Dearomatization of lube oil using polar solvents

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Abstract- Extraction of aromatics from multi-component hydrocarbon mixtures is of great commercial importance in petroleum refining industry. There exists a number of commercial extraction processes for the extraction of aromatics from aliphatics using high polar, high density, and high boiling point solvents such as dimethylsulfoxide, N-methylpyrrolidone (NMP), N-formylmorpholine (NFM), glycols, and sulfolane. Solvents for extraction should have selectivity for aromatics, high capacity, capability to form two phases at extraction temperatures, capability of rapid phase separation, good thermal stability, and should be non-corrosive, and non- reactive. In this study, the effect of adding different co- solvents to NMP solvent on the extraction process for a medium waxy distillate obtained from Western Desert crude oil. NMP was blended with water, methanol, formaldehyde, ethanol, and ethylene glycol , in order to compromise between the yield and quality of lubricating oil. The studied operating conditions are extraction temperature of 70 °C, mixing time of 15 min, settling time of 30 min, solvent to oil ratio range from 1:1 to 2:1 (wt./wt.) and co-solvent concentration from 0% to 20%. The results of the investigation show that the Increase of solvent to feed ratio led to a decrease in the raffinate yield accompanied by an increase in the quality (less sulfur content and refractive index), and increase in the yield of aromatic extract. The optimum feed: NMP ratio is 1:1.4 by mass, because it gives a reasonable yield, low sulfur content and refractive index. Increasing the concentration of the six co-solvents used increases the raffinate yield, oil density viscosity, sulfur content, refractive index, color, pour point, and average molecular weight. The best co solvent used is formamide: NMP co-solvent with 15% concentration, since it gives a reasonable raffinate yield of 78%, and acceptable sulfur content of 0.51, and acceptable refractive index of 1.4546.

Key words — Aromatics, lube oil, extraction, polar solvents, Dearomatization, formamide, N-methylpyrrolidone

1 Introduction

Lubricating base oils consist of paraffinic, aromatic and cycloparaffinic (naphthenic) molecules with small amounts of sulfur, oxygen and nitrogen containing compounds intermixed within the three basic structures. Most molecules are a combination of two or three of the basic hydrocarbon types but are classified by their dominant properties (1). Paraffins have good resistance to change in viscosity with temperature (high viscosity index) and best oxidation performance of all molecules used to blend lubricants. Naphthene ring structure with long side chains can have high viscosity index (VI) and good oxidation performance. Multi-ring structure with short side chains have low viscosity index (VI). Single ring aromatics with long side chains can have high VI and good lube properties. However multi-ring and naphtheno-aromatics are generally considered to be poor base oil molecules due to poor oxidation performance and due to that their concentration is minimized during manufacture (2). Sulfur compounds in base oils are generally benzothiophene structures that, can act as natural antioxidants. Nitrogen and oxygen containing compounds generally act as pro-oxidants and are thus considered the poorest quality molecules for use in lubricants. Base oil molecules typically contain from twenty carbon atoms, for lighter viscosity grade oils, to fifty carbon atoms or more for heavier viscosity grade oils (3).

Vacuum distillates [spindle oil, light, medium, and heavy waxy distillates] as well as deasphalted oils contain aromatics and other undesirable constituents which result in rapid darkening, oxidation and slugging in service (4). Chemicals, solvents and hydrogen refining are used to remove these undesirable constituents, reduce toxicological aggressiveness of them, and improve quality as well as viscosity index of the produced oils (5). Aromatic solvents are applied to the oil in the region of partial miscibility at which two liquid phases are formed. The phase containing the solution of oil in the solvent is known as the extract phase (containing bulk of solvent) and the solution of solvent in the oil is known as the raffinate phase (containing minor of solvent). Most of the selective solvents are heavier than the oil as well as the aromatic hydrocarbons. For this reason the extract phase always forms the bottom layer. Due to the complex structure of petroleum hydrocarbons, the aromatic solvents dissolve first the aromatics followed by alkenes, naphthenes and alkanes. Solubility of oxygen, nitrogen and sulfur compounds vary with their structures (6). Solvents for extraction should have selectivity for aromatics, high capacity, capability to form two phases at extraction temperatures, capability of rapid phase separation,

