The Influence of Water Content on the Acid Number of Diesel Engine Lubricant in Electrochemical Measurement

Fanhao Zhou1,2 and Kun Yang1,2*

1 Reliability Engineering Institute, School of Energy and Power Engineering, Wuhan University of Technology, Wuhan 430063, China;
2 National Engineering Research Center for Water Transport Safety, Wuhan University of Technology, Wuhan 430063, China.

E-mail: kunyangwhut@163.com

Abstract. Acid Number is one of the important characteristics of lubricating oil. In this study, thick film (TF) potentiometric sensors based on ion-selective electrodes (ISE) were used to determine the acid acidity of the diesel engine oil to determine the oxidation duration of the oil. This is a real-time online detection method. Two working electrodes (polymer electrode and glass electrode) and a reference electrode (bare Ag electrode) were fabricated, and the acid acidity of the diesel engine lubricant was expressed in the form of voltage, which overcomes the insufficiency of the titration endpoint in the titration method. Among oil products, most varieties only allow traces (water content below 0.3%) of moisture, and some oil products do not allow moisture. Water in oil can emulsify diesel engine lubricant, decompose additives, promote the oxidation of oil products. It affects the low-temperature fluidity of oil products. For transformer oil, extremely small amounts of water will seriously affect its insulation performance. In the experiment, the influences of water content for the acid acidity of the diesel engine lubricant were considered and tested.

1. Introduction

During the use, processing, storage and transportation of oil products, due to the influence of oxygen in the air, temperature and other conditions, it must be gradually oxidized to form a series of oxides[1]. Among them, the harmful substances are acidic substances such as naphthenic acid, Carboxylic acid etc.[2]. Generally, the higher the acid value of the oil, the deeper the aging of the oil[3]. If the insulating oil contains various acidic substances, it will increase the conductivity of the oil and reduce the insulation performance of the oil[4]. In the case of high temperatures during processing, it will also promote the aging phenomenon of solid fibrous insulating materials, especially when the content of low molecular acid increases and there is water in the oil, it will reduce the insulation performance of...
electrical equipment and shorten the operating life of the equipment\cite{5-6}. Therefore, it is a feasible method to judge the ageing process of lubricant by monitoring its acid number. It is a very effective method to monitor the change of acid value of lubricating oil by electrochemical method\cite{7}. This article first introduces the construction of the experimental platform. This experiment consists of a thick film sensor by connecting the manufactured thick film electrode with a high input impedance voltmeter. The oil sample provides conditions for the movement of ions as a connected environment\cite{8}. The article puts the method, results and discussion in one part, and explores the relationship between the acid value of the diesel engine lubricant and the oxidation time. As an inquiry link of the article, during the experiment, we found that the water content in the lubricant affects the acid value of the output. The electrochemical properties of oil, such as the dielectric constant, can reflect the pollution status of the oil\cite{9}, and water pollution is particularly sensitive to the electrochemical performance parameters of the oil\cite{10}. The presence of moisture will cause the dielectric constant to change\cite{11}, thereby changing the capacitance of the capacitor. Therefore, exploring the effect of water content on the acidity of diesel engine lubricant is a necessary condition for the successful monitoring of this electrochemical method.

2. Basic experiment

In these experiments, these oil samples are made from freshly lubricated oils by artificial oxidation. In addition, Star6 (R13-3622) BNOx run oil samples were prepared at the Shell Houston laboratories using a proprietary in-house blown NOx (BNOx) oxidation test. And oil samples were taken at seven oxidation intervals: 0, 2, 4, 8, 16, 20 and 24 h.

| Time of Oxidation | ID          | NO. | Source                | Supplier |
|-------------------|-------------|-----|-----------------------|----------|
| Star 6 (R13-3622) | R130003622  | 1   | MOTIVA ENTERPRISES    | Shell    |
| 0 hr BNOx RUN     | R140000119  | 1   | SOPUS PRODUCTS        | Shell    |
| Star 6 (R13-3622) | R14000120   | 1   | SOPUS PRODUCTS        | Shell    |
| 4 hr BNOx RUN     | R14000121   | 1   | SOPUS PRODUCTS        | Shell    |
| Star 6 (R13-3622) | R14000122   | 1   | SOPUS PRODUCTS        | Shell    |
| 8 hr BNOx RUN     | R14000123   | 1   | SOPUS PRODUCTS        | Shell    |
| Star 6 (R13-3622) | R14000124   | 1   | SOPUS PRODUCTS        | Shell    |
| 20 hr BNOx RUN    | R14000124   | 1   | SOPUS PRODUCTS        | Shell    |
| 24 hr BNOx RUN    | R14000124   | 1   | SOPUS PRODUCTS        | Shell    |

