000 hours. In large two-stroke marine diesel engines a normal cylinder liner (bore) wear rate is < 0.1 mm/1000 h and wear rates exceeding 1 mm/1000 hours are critical^{7,8}.

During combustion the fuel sulfur is primarily converted into sulfur dioxide (SO₂). After combustion and during the expansion stroke a fraction of the SO₂ is converted into sulfur trioxide (SO₃)^{9,10}. SO₃ can combine with available water vapor (H₂O) in the cylinder gas and form sulfuric acid (H₂SO₄) vapor. A binary mixture of H₂O and H₂SO₄ may thereby condense on the liner surface. Aqueous sulfuric acid is a strong electrolyte that is highly corrosive to various steel types, such as the cast iron liner. Previous studies have found that sulfuric acid has a significant impact on the liner wear^{11,12}. High temperature SO₂ corrosion of various metals or alloys is a known issue¹³. It requires, however, temperatures of more than 400 °C, which is well above the liner temperature in a marine engine. Nevertheless, SO₂ can dissolve (absorb) in formulated motor oils^{3,14} and the influence of SO₂-wear in combustion engines has been studied in the past. Nagaki and Korematsu^{15,16} added SO₂ to the charge air of a light duty single cylinder diesel engine and found that piston ring wear increases with the SO₂ addition. They reasoned that SO₂ absorbs in the cylinder liner oil film where it forms sulfuric acid and other sulfates that cause abrasive and corrosive wear. Similarly, Naegeli and Marbach³ operated a single cylinder light duty diesel engine. When sulfur was introduced, either as a fuel additive or as SO₂ in the charge air, increased wear was observed on engine parts. In their experiments, the sulfur to SO₃/H₂SO₄ conversion was typically less than 1 %. They stated that sulfurous acid (H₂SO₃) formed by SO₂ in the lube oil is the primary cause of cylinder wear.

Supplementary experimental research confirm the low conversion of fuel sulfur into SO₃/H₂SO₄ in light and medium duty diesel engines^{17,18}. The conversion may, however, be more than 4 % in large low speed marine engines^{9,10} partly due to much lower engine speeds. In addition, advanced computational efforts indicate that H₂SO₄ vapors will condense on the cylinder liners^{19,20}.

Cylinder lubrication oils used in large two-stroke marine engines contain alkaline additives (primarily CaCO₃) that neutralize acids²¹⁻²⁴. The content of alkaline constituents is defined by the Base Number (BN). A 10-20 BN oil is normally used for fuels with a low sulfur content, whereas 70-100 BN oils are used for high sulfur contents²⁵. In new oil types, the BN may be as high as 140.

The continuous engine improvements in combination with the broad use of “slow steaming” has led to doubts regarding the influence of SO₂-wear relative to H₂SO₄. A previous experimental study

conducted by the authors, supports the coupling between corrosive liner wear and the presence of even small concentrations of H_2SO_4 (ppm level) in the cylinder gas²⁶. The present study follows up on that work by studying the influence of SO_2 -wear relative to H_2SO_4 . The same test facility that involves a modified and motored light duty BUKH DV24 engine is used. Different concentrations of SO_2 as well as H_2SO_4 and H_2O vapors are dosed into the charge air of the BUKH engine, in order to resemble the corrosive combustion gas within the cylinder of a marine engine. Unlike atmospheric tribo-testers, the facility offers near realistic conditions of H_2SO_4 - H_2O condensation and SO_2 absorption (at the oil wetted liner surface) in realistic time scales during the cyclic gas conditions. The cylinder liner wear is measured as iron (Fe) accumulation in the ~ 0.5 kg lube oil swamp. During an experiment, oil samples are withdrawn from the swamp and the Fe-concentration is subsequently measured with an X-Ray Fluorescence (XRF) spectrometer. The ASTM D7751-16 standard for analyzing fuel oils and additive packages in lubrication oils is based on the XRF technique. Condensation and absorption of sulfur compounds are measured, likewise, as accumulated sulfur (S) in the lube oil. A blend lube oil composed of a highly sulfur free base oil and a commercially available marine engine cylinder lubrication oil is used in the experiments. The relatively low BN of ~ 8.5 of the blend oil should theoretically “speed up” the liner wear.

2. EXPERIMENTAL SECTION

2.1 Experimental Setup

A modified two-cylinder and four-stroke BUKH DV24 diesel engine is used in this work (Figure 1) with the specifications listed in Table 1. The BUKH engine is motored (no combustion) by an electric motor through a 1:15 worm gear, to keep the engine speed at 98 rpm similar to a large two-stroke marine engine. Additional weight is applied to the flywheel for smooth rotation. The test facility is schematically illustrated in Figure 2, and described in the following.

Figure 1. Modified BUKH DV24-engine. The charge gas system is the insulated duct in the background and the SO₂ supply gas bottle is positioned in front of the engine flywheel cover. An SO₂ alarm is positioned below the engine, next to the ventilated crank case/base cover.

Figure 2. Schematic test facility.

Charge Gas System: Filtered and pressurized air passes through a flow meter, a ceramic air heater and the 9-liter charge vessel that dampens pressure fluctuations. The air is considered dry, although it may contain weak traces of water vapor. A gravimetric flow rate of aqueous sulfuric acid (H₂SO₄)

in distilled water) is dosed into the charge air by a peristaltic pump. The liquid enters the charge gas after the ceramic heater, and evaporates instantly in the $\sim 400\text{ }^{\circ}\text{C}$ air stream; well above the $337\text{ }^{\circ}\text{C}$ boiling point temperature (at atmospheric pressure) of pure sulfuric acid. The sulfuric acid strength, the dosing rate and the air flow rate govern the concentration of H_2O and H_2SO_4 vapors in the charge gas. At the engine intake the charge gas pressure is slightly above the ambient pressure. In order to avoid condensation of vapors upstream the engine intake, the charge gas system is covered with electric heat bands ($\sim 200\text{ }^{\circ}\text{C}$) and is insulated, as seen in Figure 1.

