CHEMICAL ENGINEERING TRANSACTIONS
VOL. 55, 2016
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Tichun Wang, Hongyang Zhang, Lei Tian

ISBN 978-88-95608-46-4; **ISSN** 2283-9216
DOI: 10.3303/CET1655026

Analysis of the Acid Value of Engine Oil based on Square Wave Voltammetry

Yunxuan Jiang, Yonggang Shi*, Zicun Li, Guozhi Fan

Logistical Engineering University of PLA, Chongqing, China
2399135852@qq.com

The principle and method of square wave voltammetry (SWV) based measurement of the total acid number of petroleum products were introduced in this paper. The SWV-based measurement result was compared with the standard method based measurement result. Our research result shows that SWV has the advantages of quickness, sensitivity, small error, and high detection limit, and is accordingly feasible in testing engine oil acidity. Thus, this method is capable of detecting the acid value of lubricants and the law of oxidative degradation of engine lubricant.

1. Introduction

Oxidative decay is one of the most important causes to engine oil failure. The engine oil is oxidized under high temperature and pressure to form compounds such as peroxides, carboxylic acids, and ketones. These compounds are further condensed to form non-oil-soluble polymers. As a result, the kinematic viscosity increases, which reduces the service life of engine oil. Such being a case, researchers and users on engine oil are much concerned about its oxidative decay.

The acid number is the number of milligrams of potassium hydroxide required to neutralize the acidic substance in 1g petroleum product. It indicates the engine oil's deterioration degree and its corrosion to metals during work time. (Nakanishi et al., 2007) Acid products in the process of engine oil oxidation include naphthenic acid as the main component, some other organic acids, inorganic acids, glial, heavy metal salts, ammonium salts and other weak bases, etc. Some of these substances are inherent in engine oil; some are generated in the condition of storage and usage; and some are additives and their variations. Although the relationship between acid number and corrosion cannot be represented quantitatively, acid number is still widely used in representing the corrosion and mass of petroleum and petroleum products due to its easiness to gauge (Arapatsakos et al., 2012; Joseph, 2012; Sarma et al., 2012; Xi et al., 2016; Xu et al., 2016).

There are two types of titrations of oil product acid value with different principles: zeta potential titration and acid-base titration. (Arapatsakos et al., 2011; Zhou, 2016) The latter one indicates the endpoint of the titration by changing color, and the former one monitors the completion by zeta potential. However, the endpoint is difficult to judge for the acid-base titration in dark oil products or for the acid-base titration in sample products without noticeable abrupt change points. Non-aqueous buffer solutions as a must to determine the completion of the zeta potential titration have such weaknesses as high toxicity, sophisticated preparation process and short expiration date. Therefore, neither of them is perfect.

Compared with the above methods, the rapidly-developed technologies of spectrum analysis (De Rivas et al., 2017) and electrochemical method bring new thoughts to the detection of the acid value of lubricating oil. Due to its advantageous performance in such parameters as detection limit, sensitivity, quickness, accuracy and reproducibility, voltammetry has been used by researchers to study the law of oxidative decay of lubricated oil. Research findings have been obtained by using linear sweep voltammetry, cyclic voltammetry, and differential pulse voltammetry. Despite the applicability, the branches of voltammetry have several drawbacks, such as complicated resolution and insensitiveness to low concentration of solution. Compared to other voltammetry, SWV method, which has been used in many areas (Sasani et al., 2007), is more sensitive. In light of its lack of use in lubricant oil examination, we detected the acid value of engine oil on the SWV basis, which is succeeded by our preliminary laboratory work.

