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Reduce Aromatic Content using Pure Solvents in Multi-grades Lubricant Oils by n-d-m Method

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ABSTRACT: This research focuses on the three organic solvents (Benzene C_6H_6, Toluene $C_6H_5–CH_3$ and n-Hexane C_6H_{14}) different in the polarity and dielectric constant, which were subsequently evaluated as the solvents to reduce the aromatic content (XA) in the products of petroleum fraction like lubricants oils. The additives were blending with three samples of lubricants oils at mixing ratio ranging (13%, 23 and 37.5%), and the samples were characterizing by viscometer according to the ASTM D-445 and refractive index (RI) by Abbi refractometric with assist of n-d-m method. The reduction in the (XA) is starting with benzene then various at n-hexane and increasing with toluene were obtained for the samples of lubricants oils treated. Good result obtained with benzene solvent were 0.2966 (XA) at mixing ratio 37.5% in sample 2, also for reflectivity (RI) same case, but was various for other solvents. One of the important studies, n-d-m method with refractive index (RI) and viscosity showed good information to classify the aromatic content in case of the additions with suitable solvents.

KEYWORDS: Aromatic content; organic solvents; n-d-m method; refractive index

INTRODUCTION

In the production of Lubricating oils in oil refinery, a highly aromatic compounds required [1]. Aromatics are unsaturated cyclic compounds very reactive chemically, the most complex aromatics have three or more aromatic rings fused together found in the heavier fractions of petroleum [2]. Lubricant oils have a mixed from hydrocarbons (paraffins, naphthenes and aromatics) with some of additive material, so the effect of hydrocarbons properties with its contents have effects on the oils used. there are a lot of studies that shows all of factors, properties and its effects on major work of oils and its performance, such as Asaad S. Bded, his study was on evaluation properties of lubricant oils by using PNA analysis method to predicted fractions of paraffin (X_P), naphthenes (X_N), and aromatics (X_A) with kinematic viscosity and all results was good and suitable to evaluate the oils [3]. known the details and content for some of hydrocarbon in lubricant oil gives information about quality of oils or fuels products from petroleum, some of studies doing that on diesel fractions by Monika Sh., P.Sh. and J. N. Kim, they did review on the effect of reduction conditions by solvents to removal of aromatic content in fractions of petroleum, on the increase in the sulfur in diesel fuel coming from aromatic components, so the choosing the solvents criteria on properties is important in De-aromatization process [4].

Other researcher has study on the thermal, mechanical properties for gas oil and diesel fuels samples at different additive, Luma M. Ahmed, found the amount of ash content may be high at some of samples in the same time caused problems in engines [5]. There are aromatics solvents like benzene and toluene, which are obtained from petrochemical products and used to extraction the aromatics content in its. Performance of extraction aromatics from aliphatics using the water-containing DIL was done with assist of aromatics solvents and the results gave a good indicator that is deals with concept of green chemistry [6]. So, in that reason the pure solvent additives will help to reduction in XA in the heavy petrochemical products. The enhancement of the viscosity for lubricants oil occurs with additives, and some of them have effect on growth of the heavy hydrocarbon with dark color and lead to high content of aromatic XA in the lubricants oil after oxidation it. There are a lot of process to extract, reduced, and remove the metals or aromatic hydrocarbon or other additives that are present in the lubricating oil. A. Kamal,S. D. Naqvi, used process in their article was extraction of solvent by adsorption to remove the metals from re-refined oil, they found lower content for the metal in lubricating oil [7]. A. Mehrkesh, T.Tavakoli. A studies was on the removal of aromatic content by a Liquid-Liquid extraction column process to find out the lubricating oil and at the same time that aromatic contents is important factor to the final product quality [8].

There is a study on characteristic of pollution by aromatic components like polycyclic in the lubricating oil used, that shows amount of polycyclic aromatic hydrocarbons dependent on the its source in oil working temperatures [9]. Tahseen H. Khlaif, added some additives to reduce the amount of sulfur content in oils, was suitable method by assist of ultra-sound wave, reached to good results, but they neglected aromatic content estimation in the samples, this fraction if it was high aromatically will caused contamination and reduction in the viscosity index [10]. Most of companies started to increase the percentage of aromatic and paraffins contents in fuel or oil product that uses in internal combustion processes to reduce lead levels in it's; and because of the continuous uses the deposits or ash are generated and at the same time will issue pollution in the air. (A. H. Mehrkesh,S.H...etc), obtained correlations to predict the aromatic content in lubricating oil by viscosity if the temperature is known [11]. With assist ASTM D3238 standard test method can be characterize the components in petroleum mixtures, so the density, refractive index and molecular weight are parameters key to classify the product quality by determine the Aromatic content in the product mixtures [12]. So, we can show from previous literatures, the reducing of aromatic composition in the final products of lubricants oils is important factor with suitable method. Generally, the aromatic hydrocarbons non-polar and they are not soluble in water, but needed organic solvents to dissolve in it [13]. The aim of this study, used organic solvents (pure solvents) with different in dielectric constant that deals with aromatic hydrocarbon to reduce the percentage of aromatic in multi-grades lubricant oils by using n-d-m Method and refractive index (RI), and how that solvents will decrease hydrogen percentage in the blend solution of lube-oils mixtures.

