Intensification and improvement of petrolatum deoiling process by using pure n-alkanes as non-polar modifiers

Magdy T. Zaky*, Nermen H. Mohamed, Amal S. Farag, Fathi S. Soliman

Petroleum Refining Division, Egyptian Petroleum Research Institute (EPRl), Nasr City, P.O. Box: 11727 Cairo, Egypt

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A B S T R A C T

In order to intensify and improve the deoiling process, Alexandria crude petrolatum was subjected to one-stage fractional crystallization (deoiling process) using butyl acetate and methyl isobutyl ketone solvents at different solvent feed ratios of dilution ranging from 2:1 to 8:1 at fixed washing solvent ratio of 2:1 and ambient fractionating temperature of 20 °C to produce micro-crystalline waxes. Non-polar modifiers such as individual pure n-alkanes with an even number of carbon atoms such as C20H42, C22H46 and C24H50 were added to the petrolatum deoiling solvent mixture in the percentages ranging from 0.05 to 1 wt.% based on the feed to intensify petrolatum deoiling. Two tools of analysis such as XRD and SEM, beside the physical characteristics, were used to compare the crystal size and to observe the surface, shape and holes between crystals of the hard waxes separated without and with modifiers. Data revealed that, microcrystalline waxes with high quality are produced by using butyl acetate solvent at dilution and washing solvent ratios of 8:1 and 2:1 by weight, respectively with the addition of 1 wt.% of a non-polar modifier; C20-24 n-alkanes. The results are the increase of the filtration rate, growth of crystal size with more holes between the large crystals and improvement in the physical characteristics of the separated wax.

1. Introduction

Commercial processes for dewaxing and deoiling of residual feedstocks are complex and laborious. The greatest difficulties are related to the stage of filtering slurries of solid hydrocarbons that tend to form an inter-crystalline structure. Improving the filtration rate for obtaining solid hydrocarbons, use was made of various additives that have a modifying effect on the crystal structure of solid hydrocarbons. The modifiers offer a means for a considerable improvement in the basic indices of the process and in the quality of the end-product without any additional costs, using existing equipment. The effect of a modifier on the crystallization of solid hydrocarbons is usually rated on the basis of the melting point of the micro-crystalline wax, the oil content in the microcrystalline wax, and the slurry filtration rate (Kazakova et al., 1986; Soliman et al., 2014).

Some authors used ionic modifiers, surfactants and additives for optimization of crystallization of solid hydrocarbons. Nigmatullin et al. (1995) and Nigmatullin (1997) investigated the use of ionic modifiers; aqueous sodium chloride and aqueous iron sulfate; for deoiling petrolatum and slack wax, respectively. They concluded that the aqueous sodium chloride solution increases the selectivity of the highest-melting hydrocarbons from the petrolatum. But modifier did not affect the filtration rate and the modification function of iron sulfate was related to co-crystallization because crystal lattices of iron and solid paraffin waxes were similar. Zolotarev and Nigmatullin (1997) studied the purification and deoiling of slack wax with aluminum chloride complex. It can be used...
as a means for obtaining paraffin waxes with quality at the export-grade level, and for increasing the paraffin yield by 2–4%.

Trends in improving production of oils and solid hydrocarbons were examined by optimization of crystallization of solid hydrocarbons by using surfactants and ultrasound. Surfactants structural modifiers significantly affect crystallization of solid hydrocarbons. Concentrated on the phase interface, they form very thin layers that change the molecular nature and properties of the surface. Primarily resins are adsorbed on an energetically inhomogeneous surface of arising crystallization centers consisting of high melting paraffins and naphthenes due to the strongly developed hydrocarbon part of their molecules. In treating a suspension with ultrasound, the bonds between solid hydrocarbon crystals are destroyed and conditions are created for their growth, so that the rate and efficiency of separation of the solid phase from the liquid phase increase. To enhance the deoiling process, the slack wax (melting point of 54 °C, oil content of 5.5 wt.%) was treated with ultrasound. Exposure to ultrasound before deoiling stage I accelerated filtration in the following stages as well. In deoiling of slack wax in two stages with ultrasound treatment before the first stage for 10 min, the wax product contains a 0.43 wt.% oil content and has melting point of 58 °C (Sochevko and Tugusheva, 2010).