SO_2 gas (purity grade 3.8) is added to the charge gas from a SO_2 pressure bottle and through a mass flow controller (MFC). At temperatures less than $400\text{ }^{\circ}\text{C}$, SO_2 to SO_3 conversion is very slow. However, in a chemical perspective the residence time of ~ 7 seconds in the charge gas system is rather long, and SO_3 reacts rapidly with H_2O to produce H_2SO_4 vapor. The SO_2 is therefore dosed into the charge gas near the engine intake, as seen in Figure 2, in order to avoid $\text{SO}_3/\text{H}_2\text{SO}_4$ formation in the charge gas system.

Liner Temperature Control: The cooling circuit of the BUKH engine is filled with 4 liters of ethylene glycol that flows around the two cylinders and through the cylinder head. The heated glycol provides a uniform cylinder liner surface temperature of $80\text{ }^{\circ}\text{C}$ that is monitored by 8 thermocouples mounted in each liner.

Lubrication Oil System: A Danfoss BFP 21 L3 pump supplies 15 bar oil pressure for two Danfoss fuel oil nozzles (positioned in the engine base cover) that continuously spray lube oil onto the cylinders. The nozzles are electrically heated to $150\text{ }^{\circ}\text{C}$ to facilitate the oil atomization.

A Scherzinger 51 FBR/GM005 pump (replacing the original camshaft driven oil pump) provides 1-2 bar pressure in the engine oil channels and supplies oil to the crankshaft, main and connecting rod bearings etc. Lube oil continuously drains into the 600 mL oil beaker/swamp positioned on a plate heater below the engine base cover, see Figure 3. The pumps extract the oil from the bottom of the beaker. Plate heaters (set to $120\text{ }^{\circ}\text{C}$) are mounted on the base cover and on the outside of the engine block to improve the draining and keep the oil at $70\text{-}80\text{ }^{\circ}\text{C}$.

Lubrication Oil: A “sulfur-free” non-additivated base oil and an additivated commercial cylinder lubrication oil that is formulated for large two-stroke marine engine applications are used. The properties of the oils are listed in Table 2. In order to approach the preferred viscosity for the BUKH

engine, the marine oil is mixed with 50 % (mass basis) base oil. The intention with the blending is also to achieve a low BN oil with less ability to neutralize acids, while fairly keeping the properties of the marine oil.

Figure 3. Oil beaker/swamp positioned on the plate heater below the engine base cover. The lube oil nozzles are mounted in the base cover.

Oil Sample Analysis using ED-XRF: Before an experiment, the oil beaker is filled with ~0.5 kg fresh lube oil. During the experiment, several oil samples of 5 mL are extracted through a valve in the low pressure oil circuit, Figure 2, and fresh lube oil is regularly replenished to a sufficient level. The elemental Fe and S concentrations in the samples are measured using a calibrated Energy Dispersive X-ray Fluorescence Spectrometer (ED-XRF), *AMETEK SPECTRO XEPOS*.

2.2 Test Schedule

Several charge gas compositions are introduced into the cylinders of the motored BUKH engine. Since the engine experiences no combustion and therefore produces lower peak pressures than a fired marine engine, the dosing of SO_2 , H_2SO_4 and H_2O is tuned to mimic the partial pressures within the cylinder of a fired marine engine^{10,20}. The steady experimental operating conditions are listed in Table 3.

The matrix in Table 4 lists the individual experiments, i.e. the test cases (TC's) that are performed in this work. The matrix consists of four test series. The same cylinder liners are used in the test series, but each series starts with fresh oil in the oil beaker. In TC 0 no species, except heated air, are

introduced into the engine. TC 0 represents a “blank run” or “run in” case, that is used to “prepare” the engine and provide steady operating conditions prior to a series of TC’s.

3. CALCULATIONS

3.1 Cylinder Gas Pressure and Temperature

Figure 4 shows a sketch of the BUKH engine cylinder-piston configuration. The rotating crankshaft arm is connected to the electric motor via the worm gear and the reciprocating motion of the piston is realized through the connecting rod. The lube oil sprays from the nozzles positioned in the base cover reach the cylinders below the piston. “Fresh” oil is thereby continuously supplied onto the liner surface where it is distributed by the reciprocating piston rings.

Figure 4. Sketch of the BUKH-engine cylinder-piston configuration. The intake and exhaust valves are shown as closed.

When the intake valve is open, the cylinder is filled with charge gas as the piston moves downwards to its lowermost position termed the Bottom Dead Center (BDC). At the BDC the piston reverses (moves upward) and starts to compress the trapped cylinder gas as the intake valve closes. Compression proceeds until the topmost position termed the Top Dead Center (TDC) where the piston

reverses again, and the cylinder gas expands until the point where the exhaust valve opens - a little before the BDC. The cylinder gas is exhausted through the exhaust valve as the piston moves towards the TDC once more. The exhaust valve closes again and the cycle is repeated. The full cycle covers two revolutions, i.e. 720 crank angle degrees (1.22 seconds at 98 rpm) that are represented by the angular position θ of the crank shaft arm in Figure 4. $\theta = 0$ at TDC when the cylinder filling begins, and θ is coupled to the engine speed N or the angular velocity ω of the crank shaft arm as seen in eq. 1. The time t is in seconds and $t = 0$ when $\theta = 0$.