MATERIALS AND EXPERIMENTAL METHOD

Properties of Materials

The properties of all test sample type tested under ASTM as listed in the following table 1.

Table 1. Multi-grades lubricant properties [3]

Type of test	Sample 1	Sample 2	Sample 3	Test method
S_{Pg} at 15.6 °C	0.895	0.865	0.851	ASTM D-1217
Color test	L 3.5 ASTM	L 3 ASTM	L 3.5 ASTM	ASTM D-1500
Kinematic viscosity cSt	5.771	4.609	3.834	ASTM D- 445

Three types of organic solvents were collected from physical chemistry laboratory (Benzene C_6H_6, Toluene C_6H_5–CH_3 and n-Hexane C_6H_{14}), for each one of them has the density (0.879, 0.867 and 0.655) g/ml respectively. They have dielectric constant (2.2) for benzene, (2.4) toluene and (1.8) for n-hexane. Chemical characterization of toluene similar to benzene, but these characteristics is modified by the presence of the methyl substituents [13].

Experimental Method

In this research, three sample of multi-grade lubricant oil are blending with the non- polar organic solvents at different in the blend ratio ranged from (1.5, 3, 6) ml with 10 ml from lubricant oil as shown in table (2). The process of blending is doing at temperature lab., nine samples of the mixture putted on the Heidolph shaker magnetic and mixers Figure 1 at 500 rpm for 3min for each sample. Kinematic viscosity for all samples tested by Cannon-Fenske Routine Viscometer according to the ASTM D-445 [14], at temperature 39 °C and density of blending samples at 15.6 °C. The refractive index (n) estimate as the velocity of light in a vacuum with respect to the velocity of light in the medium, the reflective index (RI) for all of samples are measured at 20 °C by using instrument Abbi refrectrometr, (Atago1T- Japan), the refractivity suitable parameter to characterize and estimate the composition of hydrocarbon or samples fractions [15]. Values of refractive change from [1.3 - 1.6] respectively propane to some of aromatics, and the aromatic generally have refractive values higher than paraffinic [16]. The Specific gravity (Spg) for all blending sample are estimated from the following equation (1) [16].

$$Spg = 0.01044 + 0.9915\ D_{20} \quad (1)$$

Where the density in g/ml and the spg at 15.6 °C, after estimate all of physical properties we can use the n-d-m method that mention in the next section.

Figure 1. Shaker magnetic to prepare the samples

Table 2. Blending ratio with lubricant oil samples

No.	Blending ratio		
	37.5%	**23%**	**13%**
1	20W40 oil 1+ C6H5–CH3	20W40 oil 1+ C6H5–CH3	20W40 oil 1+ C6H5–CH3
2	10W40 oil 2+ C6H6	10W40 oil 2+ C6H6	10W40 oil 2+ C6H6
3	15W40 oil 3+ C6H14	15W40 oil 3+ C6H14	15W40 oil 3+ C6H14

N-D-M Method

The n-d-M method is required three physical properties have related to composition of hydrocarbon petroleum fraction like refractivity (n), density of mixture (d) and molecular weight (m). It is classified by Van Nes and Van Westen, also it is available in the ASTM with test method ASTM D 3238 [17,18]. In this research will be focused on the distribution of carbon in aromatics (%CA) because the controlling element in a petroleum mixture is the carbon, at the same time is proportional to aromatics content (XA) distribution in the blending mixture. For (% CA) and (XA) are calculated from the equations (2) and (3) respectively, the value of *v* predicted from equation (4) [19].

$$\%CA = av + \frac{3660}{m} \quad (2)$$

$$XA = \frac{\%CA}{100} \quad (3)$$

$$v = 2.51(n - 1.475) - (d - 0.851) \quad (4)$$

where **a** is constant 340 or 670 depended on the value of *v*

The amount of hydrogen content is lower in the aromatics than paraffinic compounds, so the hydrogen %H and aromatic (XA) content have relative relation in the blending samples, the hydrogen content %H estimated from equation (5) [19].

$$\%H = 14.9 - 6.38_{XA} \quad (5)$$

All of parameters and values have been predicted from the previous equation and necessary laboratory test and represented in the next section.

