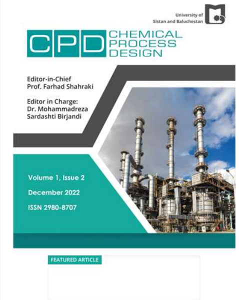
University of Sistan and Baluchestan

Chemical Process Design

Available online at http://cpd.usb.ac.ir/



Prediction of Sludge and Varnish Formation in Base-stock Lubricant using an Experimental Package

Ehsan Pashai*, Mohammad Reza Dehghani

Thermodynamics Research Laboratory, School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received: 2022-11-29
Received in revised form: 2023-01-25
Accepted: 2023-01-30
Published online: 2023-02-01

Keywords:
Lubricant degradation;
Condensation products;
Sludge; Analysis package

DOI: *10.22111/CPD.2023.44108.1014*

ABSTRACT

One of the most prevalent problems in the application of lubricants and hydraulic oils is sludge and varnish formation from lubricant degradation. It is believed that thermal degradation is the main reason for sludge formation in lubrication systems. In this study, base-stock lubricant (group I API) underwent the thermal degradation within a temperature range of 90 to 150°C for a period of 1 to 48 hours. In order to obtain a clear justification about lubricant degradation, a new analysis package of experiments consists of FTIR (Fourier Transform Infrared Spectroscopy), viscosity, TAN (Total Acid Number), IFT (Interfacial Tension measurement) and UC (Ultra-Centrifuge) test has been conducted. The results showed that the amount of sludge increases with temperature. Furthermore, all obtained results were analyzed theoretically. We found that when the surface tension suddenly decreases, the amount of sludge in the lubricant has reached its dangerous limit. Since the results of these analyses were a good predictor of sludge production, it can be claimed that the proposed package can be applied for prediction of sludge formation conditions.

1. Introduction

Rotary machines get worn out gradually, mainly because of erosion and the presence of unwanted materials in lubrication systems. Performance of lubrication oil is really effective in this regard. On the other hand, life cycle of each machine can be longer by using condition monitoring techniques. Modern lubricants are more capable in reduction of erosion and corrosion. Lubricant oil degradation under operational conditions is a problem which leads to considerable economic losses [1]. Precipitation of degradation products in lubrication cycle which results in formation of varnish is the most important factor. Varnish is an insoluble thin brown or black layer that deposits on the inner surface of bearings and hydraulic systems such as pipelines, valves, exchangers, filters, and other equipments. Fig. 1 shows an example of varnish formation on an Inlet Guide Vane (IGV) valve positioner from a large-frame turbine [2].

Corresponding author. Tel.: +98 (114) 3268678.
E-mail address: ehsan.pashai@gmail.com (E. Pashai).

Fig. 1. Varnish formation on Inlet Guide Vane (IGV) valve from a gas turbine (Courtesy of Clarus technologies)

Sludge is another possible contaminant with similar chemical properties as varnish. However, unlike varnish, sludge does not deposit on metallic surfaces; it is rather suspended in oil bulk as a semi solid black lump or something like grease [2]. In other words, varnish is the appearance of the phenomena that contaminants coat on the metallic surfaces and sludge is the mixture of the oil oxidation products and other solid contaminants in the oil bulk. It should be noted that sludge and varnish are formed as a result of oil degradation. Blockage of control valves and filters is a prevalent problem in lubrication and hydraulic systems because of sludge formation. To prevent this problem, the first step is to have the basic knowledge of the mechanism of varnish and sludge formation. In the second step, oil analyses would be useful in determination of the presence of contaminants in the lubricant. It is proved that oxidation is the main reason for oil degradation [3] and a lot of works focused on the determination of mechanism and kinetic rate of oxidation reactions [3-10].

Gatto et al. [5] focused on oxidation of turbine oil. They showed that during oil oxidation, many products such as aldehydes, ketones, water, alcohols, and carboxylic acids are produced. Presence of the mentioned products increases the oil viscosity. Meanwhile, aldehydes and ketones take part in condensation reactions named as Aldol Condensation [11]. These reactions can progress leading to the formation of polar high molecular weight oligomers and low molecular weight polymers. Presence of oligomers increases the oil viscosity significantly. These materials have a finite solubility in the lubricant. Condensation products mostly contain aromatic groups which have quite different behaviors in comparison with the paraffinic and naphthenic oil molecules [5]. This property makes them insoluble in the lubricant. Sometimes, chemical changes of oligomers make them insoluble in the non-oxidized portion of the oil. In this condition, insoluble materials are separated. In fact, after phase changes, sludge and varnish appear in the system. As discussed before, sludge remains dispersed while varnish deposits on metal surfaces. Varnish formation is further promoted by the absorption of polar oligomers on hot polar metal surfaces [5].

It is hypothesized that oligomers and condensation products are the main reasons for sludge and varnish formation. As a result, the potential of varnish formation can be easily distinguished by measuring the condensation products in the lubricant. The common oil analyses are not singly capable of detecting varnish formation potential [12]. Usually, this risk is diagnosed after the occurrence when it is too late. A number of excellent works have been published to cover this issue [13-29]. In the continuation of the mentioned works, the present study has attempted to introduce a set of analytical methods for the determination of the formation and the presence of varnish.