$$\theta = \omega t = \frac{N \cdot 2\pi}{60} t \quad \text{eq. 1}$$

The derivative of the cylinder gas volume V with respect to time is given by eq. 2 where L_R is the connecting rod length, B is the cylinder bore and L_C is the length of the crankshaft arm.

$$\frac{dV}{dt} = \omega \frac{\pi B^2}{4} L_R \left(\sin(\omega t) + \frac{L_R}{2L_C} \sin(2\omega t) \right) \quad \text{eq. 2}$$

The derivative of the internal energy U of the cylinder gas with respect to time is given by eq. 3.

$$\frac{dU}{dt} = \frac{d(m \cdot u)}{dt} = u \frac{dm}{dt} + m \frac{du}{dt} \quad \text{eq. 3}$$

During compression and expansion of the cylinder gas (the intake and exhaust valves are closed) no gas enters or leaves the cylinder and “blow by” of small gas leakages past the piston rings are neglected. The mass of the trapped cylinder gas m is then constant, and the term $\frac{dm}{dt}$ cancels. If the gas behaves as an ideal gas, the differential of its specific internal energy du is the product of the specific heat (at constant volume) c_v and the temperature differential dT as seen in eq. 4.

$$\frac{dU}{dt} = m \frac{du}{dt} = m c_v \frac{dT}{dt} \quad \text{eq. 4}$$

The energy balance for the trapped cylinder gas is now given by eq. 5 where $\frac{dQ}{dt}$ is the rate of convective heat transfer/loss from the gas to the cylinder walls and $\frac{dW}{dt}$ is the rate of work performed on the cylinder gas.

$$mc_v \frac{dT}{dt} = \frac{dW}{dt} - \frac{dQ}{dt} \quad \text{eq. 5}$$

The loss to the walls (liner surface, piston top and cylinder head) in eq. 6 is calculated from the heat transfer coefficient h_c derived by Woschni²⁷. The coefficient accounts for the instantaneous cylinder gas pressure p and mean gas temperature T , besides engine geometry and speed. The cylinder walls that are exposed to the trapped cylinder gas constitute the instantaneous heat transfer area A with the temperature $T_L = 80$ °C.

$$\frac{dQ}{dt} = h_c A (T - T_L) \quad \text{eq. 6}$$

The ideal gas law on a differential form (assuming constant mass and gas composition) in eq. 7 is used to relate T by p .

$$p \frac{dV}{dt} + V \frac{dp}{dt} = mR \frac{dT}{dt} \quad \text{eq. 7}$$

Combining eq. 5 with eq. 6 and eq. 7 and recognizing that $\frac{dW}{dt} = -p \frac{dV}{dt}$ now yields the derivative of the cylinder gas pressure with respect to time as seen in eq. 8.

$$\frac{dp}{dt} = \frac{-h_c A (T - T_L) - p \frac{dV}{dt} \left(\frac{c_v}{R} + 1 \right)}{V \frac{c_v}{R}} \quad \text{eq. 8}$$

The thermal properties of dry air are used as a good approximation in the calculations. The constant mass of the trapped cylinder gas is calculated from the ideal gas law with the charge gas pressure and temperature in Table 3.

Figure 5 shows the curve of the modeled, normalized, cylinder gas pressure during compression and expansion, i.e. when the intake and exhaust valves are closed. The pressure peaks at 37.6 bar and the heat loss explains the slightly lower pressure trace after the TDC. The curve of the mean cylinder gas temperature can be calculated from the modeled pressure and the ideal gas law. The shape is similar to the pressure in Figure 5 and peaks at 774 °C.

Figure. 5. Modeled, normalized, cylinder gas pressure relative to the piston position during compression and expansion.

The low speed of the motored BUKH engine (98 rpm) could hamper the gas seal between the piston rings and the cylinder liner surface. The sealing is tested with a cylinder compression tester that is installed in the cylinder head instead of the “dummy” fuel injector that is mounted during testing. When the compression tester is mounted, the geometric cylinder compression ratio is lowered, and the measured peak gas pressure is therefore a little lower than the calculated pressure, but it is consistent with the altered compression ratio. Moreover, as described in Figure 1, an SO₂ alarm (detection limit of 2 ppm) is used in the experiments, and is positioned next to the ventilated crankcase where lube oil drains from the base cover into the oil beaker. Traces of SO₂ gas in the ventilated crankcase would result from cylinder gas leakages past the piston rings. Yet, no such traces were detected by the alarm although the charge gas may contain more than 3000 ppm SO₂.

3.2 Cylinder Gas Dew Points and SO₂-Oil Solubility

In order to identify the cylinder liner areas that are susceptible to corrosive wear, empirical dew point correlations for pure H₂O vapor and H₂SO₄ vapor are applied. As seen in eq. 9, the distinct partial

pressure of a gas species p_i is calculated from the molar concentration x_i . The subscript i refers to H_2SO_4 , H_2O or SO_2 .

$$p_i = p \cdot x_i \quad \text{eq. 9}$$

The sulfuric acid dew point $T_{H_2SO_4,dp}$ in eq. 10 is calculated using the correlation provided by Verhoff and Banchero²⁸. It is coupled to $p_{H_2SO_4}$ and p_{H_2O} as the sulfuric acid condenses as a binary H_2SO_4 - H_2O mixture.

$$\frac{1}{T_{H_2SO_4,dp}} = 2276 \cdot 10^{-6} - 2943 \cdot 10^{-8} \ln(p_{H_2O}) - 858 \cdot 10^{-7} \ln(p_{H_2SO_4}) + 620 \cdot 10^{-8} \ln(p_{H_2SO_4}) \ln(p_{H_2O}) \quad \text{eq. 10}$$

