Utilization of Binary Mixtures of Different Solvents for Aromatics Extraction from a Petroleum Wax Distillate Feedstock

Hamida Y. Mostafa1*, Ahmed M.A. El Naggar1, Ebaa A. Elshamy1, Amal S. Farag1, Ahmed I. Hashem2
1Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727, Cairo, Egypt.
2Chemistry Departments, Faculty of Science, Ain Shams University, Cairo, Egypt.

MOST of petroleum fractions contain detectable contents of aromatic structures that include different categories. Aromatics in general and condensed aromatics particularly are of strong hazardous impact due to their toxic and carcinogenic nature. Therefore, the disposal of such compounds from the various petroleum products is powerfully advised. This research work introduces the use of various binary solvents mixtures for removal of aromatics from a petroleum wax distillate fraction. N-methyl pyrrolidone (NMP) was individually used at the first place as a main extracting agent. Significant reduction of aromatics content was noticed however not limited to the condensed aromatic structures. Binary mixtures made of NMP and different percentages of water, ethylene glycol or ethanol amine (as anti-solvent) were then utilized to improve the selectivity of removal toward condensed aromatics. Noticeable variations in the contents of di- and poly aromatics with corresponding increases in the mono-aromatics were observed. Removal of aromatic hydrocarbon compounds in general and carcinogenic; multiple-ring structures, in particular is considered one of the most important stages in lubricating oils production. One of the techniques that are used for the disposal of such aromatic compounds from lube feedstocks is solvent extraction [6,7]. The extraction of aromatics by solvents is a physical separation process. The selectivity of the solvent toward aromatics is an important parameter in its choice as a proper extracting media. In addition, the solvents of expanded selectivity towards polycyclic aromatics, that contain two or more aromatic rings, have attracted greater attentions [8].

Keywords: Aromatic removal, Physical separation, Solvent composition, Petroleum wax distillate.

Introduction

Lubricants are introduced between two moving metal surfaces to reduce friction and wear. In some cases, improving the efficiency of relative movement of two bearing surfaces is only possible if the lubricant is present [1,2]. Therefore, the manufactured lubricating base oil should have good quality and free of undesirable components such as sulfur and condensed aromatic compounds [3]. To obtain such specifications, the utilized feedstock in production of lube base-stocks; distillate or de-asphalted oil, is preceded through various processes. These processes include solvent extraction (aromatic removal stage) followed by dewaxing and finishing processes [4].

*Corresponding author e-mail: h_y_mostafa@yahoo.com, Tel: +201003650498, Fax: +2(02)227727433
Received 22/3/2019; Accepted 2/4/2019
DOI: 10.21608/ejchem.2019.11014.1705
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Experimental

In this study, a middle wax distillate fraction (b.r.400-450°C) conducted from EL-Ameria Petroleum Refining Company was used as a feedstock. NMP was introduced as the main solvent to execute the process of aromatics removal. Subsequently, the use of its binary mixtures with H₂O, Ethylene glycol and Ethanol (anti-solvents) for the aromatics removal was also studied. The extraction processes were performed via using a jacketed batch mixer-settler apparatus equipped with a mechanical stirrer. This apparatus is connected with water circulator in order to adjust the extraction temperature.

Solvent Extraction Process

The middle wax distillate fraction was subjected to the bench scale extraction using either NMP alone or its mixtures with the above stated anti-solvents. The extraction processes were carried out at fixed temperature and solvent feed ratio (S/F) of 70°C and 2 respectively. Additionally, the impact of following solvent compositions on aromatics removal was studied:

a- NMP + H₂O mixture (the percentage of H₂O from 0–5 wt%),
b- NMP + EG mixture (the percentage of EG from 0–20 wt%)
c- NMP + EA mixture (the percentage of EG from 0–20 wt%).

Characterization

The feedstock and all the acquired raffinates after each extraction process were subjected to the determination of their structural and compositional characteristics. Following techniques and methods were utilized to obtain such properties:

I- ASTM standard methods [9]: to determine the physico-chemical characteristics,
II- Liquid solid column chromatography technique [10]: obtaining hydrocarbon component analysis,
III- n-d-m method [11]: structural group analysis.