RESULTS AND DISCUSSION

Effect of Solvent Additive on Aromatic Content and %H

Different non- polar solvents were added to three sample from lubricant oil for study the amount of aromatic content in the mixture with three blending ratio 13%, 23% and 37.5% (volume basis) are clear in the Figure 2. The toluene solvent leads to increasing in the aromatic content from 0.20805 to 0.376713 for all blending ratio, but we can see the benzene solvent have effect on the XA content and reduced it to 0.2966 with blending ratio 37.5%. the n-hexane solvent has different effect on the samples, in the first blend ratio 13% gives one value to decrease the aromatic content XA reach to 0.28113 as shown in table 3. The behavior of the changing in the amount of aromatic content coming from the different in dielectric constant of solvents and power of solvent to increase the solubility of the aromatic content. The solvent benzene has (2.2) dielectric constant also non- polar solvent have increase the solubility of the aromatic content, but for toluene (2.4) dielectric constant has the methyl substituents make increasing in aromatic content. The n-hexane series solvent gives normal result because of dielectric constant equal to (1.88) and didn't have cyclic compounds. Figure 3 the sample aromatics content have lower hydrogen content %H in the benzene solvent and give good result depend on equation (5), so the %H of a mixture linked to the aromatic content [19]. The toluene solvent gives increasing in the hydrogen content %H means contain more saturated hydrocarbons leads to appear the deposit in the uses. So that the better solvent gives good results starting from benzene then n-hexane in this blending ratio.

Table 3. Value of aromatic content with blending ratio for lubricant oil samples

Samples	Blending ratio		
	37.5%	**23%**	**13%**
lubricant oil 1+ Toluene	0.376714	0.326708	0.290088
lubricant oil 2+ Benzene	0.296603	0.31924	0.320533
lubricant oil 3+ n-Hexane	0.312513	0.323053	0.281139