Please cite this article as: Jiang Y.X., Shi Y.G., Li Z.C., Fan G.Z., 2016, Analysis of the acid value of engine oil based on square wave voltammetry, Chemical Engineering Transactions, 55, 151-156 DOI:10.3303/CET1655026

2. SWV-based acid value detection for engine oil

Thermal aging of diesel engine oil: We weighed about 500ml diesel engine oil, and poured it into a four-mouth flask to be aged at 170°C, with the oxygen flow rate at 40ml / min and the speed of the tachometer staying at 200r / min. (Besser et al., 2013)Specimens were taken out every 2 hour of aging. We stopped sampling when the base value of the oil sample reached up to 2 mgKOH / g.

Figure 1: Metrohm autolab electrochemical workstation

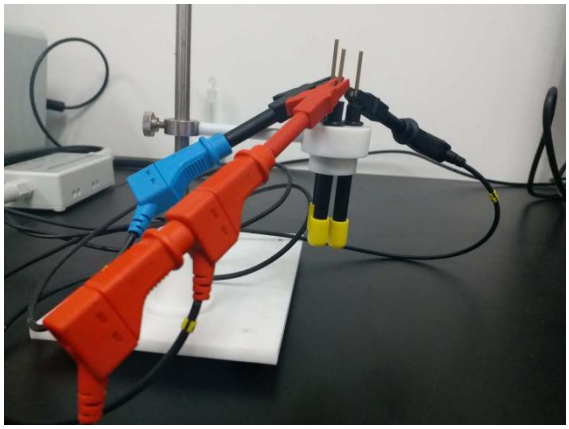

Figure 2: Bed stand of the three-electrode system

2.1 Experimental method

On the self-made support lies the three-electrode system composed of the glassy carbon electrode as the working electrode and the platinum electrodes as the reference electrode and the auxiliary electrode. We added 350ml the solution of sodium phenoxide and water / ethanol (1: 1) to the 25 × 40 measuring flask, and let the room temperature remain at 25°C. We measured the characteristic voltammetry peak H0 of the blank solution, with the representative acid value at 0mgKOH / g. 350ml electrolyte solution was poured into 50μL 0.1mol / L hydrochloric acid and given a 5s shock. The characteristic voltammetry peak H0 was measured, with the representative acid value at 0.28mgKOH / g. This was followed by the addition of 0.02 ~ 0.03g or 200μL oil sample to 350ml blank solution for a shock of 20s. The characteristic voltammetry peak was recorded as H. We repeated oil sample measurement for 3-5 times for each group, in an attempt to eliminate operational errors.

working conditions for the apparatus: initial voltage: 0V; cut-off voltage: 1V; voltage added value Step=0.005V ;amplitude: Amp=0.05V ;Pulse rate: F = 30Hz; scanning speed: 0.15 (V / s); Sensitivity: 1.0×10^{-3}(A/V)

The calculation formula of lubricant acid value:

$$\mathrm{TAN}=\frac{\mathrm{H_0}-\mathrm{H}}{\mathrm{Weight}}\times\frac{0.28}{\mathrm{H_0}-\mathrm{H_s}} \tag{1}$$

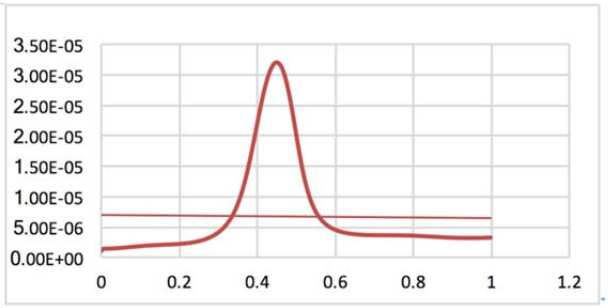

Figure 3: SWV characteristic peaks of the software in the electrochemical workstation

2.2 Experimental principle

The basic principle of SWV-based measurement of lubricant acid value is to calculate the total acid number of the sample by measuring the decrement in electroactive compounds (i.e. responsive matters in SWV), considering that part of them have reacted with lubricant acids to be converted to non-electroactive compounds (i.e. unresponsive elements in SWV). In measuring the total acid number, two requirements were posed to the activity of electroactive compounds: 1. It should be high in reacting with different acid matters in the lubricant oil; and 2. There exists electroactive responses in SWV which does not interfere with each other.

