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Characterization of Heavier Fractions of Bombay High Crude Oil

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Heavier fractions boiling above 250°C, namely gas oil (250-370°C), vacuum gas oil (350-500°C), and residue (500°C +), from Bombay High crude oil are characterized using solvent extraction and column chromatographic separations and instrumental analytical techniques such as nuclear magnetic resonance and mass spectrometries. The variation of compositional and structural data with increasing boiling range is discussed.

Bombay High crude oil, which forms a significant proportion of the crude diet in Indian refineries, has two distinct characteristics: (i) high concentration of aromatics in lower boiling distillate fractions (naphtha, kerosine), and (ii) high concentration of "wax", predominantly consisting of straight chain paraffins in the heavier boiling fractions (gas oil, vacuum gas oil and residue). These peculiar characteristics pose special processing problems, and challenges, to the petroleum refiner, especially in view of the desire of refiners in India to upgrade the heavier fractions (VGO and residue) to more valuable middle distillates (kerosine and diesel). Fluid catalytic cracking (FCC) is currently employed in Indian refineries for converting vacuum gas oil into more valuable products such as LPG, gasoline and diesel. In future the emphasis will be on hydrocracking, which produces a higher yield of middle distillates than FCC.

The design and operation of FCC and hydrocracking for maximum selectivity towards middle distillates is strongly influenced by the types of compounds present in the feedstock. In particular, the reactivities of the various compound types present in the feedstock vary significantly from one another[1,2]; these differing reactivities have a profound influence on the design of the catalyst for achieving the maximum selectivity towards middle distillates[3].

The most frequently used methods for characterizing the heavier petroleum fractions are based on the gross properties of the fractions such as refractive index, density and molecular weight in the n-d-M method[4] or average boiling point and specific gravity in K_{UOP} computation[5]. Hinds[6] has demonstrated the inadequacy of these methods in predicting the product yields and properties as well as in explaining the problems encountered during secondary processing and has emphasized the need for detailed compositional characterization of heavier fractions. The average structural parameters of asphaltenes from the hydrocracked products of petroleum residues employing NMR spectrometry have been used to clarify the hydrocracking mechanism[7]. Mauleon *et al*[8] have illustrated the use of modern analytical techniques such as NMR, mass spectrometry and HPLC for characterization and selection of heavy feeds for residue upgrading by FCC. NMR, GPC and HPLC have also been employed[9] to characterize heavy vacuum gas oil for studying the effect of composition of the feedstock on the catalytic cracking.

In this study, the heavier fractions of Bombay High crude, namely gas oil, GO (250-370°C), vacuum gas oil, VGO (350-500°C) and residue (500°C +), were separated into simpler fractions and the separated saturates and aromatics were analysed by mass spectrometry and NMR spectrometry to generate compositional and structural data. The variations of these data with increasing boiling points have also been discussed. The data generated are expected to aid technology and catalyst development for FCC and hydrocracking.

Experimental Procedure

Fraction preparation—The gas oil fraction boiling in the range 250-370°C was obtained by fractionation of Bombay High crude oil. The fraction obtained had 8% of the distillate boiling below 250°C and 3% boiling above 370°C. The VGO obtained by distillation under vacuum consisted of nearly 92% of the material boiling between 350-500°C with 8% of material boiling below 350°C. The yield on crude oil for GO, VGO and the residue boiling above 500°C is 25.0, 25.0 and 8.0 wt% respectively. GO,

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VGO and non-polar fraction of residue obtained from clay separation of deasphaltened material were separated into saturates and aromatics by classical silica gel column chromatography[10].

Fraction characterization—The molecular weights of the fractions were measured by vapour pressure osmometry in toluene solution at 60°C and elemental composition by classical methods. Saturates and aromatics from the three fractions were analysed using a Kratos MS-45 (MS-50 for VGO) mass spectrometer using direct insertion probe and ion source temperature of 200 and 250°C respectively for GO and residue, while in case of VGO both the temperatures were maintained at 250°C. The results were computed using ASTM D-2786 and D-3239 methods for saturates and aromatics respectively. The experimental conditions for recording quantitative ^1H and ^{13}C NMR spectra of fractions and the assignment of peaks and computation procedures for various parameters were the same as reported earlier[11,12].