Electrostatic discharge can lead to temperature increase and degradation in lube oils, on which a huge number of studies are reported [30-31]. These factors are highly effective in lube oil degradation containing additives and lead to a dramatic decrease in the additives. Hence, oxidation will occur faster in base-stock and sludge and varnish form consequently. Commonly, some additives are added to the base-stock to prevent the oxidation procedure in industrial applications. In the presence of enough antioxidants, degradation does not start. Therefore, for accelerating the degradation, only oxidation and thermal degradation of the base-stock are studied in this work. In this study, we presented a new analytical guidelines using common and inexpensive analyzes such as Fourier Transform Infrared (FTIR), viscosity test, Total Acid Number (TAN), Interfacial Tension Test (IFT) and ultracentrifuge to determine the time of sludge formation in lubricants in order to avoid equipment damage and inevitable compensation effects.

2. Theory of oxidation reactions

As stated in the introduction section, various theories are introduced about the mechanism of oxidation reactions. Among the different theories [3, 5], we believe that the theory introduced by Gatto et al. [5] can present a better view on this issue. In order to validate their theory through our experiments, a brief review of their method is presented in this section. Based on Gatto et al. [5], the oxidation reactions start through radicalization reaction, as shown in the following:

$$RH + O_2 \rightarrow R. + HOO. \tag{1}$$

This reaction generally occurs very slowly at room temperature, but speeds up at temperatures above 100ºC. Furthermore, metals like iron and copper can promote the initiative reactions effectively. The effects of transition metals in either catalyzing or inhibiting oil oxidation in the liquid phase have been extensively reported in the literature [32-33]. In this work, copper has been used as the reaction catalyst. The presence of copper leads to hydro peroxide decomposition reaction and formation of alkyl peroxy radical.

$$Cu^{+} + ROOH \rightarrow Cu^{2+} + RO. + OH^{-} \tag{2}$$

The second step in oxidation reaction is free radical dispersion. At this stage, an alkyl radical reacts with oxygen and forms an alkyl peroxy radical $ROO.$ (Eq. (3)). This reaction occurs very fast; its product ($ROO.$) attacks the hydrocarbon molecule, detaches the hydrogen from the former molecule, and forms a new $R.$ (Eq. (4)). Alkoxy radicals, in comparison with peroxy radical, are more active in taking part in a fast reaction with oxygen while peroxy radicals are more reactive towards Hydrogen.

$$R. + O_2 \rightarrow ROO. \tag{3}$$

$$ROO. + RH \rightarrow ROOH + R. \tag{4}$$

In the third step, water and alcohol are produced. This step is named as the branching step by Gatto et al. (2006).

$$ROOH \rightarrow RO. + HO. \tag{5}$$

$$RO. + RH \rightarrow ROH + R. \tag{6}$$

$$HO. + RH \rightarrow H_2O + R. \tag{7}$$

Finally, free radicals convert to aldehyde and ketone as follows:

$$RR'HCO. \rightarrow RCH = O + R'. \tag{8}$$

$$RR'R''CO. \rightarrow RR'C = O + R'. \tag{9}$$

$$2RR'CHOO. \rightarrow R'RC = O + RCHOHR' + O_2 \tag{10}$$

Generally, R′ and R″ are aromatic groups which do not take part in oxidation reactions. The presence of aromatic branch makes a quite different structure for ketone molecules in comparison with non-degraded part of the oil. In addition to ketones and aldehydes, molecules such as carboxylic acids are formed during the oxidation mechanism. Carboxylic acids are formed by oxidation of aldehydes and ketones. The mechanism for this oxidation varies based on the type of aldehydes and ketones derived from the lubricant [5]. The presence of these compounds leads to decreasing the oil viscosity. Aldehydes and ketones participate in poly-condensation reactions and produce oligomers and high molecular weight components, which in turn, increase oil viscosity and decrease interfacial tension. Fig. 2 shows how oligomers are produced. The oligomers have a limited solubility in the base-oil. Therefore, when oxidation reactions proceed, they separate from the non-degraded oil and precipitates as a solid phase. Two different scenarios might happen. In the first scenario, oligomers are attracted by polar metallic surfaces to form varnish. In the second scenario, the solid phase accompanied with water droplets and other particles in oil make a viscose lump which suspends in the base-oil. This viscose lump is known as sludge.

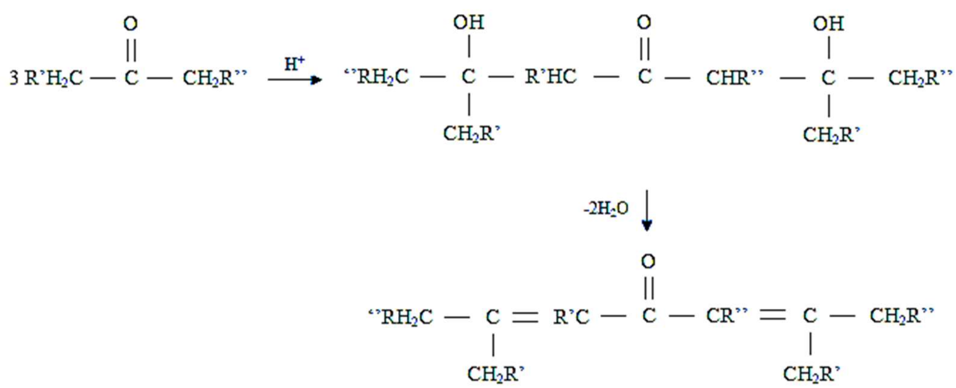


Fig. 2. Condensation of similar ketones and formation of pseudo-polymer (Courtesy of Ref [5])

