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Evaluation Properties and PNA Analysis for Different Types of Lubricants Oils

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Abstract

A study of characteristics of the lubricant oils and the physical properties is essential to know the quality of lubricant oils. The parameters that lead to classify oils have been studied in this research. Three types of multi-grades lubricant oils were applied under changing temperatures from 25 ^{o}C to 78^{o}C to estimate the physical properties and mixture compositions. Kinematic viscosity, viscosity gravity constant and paraffin (P), naphthenes (N) and aromatics (A) (PNA) analysis are used to predict the composition of lubricants oil. Kinematic viscosity gives good behaviors and the oxidation stability for each lubricant oils. PNA analysis predicted fractions of paraffin (X_P), naphthenes (X_N), and aromatics (X_A) for each one give us a good value for sample 3 (15W40) leads to suitable classification for this type multi-grade oils by kinematic viscosity

Keywords: PNA Analysis, VGC, Kinematic Viscosity, Lubricating oil

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1- Introduction

The lubricating oil is one of important industries and it is one of the applications of petroleum refining engineering which is produced from oil refining operations that have base oil because the feedstock is the reduced crude oil [1].

Crude oil compositions can be classified into hydrocarbons, paraffin, naphtha, and aromatics which are related to the classification of lubricating oils. Molecular types in the oils depend on the nature of the oils used and have an effect on the properties of the lubricating oils. The most important characteristics that determine the quality of the lubricant oil are the physical and chemical properties (density, viscosity, viscosity index, etc.) and the effect of temperatures change on the viscosity explain the ability to use oils in engines.

Density or specific gravity used to characterizing undefined lubricants because it's correlated with hydrocarbon composition (chemical composition) [2].

The basic functions of lube oils are to remove heat, reduce friction and prevent corrosion; the oils must provide these functions under operating conditions at temperatures changing.

There are a few methods available in the literature used to predict the composition so to predict properties of a mixture composition of oils requires the knowledge of PNA composition [3]. Cerny, J.and Strnad, Z.[2001].utilized a modified IP 48 procedure (200 °C, 6-hour oxidation cycle) to test the oxidation stability of SAE 15W-40 engine oils and several differences in ageing behavior were found.

Viscosity, amount of pentane insoluble within the test were chosen as the parameters to evaluate of oxidation stability of oils [4]. A. Awad, and S. Mohammed, [2014]. Have studied on the enhancements on the lubricant oil properties at different temperatures to enhance the efficiency of lubricant oil density and the thermal expansion with and without additive Poly isobutylene, but didn't have mentions on the mixture composition [5]. S. Zzeyani, M. Mikou [2018].

They used viscosity evaluation with other parameters to analysis three of synthetic lubricating by inductively coupled plasma optical emission spectrometry (ICP/OES), their investigation gives the formation of polycyclic aromatic hydrocarbons and the additives tend to thicken the lubricating oil [6].

S. Zzeyani, M. Mikou, J.Naja [2017], used the Electron Paramagnetic Resonance (EPR) and Infrared Fourier Transform (FTIR) to evaluate the rate of degradation of lubricating oil, the results were production of organic compounds from degradation and in the same time gets those FTIR techniques effective to evaluate of the lubricating oil [7].

V. Mäkelä, P. Karhunen, S. Siren, S. Heikkinen[2013], detect by software designed for mass analysis of quantitative spectra (ImatraNMR) on signals originating from napthene (cycloalkane) structures present in base oil samples to conduct the analysis of the physicochemical properties of base oils [8]

There are a lot off investigation that is depending on physical properties and chemical composition for crude oil products as in the study of Abdul-Halim A.-K. Mohammed [2007], improve the viscosity index for

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lubricant oil, explain effect of temperature and solvent on chemical composition and physical properties by using the n-d-M method for carbon distribution and analysis [9].