The pure water dew point $T_{H_2O,dp}$ is coupled to p_{H_2O} . It is calculated using the Antoine equation in eq. 11 that is listed together with the Antoine constants A , B and C in the NIST Chemistry Webbook²⁹. When calculating the cylinder gas dew points, it is fair to assume that the H_2O and the H_2SO_4 concentrations remain constant, although condensation takes place during compression and expansion.

$$T_{H_2O,dp} = \frac{B}{A - \log_{10}(p_{H_2O})} - C \quad \text{eq. 11}$$

TC 4-2 in Table 4 yields the lowest $T_{H_2SO_4,dp}$ -curve of the test matrix which is plotted against the piston position in Figure 6 (dashed curve). The curve generally exceeds the liner temperature T_L (horizontal line) which means, that in all the TC's with H_2SO_4 vapor, sulfuric acid condenses on the liner area that is exposed to the trapped cylinder gas.

TC 1-2 and TC 4-2 yields the highest and the lowest $T_{H_2O,dp}$ -curve of the test matrix respectively (dashed dotted- and dotted curve respectively). The curves lie well below the $T_{H_2SO_4,dp}$ -curve, but pure water is able to condense on the top of the liner where $T_{H_2O,dp}$ exceeds T_L .

The rate of H_2O and H_2SO_4 condensation onto the liner surface scales with p_{H_2O} and $p_{H_2SO_4}$ respectively²⁰, that “mirror” the cylinder gas pressure. Moreover, when $T_{H_2O,dp} > T_L$, the rate of pure

water condensation may highly exceed that of sulfuric acid since $x_{H_2O} \gg x_{H_2SO_4}$. Nevertheless, as the pressure falls during the expansion stroke, condensed water will begin to evaporate from the wetted liner surface when T_L exceeds $T_{H_2O,dp}$ after TDC. In large marine engines, H_2O condensation is also confined to the top of the liner, and H_2SO_4 may condense on the entire liner surface²⁰.

SO_2 is soluble in oils^{14,30} and water, especially at room temperature. Formulated motor oils exhibit a high chemical reactivity towards SO_2 that can highly exceed the SO_2 -oil solubility¹⁴. Henry's law of solubility states that the solubility of a gas species into a liquid is directly proportional to its partial pressure. The SO_2 uptake along the oil wetted liner surface is expected to “mirror” the cylinder gas pressure. In combination with condensed water, the SO_2 may lead to the formation of H_2SO_3 .

Figure. 6. Dew point temperature curves of aqueous sulfuric acid and pure water for selected (extreme) TC's in Table 4. The horizontal line represents the constant liner temperature of 80 °C.

4 RESULTS AND DISCUSSIONS

4.1 Test Series 1

Test series 1 is a preliminary test series performed with the base lube oil. It illustrates how the cylinder liner wear responds to changes in the charge gas composition. The series covers TC 1-1 through TC

1-8 as seen in Table 4, and is prepared and finalized by TC 0. Numerous oil samples are extracted from the engine during the more than 24 hours of continuous operation. Each marker in Figure 7 represents the measured Fe-concentration of a lube oil sample, extracted at a given point in time. For each TC, the linear fit represents the measured Fe-rate, i.e. the measured wear rate in $\frac{\text{mg}}{\text{kg}\cdot\text{hr}}$. The rate is displayed in the figure legend by the number in brackets. Sudden drops of the Fe-concentration are explained by oil replenishment in-between TC's, in order to avoid lube oil starvation.

Figure 7. Iron-concentration in the lube oil samples extracted from the engine during test series 1. For each TC, the number in brackets in the figure legend denote the measured wear rate (Fe-rate) that is represented by a linear fit in $\frac{\text{mg}}{\text{kg}\cdot\text{hr}}$.

As seen in Figure 7, the "run in" case (TC 0) with dry air only, produces a weak wear rate (Fe-rate). The same applies when the "wet" charge gas (i.e. H_2O is dosed to the charge gas) with 5.2 % H_2O is introduced into the engine (TC 1-1). Yet, the Fe-rate increases sharply when the H_2O concentration is increased to 10.1 % (TC 1-2). As the charge gas "returns" to the 5.2 % H_2O concentration and includes ~900 ppm SO_2 (TC 1-3) the rate drops immediately and remains flat until the point where 49 ppm H_2SO_4 is also applied to the charge gas (TC 1-4). The weak negative rate observed in TC 1-3 is not physically true, but related to the inherent uncertainties of the experimental method. A "wavy" profile of the Fe-concentration is produced as the H_2SO_4 is removed from the charge gas, while the SO_2 concentration is further increased to ~3000 ppm (TC 1-5). The overall Fe-rate is, however, "flat"

until the point where 50 ppm H_2SO_4 is also introduced into the charge gas (TC 1-6). A steep Fe-rate similar to TC 1-2 is produced when the charge gas contains 9.7 % H_2O plus ~900 ppm SO_2 (TC 1-7). The rate remains high with the addition of 47 ppm H_2SO_4 (TC 1-8). The Fe-rate tends to flatten as dry air only (TC 0) is introduced into the engine.

The distinct Fe-rates in Figure 7 indicate that the liner wear is rapidly affected by the applied charge gas composition. Sudden flattenings of the Fe-rates indicate, moreover, that the liner wear ceases as soon as the gas composition is not corrosive/wearing. It is observed that H_2SO_4 rather than the SO_2 promotes wear, which is seen by the flat rates of TC 1-3 and TC 1-5 compared to TC 1-4 and TC 1-6. When the H_2O concentration in the charge gas approaches 10 % the wear rate increases considerably, even in the absence of H_2SO_4 . The Fe-rates of TC 1-7 and TC 1-8 should not be compared directly due to oil replenishment after TC 1-7. Yet, in TC 1-8 the wear rate reduces by ~33 % relative to TC 1-7, which matches the expected decline due to the oil replenishment. It is therefore not evident that the presence of H_2SO_4 at high H_2O concentrations increases the liner wear.