Few literatures were found about using a non-polar modifier (n-alkanes) during the deoiling of petrodatum to produce microcrystalline wax. Thus, our work aims to intensify petrodatum deoiling process for improving the crystallization of solid hydrocarbons; to produce microcrystalline wax; by using a non-polar modifier; especially individual pure n-alkanes with an even number of carbon atoms in the molecule (C20–C24).

2. Materials and methods

2.1. Materials

Two crude petrolatums (petroleum wax by products) obtained from Alexandria Petroleum Company and Suez Oil Processing Company are used and evaluated in this study for deoiling process and isolation of microcrystalline waxes.

2.2. Deoiling process

Alexandria crude petrodatum was subjected to one stage fractional crystallization (deoiling process) (Zaky et al., 2007; Mohamed et al., 2008; Zaky and Mohamed, 2010) using butyl acetate (BA) and methyl isobutyl ketone (MIBK) solvents at different solvent feed ratios of dilution (S/F, by weight) ranging from 2:1 to 8:1 at fixed washing solvent ratio of 2:1 and ambient fractionating temperature of 20 °C to produce micro-crystalline waxes. In this technique, the high melting components of the wax (hard wax) got precipitated while the low melting ones (soft or slop wax) remained in the solution.

2.2.1. One stage fractional crystallization technique

A known weight of crude petrodatum was dissolved in the corresponding amount of solvent in a beaker and heated till the mixture becomes homogeneous. Then the mixture was cooled gradually at room temperature for two hours. The beaker and the Buchner funnel were transferred to a controlled temperature unit and gradually cooled to the desired temperature 20 °C for 12 h. The beaker contents were transferred to the funnel and filtered through a Whatman filter paper no.43 by using controlled suction (8.6 Psig). The wax cake was washed with an additional solvent at the same temperature and added at small increments. Solvents were removed from the wax cake by distillation.

2.3. Addition of individual pure non-polar modifiers

Non-polar modifiers of individual pure n-alkanes with an even number of carbon atoms such as Eicosane (C20H42), Docosane (C22H44) and Tetracosane (C24H48); purchased from Aldrich and Fluka Chemical Company; were added to the petrodatum-deoiling solvent mixture in the percentages ranging from 0.05 to 1 wt.% based on the feed to intensify petrodatum deoiling.

2.4. Methods of analysis

The two crude waxes and the isolated hard waxes were physically characterized according to American Society for Testing and Materials (ASTM) standard methods (ASTM, 1999). The filtration rate was calculated by the following equation:

\[
\text{Filtration rate} = \frac{\text{Weight of the filtrate}}{\text{Area of funnel bottom}} \times \text{Time of filtration} = \frac{\text{kg/m}^2}{\text{h}}
\]

where the weight of the filtrate produced through deoiling process is in kg:

\[
\text{Area of funnel bottom} = \pi r^2 \text{m}^2
\]

where \( r = 3.14 \) and \( r = \text{radius of funnel used in deoiling process} \) in m and time of filtration is in hour = h.

The type of the isolated hard waxes was specified according to Technical Association of the Pulp and Paper Industry (TAPPI) – ASTM equation (Ferris, 1963; Gottshali and McCue, 1973). The n-paraffin content was determined by using chromatographic technique (GC). The GC apparatus used was model (Perkin Elmer, Clarus 500, England), equipped with a hydrogen flame ionization detector and fused silica capillary column (30 cm \( \times 0.25 \text{ mm i.d.} \), packed with poly (dimethyl siloxane) HP-1 (non-polar packing) of 0.5 \( \mu \text{m film thickness} \). The apparatus was also equipped with an integrated data handling system for computing the peak area and concentration.

