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Study of Methanol Engine on Tribology Properties: Lubricating Oil Aging and Tribofilm Behavior

Lubricants

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ABSTRACT

The use of green methanol fuel can significantly reduce carbon emissions and pollutant discharges in internal combustion engines. However, its combustion products, such as methanol and formic acid, can infiltrate the crankcase and impact the lubrication performance of the piston ring-cylinder liner system. This study simulates the aging process of lubricating oil by introducing methanol and formic acid in a controlled environment and investigates their effects on the physicochemical properties of the oil, including neutralization number (NN), total base number (TBN), and oxidation. Furthermore, friction experiments using cylinder liner-piston ring samples were conducted to assess the tribological effects of aged oil.

The results indicate that formic acid significantly accelerates oil degradation, increases friction, and exacerbates wear, while methanol has a relatively minor impact. Surface analyses reveal that both methanol and formic acid hinder tribofilm formation, reducing protective elements on the friction surface and leading to increased wear. This study provides insights into the adverse effects of methanol fuel combustion products on lubricating oil performance and tribological behavior, contributing to the optimization of lubrication strategies for methanol engines.

1 INTRODUCTION

Renewable energy to replace the original fossil energy gradually appeared. Nowadays, with reserves of these petroleum-based fuels being rapidly depleted, various alternative resources such as methanol, ethanol, or hydrogen are needed in order to replace the non-renewable resources [1]. With global warming being a dominant environmental issue, it seems that the use of alternative fuels in the future is inevitable. Compared with other fuels, methanol has better performance. Among diesel fuel, methanol (CH_3OH) fuel has been considered to be a kind of more favorable fuel for marine engines [2,3]. Compared with diesel, methanol not only requires less oxygen in combustion but also has less heat loss in the tail gas, which can greatly improve the total thermal efficiency of the engine [4]. However, the use of methanol as an alternative fuel for the engine still has some problems. As an alternative fuel, it will cause certain corrosion to the relevant parts of the methanol supply system and the injection system. Unburned methanol in the cylinder flows into the crankcase to dilute the oil, increasing the wear between the piston and the cylinder liner. Methanol engines will also produce unconventional emissions, such as unburned methanol and formic acid generated by inadequate combustion, which have certain hazards to the lubrication oil and the wear between cylinder liner and piston ring. Hence, understanding the frictional performance and wear mechanisms at the interface under the methanol environment is crucial.

Methanol and its combustion byproducts adversely affect lubricating oil, compromising its lubrication and anti-wear properties. Shukla [5], through engine bench tests and tribological experiments, investigated the effects of methanol combustion byproducts on interface lubrication. The findings revealed that the total base number (TBN) of lubricating oil in methanol engines is lower than that in diesel engines, while the concentration of wear metals in the oil is higher. The increased wear was attributed to the emulsification effect caused by methanol and water, which reduces the anti-wear performance of the oil. Furthermore, the presence of water and formic acid in the combustion byproducts accelerates corrosive wear within the engine. The significant water production during methanol combustion can lead to electrochemical corrosion on the cylinder wall, resulting in severe wear in the upper cylinder wall and piston ring areas. Despite the valuable insights gained from bench tests, they are costly and resource-intensive for studying the impact of methanol on lubricating oil properties. Artificial aging of lubricating oil offers a cost-effective alternative by subjecting oil samples to accelerated degradation under controlled conditions, simulating real engine operation in a short period. However, artificial aging procedures must account for the actual degradation mechanisms occurring in methanol engines. Existing standardized aging methods evaluate various parameters of lubricating oil performance [6], but no dedicated aging studies have yet been conducted on the impact of methanol and its combustion products on lubricating oil properties. To address this gap, artificial aging methods tailored to methanol engine applications must be developed. These methods should incorporate periodic sampling and monitoring of oil condition to assess degradation caused by methanol-related compounds, simulating real engine operation in an economically feasible manner.

Additionally, combustion byproducts from different fuels influence the formation of tribofilm, affecting wear at the piston ring-cylinder liner interface. Research on tribofilm formation in methanol engines is relatively scarce, but insights can be drawn from ethanol-fueled engines. Hui Cen [7] employed X-ray photoelectron spectroscopy (XPS) to study the transient kinetics of zinc dialkyldithiophosphate (ZDDP) additive decomposition in the presence of water. The study found that water depolymerizes long-chain phosphates, shortening their chain length and reducing the thickness of the reaction layer as humidity increases, thereby weakening the anti-wear properties of the tribofilm. Similarly, H.L. Costa [8] used synchrotron radiation XANES and XPS techniques to investigate ZDDP-derived tribofilm formed in lubricants contaminated with anhydrous and hydrated ethanol. The presence of ethanol increased friction and surface damage, significantly reducing the content of long-chain phosphates in the tribofilm. Moreover, ethanol promoted the enrichment of iron sulfides within the film, indicating more severe wear. These findings suggest that methanol, like ethanol, may exacerbate friction and wear at the piston ring-cylinder liner interface, directly affecting lubricating oil properties and tribological performance. The internal engine environment also plays a crucial role in the formation of tribofilm and wear mechanisms, further complicating the lubrication conditions of the piston ring-cylinder liner friction pair.