The heated engine block, the ventilated crank case and the heated oil swamp beaker prevent the accumulation of condensed water in the lube oil. Liner wear caused by water “build up” in the oil is therefore unlikely, and in line with the non-continuous and dissimilar Fe-rates produced in test series 1. It will be shown in section 4.2, that the accumulation of condensed sulfuric acid in the oil swamp is not more than 13 ppm/hour (mass basis) during a TC. This would potentially yield an acid-oil mixture with very poor electrolytical properties, and liner wear due to sulfuric acid “build up” is therefore also unlikely.

A more direct comparison of H_2SO_4 - and SO_2 - related liner wear is performed with the blended lube oil in test series 2, 3 and 4 listed in Table 4. Although the BN number of the blend oil is only ~8.5, the base reserve (i.e. the CaCO_3 content of the oil) will highly exceed the sulfuric acid “build” up in the lube oil. Thus, the BN number is basically constant as the sulfuric acid is neutralized (by CaCO_3) during a TC. The neutralization will also ensure, that wear of H_2SO_4 “build up” in the oil swamp is inhibited.

4.2 Test Series 2

In test series 2, the corrosive influence of SO_2 is measured relative to H_2SO_4 in wet and in dry charge gas conditions. Prior to the four consecutive cases, TC 2-1 through TC 2-4, the series is prepared by TC 0. A mathematical representation of the Fe-content in the lube oil swamp is seen in Figure 8, and is calculated using the Fe-concentrations of the extracted lube oil samples. Each marker in the figure

denotes a lube oil sample point and the Fe-content in mg. The number is not physically genuine, yet, the linear fit of each TC represents the true Fe-rate in mg/hr. In the following, the rate is termed the measured wear rate (*MWR*). Similarly, the linear fit of the S-accumulation in Figure 8 represents the measured sulfur uptake rate (*MSR*) in the lube oil swamp.

In order to calculate the *MWR* and the *MSR*, the instant mass of the lube oil swamp is required. It is found by accounting for the oil samplings, the oil replenishments and a general oil loss. The general loss is due to small leakages in the oil circuit. It is found by measuring the difference of the oil mass in the oil swamp beaker, before and after a test series.

The measured wear rate in TC 0 represents a measured abrasive (non-corrosive) background wear rate (*MBR*), that constitutes the combined wear of all the lubed moving parts within the engine. The *MBR* may be affected by the use of the blend lube oil, as the resulting viscosity does not fully match the recommended viscosity for the BUKH engine. The wear rate that is coupled to the presence of the dosed species (SO_2 , H_2SO_4 and H_2O) in the charge gas, is termed the apparent liner wear rate (*AWR*). The *AWR* is defined as the difference between the *MWR* and the *MBR* as seen in eq. 12.

$$AWR = MWR - MBR \quad \text{eq. 12}$$

The inherent sulfur content of the applied marine cylinder oil is about 9473 ppm (Table 2). The *MSR* of TC 0 is de facto zero. Yet, an incomplete sulfur distribution within the lube oil, can result in a slightly negative (or positive) *MSR*-fit as seen for TC 0. In the dry SO_2 case (TC 2-1, 3102 ppm SO_2 in air) the steep *MSR* indicates that SO_2 is absorbed in, or reacts with the lube oil on the liner surface. Yet, the *MWR* of TC 2-1 is slightly lower than the *MBR*, which yields a negative (and unphysical) *AWR* according to eq. 12. It is presumed that the *MBR* decreases slowly over time. The *AWR* is therefore zero, as stated in Figure 8.

Figure 8. Accumulated iron and sulfur in the lube oil swamp in test series 2. The legends in the figures show the *MBR*, *MWR*, *AWR* and the *MSR* rates in $\frac{\text{mg}}{\text{hr}}$. The charge gas compositions of the TC's are listed in Table 4.

In the wet SO_2 case (TC 2-2, 3127 ppm SO_2 and 5.8 % H_2O in air) the *MWR* increases abruptly as the H_2O is introduced into the charge gas. The initial set point of the peristaltic pump (dosing of H_2O into the charge gas) was a little too high, and therefore tuned within the first 5-10 minutes of TC 2-2. As experienced in test series 1, the *MWR* is sensitive to the applied H_2O concentration. The pump tuning could therefore explain the declining *MWR*. The overall *AWR* is vague in TC 2-2. However, in the second half, the *MWR* is a little lower than the *MBR* and indicates, that the *AWR* is zero.

TC 2-2d is a duplicate of TC 2-2. It is performed with the same gas composition as in TC 2-2, but the base oil is used instead of the blended oil. From the difference between the *MSR* of TC 2-2 and TC 2-2d (in Figure 8 and in Figure 9, respectively) it is found, that the *MSR* with the blended lube oil is nearly 28 times higher than with the base oil $\left(\frac{44.9 \text{ mg/hr}}{1.62 \text{ mg/hr}} = 27.7\right)$. This indicates, that the formulated marine cylinder lube oil reacts considerably with SO_2 from the cylinder gas. In TC 2-2 condensed water on the oil wetted liner surface may hamper the SO_2 -oil reactivity, as the *MSR* is almost halved $\left(\frac{44.9 \text{ mg/hr}}{81.2 \text{ mg/hr}} = 0.55\right)$ compared to the dry SO_2 case (TC 2-1).