The aromatic content of the crude waxes and the isolated hard waxes was determined using liquid–solid column chromatography technique. Liquid–solid column chromatography technique was used to determine the molecular type composition; the total saturates and total aromatics for the crude and isolated hard waxes by using silica gel (60–200 mesh size) as an adsorbent. Stepwise elution was employed with n-heptane, benzene and mixture of methanol and benzene (Snyder, 1975). The fractionation between total saturates and total aromatics was carried out by making use of refractive indices values at 20 °C (Mair and Rossini, 1958; Deutsch et al., 1987).

2.5. X-ray diffraction

The X-ray diffraction patterns were run to study the crystal size of the hard waxes separated without and with modifiers on a Philips Analytical-XPert Pro, Netherlands, with a step size (2θ) of 0.02 and scan step time (s) of 0.4. The 2θ, full width at half maximum (FWHM) and d spacing were obtained. Wax crystal
Table 1 – Physical characteristics and molecular type composition of the two crude petrolatums.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Test method</th>
<th>Crude petrolatums</th>
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<tr>
<td></td>
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<td>Suez</td>
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<tr>
<td>Congealing point, °C</td>
<td>ASTM D-938</td>
<td>59</td>
</tr>
<tr>
<td>Kinematic viscosity, 98.9 °C</td>
<td>ASTM D-445</td>
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<td>Refractive index, 98.9 °C</td>
<td>ASTM D-1747</td>
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<td>Density, 70 °C</td>
<td>ASTM D-1418</td>
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<td>Mean molecular weight</td>
<td>ASTM D-2502</td>
<td>591</td>
</tr>
<tr>
<td>Oil content, wt.%</td>
<td>ASTM D-721</td>
<td>43.14</td>
</tr>
<tr>
<td>Needle penetration, 25 °C</td>
<td>ASTM D-1321</td>
<td>138</td>
</tr>
<tr>
<td>Sulfur content, wt.%</td>
<td>ASTM D-4294</td>
<td>1.8545</td>
</tr>
<tr>
<td>Color</td>
<td>ASTM D-1500</td>
<td>9.0</td>
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<tr>
<td>Molecular type composition</td>
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<td>Total saturates, wt.%</td>
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<td>50.13</td>
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<td>n-Paraffin content, wt.%</td>
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<td>Iso- and cyclo-paraffins content, wt.%</td>
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</tr>
<tr>
<td>Iso- and cyclo-paraffins/n-paraaffins</td>
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<tr>
<td>Total aromatics, wt.%</td>
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<td>Mono-aromatics, wt.%</td>
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<td>24.80</td>
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<tr>
<td>Di-aromatics, wt.%</td>
<td></td>
<td>25.07</td>
</tr>
</tbody>
</table>

Size was calculated according to Scherrer equation (Langford and Wilson, 1978). It is as follows:

\[
B = \frac{\lambda}{2\sin(\theta)} \times \cos(2\theta)/2
\]

where \( \lambda = 1.54 \text{ Å} \) and \( B \) is the peak width.

2.6  Scanning electron microscope (SEM)

SEM was used to observe the surface, shape and crystal size of the hard waxes separated without and with modifiers. The wax was coated with gold by K550X sputter coater, England then scanned by scanning electron microscope (SEM; Quanta 250 FEG, Netherlands).

3. Results and discussion

3.1  Characterization and evaluation of crude petrolatums

The physical characteristics and the molecular type composition for the two crude petrolatums are represented in Table 1. The physical characteristics of Suez crude petrolatum such as refractive index, density and kinematic viscosity are higher than those of Alexandria crude petrolatum. It may be due to its higher total aromatic content. The oil content is an indication of the quality of the wax whereas, the higher oil content of Suez crude petrolatum (43.14 wt.%) than that of Alexandria crude petrolatum (11.01 wt.%) is an indication of its low quality. An increase in oil content results in an increase in penetration value and decrease in congealing point (Table 1).