3. Experimental

3.1. Material

In this work all materials (toluene and normal pentane) have been prepared from Merck Ltd. The base-stock SN100 produced by Behran Iranian Oil Company has been used as the oil sample. According to manufacturer specification, this base-stock is categorized as API I or Paraffinic group. Its physical properties are reported as follows:

- Viscosity = 19.19 cSt at 40ºC (based on ASTM D-445)
- Viscosity Index = 100
- Specific Gravity = 0.836 at 15.55ºC (based on ASTM D-4052)

3.2. Experimental setup

Thermal degradation of lubricants has been achieved in a setup similar to batch distillation setup. The apparatus is equipped with thermostatic bath, thermal sensor, round-bottom flask (5 liters), condenser, small round-bottom flask (0.5 liters) for collecting condensate, and an air reflux. A copper coil (with length of 20cm) has been utilized to accelerate the rate of oxidation. In Fig. 3, the scheme of our setup is depicted. Base-stocks were heat-treated up to 90, 110, 130, and 150ºC. Different samples were withdrawn after different time intervals (including 3, 6, 12, 24 and 48 hours). Heating procedure continued for 48 hours.

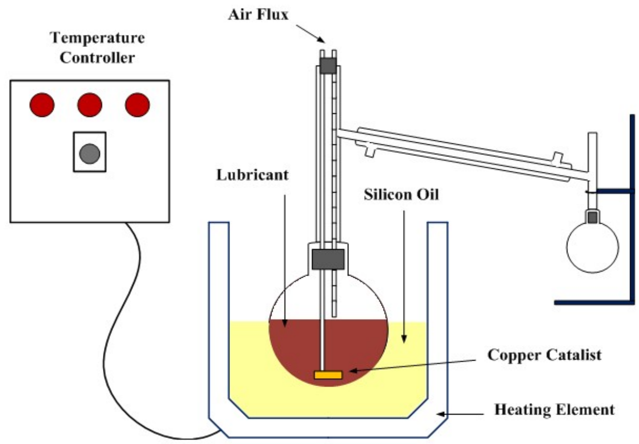


Fig. 3. Schematics of the degradation apparatus (distillation system with air reflux and copper catalyst)

3.3. Oil analysis

The conducted analyses are FTIR, viscosity test, TAN, IFT, and ultracentrifuge. FTIR has been determined by a Shimadzu FTIR-8400S with KBr pellets, in the region of 400-4000cm^{-1}. The FTIR-8400S device is combined with the IRsolution-a32 bit high performance FTIR software to analyze the samples. The IFT tests have been determined using a thermostat tension-meter KSV Sigma700. It is a computer controlled and user programmable tension meter. Interfacial tension has been measured by Du Noüy ring method by using a platinum/iridium alloy ring. The temperature was controlled with a circulation water bath Julabo F12. At least 50ml of samples was needed for measuring surface tension each time. The tension-meter device has been calibrated with de-ionized water with surface tension of about 71.7mN/m at 25°C.

Ultracentrifuge (micro high speed Centrifuge-Vision, VS-15000N) has been used for the separation of produced oligomers. This device has been equipped with one rotor with maximum 15000 rounds per minute speed. It contained 24 tubes each with 1.5ml capacity. The tubes were filled by samples and rotated for 30 minutes. The viscosity was determined by a rotary viscometer POLYVISC-VISCO STAR L. This device is able to measure the viscosity of liquids from 3 centipoises up to 1000000 Poise. The temperature of viscosity measurements is 20°C. TAN was determined according to ASTM D664 standard test measurement using Mettler-DL67. The ASTM D664 covers procedures for the determination of acidic constituents in petroleum products, lubricants, biodiesel, and blends of biodiesel. The range of acid numbers included in the precision statement is 0.1mg/g KOH to 150mg/g KOH.

4. Results and discussion

In this section, attempts have been made to find justifications for varnish and sludge formation using experimental results and theoretical concepts. In Fig. 4, the FTIR results for various lube base-stock samples are presented.