To address these challenges, this study investigates the effects of methanol and its combustion byproducts on lubricating oil properties and piston ring-cylinder liner wear. Artificial aging experiments were conducted to simulate temperature conditions in the oil sump of a diesel engine, with periodic sampling and analysis of lubricating oil properties. Aged oil samples were then used in tribological tests to evaluate the impact of methanol and its combustion products on interface friction, wear, and tribofilm growth. This approach effectively assesses the adverse effects of methanol engines on friction and wear, providing valuable insights for the development of methanol-compatible lubricants and anti-wear strategies for methanol engines.

2 OIL AGEING AND FRICTION EXPERIMENTAL METHOD

2.1 General artificial ageing and friction experiment procedure

Figure 1(a) shows the lubrication oil ageing device mainly consisted of a three-necked flask. The lubrication oil was filled at the start of the artificial ageing procedure. The contamination of the methanol engine was added to the lubrication oil every 12 hours through Neck 1. The dried compressed air that is 1 adjusted at 10 L/min by a flow controller was inlet through Neck 2. The 40 mL aged lubrication oil was extracted through Neck 3 for physical and chemical property detection introduced in Section 2.2 every 12 hours. It is noticed that aging experiments were conducted in a three-neck glass flask at 60°C, simulating medium-speed diesel engine conditions. After 96 hours of ageing procedure, the rest of the aged oil was used to carry out the friction experiment as shown in Figure 1(b). The friction pair materials will be introduced in Section 2.3.

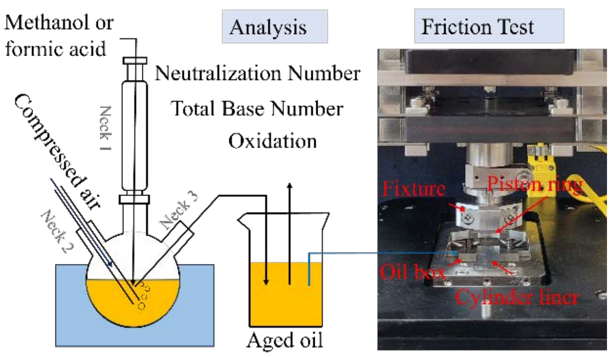

Figure 1 Schematic diagram of artificial ageing and friction experiment procedure

2.2 Lubrication oil and contamination relevant to methanol engine

The lubrication oil used in the ageing procedure is SAE30. The ZDDP (T203) is an important lubrication oil additive that helps to form the tribofilm to protect the surface added to the oil. The physical and chemical property of the oil and the element content is shown in the Table 1.

Table 1 physical and chemical property and element content

Parameters	value	units
Neutralization number	13.4	mg KOH/g
Total base number	2.06	mg KOH/g
Oxidation	3.76	A/cm
Kinematic viscosity (100 ℃)	10.15	mm2/s
P content	1096	ppm
Zn content	1193	ppm
Ca content	4580	ppm
S content	2821	ppm

Methanol and formic acid are the main contaminants of methanol engines that enter the lubrication oil. The high concentration of methanol (analytically pure, >99.0%) and formic acid (analytically pure, >99.0%) was used in ageing procedure. The addition of ethanol and acetic acid was achieved with dosing device via a Teflon tube through the cooler to the bottom of the flask. The sequence of dosing was carried out in small portions during the whole artificial ageing duration. methanol was added of 1% every 12 hours corresponding the high concentration in the methanol engine. And the formic acid was added of 0.2% every 12 hours.

2.3 Definition of parameters for oil condition monitoring

Every 12 hours, aged lubricating oil samples were extracted to analyze changes in their physicochemical properties, including the neutralization number (NN), total base number (TBN), and oxidation level. The NN was determined following the SH/T 0251-1993 standard (Positive Titration Method A), using a standard perchloric acid-acetic acid titration solution as the titrant, with the amount of perchloric acid required to titrate 1 g of aged lubricating oil measured in mg KOH/g. The TBN was measured according to the GB/T 7304-2014 standard (Method A), which defines TBN as the amount of KOH required to neutralize the aged lubricating oil, also expressed in mg KOH/g. Oxidation levels were determined using Fourier Transform Infrared (FTIR) spectroscopy following the ASTM E2412-23a standard (Direct Trend Method), where the oxidation value, given in absorbance per cm, was calculated at a wavelength of 1710 cm^{-1} using the formula: Oxidation (A/cm) = Extinction (A) / Cuvette thickness (cm). This approach provides a comprehensive assessment of the degradation characteristics of aged lubricating oil.