Results and Discussion

The details of the separation and the analytical scheme employed for the characterization of GO and VGO are given in Fig. 1 and those of residue in Fig. 2. The physicochemical properties of heavier fractions, and elemental composition and molecular weight of these fractions and their subfractions are given in Table 1. Table 2 gives the compositional da-

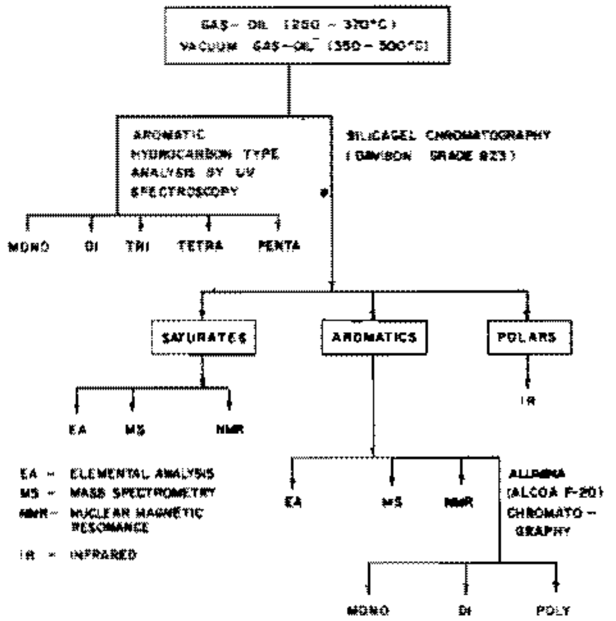

Fig. 1—Separation scheme for gas oil and vacuum gas oil

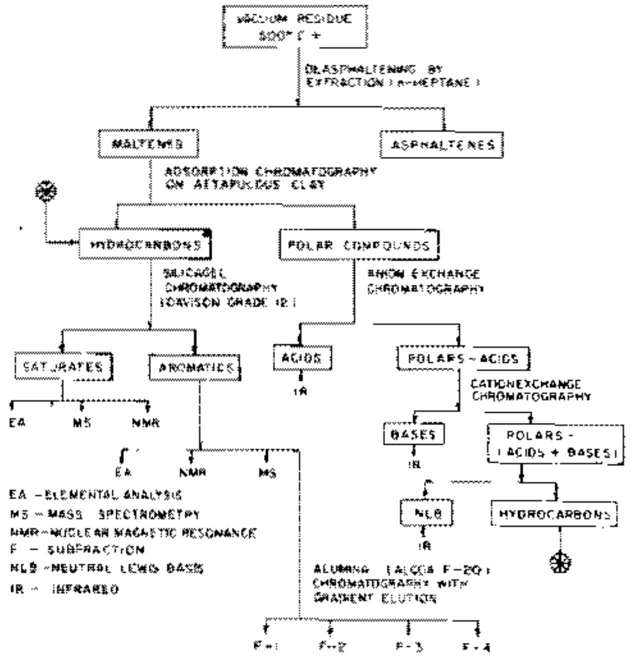

Fig. 2—Separation scheme for residue

Table 1—Physicochemical Properties of Heavier Fractions and Their Subfractions from Bombay High Crude Oil

Properties	Gas oil			Vacuum gas oil			Residue		
	As such	Saturates	Aromatics	As such	Saturates	Aromatics	As such	Saturates	Aromatics
Boiling range, °C	250-370	—	—	350-500	—	—	500 +	—	—
Yield on crude, wt% (*on fraction basis)	25.00	68.28*	28.76*	25.00	69.86*	27.60*	8.00	33.57*	40.04*
Pour point, °C	3	—	—	45	—	—	—	—	—
CCR, wt%	0.012	—	—	0.180	—	—	—	—	—
Carbon, wt%	85.90	85.10	87.40	85.86	85.15	87.00	86.50	85.10	88.00
Hydrogen, wt%	13.84	14.80	12.36	13.87	14.85	12.77	11.30	14.60	10.50
Sulphur, wt%	0.19	0.00	0.24	0.24	0.00	0.23	0.70	0.00	1.49
Nitrogen, wt%	0.07	0.00	0.00	0.03	0.00	0.00	1.20	0.30	0.10
Atomic H/C	1.93	2.09	1.70	1.94	2.09	1.76	1.57	2.06	1.43
Molecular weight (by VPO)	246	242	239	395	370	307	1102	516	688