When the SO₂ dosing is turned off (TC 2-3, 5.8 % H₂O in air) the *MWR* settles at a rate that is a little lower than the *MBR*. It indicates, that 5.8 % H₂O in the charge gas is not wearing. Moreover, the lower *MWR* supports the slowly decreasing background wear rate as stated earlier.

Figure 9. Accumulated sulfur in the lube oil swamp (base oil) of the duplicate tests, TC 2-2d and TC 2-4d. The legend in the figure shows the *MSR* in $\frac{\text{mg}}{\text{hr}}$. The charge gas compositions are the same as in TC 2-2 and TC 2-4, respectively, and are listed in Table 4

Unlike in TC 2-2, the “overdosing” of H₂O was avoided in the wet SO₂-H₂SO₄ case (TC 2-4, 74 ppm H₂SO₄, 3122 ppm SO₂ and 5.7 % H₂O in air). Yet, the first sample in TC 2-4 is omitted in the linear *MWR* and *MSR* fits, due to incomplete oil swamp mixing after the oil replenishment between TC 2-3 and TC 2-4. In TC 2-4, any possible wear influence of SO₂-chemisorption effects within the tribolayer/oil film (during TC 2-1 and TC 2-2) is sought to be hindered by introducing TC 2-3 where the SO₂ dosing is off. Hence, the steady *MWR* in TC 2-4 that yields a non-zero *AWR* indicates, that H₂SO₄ is wearing/corrosive when it is introduced into the engine. If the presence of SO₂ rather than the un-tuned H₂O-dosing causes the steep *MWR* in the first half of TC 2-2, then the same *MWR* should be approached in TC 2-4, as the SO₂ and H₂O concentrations are alike. The rate is, however, more than halved in TC 2-4 compared to TC 2-2 $\left(\frac{1.26 \text{ mg/hr}}{2.82 \text{ mg/hr}} = 0.45\right)$ and SO₂ does not seem to explain the steep *MWR* in TC 2-2.

It is presumed that the rate of H₂SO₄ condensation onto the oil wetted liner surface is not affected by the type of the lube oil (i.e. the blend- or the base oil). TC 2-4d is the duplicate of TC 2-4, but is performed with the base oil. The H₂SO₄-related sulfur uptake in the lube oil in TC 2-4 can therefore be assessed, by subtracting the *MSR* of TC 2-2d from the *MSR* of TC 2-4d (3.72 mg/hr - 1.62 mg/hr = 2.10 mg/hr). The *MSR* of TC 2-4 is the combined sulfur uptake from SO₂ and H₂SO₄, but only 5 % $\left(\frac{2.10 \text{ mg/hr}}{42.2 \text{ mg/hr}} = 0.05\right)$ seems to originate from the H₂SO₄. In light of the results

in test series 2, the presence of H_2SO_4 seems therefore much more corrosive/wearing than the SO_2 . Moreover, the sulfur rate of 2.10 mg/hr corresponds to a H_2SO_4 “build up” of ~13 ppm/hour (mass basis) in the oil swamp.

4.3 Test Series 3

Test series 3 in Figure 10 starts with a three hour wet charge gas case (TC 3-1, 5.6 % H_2O in air) in the attempt to avoid a non-steady *MWR* as experienced in TC 2-2. Due to a slight overdosing of H_2O , the *MWR* is steep in the beginning of TC 3-1. Yet, the *MWR* soon declines as the dosing is tuned, and remains steady at a rate comparable to the *MBR* in test series 2 (TC 0 in Figure 8). The applied H_2O concentration is therefore not wearing, and for that reason, the *MBR* in test series 3 is defined by the *MWR* of TC 3-1. The *AWR* is zero when the wet SO_2 gas (TC 3-2, 3094 ppm SO_2 and 5.7 % H_2O in air) is introduced into the engine, and indicates that sole SO_2 is not wearing. In contrast, the *AWR* is positive (i.e. wear occurs) when H_2SO_4 is also introduced (TC 3-3, 73 ppm H_2SO_4 , 3111 ppm SO_2 and 5.6 % H_2O in air), although the *MSR* is lowered by 1/3 compared to TC 3-2 ($\frac{54.8 \text{ mg/hr} - 37.5 \text{ mg/hr}}{54.8 \text{ mg/hr}} = 0.32$). It is presumed that condensed H_2SO_4 at the oil-wetted liner surface hampers the sulfur uptake through a lower SO_2 -oil reactivity.

Figure 10. Accumulated iron and sulfur in the lube oil swamp in test series 3. The legends in the figures show the *MBR*, *MWR*, *AWR* and the *MSR* rates in $\frac{\text{mg}}{\text{hr}}$. The charge gas compositions of the TC's are listed in Table 4.

4.4 Test Series 4

As opposed to test series 3, a wet charge gas with H₂SO₄ (TC 4-1, 49 ppm H₂SO₄ and 5.0 % H₂O in air) is introduced into the engine in test series 4, before the SO₂ dosing, in order to eliminate potential wear influences of SO₂-chemisorption in TC 4-1. At 5 % H₂O the non-steady *MWR* is avoided and the *AWR* of TC 4-1, shown in Figure 11, confirms that H₂SO₄ is wearing/corrosive. The *MSR* is slightly negative, since the sulfur uptake of condensed H₂SO₄ (in the lube oil) represents a very small amount relative to the inherent lube oil sulfur, that is not completely distributed, as mentioned earlier. When SO₂ is also introduced into the charge gas (TC 4-2, 48 ppm H₂SO₄, 2986 ppm SO₂ and 5.0 % H₂O in air) a slight increase in the *AWR* of 7 % is observed relative to TC 4-1 $\left(\frac{0.48 \text{ mg/hr} - 0.45 \text{ mg/hr}}{0.45 \text{ mg/hr}} = 0.07\right)$. Increments or reductions of this size may be within the experimental uncertainty, though. In any case, the effect of SO₂ on the *AWR* is weak (if any) compared to H₂SO₄.