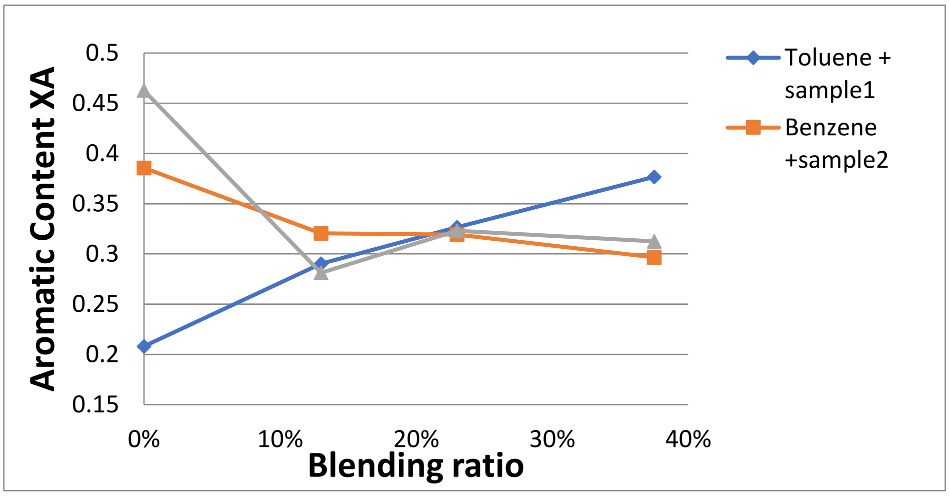

Figure 2. Illustrate the aromatic content (XA) with blending ratio

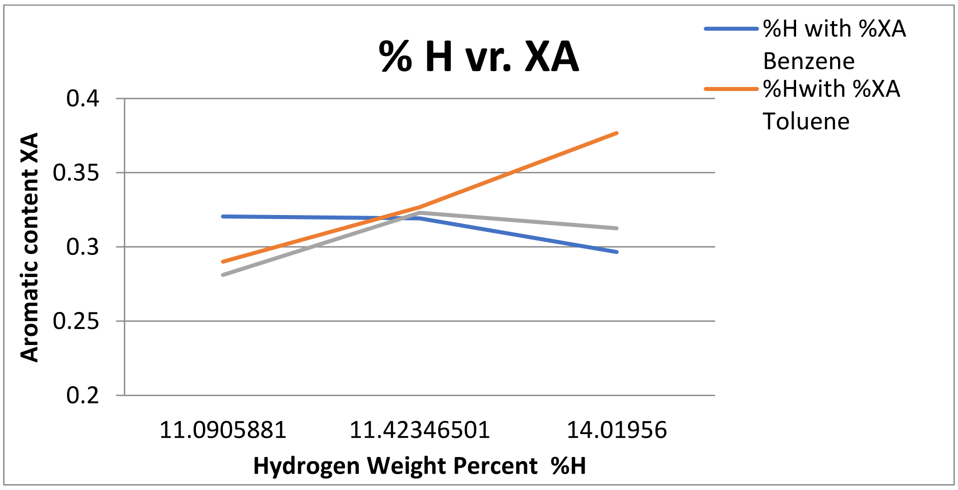

Figure 3. Illustrate the aromatic content (XA) with Hydrogen Weight Percent %H

Effect of Solvents on Refractive Index (Ri) and Specific Gravity

Refractive index is an important property to provide the clear values for hydrocarbons; the values give the information about the mixture after addition of solvents to lubricant oils. The reflectivity (RI) is shown in table 4 and Figure 4 clearly for each sample at different blending ratio and all values within range of (RI) between [1.35 - 1.6] [16]. Values of sample1 changed from 1.4850 to 1.4855 with solvent Toluene, and changed from 1.4805 to 1.4840 at blending with benzene solvent. The value of reflectivity in n-hexane blending declined from 1.4690 to 1.4350. refractive index in the aromatic hydrocarbons have values larger than naphthenes, which in turn have RI higher than compounds of paraffinic, that means the benzene solvent gives good indication for reduction aromatic content in the sample 2; in the toluene solvent the reflectivity was various, the result with n-hexane blending gives indication about effect of solvent within properties of paraffinic compounds [16]. Generally, Aromatic hydrocarbons have higher specific gravity, but we can see the values of Spg. decreases after addition solvents in all samples with different mixing ratio as shown in table 4.

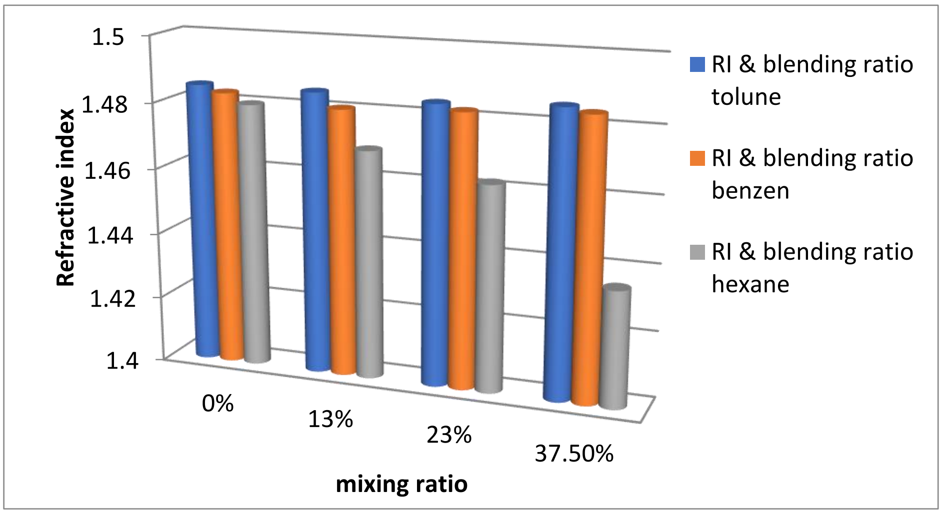

Figure 4. Illustrate the Refractive index (RI) with mixing ratio of solvent

Table 4. Value of Refractive index and specific gravity for lubricant oil samples

No.	Blending ratio	Reflectivity	Spg.
Sample 1	13% Toluene	1.4850	0.88703
	23% Toluene	1.4840	0.87999
	37.5% Toluene	1.4855	0.87503
Sample 2	13% Benzene	1.4805	0.87305
	23% Benzene	1.4822	0.85370
	37.5% Benzene	1.4840	0.84395
Sample 3	13% n-Hexane	1.4690	0.85421
	23% n-Hexane	1.4621	0.83041
	37.5% n-Hexane	1.4350	0.77330

CONCLUSIONS

In this research the effect of three types solvent have been studying to reduce the aromatic content in three samples of lubricant oils. the blending ratio 13%, 23% and 37.5% (volume basis) for each of toluene, benzene and n-hexane as solvent, the solvent benzene gives good indication to reduce of aromatic content (XA) because of dielectric constant of solvent and non- polar solvent to 0.2966 at mixing ratio 37.5% and same case to the %H. good results starting from benzene then n-hexane in all blending ratio but at toluene solvent was higher. N-D-M method with assist refractive index (RI) gives good information and results to classify the aromatic content in case of pure addition solvents.

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