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good thermal stability, and should be non-corrosive, and non-reactive a large number of solvents have been used commercially such as N-methyl-2-pyrrolidone (NMP), furfural, phenol, liquid sulfur dioxide nitrobenzene and chlorex (β,β dichloro ethyl ether). In some cases a solvent mixture may be also used to derive properties that cannot be achieved with pure solvents (7). Although liquid sulfur dioxide, nitrobenzene and chlorex have good solvent power, the requirement of low extraction temperature prevents its wide use for extraction of high pour paraffinic lubricating stocks. Other disadvantages of use liquid sulfur dioxide are its toxicity and air pollution control requirements (8). N-methyl-2-pyrrolidone exhibits better solvent power, better chemical and thermal stabilitie, and lower toxicity than either furfural or phenol, also it is the best in the areas of solvent circulation and it requires less corrosion protection (9). It is adaptable to the extraction of both paraffinic and naphthenic feed stocks. Furthermore, NMP is an attractive alternative to furfural for extraction of high viscosity feed stocks and oils which have poor refining response or which require high solvent to oil ratios. On the other hand, it has been reported that the temperature has a greater effect on the selectivity and solvent power of NMP than with other solvents (10-11).

The aim of the present study is to improve NMP selectivity for aromatic extraction from a medium waxy distillate obtained from the Western Desert in Egypt. This improvement is made by adding different co- solvents to NMP solvent such as water, methanol, formamide, ethanol, and ethylene glycol to maximize the yield of raffinate production within the required specifications, and to improve the quality of lubricating oil. Also, the effect of various parameters on the extraction process is studied such as the co-solvent to oil feed ratio, type of co-solvent, and concentration of co-solvent.

2 MATERIALS AND METHODS:

2.1 Materials:

Lube oil, N-Methyl-2-Pyrrolidone (NMP) solvent obtained from Alexandria Mineral Oils Company (AMOC) in Egypt, Methanol, Ethanol, Formamide, and Ethylene glycol all are obtained from Elnasr Company for chemicals and Drugs in Egypt.

2.2 Extraction Apparatus:

The following figure shows the apparatus used in the extraction of aromatics from lube oil.

2.3 Experimental procedures:

The oil container is warmed by placing it on a hot plate to reduce viscosity for easy handling, the feedstock is weighed and introduced into a 5 liters flask, the required amount of solvent (according to the applied solvent to feed ratio) is carefully poured into the flask, after that it is placed in oil bath, the oil bath is switched on, and the set point in the controller is adjusted according to the required extraction temperature. The operation is conducted under a continuous inlet and outlet of nitrogen gas to prevent solvent oxidation, and with continuous stirring for about 30 minutes, to ensure a complete mass transfer between the two phases. The stirrer is turned off and the mixture is allowed to settle at room temperature for appropriate settling time in a separating funnel. A clean weighed receiver is put under the outlet pipe of the separating funnel to collect the extract phase (heavy phase) followed by the raffinate phase (the oil). The raffinate and extract are distilled under vacuum to recover all furfural and N-methyl-2-pyrrolidone, present with the oils. The oils are weighed and determined as weight percent related to the feedstock. The amount of furfural or NMP in the raffinate and extract were determined. The solvent percentage should not exceed 100 ppm for the raffinate and 300 ppm for the extract. The properties of raffinate and aromatic extract are determined