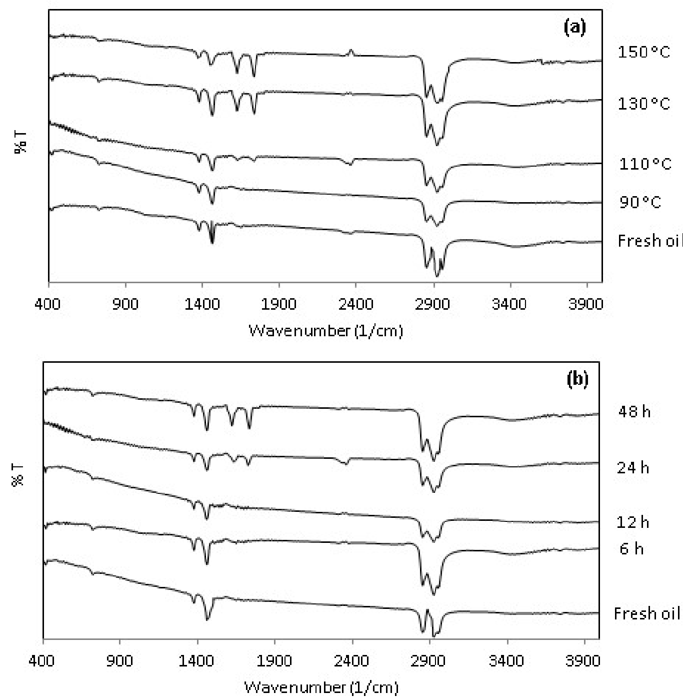


Fig. 4. FTIR spectra of lubricants: (a) Samples degraded for 48hr at different temperatures; (b) Samples degraded at 130ºC for different times

Fig. 4(a) contains the results of FTIR for different samples including degraded and non-degraded oil at four different temperatures (90, 110, 130, and 150ºC) after 48hours. In order to find the variation of FTIR spectra with respect to time, the temperature was kept constant at 130ºC. Then, at different time intervals, samples were withdrawn and tested. The results are presented in Fig. 4(b). Comparison of different samples showed that new peaks have been created gradually. It implies that the oxidation reaction as well as partial thermal decomposition has been progressed and new materials were produced. The breakage of the carbon chain leads to formation of free radicals (Eq. (1)). Free radicals are highly active and are responsible for speeding up the chemical chain reactions [12]. Fig. 4 shows that in the region of 1700–1750cm^{-1}, some changes have occurred. These changes can be the result of oxidation products, mainly ketones formation. In the present spectra, observed band at 1730cm^{-1}, shows that at temperatures 110, 130 and 150ºC, thermal degradation has happened; meanwhile the presence of ketones is also justified.

In Fig. 5, the results of TAN analysis for oil samples withdrawn at 90, 110, 130, and 150ºC is presented. The results reveal that TAN increases with respect to temperature and time. This phenomenon can be the result of the formation of acidic compounds due to the oxidation reactions. However, no significant changes in TAN at 90ºC is observed. It is mentioned that oligomer compounds are produced during oil degradation because of Aldol Condensation [11]. The presence of oligomers changes the oil viscosity. In order to investigate these effects, the viscosity of samples at different temperatures and time intervals has been measured the results of which are presented in Fig. 6. It is observed that viscosity of all samples increased at the beginning of the experiments as a result of vaporization of available light components. After the first peak, viscosity decreases because of formation of ketones, aldehydes and acidic compounds. Finally, poly condensation reactions start and consequently viscosity increases. It can be deduced that the oxidation process starts when viscosity decreases.

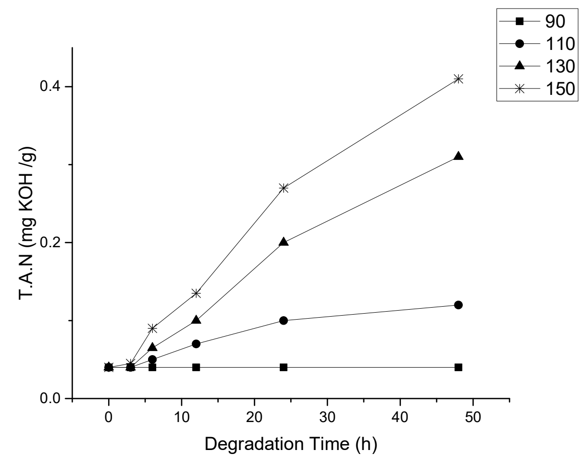


Fig. 5. Total acid number variation as a function of time and temperature

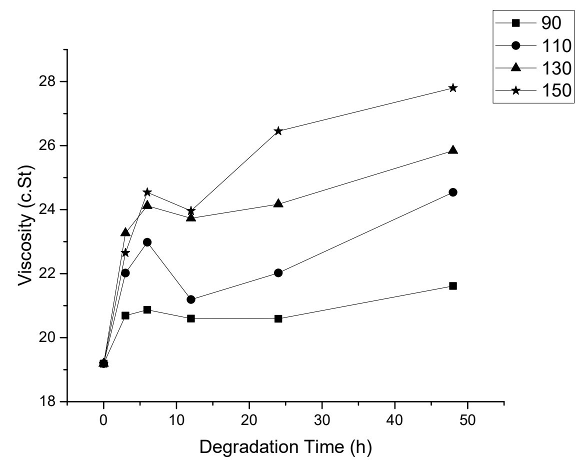


Fig. 6. Viscosity variation as a function of time and temperature

The IFT tests are usually used as an analytical tool in monitoring transformer oil [14]. In this work, the variation of IFT has also been monitored. The interfacial tension of water and oil is expected to decrease when polar surface-active compounds appear at the interface. Fig. 7 shows the results of IFT analysis for the oil samples withdrawn at 90, 110, 130, and 150ºC temperatures.

