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High molecular weight waxes from Short Path Distillates of vacuum residue

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ABSTRACT

Short Path Distillates of vacuum residue (boiling above 545 °C) is taken as feedstock for this study. Wax from this fraction is separated by solvent extraction method using methyl iso-butyl ketone (MIBK) as solvent. Both wax and the feedstock are characterised with the help of ASTM and IP procedures. Separated wax is fractionated at different temperatures, say 0–30 °C using MIBK as solvent. High temperature gas chromatography (HTGC) technique is used to study the distribution of alkane carbon number in all the fractions. It is observed that the wax contains very high molecular weight hydrocarbons as high as $C_{67}H_{136}$. HTGC technique as well as the Differential Scanning Calorimetry (DSC) indicates that all the fractions of the wax contain two types of hydrocarbons, one having high molecular weight alkanes (>600) and another having low mol. wt. alkanes (~400). Thermal analysis by DSC technique further indicates that the wax is microcrystalline in nature having a low degree of crystallinity, 17%, as evidenced by XRD studies. Both high and low molecular weight waxes can also be separated based on their solubility characteristics.

1. Introduction

Petroleum waxes are generally produced from lubricating oil base stocks, residual distillates, tank bottoms and sucker rod waxes [1]. The chemical composition of wax is complex, all of the products have relatively high molecular weight profiles with the functionality ranging from products which contain n-alkanes to those which are mixtures of hydrocarbons and reactive functional species. Waxes are classified into three categories, paraffin, intermediate and microcrystalline waxes. Paraffin wax contains individual alkane range from about 18-carbon atoms to about 45, Intermediate waxes contain individual alkane chain length up to 60 carbons whereas microcrystalline waxes contain mixtures of saturates, branch chain and also cyclo alkanes. The Carbon No. content per molecule may vary from about mid-thirties to well over eighty [2]. Thus alkanes are the basic building block unit in most naturally occurring organic linear chain molecular species such as wax. A number of studies have been undertaken to investigate the ability of n-alkane to form polydispersed crystalline aggregates using calorimetry [3–5], powder X-ray diffraction techniques [6–9], electron diffraction [5,10–12], FT-IR spectroscopy [13] and atomic force microscopy [9]. These studies revealed that these materials crystallise in the form of thin plates with regular faces in which the chain diffraction is more or less perpendicular to the lamella surface. Prior to melting the alkanes are known to exhibit solid–solid phase transition to crystalline rotor phases [14]. At low temperature the chains undergo hindered rotation about the main carbon axis and the molecules are hexagonally packed. In this present communication, Short Path Distillates of vacuum residue (VRS) i.e. boiling range, 545–740 °C, is taken as feedstock. Wax from this fraction of crude oil is separated by solvent extraction method using methyl iso-butyl ketone (MIBK) as solvent and characterised by different techniques. Attempt is also taken to understand the composition of wax and their behaviour of crystal packing and to understand its possible utility.

2. Experimental details

2.1. Separation of wax

A number of techniques are well documented for the separation of waxes from petroleum feedstock by solvent extraction method [3,15–18]. In this present communication methyl isobutyl ketone (MIBK) is used as extraction solvent whereby waxes precipitate at low temperature. The feedstock is heated to 60–70 °C to melt and make a homogeneous liquid (about 10 g) in MIBK. Stirring is continued at that temperature at least for a period of half an hour. The mixture solvent is then kept in cooling water bath at 0 °C for 2–3 h, filtered through Grutch Crucible containing Whatman No. 2 filter paper kept at 0 °C by applying vacuum. The separated wax on filter paper is washed several times with MIBK to remove the adhered oil from the wax. The wax on filter paper is then dissolved by pouring hot hexane over it. Then the colour of the wax is removed by adding activated alumina (dried at 120 °C overnight) to the wax solution with constant stirring till the solution becomes colourless. The solution is filtered off and the solvent from the filtrate is removed to get the wax.

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Table 1
Physical characteristics of VRS.

1. Density	0.999
2. Metal cont. (Fe/Ni/V) ppm	12/2/0.2
3. Wax cont. (%)	16.2
4. Asphaltenes cont. (%)	1.6
5. Aromatics (%)	22.14
6. Resin cont. (%)	12.07
5. Penetration (1/10 mm)	3
6. Softening point (°C)	70
7. Flash point (°C)	228
8. Conrudson carbon	17.8
9. Ductility at 27 °C	3.3
10. Sulphur cont. (wt.%)	0.075

Table 2
Physical characteristics of VRS wax.