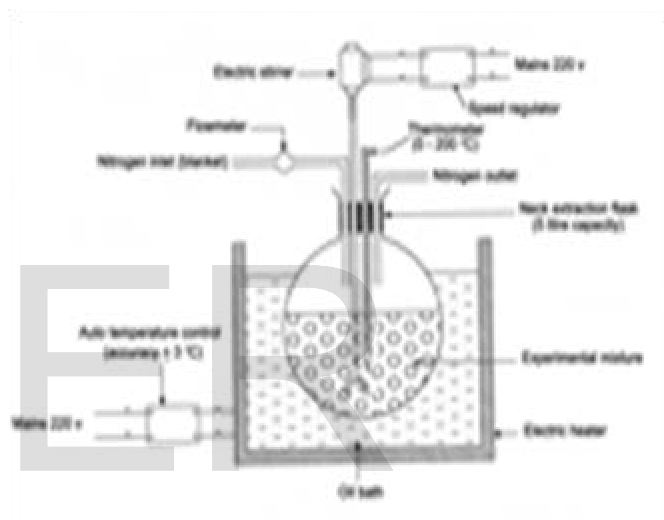

Figure (1): Extraction apparatus

3 RESULTS AND DISCUSSIONS:

3.1 Comparison of the effect of different co-solvent types on lube oil properties:

Five different co-solvents were used with NMP solvent such as water, methanol, formaldehyde, ethanol, and ethylene glycol with different concentrations varying from 0% to 20%. The following figures show a comparison of the effect of these different co-solvent types on the following: Raffinate yield, oil density, oil viscosity, sulfur content, refractive index, color, pour point, and average molecular weight.

3.1.1 Comparison of the effect of different co-solvent types on raffinate yield:

Figure (2) shows a comparison of the effect of different co-solvent types on raffinate yield at different concentrations.
As seen from the figure, the highest raffinate yield is obtained

at 15% and 20% concentration. Water: NMP co-solvent gave the highest raffinate yield. Methanol: NMP co solvent, and formamide: NMP co solvent also gave high raffinate yield compared to ethanol: NMP co-solvent, and ethylene glycol: NMP co-solvent.

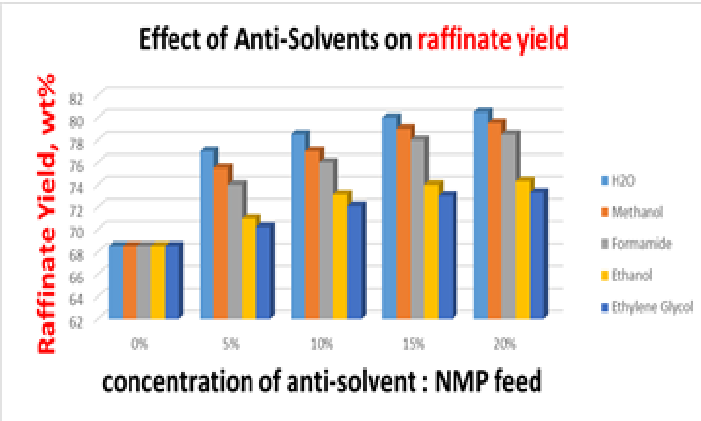

Figure (2): Comparison of the effect of different co-solvent types on raffinate yield

3.1.2 Comparison of the effect of different co-solvent types on oil density:

Figure (3) shows a comparison of the effect of different co-solvent types on oil density at different concentrations. As seen from the figure, the highest oil density is obtained at 15% and 20% concentration. Water: NMP co-solvent gave the highest oil density. Methanol: NMP co-solvent, and formamide: NMP co solvent also gave high oil density compared to ethanol: NMP co-solvent, and ethylene glycol: NMP co-solvent