Molecular type composition data indicate that Suez crude petrolatum has appreciable total aromatic content (49.87 wt.%) as compared with that of Alexandria crude petrolatum (26.17 wt.%). These aromatic constituents are mainly mono and di-aromatic ones of nearly equal contents (24.80 and 25.07 wt.%, respectively) for Suez crude petrolatum.

Meanwhile, Alexandria crude petrolatum has higher saturate content (73.83 wt.%) specially, n-paraffin content (43.92 wt.%) which is about four folds the n-paraffin content of Suez crude petrolatum (10.52 wt.%). This value of n-paraffin content (10.52 wt.%) is lower than the n-paraffin content limit (15 wt.%) of microcrystalline wax crude (Edwards, 1963). Thus, it can be deduced that Alexandria crude petrolatum is a preferable crude petrolatum for deoiling process.

3.2  Solvent deoiling of crude petrolatum without using a modifier

Alexandria crude petrolatum was subjected to fractional crystallization technique (deoiling process) by using butyl acetate (BA) and methyl isobutyl ketone (MIBK) solvents under different dilution solvent ratios (S/F by weight) and at ambient fractioning temperature of 20 °C. Data are represented in Table 2.

![Fig. 1 – Correlation between filtration rate with the yield and oil content (a), and congealing point and needle penetration (b) of the hard waxes isolated by using BA and MIBK solvents at different dilution solvent ratios.](image-url)
The dilution has an obvious effect upon the yield and quality of the waxes isolated from Alexandria crude petrolatum by using the two solvents. The wax yield decreases with increasing of solvent dilution ratio. It may be attributed to the increase of the solvent power toward the oil inherent to such wax crystals. This conclusion is in line with the data of congealing points and mean molecular weights of the isolated waxes which give higher values on increasing the dilution solvent ratio. Also, it can observe that the wax yield isolated by using BA solvent is lower than that obtained with MIBK solvent. This may be related to the higher solvent power for BA over MIBK solvent (Table 2).

Generally, the rate of filtration increases with dilution and is accompanied with a decrease in the oil contents, viscosities and refractive indices of the hard waxes separated from crude petrolatum. This attributed to the removal of the oil which is mainly aromatic constituents. Consequently, the sulfur content and color value of the isolated hard waxes decrease with increasing the dilution solvent ratios. Data of molecular type composition confirm the previous results as there is a valuable decrease in the total aromatic contents specially the di-aromatic constituents which disappeared by using BA solvent at dilution solvent ratio of 8:1 by weight. Consequently, the total saturate contents of the isolated hard waxes increase (Table 2).

Fig. 1 exhibits the correlations between rate of filtration with the yield, oil content, congealing point and needle penetration of the hard waxes isolated from Alexandria crude petrolatum. It is clear from the plots that, as the filtration rate increases, the yield, the oil content and consequently the needle penetration of the wax decrease while the congealing point increases and the hard waxes isolated by using BA solvent have higher filtration rate and congealing point

Table 2 – Effect of dilution solvent ratio on the physical characteristics, molecular type composition and type of the isolated waxes by deoiling of Alexandria crude petrolatum using BA and MIBK solvents at fractionating temperature of 20°C and 5/1 for washing of 2:1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Yield on crude petrolatum, wt.%</th>
<th>Congealing point, °C</th>
<th>Kinematic viscosity at 98.9°C, mm²/s</th>
<th>Refractive index at 98.9°C</th>
<th>Refractive index by TAPPI-ASTM equation</th>
<th>Mean molecular weight</th>
<th>Oil content, wt.%</th>
<th>Needle penetration at 25°C</th>
<th>Sulfur content, wt.%</th>
<th>Color</th>
<th>Filtration rate, kg/m² h</th>
<th>Crystal size (X-ray diffraction)</th>
<th>Molecular type composition</th>
<th>Total saturates content, wt.%</th>
<th>Total aromatics content, wt.%</th>
<th>Mono-aromatic content, wt.%</th>
<th>Di-aromatic content, wt.%</th>
<th>Type of wax</th>
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<tr>
<td>BA</td>
<td>MIBK</td>
<td>BA</td>
<td>MIBK</td>
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<tr>
<td>2/1</td>
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<td>78.50</td>
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</table>