In the other studies, the characterizations of extract lubricating oil at different conditions to make a comparison between the percent of conversion to reduce the aromatic compounds in that's products, this is done by Fatimah Kadhim [2018] [10].

Ibtehal k. Shakir [2015] used two types of co-solvents to decreases undesirable materials in raw lubricating oil to improve the viscosity index at the temperature range from 70 to 110 °C [11]. We can conclude from all of them the chemical composition and analysis for lubricating oil very important before and after used in the market.

In order to provide basic function of lubricants oils under changing in the temperatures, the quality and properties of lubricants oils depend mainly on the mixture composition, and characterization parameters that are useful for molecular type in PAN analysis, this was aim of study by using (Riazi-Daubert) Methods [3] and all assumption was for three types multi-grades oils.

2- Characterization Parameters and Experimental Test

2.1. Properties of Lubricants Oils

Three types of multi-grades oils properties were measured in laboratories of petroleum Eng. according to ASTM tests, as shown in the Table **1**.

Table 1. Lubrication oils parameters and properties

parameters	Sample 1	Sample 2	Sample 3	Test method
SAE Viscosity Grades	20W40	10W40	15W40	------
SG at 15.6 ºC	0.895	0.865	0.851	ASTM D-1217
Color	L3.5 ASTM	L 3 ASTM	L3.5 ASTM	ASTM D-1500
API requirements	SL	SN	SF	------
Molecular Weight	109.358	101.816	98.545	(Pedersen.,1989) [12]
Kinematic viscosity cSt at 25 ºC – 78 ºC	5.7702–0.513	4.609–0.545	3.834- 0458	ASTM D- 445

All physical properties and other parameters are estimated as the following:

2.2. Tests of Density, Specific Gravity, color, and Viscosity

Density and Specific Gravity(SG): The concept of density is unit weight to unit volume of a fluid and liquid density for hydrocarbons is usually reported in terms of (SG) or relative density defined as, the ratio of the weight of a unit volume of oil to the weight of the same volume of water at a standard (0.999 g/cm^3 (999 kg/m^3) at 60^{0}F) [13], Both of relative density and API degree used for characterizing unknown oils because they have relation with hydrocarbon composition and, therefore, with the nature of the source oil (ASTM D-l298, IP 160) [14]. In the present research, the method of Pycnometer (ASTM D-1217/ 941) used to determine value of density for three type of lubricant oil and then value of SG that needed in calculation of API , VGC, Ri and other parameters.

Kinematic Viscosity: Kinematic viscosity used to estimate some of physical properties as well as the composition and quality of lubricant oils. In this research the viscosity of lubricating oil is a measure of its flow characteristics at different temperatures experimentally by using Cannon-Fenske Routine Viscometer according to the ASTM D-445[14]. The Kinematic viscosity (v), (mm^2/s) of a Newtonian liquid calculated from the mean measured flow time (t) (in seconds) and with viscometer constant (c) (mm^2/s)/s) using the following equation:

$$\boldsymbol{v = c*t} \qquad (1)$$

The constant (c) of the viscometer found to be 0.45868. Three types of lubricant oil were tests at different temperatures in two times, the first before oxidation of lubricant oil (normal conditions) and the second after oxidation of lubricant oil as shown in. Fig.1. The selection of the correct viscosity for the oil is aimed at a balance between a viscosity high enough to prevent the lubricated surfaces from contacting and low enough to minimize energy losses through excessive heat generation caused by having too viscous lubricant (ASTM D-2422, BS-4231) [14], because the main objective of lubrication is to provide a film between load-bearing surfaces.