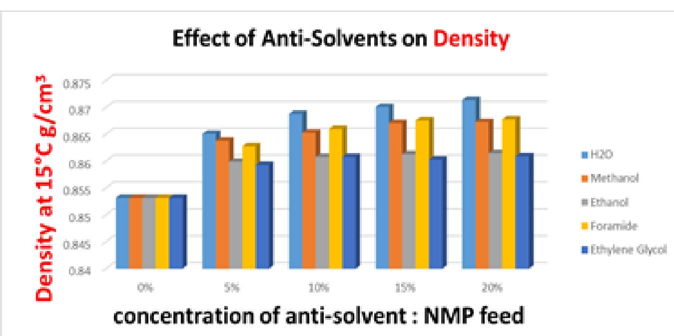

Figure (3): Comparison of the effect of different co-solvent types on oil density

3.1.3. Comparison of the effect of different co-solvent types on oil viscosity:

Figure (4) shows a comparison of the effect of different co-solvent types on oil viscosity at different concentrations. As seen from the figure, the highest oil viscosity is obtained at 15% and 20% concentration. Water: NMP co-solvent gave the highest oil viscosity. Methanol: NMP co solvent, ethanol: NMP co-solvent and formamide: NMP co solvent also gave high oil viscosity compared to glycol: NMP co-solvent

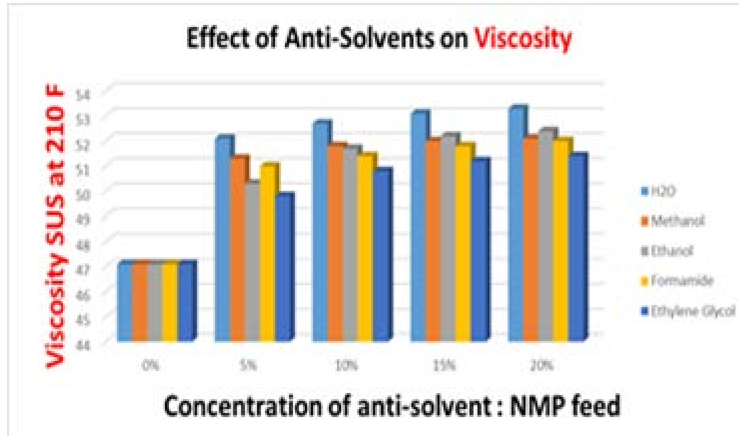

Fig (4): Comparison of the effect of different co-solvent types on oil viscosity

3.1.4. Comparison of the effect of different co-solvent types on sulfur content:

Figure (5) shows a comparison of the effect of different co-solvent types on sulfur content at different concentrations. As seen from the figure, the highest sulfur content is obtained at 15% and 20% concentration. Water: NMP co-solvent, Methanol: NMP co solvent, formamide: NMP co gave the highest sulfur content, compared to ethylene glycol: NMP co –solvent, and ethanol: NMP co-solvent.

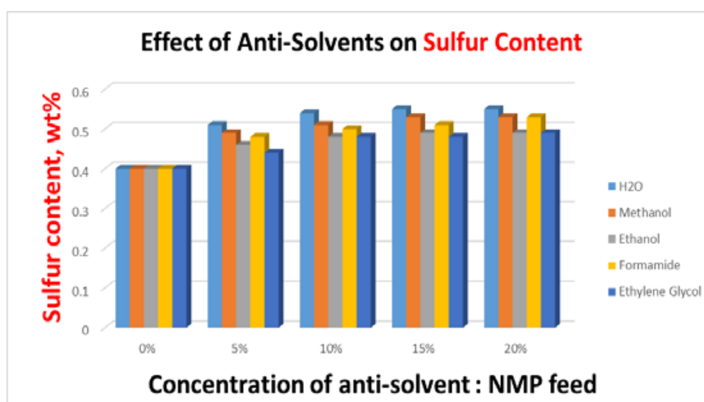

Figure (5): Comparison of the effect of different co-solvent types on sulfur content

3.1.5. Comparison of the effect of different co-solvent types on refractive index:

Figure (6) shows a comparison of the effect of different co-solvent types on refractive index at different concentrations. As seen from the figure, the highest refractive is obtained at 20% which indicates high the presence of high aromatics. Water: NMP co-solvent, gave the highest refractive index which indicates high the presence of high aromatics. Formamide: NMP co-solvent gave a reasonable sulfur content of all co solvents.