Fig. 2 – SEM photographs of the hard waxes isolated from Alexandria crude petrolatum by using BA (a) and MIBK (b) solvents at dilution solvent ratio of 8:1 by weight.
and lower oil content than those separated by using MIBK solvent.

SEM photographs of the isolated hard waxes are parallel to the above findings as the hard waxes isolated by using BA solvent seem to be somewhat more crystalline and possess more holes than those separated by MIBK solvent at the same dilution solvent ratio of 8:1 by weight (Fig. 2).

Moreover, X-ray diffraction patterns confirm the previous results whereas, the hard waxes isolated by using BA and MIBK solvents become well crystalline and have high crystal size with dilution; as an example from 2:1 to 8:1 by weight. Also, it is interesting to observe that, the hard waxes isolated by using BA solvent appear to be more crystalline and have higher crystal sizes than those isolated by using MIBK solvent.

Fig. 3 – X-ray diffraction patterns for the hard waxes separated by using BA and MIBK solvents at dilution solvent ratios of 2:1 (a and b) and 8:1 (c and d), respectively.

Fig. 4 – Effect of non-polar modifier addition on the yield (a), congealing point (b), mean molecular weight (c) and needle penetration (d) of the hard waxes isolated from Alexandria crude petrolatum by using BA solvent.
Fig. 5 – Effect of non-polar modifier addition on the filtration rate (a), oil content (b), viscosity (c) and refractive index (d) of the hard waxes isolated from Alexandria crude petrolatum by using BA solvent.

Fig. 6 – X-ray diffraction patterns for the hard waxes separated by using BA solvent without modifier (a) and with 1% of pure n-C_{20} (b), 1% n-C_{22} (c) and 1% n-C_{24} (d) at dilution solvent ratio of 8:1 by weight.
MBK solvent at all the dilution solvent ratios (Fig. 3a-d and Table 2).

Examining the isolated wax type in Table 2; on the basis of TAPPI-ASTM equation (Ferris, 1963; Gottshall and McCue, 1973) and petroleum wax specifications (Sequeria, 1994), it can be noticed that all the hard waxes isolated from Alexandria crude petroleum by using BA and MBK solvents at all the dilution solvent ratios lie in the category of microcrystalline waxes as they characterized by refractive indices higher than those obtained by the equation and by viscosities at 98.9 °C higher than 10.2 centistokes.

Also, it can be deduced that, the microcrystalline waxes; isolated by using butyl acetate solvent at dilution solvent ratio of 8:1 by weight; have the highest filtration rate, crystal size and congealing point and they possess more holes and the lowest oil content and total aromatics whereas, the di- aromatic constituents disappeared. Thus, it can be deduced that BA solvent is suitable for deoiling of crude petroleum at dilution solvent ratio of 8:1 by weight.

3.3. Solvent deoiling of crude petroleum using individual n-alkane modifiers

The effect of addition of a non-polar modifier; pure C20–24 n-alkanes with an even carbon number in the range of 0.05–1 wt.%, during the deoiling process of Alexandria crude petroleum on the filtration rate and the isolated hard wax quality was studied at fractionating temperature of 20 °C and dilution solvent ratio of 8:1 by weight by using BA solvent.