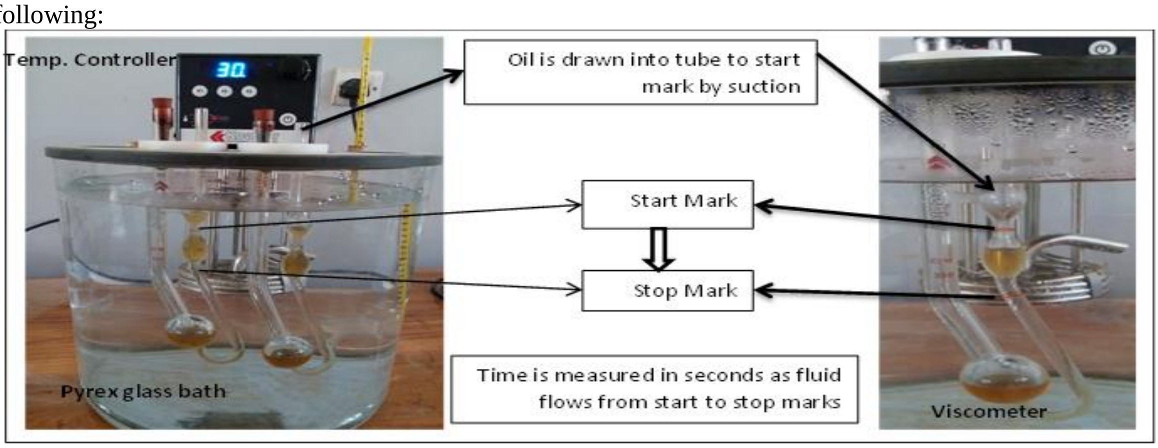


Fig. 1. Instrument description of Kinematic viscosity test

The Color- ASTM D-1500: (ASTM Color Scale) this method used for determination of the color of lubrication oils in this research, three glass samples and reference container tubes are used with the AF 650 comparator together with two discs of color standards [14].

All tests done with two cases, case1 normal condition for lubricant oil and the case2 lube oil has a boiling range up to 200^{o}C, (in the case2 lube oil heated to temperature of 200 °C with high airflow for six hours to compare the results), and its physical properties were determined according to standard test methods in ASTM to find oxidation stability from the following ratio [15]:

$$\text{Oxidation Stability} = \frac{\text{The Kinematic viscosity } (v) \textit{ in case } 2at \text{ 100 F}}{\text{The Kinematic viscosity } (v) \textit{ in case } 1at \text{ 100 F}} \qquad (2)$$

Equation (2) leads us to know the oils deterioration by oxidation under specified conditions.

3- Estimation of Viscosity Gravity Constant (VGC)

The parameter viscosity gravity constant **(**VGC) with other parameters were used in this research to estimate samples of lubricant oil compositions by equation (3) [13]. VGC is defined in terms of kinematic viscosity and specific gravity and determined experimentally.

$$\text{VGC} = \frac{10\,SG - 1.0752\,log_{10}(V_{38} - 38)}{10 - log_{10}(V_{38} - 38)} \qquad (3)$$

Where: SG and V_{38} are specific gravity and kinematic viscosity at 38^{o}C (100^{o}F in SUS) (Saybolt Universal Seconds). VGC arranged for paraffinic (P) from (0.74 - 0.75), naphthenic (N) (0.89 - 0.94), and for aromatics between 0.95 and 1.13 [16], as shown in Fig. 2, to predict the composition of three types from lubricant oil in this research with the refractivity intercept (Ri) determined from the refractive index(n) at 20 ^{o}C and density (ρ) of each sample by the equation below:

$$R_i = n - \frac{\rho}{2} \qquad (4)$$

4- PNA Analysis

PNA analysis is a method used to predict the quantitative determination of paraffin (P), naphthenes (N) and aromatics (A) (PNA) in oil mixture. The nature of lubricant oil content on different amounts of paraffin, naphthenes and aromatics groups, this method used to predict the characterizes and quantifies the components in lubricant oil and classifying it. The method of Riazi-Daubert (PNA analysis) adopted by the API Committee on the characterization of petroleum fractions and is included in the fourth and subsequent editions of the API-TDB [13].