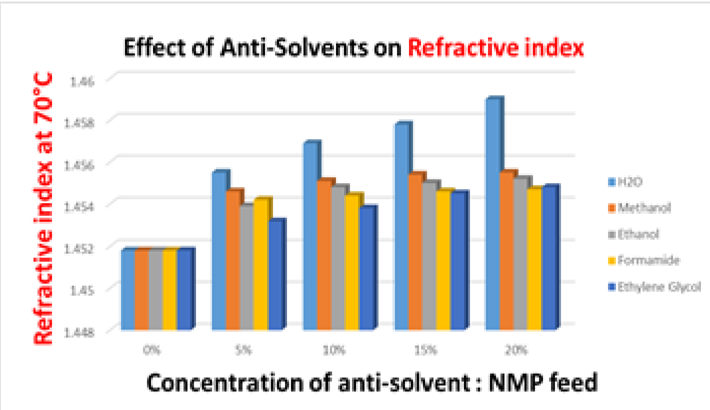

Figure (6): Comparison of the effect of different co-solvent types on refractive index

3.1.6. Comparison of the effect of different co-solvent types on color:

Figure (7) shows a comparison of the effect of different co-solvent types on color at different concentrations. As seen from the figure, at 20 % concentration all co-solvents almost gave the same effect on color clarity. Also, at 15% concentration, all co-solvents almost gave the same effect on color clarity except ethanol: NMP co-solvent.

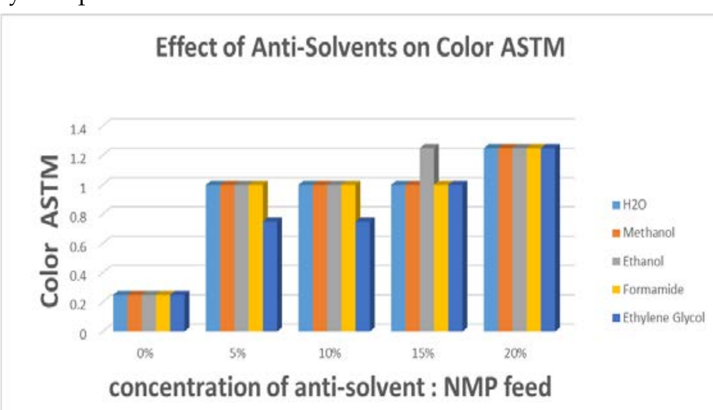

Figure (7): Comparison of the effect of different co-solvent types on color

3.1.7. Comparison of the effect of different co-solvent types pour point:

Figure (8) shows a comparison of the effect of different co-solvent types on pour point at different concentrations. As seen from the figure, at 15 % concentration all co-solvents almost gave the same effect on pour point except ethylene glycol: NMP co-solvent. Also, at 20% concentration, all co-solvents almost gave the same effect on pour point except ethanol: NMP co-solvent, and ethylene glycol co-solvent.

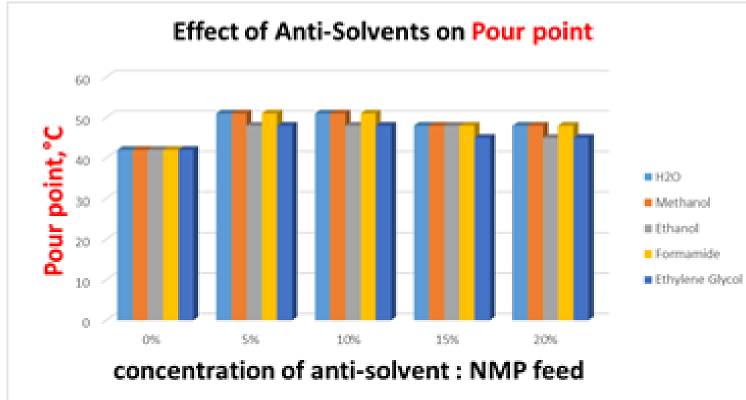

Figure (8): Comparison of the effect of different co-solvent types on pour point

3.1.8. Comparison of the effect of different co-solvent types molecular weight:

Figure (4.56) shows a comparison of the effect of different co-solvent types on pour point at different concentrations. As seen from the figure, 20 % concentrations for all co-solvents gave the highest effect on molecular weight.