Results and Discussion

At the beginning of aromatics removal investigation, the full characteristics of the feedstock (using the stated methods in section 2.2) were determined. Then, the aromatics extraction process using pure NMP was executed at the pre-determined conditions in section 2.1. The full characteristics of both the feedstock and collected raffinate after the extraction process are presented in Table 1. It can be obviously noticed that the implementation of solvent extraction stage could reduce the aromatics content of raffinate, compared to feedstock. Specifically, about 22% of the aromatics content was reduced in the produced raffinate. However, the detected removal had included all the existing aromatics categories in the feedstock, with no strong orientation towards condensed aromatic structures. Thus, the addition of other solvents to the NMP, in order to improve its selectivity to di- and poly-aromatics, was necessary. Generally, the change in aromatic content was accompanied with observable changes in the features of the gained raffinate. Exactly, the reduction if aromatics was joined by reductions also in values of sulfur compounds, viscosity, density and viscosity gravity constant (VGC). Also decrease in aromatic carbon percentage (%Cₐ) as well as the total ring content Rₚ of raffinate could be displayed. These reductions were compromised by the increase of paraffinic nature of raffinate; hence its viscosity index and mean molecular weight were enhanced.

Raffinate I is the product of extraction process at temperature of 70 °C and solvent oil ratio of 2/1 these conditions has been chosen because of using in industry scale.

Effect of Solvent Composition

In the current stage, three binary mixtures made of mixing NMP solvent with water, ethylene glycol and ethanolamine respectively, as anti-solvents, were used for the process of solvent extraction. The use of these anti-solvents was meant to control the solvency power of NMP and enhance its selectivity toward the extraction of condensed/ poly aromatic structures. The critical solution temperature (CST) for each of the binary mixtures was firestly measured at a solvent feed ratio of 2/1. Figure 1 illustrates the CST values of feed-solvent system at different concentrations of water, ethylene glycol (EG) and ethanolamine (EA). It can be clearly noticed that increasing the concentration of H₂O, EG and EA in NMP elevates the CST of the system. This may consequently refer to the decrease in solvent power of NMP with a simultaneous increase in its selectivity. It can also be seen that the lowest CST value for the mixtures could be detected around 100 °C. Therefore, the utilization of 70°C as the operational temperature, at this stage of extraction, could be then validated.

After determining the CST values, the different binary mixtures were forwarded for the aromatics removal process. The physical features, component analysis, carbon distribution and ring content of the obtained raffinates are exhibited in

*Egypt.J.Chem. 62, No. 9 (2019)*
TABLE 1. Physical Characteristics, Hydrocarbon Component Analysis and Structural Group Analysis of the Feedstock (400-450°C) and raffinate I.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Raffinate I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield, wt.%</td>
<td>---</td>
<td>63.03</td>
</tr>
<tr>
<td>Refractive index, 70°C</td>
<td>1.4875</td>
<td>1.4650</td>
</tr>
<tr>
<td>Density, gm/cc, 70°C</td>
<td>0.8782</td>
<td>0.8434</td>
</tr>
<tr>
<td>Mean molecular weight</td>
<td>391</td>
<td>415</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>39</td>
<td>42</td>
</tr>
<tr>
<td>Sulfur content, wt%</td>
<td>2.41</td>
<td>1.16</td>
</tr>
<tr>
<td>Kinematic viscosity,40°C, cSt</td>
<td>39.28</td>
<td>26</td>
</tr>
<tr>
<td>Kinematic viscosity,100°C, cSt</td>
<td>5.68</td>
<td>4.98</td>
</tr>
<tr>
<td>Viscosity index</td>
<td>76</td>
<td>118</td>
</tr>
<tr>
<td>Viscosity-gravity constant (VGC)</td>
<td>0.8694</td>
<td>0.8341</td>
</tr>
</tbody>
</table>

**Component analysis:**

- Total saturates, wt%: 50.03, 61.16
- Total aromatics, wt%: 49.97, 38.84
- Mono aromatics, wt%: 14.51, 12.53
- Di aromatics, wt%: 25.46, 19.55
- Poly aromatics, wt%: 10.00, 6.76

**Structural group analysis:**

**Carbon distribution**

| %C<sub>A</sub> | 18.27 | 6.88 |
| %C<sub>N</sub> | 20.39 | 27.60 |
| %C<sub>R</sub> | 38.66 | 34.47 |
| %C<sub>P</sub> | 61.34 | 65.53 |

**Ring content analysis**

- R<sub>A</sub>: 0.89, 0.34
- R<sub>T</sub>: 2.06, 2.00
- R<sub>N</sub>: 1.17, 1.66

- C<sub>A</sub> = Aromatic carbon; C<sub>N</sub> = Naphthenic carbon; C<sub>P</sub> = Paraffinic carbon; R<sub>A</sub> = Aromatic ring; R<sub>N</sub> = Naphthenic ring; R<sub>T</sub> = R<sub>A</sub> + R<sub>N</sub>.