This method used both of (Ri) and (VGC) to develop a predictive the composition of viscous petroleum fractions as shown in Fig.2 indicates the value of Ri and VGC are the most suitable parameters to identify hydrocarbon type. [3]

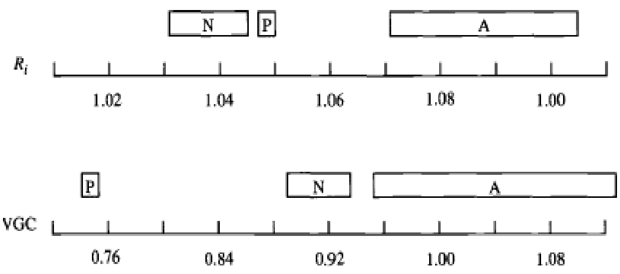


Fig. 2. Characterization factors for viscous of oil fractions [3]

PNA analysis provides a good knowledge of molecular type of lubricant oil mixture constituents, the first equation is known from the material balance:

$$X_P + X_N + X_A = 1 \qquad (5)$$

Based on the values of Ri and VGC that determine from equation (3) and (4) for all type of lubricant oil, average values of these parameters were determined for the groups of paraffins, naphthenes, and aromatics by applying the following equations for estimation of the PNA composition in lubricant oil for heavy fractions at 37.8 ^{o}C (100^{o}F) [3]:

$$\begin{aligned} X_P &= a + b\,R_i + c\,VGC \\ X_N &= d + e\,R_i + f\,VGC \\ X_A &= g + h\,R_i + I\,VGC \end{aligned} \qquad (6)$$

X_P, X_N, and X_A calculated from the above relations may represent volume, mole, or weight fractions and a, b, c, d, e, f, g, h, and i are the constants varying with molecular weight range as given in Table **2** [17]. The information available for three types of lubricant oils with experimental values are used as input parameters to predict PNA composition for each other as shown in discussion.

Table 2. Constants equation (6) [17]

constant	Light fraction	Heavy fractions	constant	Light fraction	Heavy fractions
a	-13.359	2.5737	f	0.81517	1.96312
b	+14.4591	1.0133	g	-9.6235	-4.0377
c	-1.41344	-3.573	h	8.8739	2.6568
d	+23.9825	2.464	i	0.59827	1.60988
e	-23.333	-3.6701			

5- Results and Discussion

5.1. Effect of Temperature on Kinematic Viscosity:

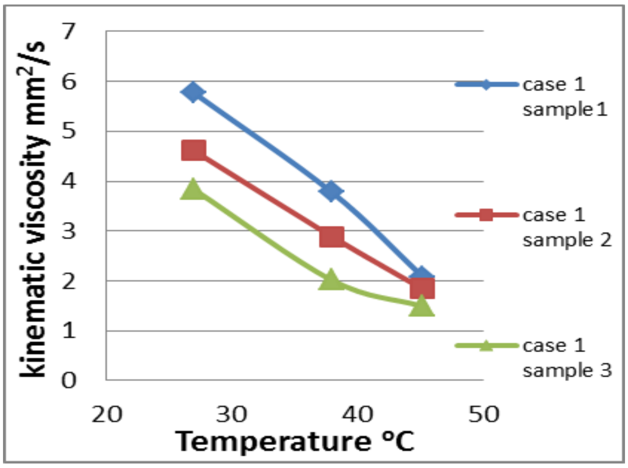
Values of kinematic viscosity of lubricant oil are usually measured and reported at different temperatures also it's decreased with temperatures increasing. **Fig. 3** illustrates the variation of kinematic viscosity (cSt) of three sample from lubricant oils with different temperatures (^{o}C) at two cases.

First case (case 1) shows in (a) we can see from the Fig. there is different value of kinematic viscosity for each sample under normal conditional and that is clear in the first reading for sample 1 at temperature 27 ^{o}C needed efflux time 12.58 seconds as fluid flows from start to stop marks in the viscometer, but the sample 2 was needed 10.05 seconds to measured its kinematic viscosity and 8.36 seconds for sample 3.