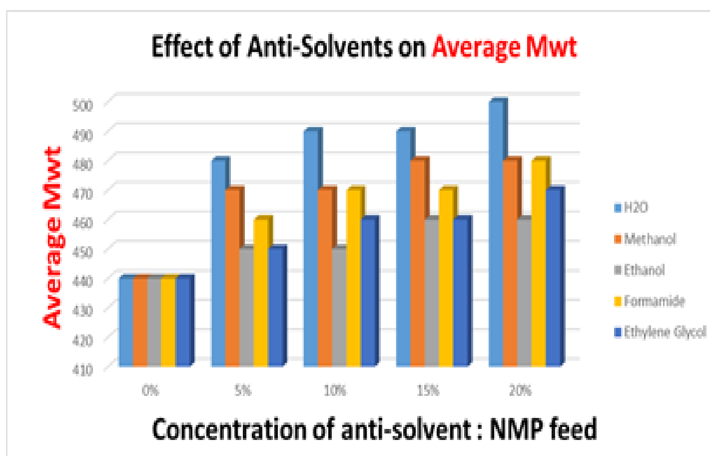

Figure (9): Comparison of the effect of different co-solvent types of molecular weight

4 Conclusions:

- In the present work, six different co-solvents (pure

NMP, NMP : H2O, Methanol: NMP, Formaldehyde: NMP, Ethanol: NMP, and ethylene glycol :NMP) with different concentrations were used and their significant effects on the properties of the lube oil such as yield and quality determined by: density, viscosity, sulfur content, refractive index, color, pour point, and average molecular weight was studied.

- The extraction temperature remained constant at 70° C, the mixing time, and the settling time were fixed at 15 min, and 30 min respectively

- Increase solvent to feed ratio led to a decrease in the raffinate yield accompanied by an increase in the quality (low sulfur content and low refractive index), and increase in the yield of aromatic extract.

- The optimum feed: NMP ratio is 1:1.4 by mass, because it gives a reasonable yield, low sulfur content and low refractive index.

- Increasing the concentration of the six co-solvents used increases the raffinate yield, oil density viscosity, sulfur content, refractive index, color, pour point, and average molecular weight.

- For water and NMP co-solvent, the best concentration for co-solvents used was 15%, and (1.4:1) solvent to lube oil ratio, to produce a yield of 80%, sulfur content of 0.55, and refractive index of 1.4578.

- For methanol and NMP co-solvent, the best concentration for co-solvents used was 15%, and (1.4:1) solvent to lube oil ratio, to produce a yield of 79%, sulfur content of 0.53, and refractive index of 1.4554.

- For formamide and NMP co-solvent, the best concentration for co-solvents used was 15%, and (1.4:1) solvent to lube oil ratio, to produce a yield of 78% sulfur content of 0.51, and refractive index of 1.4546.

- For ethanol and NMP co-solvent, the best concentration for co-solvents used was 15%, and (1.4:1) solvent to lube oil ratio, to produce a yield of 74%, sulfur content of 0.49, and refractive index of 1.4550.

- For ethylene glycol and NMP co-solvent, the best concentration for co-solvents used was 15%, and (1.4:1) solvent to lube oil ratio, to produce a yield of 73%, sulfur content of 0.48, and refractive index of 1.4545.

- The best co solvent used is formamide and NMP co-solvent, since it compromises between a reasonable yield, and acceptable sulfur content and acceptable refractive index.