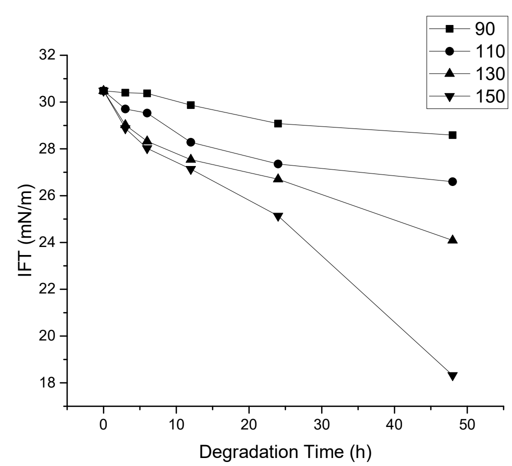


Fig. 7. Interfacial tension variation as a function of time and temperature

In this figure, it is observed that the rate of decrease of IFT increases with increasing temperature. In the case of samples withdrawn at 150ºC, after 24 hours a sharp change in slope can be observed. In the interfacial tension, this behavior can be attributed to the formation of impurities in the oil. The highest production of oligomers with high molecular weight is observed at 150ºC for 24hr as well as 48hr of heat treatment.

The ultracentrifuge test confirms the same results. In this regard, all samples were placed in a dark room for three days to let the degradation products deposit. The formed sludge was separated using a micro centrifuge device at 15000rpm. The results showed that the amount of sludge increases with temperature. Fig. 8 shows that at 90ºC the minimum amount of sludge is produced while Fig. 9 illustrates that at 150ºC the maximum amount of sludge is created. The summary of these results can be seen in Table 1.

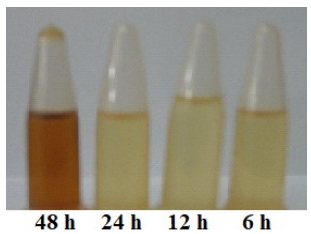


Fig. 8. No deposit products were observed for the samples at 90ºC in ultracentrifuge tube

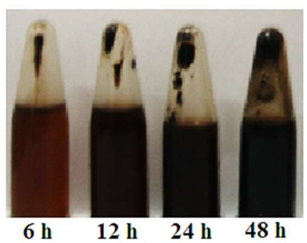


Fig. 9. An increase in amount of deposit products in ultracentrifuge tube as a function of time for samples withdrawn at 150ºC

Sasaki et al. [34] reported that while the sludge sampled from a gas turbine lubrication cycle is insoluble in normal pentane, it is soluble in toluene. In this work, in order to check whether the separated sludge included polar oligomer compounds or not, it was dissolved in normal pentane. Afterwards, the insoluble part was separated and dissolved in toluene as a polar solvent. It was observed that the most part of the sludge was completely soluble in toluene. Hence, it can be concluded that the main part of the sludge includes polar oligomers. The FTIR results of dried sludge confirm these results in Fig. 10.

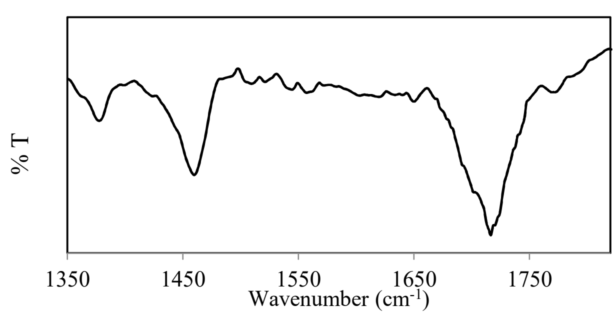
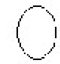
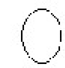
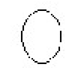
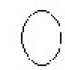
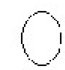
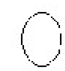
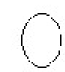
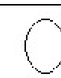
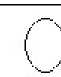
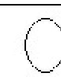
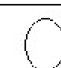
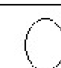
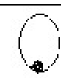
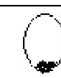
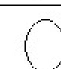
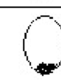
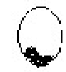


Fig. 10. The strong absorption at 1730cm^{-1} suggests that the toluene soluble fraction was oil oxidation products with carboxylic acid

In summary, in Fig. 11, it is shown that how varnish formation potential can be detected using the presented test package.