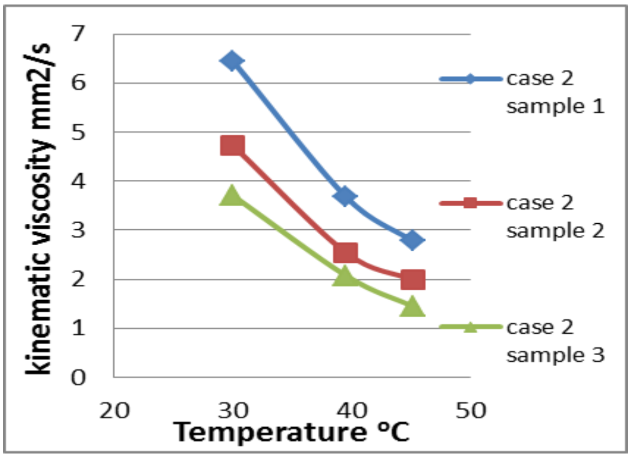
So the time taken for gravity flow of samples through a restriction is proportional to the kinematic viscosity.

After rising in the temperature the kinematic viscosity decreases with an increase in temperature as shown in **Fig. 3** (a).

In the second case (case 2) the lubricant oil was heated up to 200 ^{o}C to study of viscosity with change in temperatures and its behavior as shown in Fig. **3** (b), the kinematic viscosity decreases with efflux time less than case 1 at same temperature and the comparison for each sample with two cases are shown in **Fig. 4- Fig. 6**.



(a)



(b)

Fig. 3. Variation of kinematic viscosity of lubricant oils with Temperature ^{o}C

Fig. **4** explain the sample 1 has kinematic viscosity different in both cases but there is a simple converges at 40 ^{o}C needed times flow between (6.05 - 4.55) seconds, in this concept the sample 1 have low viscosity index and extracted from naphthenic oil as shown in table (4) and depended on equation (2) the oxidation stability equal to 0.973 are not critical.

Fig. **5** illustrate behavior the sample 2 between change in temperature and kinematic viscosity , we can see at 39 ^{o}C in both cases have same kinematic viscosity with efflux time between (2.889 - 2.536) seconds that means the sample2 remain in a relatively unchanged condition with higher temperature and have oxidation stability equal to 0.877 less than sample1. Fig. **6** the sample 3 has very converges in kinematic viscosity with both cases at efflux time between (1.44 - 1.45) seconds in 45 ^{o}C and remain relatively unchanged condition with higher temperature and has oxidation stability equal to 1.02.

From all above is the basic functions of lubricants should possess and maintain proper viscosity, flow as a liquid at the operating temperature and have good oxidation stability.

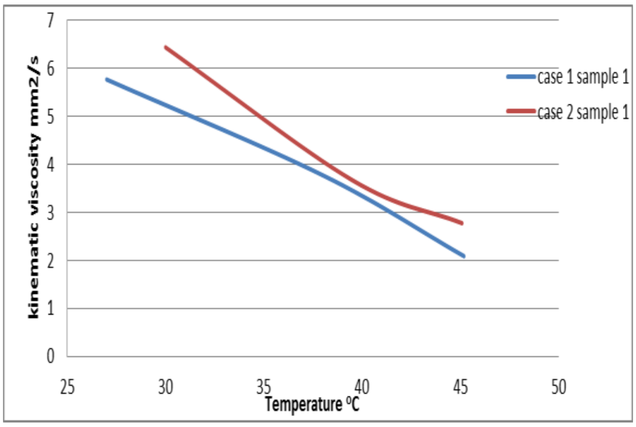


Fig. 4. Comparison of kinematic viscosity of lubricant oil (sample1) with two cases with change in Temperature ^{o}C