It can be observed that, the yield of the isolated hard waxes decreases with increasing the modifier concentration; n-alkanes (Fig. 4a). It may related to the improvements of the crystallization of the solid hydrocarbons by creation of the crystal nuclei with a portion of the modifier, C20-24 n-alkanes, and the remainder built in the surface of the growing crystals. This enhanced on contact with other crystals that include alkyl radicals and formed densely packed coagulated structures. The result was the squeezing of substantial amount of oil and low molecular weight components to the solvent layer, which decreased the yield of the isolated hard waxes. This conclusion is in line with the data of congealing points and mean molecular weights (Fig. 4b and c) of the isolated waxes which are increased by increasing the non-polar modifier concentrations and consequently the penetration value decreases (Fig. 4d). The rate of increase is smaller by increasing the modifier concentration from 0.5 to 1 wt.% than that obtained by increasing the modifier concentration from 0.05 to 0.5 wt.% (Fig. 4b and c).

It is interest to note that, the filtration rate; the most important property for the fractional crystallization process; increases by the addition of a modifier; C20-24 n-alkanes. It increases smoothly with increasing the modifier concentration,
Fig. 8 – Effect of non-polar modifier concentration on the experimental and calculated refractive indices of the hard waxes isolated from Alexandria crude petrolatum.

concentration from 0.05 to 0.5 wt.% and then increases sharply when the modifier concentration reaches 1 wt.% (Fig. 5a).

Also, it can be noticed that the filtration rate increase is accompanied with decrease in the oil contents, viscosities and refractive indices of the hard waxes separated from crude petrolatum. This attributed to the removal of the oil which is mainly low melting point wax; cyclo-paraffin and aromatic constituents which have higher viscosities and refractive indices than the other constituents of the wax (Fig. 5b–d).

Moreover, it can be observed that, the highest filtration rate was achieved by using 1 wt.% of a modifier; C20-24 n-alkanes and the three membered n-alkanes C20, C22 and C24 gave more or less the same filtration rates, yields, congealing points and oil contents at the same modifier concentration (Figs. 4a and b and 5a and b).

Comparing between the X-ray diffraction patterns of the hard waxes isolated without and with addition of 1 wt.% of a modifier; C20-24 n-alkanes, it can be observed that the peaks of hard waxes isolated appear to be well crystalline and have the higher crystal sizes by the addition of 1 wt.% of a modifier; C20-24 n-alkanes (compare Fig. 6a with b–d).

SEM photographs of the isolated hard waxes are parallel to the above findings whereas, the crystals of the hard waxes isolated are growing up and became more crystalline and possess more holes with addition of 1 wt.% of a modifier; C20-24 n-alkanes (compare Fig. 7a with b–d).

Examining the type of the isolated waxes from Alexandria crude petrolatum with addition of many concentrations of a non-polar modifier (C20-24 n-alkanes) (Fig. 8); on the basis of TAPPI–ASTM equation (Ferris, 1963; Gottshall and McCue, 1973) and petroleum wax specifications (Sequeria, 1994); it can be noticed that all the hard waxes isolated lie in the category of microcrystalline waxes. Thus, it can be concluded that, intensifying and improvement of the fractional crystallization of crude petrolatum to isolate the hard wax; microcrystalline wax with high quality are achieved by using butyl acetate solvent with addition of 1 wt.% of a non-polar modifier; C20-24 n-alkanes. The results are the increase of the filtration rate, growing up of crystal size, elevation of the congealing point of the wax and the decrease in its oil content, needle penetration and viscosity.

4. Conclusions

The study shows that Alexandria crude petrolatum is the preferable crude for deoiling process and butyl acetate solvent is suitable for deoiling of crude petrolatum at dilution solvent ratio of 8:1 by weight at fixed washing solvent ratio of 2:1 and ambient fractionating temperature of 20 °C to produce micro-crystalline waxes. Also, addition of 1 wt.% of a non-polar modifier; C20-24 n-alkanes is highly effective to intensify and improve the fractional crystallization of crude petrolatum to isolate the hard waxes; microcrystalline waxes with high quality, filtration rate, crystal size, congealing point and having more holes between their large crystals and low oil content.

References