REFERENCES

[1]Zhao, G., Chunlei Yao, Hui Quan. The Prospects of Shale Oil Utilization , Cont. Chem. Ind., 2008. vol. 10, no. 5. pp. 496–499.

[2] Zhao, Y. Research on Processing Plan of Shale Oil , Shenyang Chem. Ind. 2000. Vol. 29, No. 1. P. 78–80 .

[3] J. Williams, “Narrow-Band Analyzer,” PhD dissertation, Dept. of Electrical Eng., Harvard Univ., Cambridge, Mass., 1993. (Thesis or dissertation)

[3] Li, X,” Study on light diesel and blend oil from shale oil, “ PhD dissertation, University of Petroleum, Beijing, 2003. (Thesis or dissertation)

[4] Koski, A., S. Pekkarinen, A. Hopia, K. Wähälä, and M. Heinonen, “ Processing of Rapessed Oil: Effects on Sinapic Acid Derivative Content and Oxidative Stability”, Eur. Food Res. Technol., vol 217, pp.110–114 ,2003.

[5] Brenes, M., C. Romero, A. García, F.J. Hidalgo, M.V. Ruiz-Méndez, “Phenolic Compounds in Olive Oils Intended for Refining: Formation of 4-Ethylphenol During Olive Paste Storage”, J. Agric. Food Chem., vol 52, pp.8177–8181, 2004.

[6] Nogala-Kalucka, M., J. Korczak, K.H. Wagner, I. Elmadfa, “Tocopherol Composition of Deodorization Distillates and Their Antioxidative Activity, Nahrung, vol 48, pp.34–37, 2004.

[7] García, A., M. Brenes, P. García, C. Romero, and A. Garrido, “Phenolic Content of Commercial Olive Oils”, Eur. Food Res. Technol, vol 216, pp.520–525 ,2003.

[8] A. Chin, Cherry Hill, Bryan M. Knickerbocker, Beaumont; C. Trewella, Kennett Square; Terry R. Waldron; PT Neches; Lloyd S. White, “Recovery of aromatic hydrocarbons using lubricating oil conditioned membranes”, United States Patent, no US 6,187,987 B1,2001.

[9] M. Hussein; A. A. Amer; A. S. Gaberah, “Used lubricating oils re-refining by solvent extraction”, Am.J. Environ. Eng. Sci., 1(3): pp.44-50,2014.

[10]- BIAOHUA CHEN; ZHIGANG LEI; AND JIANWEI LI," Separation on Aromatics and Non-aromatics by Extractive Distillation with NMP”, J. Chem. Jpn. ,vol. 36(1), pp. 20–24, 2003.

[11] Gholam R. Vakili-Nezhaad; Hamid Modarress; and Gholam A. Mansoori, “Solvent Extraction of Aromatic Components from Lube-Oil Cut by N-methylpyrrolidone (NMP), Chem. Eng. Technol., vol 22 (10), pp.847-853,1999

[12] Eman A. Emam; Abeer M. Shoaib,” Re-refining of used lube oil, i- by solvent extraction and vacuum distillation followed by hydrotreating, Petrol.& Coal , vol 55 (3),pp. 179-187, 2013.

[13] E. Epelle, Y. Lukman and A. J. Otaru, “A comparative study of the solvent powers of phenol, furfural and NMP in improving the viscosity index of spent lubricating oil”, Int. Res. J.Eng., vol. 3 no 1, pp. 008-024, April, 2016.

[14] Ibtehal k. Shakir , Muslim A. Qasim, “ Extraction of Aromatic Hydrocarbons from Lube Oil Using Different Co-Solvent”, Iraqi J. Chem. Petrol. Eng. ,vol.16 no.1,pp. 79- 90, 2015.

[15] Zhang, S., Yang, Q., Li, S, “ Refining of Fushun shale oil by complexation , J. Petrol. Uni, vol 20, pp.77-80, 1996.