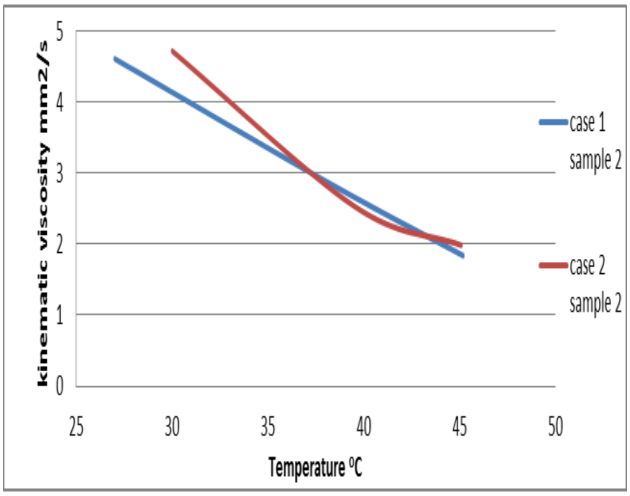


Fig. 5. Comparison of kinematic viscosity of lubricant oil (sample2) with two cases with change in Temperature ^{o}C

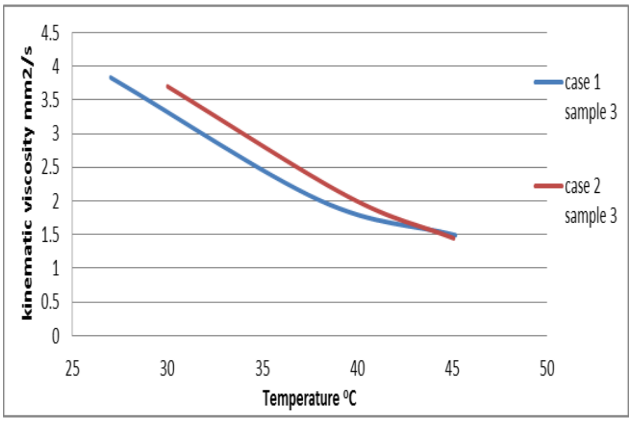


Fig. 6. Comparison of kinematic viscosity of lubricant oil (sample3) with two cases with change in Temperature °C

5.2. Prediction of PNA Composition

PNA analysis used to predict of lubricants oils compositions by analysis some of depended characterization (VGC, Ri, SG), Table **3** and Table **4** show value and characterization parameters for three samples.

Table 3 predicts value of VGC and Ri from equations (3) and (4) compared with Fig. 3, it is clear VGC evaluated have little value for paraffinic oil, while inversely value for VGC in naphthenic oils. The sample 1 has high value of VGC in type naphthenic and low value in paraffinic but in sample 2 has medium value in both naphthenic and aromatics type.

The aromatics are undesirable because it have effect on the oils properties, that seen in sample 3 it was divided value of VGC between high value in naphthenic type and the remained have medium values in both of aromatics and paraffinic type as shown in Fig. **7** to explain the variation of composition of lubricant oil types with PNA analysis and show us that Ri and VGC are the most suitable parameters to identify hydrocarbon type and that leads to applied both of equations (5) and (6) to obtain fractions of paraffins (X_P), naphthenes (X_N), and aromatics (X_A).

As in Table **4** and high values for fraction of naphthenes (X_N) equals to 0.699133197, 0.4291149, and 0.5167164 for Sample 1 (20W40), Sample 2 (10W40) and Sample 3 (15W40) .

PNA analysis gives us a good value for sample 3 (15W40) leads to suitable classification for this type multi-grade oils by viscosity or kinematic viscosity.