2.4 Friction materials

The cylinder liner and piston ring samples were used in this study were cut from an internal combustion engine with a bore diameter of 270 mm. The cylinder liner material is gray cast iron with flake graphite. In order to avoid the influence of surface roughness, 400#, 1000#, 2000#, and 3000# diamond sandpaper were used to grind the cylinder liner samples and then polished to obtain a smooth surface with roughness Ra ⩽0.2. The substrate material of the piston ring is gray cast iron, with a chromium plating coating approximately 300 μm thick. The roughness of the ring surface is 0.2 μm. And the contact form and the size of the cylinder liner and piston ring samples are shown in Figure 2.

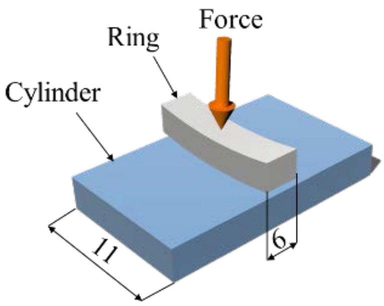

Figure 2 Cylinder liner-piston ring samples contact form

2.5 Friction experiment method and wear scar analysis

Friction experiments were conducted on a multifunctional wear testing machine (BULUKE, UMT TriboLab), as shown in Fig. 1(b). During the experiment, the piston ring sample was fixed in the upper fixture and remained stationary, and the vertical downward load was applied to the piston ring through the upper fixture. The temperature chamber regulates the lubrication ambient temperature to a precise set value. The reciprocating motion is performed according to the set speed during each test. Approximately 25 ml different oil of fresh oil, aged oil with methanol, and aged oil with formic acid were used in each experiment. Before and after the friction experiment, the samples were cleaned by absolute ethyl alcohol in an ultrasonic cleaner for 10 min to remove residual impurities and lubricating oil. The specific parameters in the friction experiment are shown in Table 2.

Table 2 Friction experiment parameters

Parameters	value	units
Load	500	N
Temperature	120	℃
Frequency	2	Hz
Stroke	6	mm

After the friction experiment, the white light interferometer (Zegage, Zygo) was utilized to measure the wear morphology. Post-test surface observations were conducted using a scanning electron microscope (SEM, HITACHI SU5000), and an energy dispersive spectrometer (EDS, Oxford Instruments Ultim Max) was used to measure the elemental composition of the surface.

3 RESULTS AND DISCUSSION

3.1 Change of physicochemical properties of lubricating oil

Figure 3 illustrates the changes in neutralization number (NN), total base number (TBN), and oxidation value over time. Fresh oil has an initial NN of 3.12 mg KOH/g, and the addition of methanol causes only a slight increase. The NN remains unchanged for the first 24 hours, then gradually rises, reaching 4 mg KOH/g at 96 hours. In contrast, formic acid has a much more pronounced effect on NN. During the first 36 hours, NN increases rapidly due to the reaction between formic acid and ZDDP, continuing until the additive is depleted. After depletion, the formic acid content increases significantly, and NN stabilizes. TBN remains stable at 13.1 mg KOH/g in formic acid-containing oils, similar to fresh oil, indicating that formic acid does not react with base additives such as calcium sulfonate. In contrast, methanol causes a slight decrease in TBN, though the effect is negligible. Oxidation levels remain similar to fresh oil in the presence of methanol but increase significantly with formic acid. Since ZDDP is a key antioxidant additive, its reaction with formic acid leads to a sharp rise in oxidation value within the first 36 hours, followed by a slower increase. Overall, formic acid significantly affects NN due to its reaction with the ZDDP additive but has minimal impact on TBN, while methanol has a negligible effect, likely due to its volatility at low temperatures. Further investigations are needed for a more comprehensive understanding of this aging behavior.