Sl. no.	Total wax				n-Paraffin			
	Wax conc. (wt.%)	Mol. wt.	Penetration no. (1/10 mm)	Drop m. pt. (°C)	wt.%	Mol. wt.	Penetration no. 1/10 mm)	Drop m. point (°C)
1	15	700	38	78	20	570	3	90
2	14.5	650	42	82	18	600	4	89

2.2. Fractionation of wax

Wax separated as above is subjected to fractionation at different temperatures. Fractionation is carried out by dissolving the separated wax in MIBK (1:3) at 70 °C. A clear homogeneous liquid is obtained. It is then cooled slowly to 30 °C and kept at that temperature at least for a period of 1 h. At this temperature a part of this wax separates out from the liquid. It is then filtered off at that temperature. The solid in the filter paper is processed to get the first fraction (F1). The filtrate is further processed to fractionate the waxes at 20, 10 and 0 °C by following the same procedure as stated above. Altogether four fractions are obtained.

2.3. Analysis of wax by HTGC

Gas chromatography is the simple analytical method for the determination of the alkane constituents in wax sample. del Carmen GarcĀ et al. [15] analysed the tank bottom wax by applying high temperature GC programme. GLC–MS analysis was done to obtain information on the type of branching [17]. In these present studies the wax fraction separated as above are analysed by a Thermo Ultra Trace Gas Chromatograph equipped with a 30 m × 0.25 mm DBI HT fused silica capillary column. 2 µl of 1% wax solution in hexane is injected to the GC. The GC is programmed as constant injector temperature programmed from 80 °C with 0 min hold time to 380 °C with 10 min hold time at 8 °C/min heating rate. Total time of analysis is only 46.5 min.

2.4. Differential Scanning Calorimetry (DSC) studies

The analysis is carried out by Mettler Toledo DSC 822(Switzerland) instrument. About 5 mg of wax sample is taken in an aluminium sample holder. The holder is then put in the heating chamber of the DSC system. The analytical method is: initial temperature 25 °C, initial hold time 0 min, final temperature 100 °C; final hold time 0 min heating rate 5 °C/min, segment gas used is nitrogen at a flow rate of 40 ml/min. Total time of analysis was 15 min.

2.5. TLC-FID analysis

A latroscan TLC-FID model MK 10 is used to determine the composition of the feedstock. The chromatography elution is done to develop tanks using n-hexane to elute saturates, toluene to elute aromatics, and dichloromethane:methanol (95:5 v/v) to elute resins. All the other analyses are carried out as per ASTM/IP procedures.

2.6. XRD studies

The X-ray crystallographic studies consist of a Philip PW 1730 generator, Cu tube PW 1710 diffractometer control unit. Data is collected by X'pert Industry software. A small amount of wax is uniformly spread over a glass slide with a length of 5 cm and breadth of 2.5 cm by heating the solid on a hot plate. The slide is then placed on the slide holder of the X-ray system. The X-ray system is then programmed as; start angle(°C Theta); 1.5, end angle(°C Theta): 40, step size(02 Theta): 0.0.3, time per step(s) 1.2, scan speed(02 Theta); 0.025, no. of steps; 1283, total time 0;25;40 min-part.

3. Results and discussions

The physical characteristics of VRS feedstock are presented in Table 1. This feedstock is obtained after Short Path Distillation of the vacuum residue from an Indian Refinery. After atmospheric distillation, vacuum distillation is applied to crude oil till 545 °C, the residue left is further distilled with the help of SPD technique. The distillated fraction is the feedstock for the present studies. Composition of the feedstock is determined with the help of TLC-FID technique. As presented in Table 1, it contains 16.2% wax, 1.6% asphaltenes, exhibits density of 0.999 at 20 °C and softening pt. of about 70 °C. The wax present in the feedstock is separated by solvent extraction method using MIBK as solvent, the details of which are presented above. In Table 2 two repeated experimental results are documented. It shows that mol. wt. of wax is very high (~700), and drop melting point and penetration no. are also presented in the table. N-paraffin content of the wax is separated by urea adduction method. It is observed from the data in Table 2 that the wax contains about ~20% n-paraffin hydrocarbons, hard in nature, having very high mol. wt. (~600) high drop melting point (>85 °C) and low penetration (pent. no 2).

3.1. Studies of wax C-No

The separated wax is fractionated at different temperatures from 0 to 30 °C. The yield and the average C-No of each fraction are presented in Table 3. The distribution of n-paraffin in waxes separated

Table 3
Physical characteristics of fractionated VRS wax.

Wax sep. temp. (°C)	Yield (wt.%)	Average C-No	Mol. wt.	Low mol. wt. fraction			High mol. wt. fraction		
				Conc. wt.%	Range of C-No	Peak range of C-No	Conc. wt.%	Range of C-No	Peak range of C-No
0	2.1	41	576	28.5	17–35	31–32	70.6	36–54	43–45
10	2.3	37	520	47.5	22–35	29–32	52.0	36–50	31–46
20	2.5	42	590	43.5	22–35	31–34	55.6	41–66	57–59
30	3.1	40	562	45.5	22–35	32–35	55.5	41–66	57–50