— not measured

Table 2—Compositional Analysis of Heavier Fractions of Bombay High Crude Oil

			Gas oil wt %			Vacuum gas oil wt %			Residue wt %		
Saturates			68.28			69.86			33.57		
	n-paraffins				32.41			40.50			
	Isoparaffins				28.91			12.50			13.04
	Monocycloparaffins				1.72			5.50			9.61
	Dicycloparaffins				3.52			4.55			6.47
	Tricycloparaffins				1.57			3.43			3.64
	Tetracycloparaffins				0.00			2.54			0.81
	Pentacycloparaffins				0.07			0.68			0.00
	Hexacycloparaffins				0.07			0.16			0.00
Aromatics			28.76			27.60			40.04		
	Monoaromatics			10.69			9.23			15.79	
		alkyl benzenes			5.10			3.87			5.50
		naphthenebenzenes			2.48			2.32			4.75
		dinaphthenebenzenes			3.11			3.04			5.54
	Diaromaties			15.65			8.92			12.86	
		naphthalenes/ aeenaphthenes			8.66			2.92			4.30
		dibenzofurans			5.26			3.00			4.51
		fluorenes			1.73			3.00			4.05
	Triaromatics			1.58			3.85			7.23	
		phenanthrenes			1.43			2.82			6.15
		naphthenephenanthrenes			0.15			1.03			1.03
	Tetraaromatics			0.07			1.52			1.87	
		pyrenes			0.07			1.13			1.36
		chrysenes			0.00			0.39			0.51
	Pentaromatics			0.00			0.25			0.59	
		benzopyrenes			0.00			0.24			0.46
		dibenzanthracenes			0.00			0.01			0.13
	Thiophene aromatics			0.77			0.45			0.53	
		benzothiophenes			0.46			0.11			0.34
		dibenzothiophenes			0.31			0.32			0.19
		naphthobenzothiophenes			0.00			0.02			0.00
	Unidentified compounds			0.00			3.38			1.17	
Polars			2.96			2.50			16.78		
	Acids									4.31	
	Bases									6.47	
	Neutral Lewis bases									6.00	
Asphaltenes			0.00			0.04			9.61		
			100.00			100.00			100.00		

ta of GO, VGO and residue from Bombay High crude oil obtained through solvent extraction, column chromatography and mass spectrometry. The distribution of hydrogen and carbon obtained by ^{1}H and ^{13}C NMR spectrometry and a few average structural parameters of saturates and aromatics of heavier fractions of BH crude are given in Table 3.

From Table 1 it is evident that fractions as such have relatively higher molecular weight than their subfractions which is due to presence of polar compounds, which yield artificially higher molecular weight due to molecular associations. Due to the significant amount of polars and asphaltenes in the residue as compared to other fractions, the difference is quite large. The comparison of saturates and aromatics molecular weights of respective fractions (GO and VGO) shows that saturates comprise of relatively larger molecular mass compounds than aromatics. The opposite trend in the subfractions of residue is due to the presence of some polars as well as highly condensed aromatics in aromatic subfraction which form molecular associations and in turn

Table 3—Structural Data of Saturates and Aromatics from Heavier Fractions of Bombay High Crude Oil Derived from ^{1}H and ^{13}C NMR Spectrometry

	Gas oil		Vacuum gas oil		Residue	
	Saturates	Aromatics	Saturates	Aromatics	Saturates	Aromatics
%H						
H_{ar}	0.0	23.0	0.0	14.4	0.0	7.7
H_{sat}	100.0	77.0	100.0	85.6	100.0	92.3
H_{α}	0.0	30.5	0.0	21.9	2.5	11.5
$H_{\alpha\text{-alk}}$	0.0	-	0.0	5.5	0.0	1.3
$H_{\alpha\text{-}CH_3}$	0.0	—	0.0	16.4	0.0	10.2
H_{β}	67.6	33.7	75.7	44.3	74.4	57.7
H_{γ}	32.4	12.8	24.3	19.4	23.1	23.1
Branchiness index	0.48	0.38	0.32	0.44	0.31	0.40
% C						
C_{sat}	100.0	71.0	100.0	64.6	100.0	69.9
C_{p}	81.3	47.7	84.8	49.3	93.7	44.7
$C_{n\text{-}p}$	55.4	11.1	67.7	22.7	58.9	34.5
$C_{i\text{-}p}$	25.9	36.6	17.1	26.6	34.8	10.2
C_{N}	18.7	23.3	15.2	15.3	6.3	25.2
C_{ar}	0.0	29.0	0.0	35.4	0.0	30.1
$C_{ar,H}$	0.0	23.0	0.0	21.5*	0.0	10.9*
C_{ar,CH_3}	0.0	3.0	0.0	8.2*	0.0	4.8*
$C_{ar,alk}$	0.0	0.0	0.0	4.1	0.0	0.9
$C_{ar,br}$	0.0	3.0	0.0	1.6	0.0	13.5
C_{sat}/H_{sat}	—	0.541	—	0.458	—	0.446
Chain length, *n*	20	7	27	9	36	15

– not measured

*computed from ^{1}H NMR data

give higher molecular weight. The atomic H/C ratio varies from 1.93-1.94 for GO and VGO to 1.57 for residue. The relatively high value of H/C ratio in case of VGO is due to high concentration of *n*-paraffinic hydrocarbons in this fraction. This explains the erratic variation of H/C ratio with increasing boiling range of fractions. The H/C ratio of all the three saturates range from 2.06 to 2.09 which suggests, in general, the presence of long chain molecules. The heteroatomic content is also found to increase with increasing boiling point of the fractions. This implies that these atoms are either incorporated in the larger molecules or increase the boiling point due to introduction of polar character to the molecules.