In this paper, sodium phenoxide was used as an electroactive compound to react with the acid in the lubricating oil (the acid in standard test was 0.1 mol / L of hydrochloric acid, whilst the acid in the test sample was derived from acidic substances in internal combustive engine oil). Overbased sodium benzoate reacted with acids in lubricant oils and turned into phenol. As phenol is a non-electroactive compound unresponsive in SWV, SWV is feasible in measuring the total acid number of samples by determining the decrement of electroactive compounds after sodium phenoxide reacts with acids.

3. Control experiments: automatic zeta potential titration

3.1 Equipment and materials

Equipment: 877 Tirino Plus automatic point potential tetrameter, Metrohm Co. Ltd.; glassy electrodes; analytical balance.

Titrant: c(TBAOH) = 0.1 mol/L; isopropyl alcohol solution; or c(KOH)=0.1 mol/L; isopropyl alcohol solution.

Solvent: 500mL methylbenzene +495mL isopropyl alcohol solution +5mLH2O. chlorinated solvent is not an option in this test because it is environmentally unfriendly.

electrode/electrolyte: tetraethyl ammonium bromide c(TEABr)=0.4mol/L;ethylene glycol solution(Metrohm no.6.2320.000)

standard： c(benzoic acid) = 0.100 mol/L; ethanol solution(prepared by mixing 1.220g benzoic acid with 100ml ethanol).

Measurement method: Chinese Standard: GB/T 264 (Petroleum products. Determination of Acid Number)

3.2 Determination of acid number

$$\text{mg KOH/g} = (\text{EPn} - \text{C31}) \times \text{C01} \times \text{C02} \times \text{C03}/\text{C00} \quad (2)$$

EPn =the volume consumed at the nth (last) equivalent point. Most often, there is only one equivalent point, but the number may exceed 1 at the existence of strong acid. The acidity is computed at the last equivalent point (EP1 can be used to calculate the acid value of strong acid).

C00 = sample mass (g)

C01 = 0.1(concentration of titrant,mol/L)

C02 = titer

C03 = 56.106[KOH molar mass,g/mol]

C31 = solvent blank

4. Result and analysis

4.1 The law of lubricant oxidation value changing with time

With infrared spectroscopy, we determined the time-related law of lubricant oxidation value, as plotted in the following figure. As can be seen, oxidative decay is slow at the initial stage of the thermal oxidation of engine oil, and begins to accelerate 10 hours later (Al-Shyyab and Khadrawi, 2011). This is because the reduction in

antioxidant agents and the rise in acid matter in oil as a result of the oxidative decay of lubricants accelerates the aging the engine oil (Barik et al., 2015).

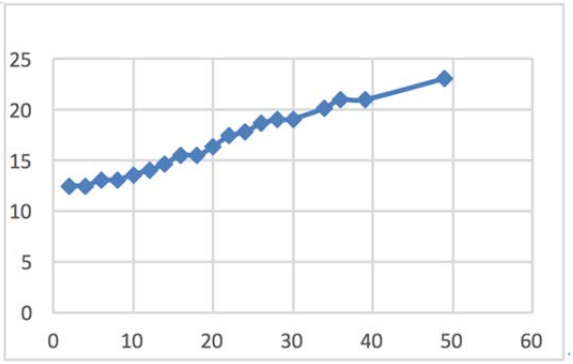

Figure 4: The law of lubricant oxidation value changing with time

Table 1: measurement result of the electrochemical analysis of engine oil acid number