Two TF ruthenium oxide pH electrodes are connected as working electrodes to a high input impedance voltmeter. The other end of the voltmeter is connected to the bare silver reference electrode. The Metrohm 827 pH lab measures the potential between the working electrode and the reference electrode and expresses it as pH. Therefore, connecting two working electrodes separately can provide the baseline response of the TF sensor and confirm its function. In Metrohm 827 pH Lab, the output voltage can be converted to pH value through a certain model. Therefore, the main body of the experiment is shown in Figure 1, putting the printed working electrode and reference electrode into
seven sets of oil samples, getting the pH (voltage) of seven sets of oil samples by Metrohm 827 pH Lab. Then analyzing the seven sets of data to obtain the change law.

![Figure 1. Oil acidity measurement setup using thick film electrodes](image)

3. Experimental method, results and analysis

The results of the experiment are consistent with known laws. The longer the oxidation time of the lubricant, the stronger its acidity. However, individual oil samples do not conform to this rule. It is speculated that the moisture produced in the lubricant affects the experimental results.

During the experiment, the diesel engine lubricant will generate a part of water while oxidizing itself. The generated water will react with sulfur and chloride ions in the diesel engine lubricant to form sulfuric acid and hydrochloric acid\(^{[12]}\). Therefore, the water content in the diesel engine lubricant affects the experimental results to some extent. In addition, the trace water contained in the diesel engine lubricant will affect the acid value, so it is necessary to investigate the influence of the water content.

An online moisture sensor developed by Kittiwake was used to measure the moisture content of each group of oil samples. The oil online moisture monitoring sensor technology mainly adopts the electrical method. The principle is that the electrochemical properties of the oil such as the dielectric constant can reflect the pollution status of the oil, and the water pollution is particularly sensitive to the electrochemical performance parameters of the oil. The capacitance method changes the capacitance of the capacitor by using the oil and its contaminants as the specially constructed capacitor dielectric. The presence of moisture causes a change in the dielectric constant that changing the capacitance of this capacitor. The sensor monitors the state of moisture in the oil by detecting the change in capacitance.

The water content of the seven sets of Star6 R13-3622 BNOx RUN oil samples was determined and compared to the changes in the voltage output (obtained by Metrohm 827 pH Lab) of the seven
groups of oil samples.

**Table 2. Testing for water content of oil**

| star6 R13-3622 BNOx RUN | oxidized time | water content % | mv output |
|-------------------------|---------------|-----------------|-----------|
| 0                       | 0             | 0               | 135       |
| 2                       | 1.1           | 59.3            |
| 4                       | 3.8           | 91.7            |
| 8                       | 2.2           | 215.3           |
| 16                      | 0.7           | 197.2           |
| 20                      | 0             | 274.2           |
| 24                      | 0.2           | 328.4           |

The Figure 2 shows that the variable relationship between water content and the voltage output over the period of the oxidized time from 0 to 24 hours. It is significant that the variation of voltage output is irregular when the water content in the oil is different. For example, the voltage output initially reduced from 135 to 59.3 within 2 hours, accompanying the increase of water content from 0 percent to one percent. Then the voltage output began to rise to 215.3 over the period of the oxidized time from 2 to 8 hours, at the same time, the water content of the diesel engine lubricant increased to 2.2 percent. At this stage of oxidized time, the increase of water content did not allow the voltage output to change regularly. Then, the voltage output was gradually raised to 215.3. However, the water content was declining during the oxidized time of 5 to 10 hours. Moreover, the voltage output increased along with a gradual reduction of the water content after the oxidized time of 15 hours. As can be seen, the water content of the oxidised oil samples increases with the oxidation hours for the first three oil samples and decrease considerably for the last four oil samples. Water is a by-product of oil oxidation, hence, as expected, the water content rises as oxidation progresses. The decline in the water content of the last four oil samples may be caused by solubility issues as a result of excessive oil viscosity, i.e. the oil is not fully dissolving within the timescale allowed for the testing. As discussed, the TF electrodes demonstrated a correlation with oil voltage output, and water content increase may have accelerated the disassociation of acid in oil. This effect might have improved the performance of the TF electrodes in detecting the $\text{H}^+$ concentration in the oil samples. However, the unicity of this experiment cannot effectively demonstrate how the water content how affect the voltage output. In addition to excessive oil viscosity, another reason why the lack of regularity in results might be that the water on the sensor of the instrument is not dried. In order to rigorously acquire the relationship between the water content and the voltage output, subsequent experiments have been supplemented below to achieve the goal.
The water in oil supplementary tests were divided into two sets at two temperature conditions. The first set was carried out at 120℃, measuring the water content of oil samples which are the seven sets star6 R13-3622 BNOx RUN oil samples. All results displayed by the instrument was 0% that directly caused by high temperature. The 120 ℃ is higher than the boiling point of water, so the water in the oil is basically evaporated at this high temperature. The water content in oil is too low (less than 200ppm), so that the instrument was unable to measure it. Maybe this is the reason that when the voltages of star6 R13-3622 BNOx RUN oil samples were tested at 120℃, the data of each sets is basically the same. Despite the influence of water content at 120℃ can be ignored, the influence of water content on the output still need to be evaluated at room temperature. It is necessary to supplement experiments to measure the output at the temperature which is under 100℃.