Table 1. The summarized results of proposed analytical package

Temperature (ºC)	Time range of degradation (h)	Change of analysis result					
		TAN (mg KOH/g)	**FTIR**	**IFT (mN/m)**	**Viscosity**	**UC**	**TAN (mg KOH/g)**
90	0-3	0	Oxidation	No	-0.082	1.5	 a
			Thermal degradation	No			
	3-6	0	Oxidation	No	-0.027	0.18	
			Thermal degradation	No			
	6-12	0	Oxidation	No	-0.503	-0.274	
			Thermal degradation	No			
	12-24	0	Oxidation	No	-0.789	-0.007	
			Thermal degradation	No			
	24-48	0	Oxidation	No	-0.494	1.026	
			Thermal degradation	No			
110	0-3	0	Oxidation	No	-0.779	2.828	
			Thermal degradation	No			
	3-6	0.01	Oxidation	No	-0.171	0.962	
			Thermal degradation	No			
	6-12	0.02	Oxidation	No	-1.249	-1.79	
			Thermal degradation	No			
	12-24	0.03	Oxidation	Yes	-0.931	0.83	
			Thermal degradation	No			
	24-48	0.02	Oxidation	Yes	-0.753	2.52	
			Thermal degradation	Yes			
130	0-3	0	Oxidation	Not	-1.461	4.078	
			Thermal degradation	Not			
	3-6	0.015	Oxidation	Not	-0.694	0.852	
			Thermal degradation	Not			
	6-12	0.035	Oxidation	Not	-0.789	-0.39	
			Thermal degradation	Not			
	12-24	0.1	Oxidation	Yes	-0.835	0.44	 b
			Thermal degradation	Yes			
	24-48	0.11	Oxidation	Yes	-2.612	1.67	
			Thermal degradation	Yes			
150	0-3	0.005	Oxidation	Not	-1.607	3.459	
			Thermal degradation	Not			
	3-6	0.045	Oxidation	Yes	-0.85	1.891	
			Thermal degradation	Not			
	6-12	0.045	Oxidation	Yes	-0.888	-0.58	
			Thermal degradation	Not			
	12-24	0.135	Oxidation	Yes	-1.999	2.49	
			Thermal degradation	Yes			
	24-48	0.14	Oxidation	Yes	-6.813	1.35	

			Thermal degradation	Yes			
a: centrifuge tube without sludge, b: centrifuge tube with sludge. more black region, more sludge							

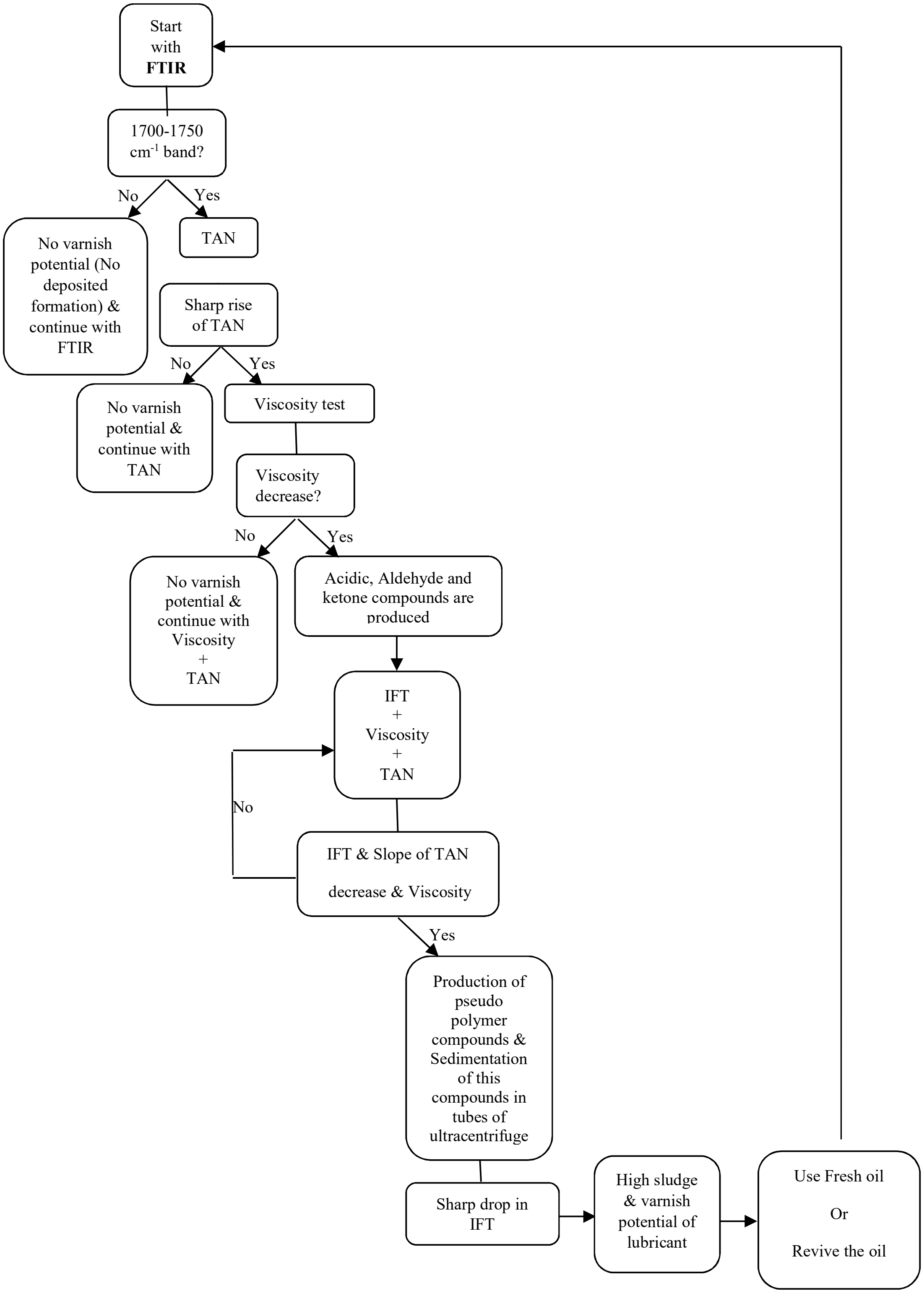


Fig. 11. A procedure for detecting varnish potential of lubricant by an analysis package