The data in Table 2 reveal that the concentration of polar compounds is nearly of the same order in GO and VGO, while the residue shows quite high concentration of polars as well as asphaltenes. Owing to the appreciable overlapping properties and multifunctionality, it is difficult to separate polar compounds in the residue, and acids and bases are not chemically separated from each other. The higher concentration of neutral Lewis bases is due to the presence of polycondensed aromatic rings and methyl substituted non-condensed aromatic rings which are capable of forming charge transfer weak complexes with $FeCl_3$. The distribution of saturates is nearly the same in both the gas oils, while there is a significant reduction in the saturate content of residue. This reduction is due to separation of larger *n*-paraffinic compounds with asphaltenes due to poor solubility in *n*-heptane. The high yield of aromatics for residue together with high polar and asphaltene contents indicate the magnitude of structural diversity in this fraction.

The hydrocarbon type distribution data for saturates (Table 2) indicate that naphthenic content increases with increasing boiling point of the fraction. This increasing trend is observed in mono-, di- and tricycloparaffins individually as well. Although, the total paraffinic content in GO saturate is larger than that in VGO, the *n*-paraffins are present in significantly higher amount in the latter than in the former as determined by urea adduction. Table 2 also shows significant amount of isoparaffinic compounds in GO saturate.

The compositional data of aromatic subfractions (Table 2) show the dominance of monoaromatics in all the fractions. The aromatics from residue contains the largest amount of monoaromatics followed by GO and VGO. A similar trend is observed in alkyl benzene concentration. In all the fractions, dinaphthenebenzenes are in larger concentration as compared to naphthenebenzenes, the individual values being higher in residue. The gas oil aromatics contains largest amount of diaromatics followed by residue and VGO. The same trend is observed in naphthalene content of these subfractions. But naphthenenaphthalenes show increasing concentration with increasing boiling range. Similar trends are observed in concentrations of polyaromatic hydrocarbons.

Besides having a knowledge of the hydrocarbon type compositional data for the various fractions it is also essential for one to have an idea of the chemical structures. For example, the knowledge of branching of the aromatic structures is important because side chain scission is the most facile of the cracking reactions. NMR spectroscopy has potential capability for identifying chemically significant molecular species in heavier petroleum fractions. The precise breakdown of feed carbon and hydrogen atoms can be used to generate average structural data which can be employed to explain the behaviour of the feed under different operating conditions. The coking tendency of the feed is found to be more accurately correlated with different types of aromatic carbons derived from NMR rather than with Conradson carbon residue[8].

The decreasing aromatic hydrogen in the aromatics from GO to residue (Table 3) indicates an increasing trend in the substitution and/or condensation. This is also corroborated by the increasing trend of $(C_{ar,CH_3} + C_{ar,alk} + C_{ar,br})$ from GO to residue. The protons in the methyl groups of paraffinic structures of saturates decreases from GO to residue indicating the decrease of branching in the chains. On the other hand, the methyl protons in the alkyl substituents on the aromatic rings increases from GO to residue indicating the increase of branching in the chains. Normal paraffinic carbons are maximum in VGO saturates and naphthenic carbons are predominant in GO saturates. The higher isoparaffinic carbons in the residue saturate is due to the removal of longer *n*-paraffins with asphaltenes. The trends of naphthenic carbons and naphthenic compounds in the saturates of the three fractions (Tables 2 and 3) are contradictory to each other. This inconsistency may be due to some contributions of short chain isoparaffinic structures which may not produce sharp peaks and are included in the broad overlap used for estimating naphthenic carbons. Different trends in the richness of different carbons are indicated in the aromatics (Table 3). While *n*-paraffinic carbons are increasing with an increase in boiling range, isoparaffinic carbons show an opposite trend. The naphthenic carbons in VGO aromatics are less than GO and residue aromatics. The average chain lengths in the saturates and aromatics are found to increase with the boiling range of the fractions, while C_{sat}/H_{sat} ratio in the aromatic fractions decreases. Table 3 shows an increase in the aromaticity (C_{ar}) from GO to VGO aromatics and a reduction in the residue aromatics. The reduction in the latter is due to the presence of higher condensation, i.e. higher $C_{ar,br}$ and longer chain length in residue, although percentage of total aromatics is higher in this fraction (Table 1).

Conclusions

From this study the following conclusions can be drawn abour changes in composition with increasing boiling points of heavier fractions of BH crude:

The *n*-paraffinic compounds increase, with appreciable dominance in VGO.

- Naphthenic compounds increase.
- Amount of polyaromatics increases.
- Average chain length in saturates and aromatics increases.
- Bridgehead aromatic carbons ($C_{ar,br}$) increase.
- Branching in the chains of saturates decreases, and the amount of alkyl groups on aromatic rings increases.

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