Table 3. Characterization Parameters for samples types Analysis

Hydrocarbon type	Sample 1 (20W40)			Sample 2 (10W40)			Sample 3 (15W40)		
	VGC	Ri	SG	VGC	Ri	SG	VGC	Ri	SG
Paraffins	few	few	few	few	few	few	few	few	few
Naphthenes	high	high	medium	high	few	medium	high	high	medium
Aromatics	medium	few	few	medium	medium	few	medium	few	few

Table 4. Values of PNA Analysis for types of lubricant oils

Sample type	Paraffins (X_P)	Naphthenes (X_N)	Aromatics (X_A)
Sample 1 (20W40)	0.026026213	0.699133197	0.27484059
Sample 2 (10W40)	0.26023	0.4291149	0.31065543
Sample 3 (15W40)	0.21233	0.5167164	0.270953832

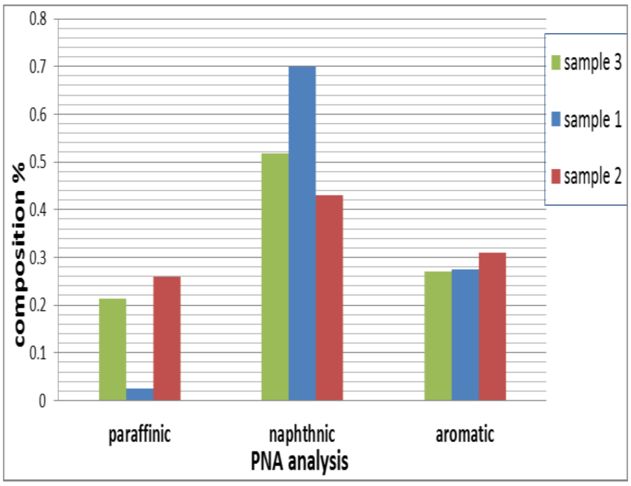


Fig. 7. Variation of composition for lubricant oil types with PNA analysis

6- Conclusions

- Kinematic viscosity measured at different temperatures (25 °C – 78 °C) at two conditions to explain oxidation stability for Sample 1 (20W40), Sample 2 (10W40) and Sample 3 (15W40) equal to 0.973, 0.877, and 1.02 respectively oxidation stability, leads to the basic functions of lubricants oils should maintain suitable viscosity at the operating temperature with a good oxidation stability.
- PNA analysis gives a clear value to three groups for each Sample and high values for fraction of naphthenes (X_N) equals to 0.699133197, 0.4291149, and 0.5167164 for Sample 1 (20W40), Sample 2 (10W40) and Sample 3 (15W40) respectively, this method leads to classification of multi-grade oils by kinematic viscosity depended on the original hydrocarbons composition in the lubricants oils.

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تقييم خصائص وتحليل(PNA) لانواع مختلفة من زيوت التزييت

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الخلاصة

دراسة الخصائص الفيزياوية لزيوت التزييت وتصنيفها تعتبر مهمة لمعرفة نوعية الزيوت وجودتها. في هذا البحث تم دراسة المعاملات الاساسية التي تدخل في تصنيف الزيوت. استخدمت ثلاث انواع من الزيوت التزييت ذات نوع متعددة– الدرجة حيث تم حساب الخصائص الفيزياوية لها ومكونات المزيج بدرجات حرارة متغيرة تتراوح بين $25^{o}C - 78^{o}C$.تم استخدام كل من اللزوجة الكينماتيكية وثابت اللزوجة وطريقة تحليل المكونات كل من البرافينات والنفثينات والعطريات (PNA) لتنبأ المكونات لزيوت التزييت. اللزوجة الكينماتيكية اعطت سلوك جيد مع ثابت استقرارية لكل زيت. طريقة التحليل (PNA) اعطت نسب كل من المكونات البرافينات (X_P) والنفثينات(X_N) والعطريات (X_A) الداخلة في تركيب كل نوع من الزيوت المستخدمة وكذلك استنتجت الطريقة قيم جيدة للنوع الثالث من الزيوت (15W40) وهذا مؤشرمناسب لتصنيف الزيوت متعددة –الدرجات بواسطة اللزوجة الكينماتيكية

الكلمات الدالة: تحليل PNA, اللزوجة الحركية, زيوت التشحيم