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**Fig. 1.** Effect of Solvent Composition on the Critical Solution Temperature of the Feed-Solvent Systems.

Fig. 2-7.

It can be observed that the increase of $\text{H}_2\text{O}$, EG and EA concentrations in the solvent mixtures could increase the yield of obtained raffinates (Fig. 2a, 4a & 6a). This increase in yield percentages of raffinates was accompanied with improvement in

Fig. 2. Effect of Solvent Composition (NMP+$\text{H}_2\text{O}$) on the Yield and Physical Characteristics of the Raffinates.
Fig. 3. Effect of Solvent Composition (NMP+ H₂O) on Component Analysis, Carbon Distribution and Ring Content of the Raffinates.
Fig. 4. Effect of Solvent Composition (NMP+EG) on the Yield and Physical Characteristics of the Raffinates.
Fig. 5. Effect of Solvent Composition (NMP+EG) on Component Analysis, Carbon Distribution and Ring Content of the Raffinates.
Fig. 6. Effect of Solvent Composition (NMP+EA) on the Yield and Physical Characteristics of the Raffinates.

Fig. 7. Effect of Solvent Composition (NMP+EA) on Component Analysis, Carbon Distribution and Ring Content of the Raffinates.
their qualities in terms of elevating the values of mean molecular weight and viscosity index (Fig. 2d, 2e, 4d, 4e, 6d & 6e).

Correlating data of component analysis, carbon distribution and ring content with those of viscosity index and mean molecular weight of the raffinates, it can be noticed that the percentages of both di- and poly-aromatics of raffinates had decreased by increasing the amount of anti-solvents (Fig. 3b, 5b & 7b). These declines were accompanied by corresponding increases in the mono-aromatics contents and subsequently the percentages of aromatic and naphthenic carbons (\( \% C_A \) & \( \% C_N \)) and aromatic and naphthenic rings (\( R_A \) & \( R_N \)) per molecule (Fig. 3, 5 & 7). This findings could explain the increase of mean molecular weight and viscosity indices since such aromatic structure may contain long paraffinic side chain and/or of naphthenic structure attached to its ring. This attitude had continued until the concentration of anti-solvents reached 3, 10 and 15\% for \( H_2O \), EG and EA respectively. Above these percentages of anti-solvents in the extracting mixture, the behavior had been reversed. This can be explained by increasing the selectivity of extracting mixtures toward di- and poly-aromatic structures (most polar compounds) by the increase of anti-solvent concentrations to prior-stated percentages. Above these concentrations, selectivities of these mixtures were partly lost and their solvent power could consequently increase.

**Conclusion**

Removal of different aromatic structures from a petroleum wax distillate fraction was performed using the solvent extraction technique. Individual extracting agent (NMP) as well as its sub-driven binary mixtures were utilized during the elimination of aromatics. The collected results of this study reveal that the addition of anti-solvents (\( H_2O \), ethylene glycol and ethanol amine) to NMP could improve its efficiency in reducing the polycyclic aromatics content. The most suitable combinations of these mixtures were found to be those containing 3 % \( H_2O \), 10 % ethylene glycol and 15 % ethanol amine in NMP.

**References**


UTILIZATION OF BINARY MIXTURES OF DIFFERENT SOLVENTS FOR AROMATICS...


Utilization of the二元混合物的二元混合物的不同溶剂进行芳香烃的选择性

دميا بوسف منظفي، أحمد أوائل الجمال، إسماعيل عبد المنعم الشامي، أمال سعد فرج و أحمد إسماعيل

قسم التكرير - معهد بحوث البترول - القاهرة - مصر.
قسم الكيمياء - كلية العلوم- جامعة عين شمس - القاهرة - مصر.

القيام بعملية استخدام البترول الشمالي المقطر، حيث يتم استخدام بيروليدون ميثيل من المصنوعة من المذيبات الثنائية بطريقة مماثلة.

التخلص من المحتويات في ملحوظة مختلفة للإثاثي، يتم تحديد أمثلية التركيب الأسبل لكل من المخلوات الثنائية بناءً على خصائص المنتجات المكثفة من عمليات الاستخراج.

Confirmation of the results was obtained through a series of experiments including the use of binary solvent mixtures for the extraction of aromatics from different petroleum fractions. The results indicated that the use of binary solvent mixtures is an effective method for the extraction of aromatics from petroleum fractions.