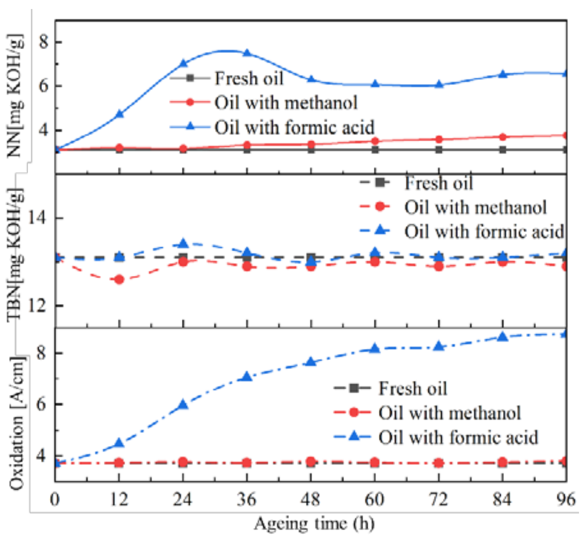

Figure 3 Change of physicochemical properties of lubricating oil

3.2 Friction and wear characteristics

Figure 4 shows the friction coefficient change of fresh oil, methanol- and formic acid-aged oil. For fresh oil, at first 1200s, the friction coefficient is high due to the run-in stage between the cylinder liner-piston ring samples. Then the tribofilm grows on the cylinder liner surface, the friction coefficient decreases significantly during the 1200s and 2400s until the friction coefficient value achieves a stable value. Similarly, the friction coefficient of methanol aged oil performs the same trend as fresh oil. In contrast, the formic acid-aged oil performed a high friction coefficient value from beginning to end, increasing the friction coefficient by 10% compared with the fresh oil, due to the formic acid consuming the ZDDP significantly, causing the tribofilm not to grow on the cylinder liner surface.

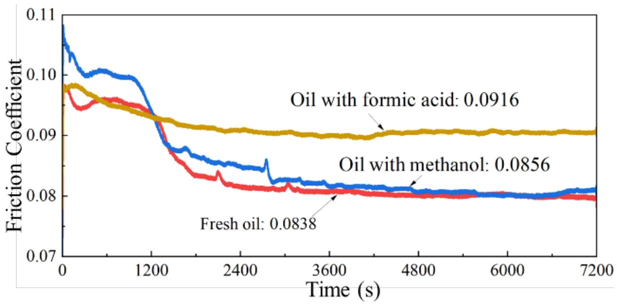

Figure 4 Friction coefficient change varying the time

The two-dimensional wear profiles of the three oils are shown in Figure 5. The wear volume of fresh oil and methanol-aged oil is almost the same. In contrast, the formic acid aged oil increased the wear greatly without the protection of the tribofilm. There also may be the influence of the corrosion of formic acid caused by the increased wear volume that should be studied corrosion of cylinder liner piston rings by formic acid separately.

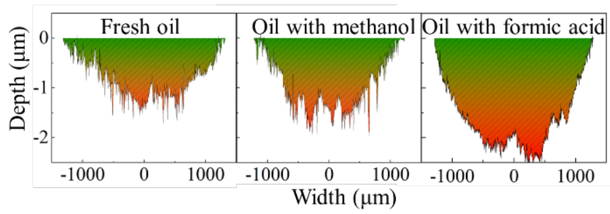

Figure 5 Two-dimensional wear profile of (a) fresh oil (b) methanol-aged oil (c) formic acid-aged oil

3.3 Wear scar analysis

As shown in Figure 6(a), the friction surface of fresh oil shows scratching, spalling, and delamination wear. In the meantime, the ZDDP and Ca tribofilm grow on the cylinder liner surface significantly, which can be illustrated by the O, Ca, and Zn element distribution. The tribofilm effectively avoids direct contact between the asperities on the cylinder liner and the piston ring surface, which decreases the wear amount. The wear scar surface of the methanol-aged oil exhibits more cracks, spalling, and wear debris, as shown in Figure 6 (b), with the decrease of O, Zn, P, S, and Ca elements, which means the tribofilm amount decreases. Direct asperity contact during the wear generates significant shear stress, which can induce plastic deformation. Deformation increases with larger stresses, leading to spalling. Additionally, graphite can easily detach from the material, causing spalling and cracking around the graphite particles.

Figure 7 shows the wear surface SEM pictures of the formic acid aged oil that mainly shows the scratch wear along with the slight delamination wear and cracks. The element distribution shows the Zn, P, S, and Ca elements decreased significantly, the tribofilm cannot effectively grow on the cylinder liner surface due to the ZDDP consumption or the influence of the formic acid on tribofilm growth, which results in increased wear due to insufficient tribofilm protection. Therefore, both methanol and formic acid hinder tribofilm formation, with formic acid having the most significant impact.