Sample No. /10-2g	SWV peak amplitude/10-5 A	SWV-based measurement result (mgKOH/g)	GB/T264-based measurement result (mgKOH/g)	Mean measurement value mg (KOH/g)
2.13	7.5432	0.489	0.38	0.109
2.31	7.384	0.467	0.39	0.077
2.22	7.2612	0.498	0.41	0.088
2.72	7.1425	0.417	0.41	0.007
2.54	7.0526	0.454	0.43	0.024
2.31	6.9882	0.506	0.47	0.036
2.54	6.7879	0.478	0.45	0.028
2.32	6.5289	0.549	0.53	0.019
2.71	5.1939	0.582	0.58	0.002
2.07	6.2142	0.649	0.66	-0.011
2.39	4.8356	0.694	0.68	0.014
2.51	3.2715	0.803	0.76	0.043
2.28	3.0415	0.906	0.86	0.046
2.31	2.8716	0.909	0.89	0.019
2.16	2.2142	1.044	0.98	0.064
2.17	1.6229	1.101	1.08	0.003

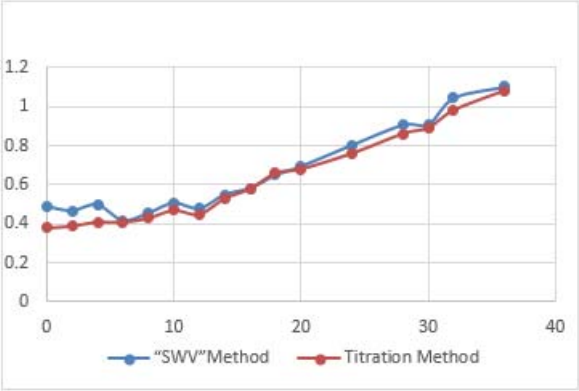

Figure 5: Comparison of the time-related law of SWV-based measurement result and law of titration-based measurement result

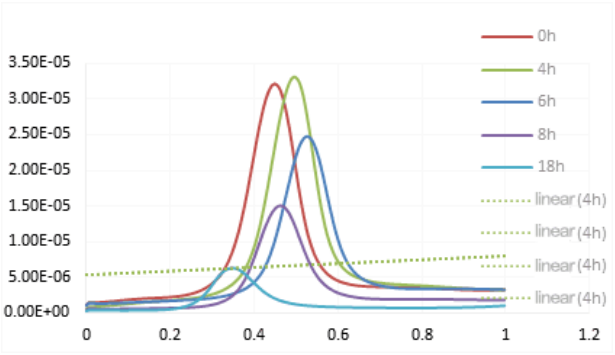

Figure 6: SWV-based measurement peak amplitude

4.2 Result analysis

It can be seen from the table that with the increase of oxidation time, the aging degree of diesel engine oil has been deepened and the acid value has been increasing continuously. In terms of the automatic zeta potential titration of national standard, the measured value has a remarkably upward trend, soaring at the 5th sampling. The reason for this phenomenon is that the oxidation of engine oil leads to the decrease in antioxidant agents at the same time when generating acid products. When the antioxidant agent is consumed to a certain degree, the balance between the antioxidant agent and the new products are damaged, and thus the acid value surges. The changing trend of SWV-based acid number determination is obvious in comparison to the national standard method. The good consistency and repeatability between the two measurement results proves that SWV satisfies the requirements of acidity determination.

4.3 Comparative analysis

By comparing the two methods, it can be seen that the acid number of engine oil measured by SWV is higher than that measured by KOH-based titration of national standard, in that sodium benzoate reacts sensitively to both strong acid and weak acid in engine oil.

4.4 Analysis of experimental samples

Experimental control in the method is divided into two parts: 1. Condition control, which constitutes hierarchical value, amplitude and frequency; the scanning speed is controlled simultaneously by hierarchical value and frequency; reaction conditions have been determined according to single-index method and orthogonal experimental method before conducting the test; 2. Test sample control, which mainly includes temperature and sample mass; the temperature is controlled constant at 25°C; After the blank samples stand still for 20s, we begin our test; the laboratory is kept dry by using dehumidifier; the measurement precision of equipment is also controlled. In the experiment, it is found that the small change of sample size does not lower the experimental precision, but a certain amount of mass deviation will change the measurement result greatly. For example, when the deviation value of sample mass reaches 0.02g, the measurement result rockets. Therefore, the mass deviation should be controlled less than 0.005g for the SWV.