5. Conclusion

In this study we have discussed the procedure of predicting the potential of varnish formation of lubricating oils. We have studied oil degradation mechanism utilizing different analytical tests such as Fourier Transform Infrared (FTIR), viscosity test, Total Acid Number (TAN), Interfacial Tension Test (IFT) and ultracentrifuge. The result of these tests is summarized in Table 1. The procedure of oil monitoring can be summarized as follows: observation of band in the range of 1700-1750cm^{-1} in the FTIR spectra (in Fig. 4) shows the occurrence of oxidation reactions (initiation stage and then propagation stage) that can be shown in 130ºC and 150ºC samples at 48hr. This phenomenon is the first step of varnish formation. In order to control the oxidation reactions TAN tests must be carried out. The sharp rise of TAN and decrease of viscosity (which can be shown in 130ºC and 150ºC samples in Fig. 5) are indications of aldehyde and ketone formation. Aldehydes and ketones participate in poly condensation reactions and, as a result, oligomer components are produced. The presence of heavy compounds increases the viscosity of the lubricant; this increase has been shown higher in 150ºC samples (in Fig. 6). The heavy components are surface active as well as polar and decrease the value of interfacial tension. It is observed that the rate of decrease of IFT increases with increasing temperature. In the interfacial tension, this behavior can be attributed to the formation of impurities in the oil. As would be expected, the highest production of oligomers with high molecular weight is observed at 150ºC for 24hr as well as 48hr of heat treatment. Finally, ultracentrifuge test can be utilized to prove the presence of insoluble oligomer compounds. The results showed that the amount of sludge increases with temperature. In general, we showed the consistency of the analysis results with the chemistry of the sludge formation process.

References

[1] Rauscher, M.S., Tremmel, A.J., Schardt, M., Koch, A.W., 2017. Non-Dispersive Infrared Sensor for Online Condition Monitoring of Gearbox Oil, Sensors, 17 (2), 399-407. https://doi.org/10.3390/s17020399
[2] Fitch, J.C., Gebrain, S., 2006. Review of Degradation Mechanisms Leading to Sludge and Varnish in Modern Turbine Oil Formulations, Journal of ASTM International, 3 (8), 1. https://doi.org/10.1520/JAI13504
[3] Ingold, K.U., 1961. Inhibition of the Autoxidation of Organic Substances in the Liquid Phase, Chemical Reviews, 61,563-589. https://doi.org/10.1021/cr60214a002
[4] Stark, M.S., Wilkinson, J.J., Smith, J.R.L., Alfahad, A., Pochopien, B.A., 2011. Autoxidation of Branched Alkanes in the Liquid Phase, Industrial & Engineering Chemistry Research, 50, 817-823. https://doi.org/10.1021/ie101695g
[5] Gatto, V.J., Moehle, W.E., Cobb, T.W., Schneller, E.R., 2006. Oxidation Fundamentals and Its Application to Turbine Oil Testing, Journal of ASTM International, 3(4), 1-20. https://doi.org/10.1520/JAI13498
[6] Migdal, C.A., 2003. Antioxidants, in: Rudnick LR (Ed.), Lubricant Additives Chemistry and Applications, Marcel Dekker Inc, New York.
[7] Rasberger, M., 1997. Oxidative Degradation and Stabilization of Mineral Oil Based Lubricants, in: Motier RM, Orszulik ST, (Eds.). Chemistry and Technology of Lubricants, Blackie Academic and Professional, London.
[8] Colclough, T., 1993. Lubricating Oil Oxidation and Stabilization, in: Scott G. (Ed.), Atmospheric Oxidation and Antioxidants, Elsevier Science Publishers, Amsterdam.
[9] Shlyapnikov, Y.A., 1981. Antioxidant Stabilization of Polymers, Russian Chemical Reviews, 50, 581-600. https://doi.org/10.1070/RC1981v050n06ABEH002652
[10] Scott, G., 1965. Atmospheric Oxidation and Antioxidants, Elsevier Publishing Company, Amsterdam.
[11] March, J., 1985. Advanced Organic Chemistry, 3nd ed., John Wiley & Sons Inc, New York.
[12] Thompson, B.T., Livingstone, G., 2004. Using Quantitative Spectrophotometric Analysis as a Predictive Tool to Measure Varnish Potential, Lubrication Excellence 2004 Conference, March 23-25, Nashville, USA.
[13] Livingstone, G., Thompson, B., 2005. New Varnish Test Improves Predictive Maintenance Program, Lubrication Excellence 2005 Conference, April 25-29, San Antonio, USA.
[14] Livingstone, G., 2003. Detecting Thermal Failure and Varnish Potential, Lubrication Excellence 2003 conference, April 1-3, Houston, Texas, USA.
[15] Yano, A., Watanabe, S.H., Miyazaki, Y., Tsuchiya, M., Yamamoto, Y., 2004. Study on Sludge Formation during the Oxidation Process of Turbine Oils, Tribol. Trans. 47, 111-122. https://doi.org/10.1080/05698190490278985
[16] Kouame, S.D., Liu, E., 2014. Characterization of fully and partially additized lubricant deposits by Temperature Programmed Oxidation, Tribology International. 72, 58–64. https://doi.org/10.1016/j.triboint.2013.11.001

