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FULL LENGTH ARTICLE

Evaluation of various techniques for separation of non-polar modifier concentrates from petroleum waxy by-products

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Abstract Two petroleum waxy by-products (light and middle slack wax crudes) were evaluated for separation of non-polar modifiers by using different techniques. The results showed that, the light slack wax is selected as a suitable wax for separation of n-alkanes with even number of carbon atoms ranging from C_{20} to C_{26} for their high n-paraffin contents and can be used as non-polar structural modifiers. Different separation techniques; multistage fractional crystallization and liquid–solid chromatography; followed by the urea adduction technique have been used to separate non-polar modifier concentrates from the light slack wax crude. The light slack wax, its saturate components, the hard wax fractions isolated from light slack wax by the multistage fractional crystallization technique and their adducts were analyzed by GC to characterize and compare the produced components. The resulting data reveal that, the adducts of light slack wax and its saturate components; can be used as non-polar modifier concentrates of low carbon atoms (C_{20} + C_{22}). From an economic point of view, the light slack wax adduct is selected as a non-polar modifier concentrate whereas, the separation step can be neglected to save energy. Meanwhile, the adduct of the hard wax isolated at 30 °C can be used as the preferable non-polar modifier concentrate of the high carbon number atoms (C_{24} + C_{26}).

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

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modifier on the crystallization of solid hydrocarbons is usually rated on the basis of the melting point of the microcrystalline wax, the oil content in the microcrystalline wax, and the slurry filtration rate such as ionic and non ionic modifiers, surfactants and additive [1].

Zolotarev and Nigmatullin, 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% [2]. Nigmatullin et al. 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 [3,4].

Trends in improving production of oils and solid hydrocarbons were examined by optimization of crystallization of solid hydrocarbons by using surfactants and ultrasound. Surfactant 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. The metal containing additives and fractions of solid hydrocarbons are used as structure modifiers. Incorporation of the modifier in the concentration of 0.001–0.1 wt.% increases the yield of oil by 2–4 wt.% and the filtration rate and reduces the oil content in the solid phase by 2–3 times. 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 a melting point of 58 °C [5].

For improving the crystallization of solid hydrocarbons; during the deoiling of petrolatum to produce microcrystalline wax; a non-polar modifier (pure n-alkane from C_{20}–C_{24}) was added to the wax deoiling solvent mixtures. Kazakova et al. showed that non-polar modifiers, especially individual n-alkanes with an even number of carbon atoms in the molecule (C_{20}–C_{24}) are very important when added in amounts highly effective for crystallization of petroleum solid hydrocarbons. A portion of the modifier; C_{20}–C_{24} n-alkanes; participated in the creation of the crystal nuclei, and the remainder built in the surface of the growing crystals. This not only altered the surface but also enhanced interaction contact with other crystals that include long alkyl radicals. During this interaction, microcrystalline wax crystals and the modifier formed densely packed coagulated structures; the result was the squeezing of substantial amounts of oil and lower molecular weight components to the solvent layer. The filtration rate was greatly increased and the resulting microcrystalline wax contained 0.5 wt.% oil [1,6,7].

No literature was found about separation of non-polar modifiers from petroleum products for intensification of deoiling residual stocks. Thus, the present work deals with the use of the light slack wax; which is a dewaxing by-product obtained from dewaxing of the light wax distillate fraction through the manufacture of lubricating oil; for separation of non-polar modifier concentrates having the carbon numbers of C_{20}–C_{26} by applying two different techniques: multistage fractional crystallization and liquid–solid chromatography, followed by the urea adduction technique.

2. Experimental

2.1. Material

Two slack wax crudes (petroleum by-products) were obtained from light and middle wax distillate fractions from El-Ameria Refining Company and Butyle acetate.

2.2. Methods

2.2.1. Separation of non-polar modifier concentrates

Two different techniques: multistage fractional crystallization and liquid–solid chromatography, followed by the urea adduction technique were used to separate non polar modifier concentrates containing high contents of C_{20}–C_{26} n-alkanes.

2.2.2. Multistage fractional crystallization technique

Light slack wax was subjected practically to multistage stage fractional crystallization process by using butyl acetate solvent [8] at different fractionating temperatures under fixed dilution and washing solvent ratios (S/F) of 6:1 and 2:1 by weight, respectively. At each fractionating temperature the high melting point components of the slack wax were precipitated, while the low melting ones remained in the solution. The process of solvent fractionation was repeated on the soluble components at different fractionating temperatures ranging from 40 to 20 °C at intervals of 5 °C.

2.2.3. Liquid–solid chromatographic technique

Light slack wax was subjected to liquid–solid column chromatography to separate its total saturate components [9].

2.2.4. Urea adduction technique

The light slack wax, its saturate components and the hard wax fractions isolated from the light slack wax were subjected to the urea adduction technique [10] to separate pure non-polar modifier concentrates containing high contents of C_{20}–C_{26} n-paraffins.

2.3. Methods of analysis

The light and middle slack waxes, the light slack wax saturate and the isolated hard waxes from light slack wax and their adducts were physically characterized according to American Society for Testing and Materials (ASTM) standard methods [11]. The aromatics and n-paraffin contents were determined by using the liquid–solid column chromatographic technique [9] and by using the GC technique, respectively. The GC apparatus used was of model Perkin Elmer, Clarus 500, England, equipped with a hydrogen flame ionization detector and fused silica capillary column (30 cm × 0.25 mm i.d.), packed with