Figure 11. Accumulated iron and sulfur in the lube oil swamp in test series 4. The legends in the figures show the *MBR*, *MWR*, *AWR* and the *MSR* rates in $\frac{\text{mg}}{\text{hr}}$. The charge gas compositions of the TC's are listed in Table 4.

4.5. Visual Inspection of Cylinder Liner Wear

After the four test series, the cylinder liners of the BUKH engine were unmounted for a visual inspection of wear. A photograph of one of the liners is seen in Figure 12. Above the TDC position of the top piston ring, a protective “coked” lube oil layer covers the 18 mm “static” liner top. The top is exposed to the highest cylinder gas temperatures (above 700 °C) that provide a hot surface where H_2O and H_2SO_4 condensation is not favored, as opposed to the cooled liner surface below.

Below the “static” top, the liner surface is swept by the moving piston rings. As seen in Figure 12, the wear is concentrated in the upper 11 mm of this “non-static” part. The motion of the piston rings ceases as the piston approaches the TDC, which inhibits the hydrodynamic lubrication and the oil’s ability to separate the liner surface from the piston rings. The oil film thickness (of a few microns) is therefore known to be corresponding thin in this location^{31,32}. In addition, the upper swept part is exposed to high gas pressures, and is therefore exposed to significant deposits of H_2O and H_2SO_4 condensate.

Figure 12. Photograph of the surface of a used cylinder liner. The “static” top of the cylinder liner (upper 18 mm) is covered by a protective “coked” lube oil layer. Wear is concentrated on the swept liner surface 11 mm below the “static” top. Further below, the honed surface is still visible.

Despite of the exposure to H_2SO_4 condensation for many hours, most of the swept liner surface appears as new. In fact, the crosshatch-honed liner surface is still visible, as seen in Figure 12. Most of the swept surface seems therefore to be safely protected by an oil layer, even at the BDC where

the piston motion also ceases and challenges the hydrodynamic lubrication. The locus of the liner wear in the figure is analogous to large two-stroke marine engines. In these engines, the corrosive wear is primarily concentrated at the TDC position of the piston ring pack ^{11,12}.

4.6 Discussion

The liner wear rates presented in this work are based on the elemental iron build up in a series of oil samples that are extracted from the engine during a test case, and do not differentiate between the type of wear, i.e. corrosive or abrasive. In test cases that involve H_2SO_4 and H_2O concentrations of less than ~6 % the wear is considered corrosive. When H_2SO_4 condenses, a thin film of aqueous acid forms on the oil wetted liner surface. The acid mixture can corrode the surface through a sequence of electrochemical reactions that form the compound termed iron sulfate (FeSO_4). In this work, pure water condensation has a tendency to increase the liner wear rate significantly at H_2O concentrations exceeding ~6 %. The wear is then considered to be abrasive rather than corrosive, due to the weak electrolytical properties of demineralized water, and since water is known to increase oil viscosity, cause water in oil emulsions and reduce the load carrying capacity of an oil film.

The current focus for marine engines is the application of dual fuel concepts with sulfur free low carbon fuels, such as natural gas (primarily CH_4) or even methanol (CH_3OH) and ammonia (NH_3). Without sulfur the premise for H_2SO_4 corrosion is absent. Yet, in large marine engines a mild corrosive wear is considered to enhance the lubrication, as it creates small oil “pockets” on the liner surface that support the hydrodynamic lubrication. The lack of corrosion may in fact hamper the creation of the oil film, promote liner polish and eventually accelerated scuffing wear. Another aspect with the low carbon fuels is that more H_2O vapor will form in the cylinder gas compared to conventional fuels, due to the higher hydrogen to carbon ratio. Elevated H_2O concentrations within the cylinder gas tends to increase the liner wear, as experienced when ships operate in “wet” tropical regions. The same trend is observed in this work when the H_2O concentration is increased in the charge gas. Therefore, low carbon fuels could involve the risk of increased abrasive (H_2O) wear.

When a fuel contains sulfur, and is combusted in a diesel engine, the sulfur rapidly converts into SO_2 in the hot flame that may exceed 2000 °C. A fraction of the SO_2 is subsequently converted into SO_3 and ultimately H_2SO_4 , as the combustion gasses cool during the expansion stroke ^{9,10}. Adding SO_2

into the charge air of a fired diesel engine has the same effect as increasing the fuel sulfur content - more $\text{SO}_3/\text{H}_2\text{SO}_4$ will form. From the authors point of view, the distinct SO_2 -wear is therefore not examined when SO_2 is added into the charge air of a fired engine, as attempted by Nagaki and Korematsu^{15,16} as well as Naegeli and Marbach³. In the present experiments, the cylinder gas temperature peaks below 800 °C. At this temperature, the SO_2 to SO_3 conversion is basically frozen, and the distinct SO_2 -wear can therefore be examined.

Lejre³³ performed model simulations in order to examine the depletion of lube oil BN under engine conditions. It was concluded, that the H_2SO_4 - CaCO_3 reaction is generally dominant over the SO_2 - CaCO_3 reaction. If SO_2 does not deplete the BN, it could then partly explain the very low impact (if any) of SO_2 on wear, as found in this work.