The second set was conducted at room temperature. Since it is the H⁺ concentration in oil that is the reason for the voltage output of the TF sensor, water content was gradually increased to test its relationship with response potential output of the sensor (mv) at constant indoor temperature. The base oil was used to make 4 samples of 4 water contents to analyze the linearity. The principle is to add 400 ppm, 800 ppm, 1000 ppm, and 1600 ppm water to the four groups of base oil without water. The Figure 3 illustrates that the variation tendency of voltage output is declining as increasing water content. The voltage output closed to 108.4 when the water content was 400 ppm, and it reduced to 90.1 when the water content increased by 800 ppm. Eventually, the voltage output dropped to 70.1 in terms of water content of 1600 ppm. It is obvious that the voltage output continues to decreasing with the increase of the water content from 400 ppm to 1600 ppm. The experimental results showed that increased water content led to a negative impact on the voltage output. The increase of water content output directly reduced the voltage output at indoor temperature. The electromotive force output by the sensor is inversely proportional to the acidity of the lubricant. This means that within a certain range, the more water in the lubricant, the greater the acid value, and the worse the quality of the oil.

![Relation between water in oil and mv output](image)

**Figure 2.** Relation between water in oil and mv output
This part of experiments showed that the effect of water content on output under different temperature conditions. The high temperature that exceeds the boiling point of water contributes to the evaporation of water. The influence caused by the water content under this condition cannot be considered. However, the excessive water content at indoor temperature has an obvious negative effect on output according to the second experiments. Excessive water content will deteriorate oil performance, which needs to be eliminated at the indoor temperature.

4. Research conjecture
To study the water content in diesel engine lubricant, it is first necessary to investigate the source of water in diesel engine lubricant. Because the new base oil is free of water\textsuperscript{[13]}, the water in the lubricant should be the oxidation product of the lubricant. In addition, in this study, due to the presence of additives and wear particles in the diesel engine lubricant, taking iron powder as an example and using water as a medium, the iron powder will react with the organic acid generated during the oxidation process\textsuperscript{[14]}. Therefore, the organic acid in the diesel engine lubricant is consumed, affecting the monitoring of the acid value in the diesel engine lubricant. Because the organic acid in oil is relatively rare, and the volume (radius) of H\textsuperscript{+} is particularly small \textsuperscript{[15]}, the polarizing ability is very strong, and it can be drilled into O\textsuperscript{2-}, so that the stability of anions is destroyed. On the other hand, during the storage of diesel engine lubricant, once the container is not properly sealed, water will enter the diesel engine lubricant, or condensate will be generated when the container breathes.

5. Conclusion
The objective of the study is to make a thick film sensor to monitor the acid value of the lubricant in real time. Through the modification of Metrohm 827 pH Lab, the sensor has the ability to monitor the quality of diesel engine lubricant under more severe conditions. Meanwhile, it has the advantage of more convenient operation. The trace water generated in the lubricant due to oxidation may affect the change in the acid value. It is instructive for this sensor system to explore what mapping relationship exists between water and lubricant acid value. The online monitoring technology of diesel engine lubricant is one of the key points and difficulties of current fault diagnosis. The monitoring mode is developing towards integrating multiple parameters. In addition, exploring the effect of moisture on diesel engine lubricant is conducive to timely evaluation of the quality of diesel engine lubricant,
monitoring the state of the machine, and ensuring the safe use of diesel engine lubricant. In later research, infrared spectroscopy will be applied. Combined with the change of the infrared absorption peak of the diesel engine lubricant component, the diesel engine lubricant with a water content of more than 1% can be effectively monitored to locate the quality of the diesel engine lubricant. Based on infrared spectroscopy, miniaturization and multi-functionalization are the future development trend of acid value sensors.

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