[17] Sinha, S., Agarwal, A.K., 2010. Experimental investigation of the effect of biodiesel utilization on lubricating oil degradation and wear of a transportation CIDI engine. Journal of Engineering for Gas Turbines and Power. 132 (4), 1-9. https://doi.org/10.1115/1.3077659

[18] Perez, J.M., 1999. Oxidative properties of lubricants using thermal analysis, Thermochimica Acta. 357–358, 47–56. https://doi.org/10.1016/S0040-6031(00)00367-1

[19] Kurre, S.K., Garg, R., Pandey, S., 2017. A review of biofuel generated contamination, engine oil degradation and engine wear, Biofuels. 8(2), 273-280. https://doi.org/10.1080/17597269.2016.1224291

[20] Altaie, M.A.H., Janius, R.B., Yunus, R., Taufiq-Yap, Y.H, Zakaria, R., 2016. Degradation of enriched biodiesel under different storage conditions, Biofuels. 8(2), 181-186. https://doi.org/10.1080/17597269.2016.1215070

[21] Coates, J.P., Setti, L.C., 1986. Infrared Spectroscopic Methods for the Study of Lubricant Oxidation Products, ASLE Transactions. 29(3), 394-401. https://doi.org/10.1080/05698198608981701

[22] Liu, Z., Wang, H., Zhang L., Sun, D., Cheng, L., Pang, C., 2016. Composition and degradation of turbine oil sludge, Journal of Thermal Analysis and Calorimetry. 125(1), 155–162. https://doi.org/10.1007/s10973-015-5200-1

[23] Fitch, J.C., Gebarin, S., 2006. Sludge and varnish in turbine systems, Practicing Oil Analysis. 5, 28–36.

[24] Shima, M., Kumazaki, O., Hashimoto, K., Yoshida, T., 2000. Development of lubricant deterioration evaluation method using chemical analysis; Sanka boshizai no kagaku bunseki ni yoru tabinyu rekka hanteiho no kaihatsu, Karyoku Genshiryoku Hatsuden. 51, 108–112. https://www.osti.gov/etdeweb/biblio/20092463

[25] Hussain, S.K.A., Usman, M., Umer, J., Farooq, M., Noor, F., Anjum, R., 2022. A novel analysis of n-butanol–gasoline blends impact on spark ignition engine characteristics and lubricant oil degradation, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 1-15. https://doi.org/10.1080/15567036.2022.2036874

[26] Dörr, N., Agocs, A., Besser C., Ristić A., Frauscher M., 2019. Engine Oils in the Field: A Comprehensive Chemical Assessment of Engine Oil Degradation in a Passenger Car. Tribology Letter. 67, 68. https://doi.org/10.1007/s11249-019-1182-7

[27] Jamil, M.K., Akhtar, M., Farooq, M., Abbas, M.M., Saad., Khuzaima, M., Ahmad, K., Kalam, M.A., Abdelrahman, A., 2022. Analysis of the Impact of Propanol-Gasoline Blends on Lubricant Oil Degradation and Spark-Ignition Engine Characteristics. Energies. 15, 5757. https://doi.org/10.3390/en15155757

[28] Ahme, L., Kuhn, E., Canto, M.A.D., 2022. Experimental Study on the Expended Energy on Structural Degradation of Lubricating Greases. Tribology Letter. 70, 81. https://doi.org/10.1007/s11249-022-01622-2

[29] Ribeiro, F.C.P, Oliveira, A.S., Araújo, A., Marinho, W., Schneider, M.P., Pinto, L., Gomes, A.A., 2019. Detection oxidative degradation in lubricating oil under storage conditions using digital images and chemometrics. Microchemical Journal. 147, 622. https://doi.org/10.1016/j.microc.2019.03.087

[30] Sasaki, A., Uchiyama, S., Yamamoto, T., 1999. Generation of Static Electricity during Oil Filtration. Lubrication Engineering. 55(9), 24-27.

[31] Sasaki, A., Uchiyama, S., Yamamoto, T., 1999. Free Radicals and Oil Auto-Oxidation Due to Spark Discharges of Static Electricity. Lubrication Engineering. 55 (9), 24.

[32] Gunsel, S., Lockwood, F.E., 1995. The Influence of Copper-Containing Additives on Oil Oxidation and Corrosion, Tribology Transactions. 38(3), 485-496. https://doi.org/10.1080/10402009508983434

[33] Lahijani, J., Lockwood, F.E., Klaus, E.E., 1982. The Influence of Metals on Sludge Formation. Tribology Transactions. 25, 25-32. https://doi.org/10.1080/05698198208983060

[34] Sasaki, A., Uchiyama, S., Kawasaki, M., 2008. Varnish Formation in the Gas Turbine Oil Systems, Journal of ASTM International. 5(2), 1-12. https://doi.org/10.1520/JAI101419