5. Conclusion

Square wave voltammetry is an excellent, fast method to determine the acid value of engine oil. The measurement results reflect the law of oxidant degradation of engine lubricant. The proposed SWV-based measurement method can be used as a means of engine oil acid number detection.

Reference

Al-Shyyab A., Khadrawi A.F., 2011, Effect of Magnetic Field on Boundary Layer Flow over an Unsteady Streching Surface in a Micropolar Fluid, International Journal of Heat and Technology, 29(1), 75-82.

Arapatsakos C., Christoforidis D., Karkanis A., 2011, The Fuel Temperature Impact in the Diesel Engine When Mixtures of Diesel-Soy Oil are Used as Fuel, International Journal of Heat and Technology, 29(1), 107-112.

Arapatsakos C., Christoforidis D., Karkanis A., 2012, The use of vegetable oils us fuel on diesel engine, International Journal of Heat and Technology, 29(1), 25-32.

Barik M., Dash G.C., Barik R.N., 2015, The Effect of Magnetic Field and Fluid Inertia on the Film Pressure between Two Axially Oscillating Parallel Circular Plates with a Second Order Fluid as Lubricant, International Information and Engineering Technology Association, 84(2), 39-51.

Besser C., Dörr N., Novotny-Farkas F., Varmuza K., Allmaier G., 2013, Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation, Tribology International, 37-47, 65.

De Rivas B.L., Vivancos J.L., Ordieres-Meré J., Capuz-Rizo S.F., 2017, Determination of the total acid number (TAN) of used mineral oils in aviation engines by FTIR using regression models, Chemometrics and Intelligent Laboratory Systems, 32-39, 160,15.

Nakanishi H, Utsui S, Yuki T., 2007, Method for producing alpha, beta-unsaturated carboxylic acid ester, and alpha, beta-unsaturated carboxylic acid ester, and lubricating oil additive: US, US20070173421[P]. 526/318.43, 560/205.

Joseph A.M.F., 2012, Effects of thermal modification by the hot oil treatment process on some physical properties of two cameroonian hardwwod species, International Journal of Heat and Technology, 30(2), 43-50. DOI: 10.18280/ijht.300206.

Sarma P.K., Radha Krishna D., Ramanarayanan C.P., Dharmarao V., Srinivas V., 2012, Analysis of engine oil cooler of an unmanned aero-engine at various altitudes, International Journal of Heat and Technology, 30(1), 45-50. DOI: 10.18280/ijht.300107.

Sasani M., Bazan M., Sagiroglu S., 2007, Experimental and analytical progressive collapse evaluation of actual reinforce concrete structure, Structural Journal, 104, 6, 731-739, DOI: 10.1061/(ASCE)0733-9445.

Xi G.Q., Tan F., Yan L., Huang C.J., Shang T.Y., 2016, Design of an oil pipeline nondestructive examination system based on ultrasonic testing and magnetic flux leakage, Revista de la Facultad de Ingeniería, 31(5), 132-140. Doi:10.21311/002.31.5.14.

Xu D.J., Liao R.Q., Li D.S., Wang M.F., Su Y.B, 2016, Experimental study and application of seepage characteristics of chang 72 tight oil reserves in ordos basin, Revista de la Facultad de Ingeniería, 31(8), 187-196. DOI: 10.21311/002.31.8.18.

Zhou Y., 2016, Experimental Research of Progressive Collapse Resistance of RC Frame Structure, Revista de la Facultad de Ingeniería U.C.V., 31, 7, 152-161, DOI: 10.21311/002.31.7.15.