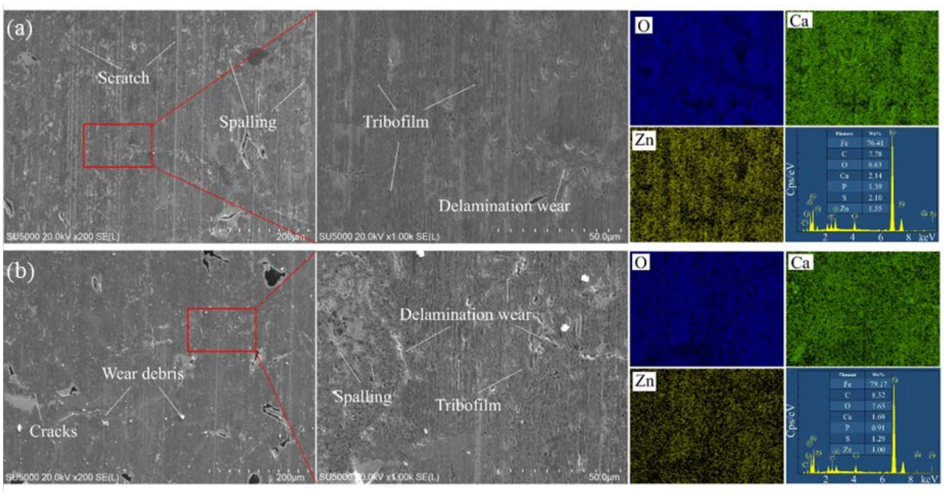

Figure 6 SEM pictures and element distribution of (a) fresh oil, (b) oil with methanol

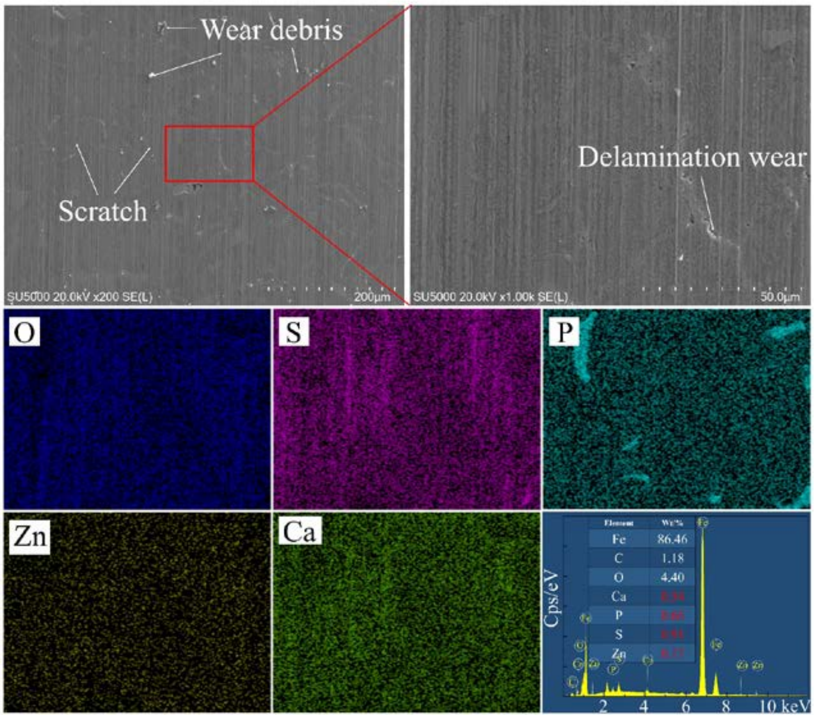

Figure 7 SEM pictures and element distribution of formic acid

4 CONCLUSIONS

This study simulates the aging process of lubricating oil by introducing methanol and formic acid in a controlled environment and investigates their effects on the physicochemical properties of the oil, including the neutralization number (NN), total base number (TBN), and oxidation. Furthermore, friction experiments using cylinder liner-piston ring samples were conducted to assess the tribological effects of aged oil. The results can be concluded below.

1. Lubricating Oil Aging Characteristics: During the aging process, methanol has little effect on the neutralization number (NN) and total base number (TBN), while formic acid significantly increases NN, decreases TBN, and accelerates oil oxidation.

2. Tribological Performance: Compared to fresh oil, lubricating oil with formic acid exhibits a 10% increase in friction coefficient and a 77% increase in wear volume, indicating a significant impact on tribological performance, whereas methanol has minimal influence.

3. Tribofilm Formation: Both methanol and formic acid inhibit the formation of ZDDP and Ca-based tribofilm, reducing the content of P, S, Zn, and Ca elements on the friction surface. Formic acid has the most pronounced effect, leading to increased wear.

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