CONCLUSION

Various charge gas compositions with SO_2 , H_2SO_4 , and H_2O in air that resemble the corrosive cylinder gas in a large two-stroke marine engine, are introduced into a motored two-cylinder BUKH DV24 engine operating at 98 rpm. In the motored engine, the cylinder gas pressure peaks at 37.6 bar (modeled) and the surface temperature of the cylinder liners are fixed at 80 °C. Cylinder liner wear, SO_2 absorption and H_2SO_4 condensation at the oil wetted liner surface are measured as elemental Fe- and S-accumulation, respectively, in the lube oil swamp.

The various charge gas compositions yield distinct liner wear rates that can rapidly change when the composition is altered.

Even though the SO_2 exhibits a high chemical reactivity towards the applied marine engine cylinder lube oil, wear of sole SO_2 is not measured, neither in dry nor in wet charge gas conditions. Moreover, adding SO_2 into a charge gas that contains H_2SO_4 has a weak (if any) additional effect on the liner wear relative to sole H_2SO_4 in the charge gas.

The liner wear rate increases considerably at H_2O concentrations exceeding ~6 % in the charge gas. In fact, the highest wear rates are measured - in the absence of H_2SO_4 - when the H_2O concentration approaches 10 %.

It is found, from a visual inspection of the cylinder liners, that the wear only takes place in the top of the swept liner surface. The top is also most prone to H_2SO_4 and H_2O condensate.

NOMENCLATURE

Symbol		Unit
A	Surface area of the cylinder walls that encloses the trapped cylinder gas	m^2
AWR	Apparent cylinder liner wear rate	mg/hr
B	Cylinder bore	m
c_v	Specific heat capacity of the cylinder gas (constant volume)	J/kg-K
h_c	Specific heat transfer coefficient	$\text{W/m}^2\text{-K}$
L_C	Length of the crank shaft arm	m
L_R	Length of the connecting rod	m
MBR	Measured background wear rate	mg/hr
MWR	Measured wear rate	mg/hr
MSR	Measured sulfur accumulation rate in the lube oil swamp	mg/hr
m	Mass of the trapped cylinder gas	kg
N	Engine speed	rev/min
p	Pressure of the trapped cylinder gas	Pa
p_i	Partial pressure of H_2SO_4 , H_2O or SO_2	Pa
Q	Convective heat transfer/loss from the trapped cylinder gas	J
R	Specific gas constant of the trapped cylinder gas	J/kg-K
T	Mean temperature of the trapped cylinder gas	K
T_L	Cylinder liner temperature	$^{\circ}\text{C}$
$T_{\text{H}_2\text{O},dp}$	Dew point temperature of pure water	$\text{K}, ^{\circ}\text{C}$
$T_{\text{H}_2\text{SO}_4,dp}$	Dew point temperature of sulfuric acid	$\text{K}, ^{\circ}\text{C}$
t	time	s
u	Specific internal energy of the trapped cylinder gas	J/kg
U	Internal energy of the trapped cylinder gas	J
V	Volume of the trapped cylinder gas	m^3
W	Work performed on the trapped cylinder gas	J
x_i	Molar concentration of H_2SO_4 , H_2O or SO_2	-
ω	Angular velocity of the crank shaft arm	rad/s
θ	Angular position of the crank shaft arm	rad

ABBREVIATIONS

BDC	Bottom Dead Center
BN	Base Number
rpm	Revolutions per minute
TDC	Top Dead Center

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TABLES

Working principle	Four stroke
Number of cylinders	2
Bore/stroke/connecting rod	85 mm/85 mm/159.8 mm
Swept volume per cylinder	482 cm ³
Geometric compression ratio	18.5:1

Table. 1. BUKH DV24-engine specifications

	Base oil	Marine cylinder oil
Appearance	Bright , clear	Brown
Density @ 15.6 °C	0.87 g/cm ³	0.96 g/cm ³
Viscosity @ 40 °C	102 cSt	520 cSt
Viscosity @ 100 °C	12.0 cSt	22.0 cSt
Sulfur Content	< 6 ppm	9473 ppm*
Base Number (BN)	0	17

Table 2. Properties of the base- and the marine cylinder lubrication oils. *measured using XRF apparatus.

Cylinder liner temperature	80 °C
Charge gas temperature (at engine intake)	~160°C
Charge gas pressure (at engine intake)	1.05-1.1 bar
Lube oil temperature (in oil beaker)	70-80 °C
Intake air flow (@ 25°C and 1 atm.)	47-50 L/min
Mass flow of dosed liquid (water or aqueous H ₂ SO ₄)	130-265 g/h
Engine rotational speed	98 rpm
Maximum pressure of the cylinder gas*	37.6 bar
Maximum temperature of the cylinder gas*	774 °C

Table 3. Steady operating conditions during testing. *Maximum pressure and temperature are modelled non-adiabatic values.

TC	Oil	H ₂ O [%]	H ₂ SO ₄ [ppm]	SO ₂ [ppm]
0	Base/Blend	0	0	0
1-1	Base	5.2	0	0
1-2	Base	10.1	0	0
1-3	Base	5.2	0	906
1-4	Base	5.1	49	927
1-5	Base	5.2	0	2999
1-6	Base	5.1	50	2997
1-7	Base	9.7	0	904
1-8	Base	9.7	47	909
2-1	Blend	0.0	0	3102
2-2	Blend	5.8	0	3127
2-3	Blend	5.8	0	0
2-4	Blend	5.7	74	3122
3-1	Blend	5.6	0	0
3-2	Blend	5.7	0	3094
3-3	Blend	5.6	73	3111
4-1	Blend	5.0	49	0
4-2	Blend	5.0	48	2986

Table 4. H₂O, H₂SO₄ and SO₂ concentrations in the charge gas (the rest of the charge gas is air) introduced into the BUKH engine cylinders in the individual Test Cases (TC's).