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Characterization of Vacuum Gas Oil from North Gujarat Crude Mix

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Compositional and structural data of North Gujarat mix vacuum gas oil (370-530°C) have been derived employing separation procedures and instrumental analytical techniques, viz. IR, NMR and MS. The repeatability of the separation procedure is found to be satisfactory and the compositional data derived by alumina chromatography and mass spectrometry are in good agreement. Among the different types of heteroatomic functionalities estimated by IR spectroscopy, phenols are found to be predominant followed by carboxylic acids. Various average structural parameters of saturate and aromatic subfractions have been derived by proton and ^{13}C-NMR spectroscopy. The compositional and structural data thus obtained are compared with those of vacuum gas oil from Bombay High crude.

With increasing demand for transportation fuels, mainly diesel, there is enhanced interest in converting high-boiling material into middle distillates. Catalytic cracking is one of the most important secondary processing techniques, which commonly employs vacuum gas oil (VGO) as feedstock. A knowledge of the chemical composition of the feed is essential for the purposes of choosing, or designing, the ideal catalyst for a given objective and also for selecting the optimum set of operating conditions; this is so because the adsorptivity and crackability of the reactants are dependent on the chemical structures[1].

The inadequacies of feed characterization methods based on gross properties have been demonstrated by Hinds[2]. In a recent study, Nilsson and Otterstedt[3] have employed modern analytical techniques such as NMR, GPC and HPLC to determine the composition of VGO feeds with the objective of interpreting the results of catalytic cracking. The heavier fractions, including VGO, of Bombay High crude have been characterized[4] employing column chromatographic and various instrumental analytical techniques. In this communication, vacuum gas oil (370-530 °C) from North Gujarat mix crude (NGM VGO) is characterized employing chromatographic and various instrumental analytical techniques. The compositional and structural data are compared with those of vacuum gas oil from Bombay High crude (BH VGO) boiling in the range 350-500 °C.

Experimental Procedure

The vacuum gas oil (VGO) fraction from NGM was obtained by distillation under vacuum; more than 95% of the material distilled was in the boiling range 370-530 °C. The VGO was separated into saturate, aromatic and polar fractions on silica gel (Davison grade 923) and bauxite column according to ASTM D-2549 method with slight modifications in the concentration procedure. The aromatic concentrate was further fractionated into mono-, di- and polyaromatics on alumina gel (Alcoa F20) according to a standardized procedure[5] with slight modification in the cut point for di- and polyaromatics separation, based on the ultraviolet absorptivity values at 270 nm measured on a Shimadzu UV-VIS spectrophotometer (model UV-240).

The quantitative infrared spectra of the VGO and its subfractions were recorded on a Perkin-Elmer 399 B spectrophotometer in CCl_4 and CS_2 solutions using 5.0 and 0.5 mm KBr cells. The mass spectral data were obtained on a Kratos MS-50 mass spectrometer using direct insertion probe and ion source temperature of 200 °C and 250 °C for saturates and aromatics. The detailed distributions of the hydrocarbon types were computed using D-2786 and D-3239 ASTM procedures for saturates and aromatics respectively. The NMR spectra (^{13}C and ^{1}H) of saturate and aromatic subfractions were recorded on a Bruker NR/80 AF spectrometer in $CDCl_3$ solution at observing frequencies of 20.15 and 80.13 MHz respectively using optimum instrumental and experimental conditions to yield quantitative spectra.

Results and Discussion

The repeatability of the column chromatographic methods are shown in Table 1 using duplicate experiments. The coefficients of variation for saturates and aromatics on silica gel-bauxite column are very good. The maximum coefficient of variation on alumina column is found to be ± 8.9% of the value present. The elemental analysis as well as molecular weight data on VGO and its saturates and aromatics are given in Table 2; this table also presents the compositional data obtained by column chromatography and infrared analyses. The somewhat lower value of H/C atomic ratio (1.88) in NGM VGO as compared to that of BH VGO (1.94)[4] is due to the dominance of naphthenic compounds in the former and normal paraffinic compounds in the latter. The distribution of saturates, aromatics, polars and asphaltenes in NGM VGO is nearly same as that obtained in BH VGO[4]. The distribution of compound types in the aromatic concentrate shows relatively higher concentration of monoaromatics and lower concentration of diaromatics in NGM VGO as compared to BH VGO. The polar compounds in NGM VGO are found to be rich in phenolic structures followed by carboxylic acids.

Table 1 — Repeatability of the Chromatographic Methods for the Separation of Hydrocarbon Types in Vacuum Gas Oil

	Concentration, wt %		Average	Coefficient of variation
	Expt No.1	Expt No.2		
Silica-bauxite chromatography				
Saturates	68.63	68.81	68.72	0.19
Aromatics	28.65	28.69	28.67	0.99
Polars	2.66	2.44	2.55	6.10
Alumina chromatography				
Monoaromatics	11.03	9.93	10.48	7.42
Diaromatics	7.76	8.80	8.28	8.88
Polyaromatics	9.88	9.94	9.91	0.43

Table 2 — Elemental Analyses, Molecular Weight, Column Chromatographic and Infrared Spectroscopic Data on NGM Vacuum Gas Oil and Its Subfractions

(a) Elemental Analyses

	Fraction as such	Saturates	Aromatics
Carbon, wt %	85.60	84.60	87.90
Hydrogen, wt %	13.40	15.00	11.40
H/C	1.88	2.13	1.56
Sulphur, wt %	0.124	0.005	0.290
Molecular weight (VPO)	388	396	356

(b) Column chromatographic data

Hydrocarbon type	Concentration wt %
Saturates	68.72
Aromatics	28.67
Monoaromatics	10.48
Diaromatics	8.28
Polyaromatics	9.91
Polars	2.55
Asphaltenes	0.06

(c) Infrared spectroscopic data

	Number of paraffinic methylene groups per av. molecule (N)	CH_3/CH_2	Concentration mol/L
Fraction as such	8.26	0.4485	—
Saturates	11.06	0.3993	—
Aromatics	1.65	—	—
Polars	—	0.4016	—
Phenols	—	—	0.5360
Carbazoles	—	—	0.0034
Esters	—	—	0.0851
Carboxylic Acids	—	—	0.1930

The compositional data on NGM VGO obtained by mass spectrometry of saturates and aromatics are presented in Table 3. Nearly 59% of the total saturates is naphthenes, whose concentration decreases as the number of rings increases. The ring type distribution obtained by mass spectral analysis of aromatic concentrate compares well with the compositional data from alumina chromatography (cf. Table 1). When comparison

Table 3 — Mass Spectral Data on the Saturates and Aromatic Subfractions of NGM Vacuum Gas Oil

Hydrocarbon types	Concentration, wt %		
Saturates	68.72		
Paraffins			28.34
Monocycloparaffins			15.71
Dicycloparaffins			10.81
Tricycloparaffins			8.19
Tetracycloparaffins			3.06
Pentacycloparaffins			2.37
Hexacycloparaffins			0.24
Aromatics	28.67		
Monoaromatics		10.82	
Alkylbenzenes			3.38
Naphthenebenzenes			3.86
Dinaphthenebenzenes			3.58
Diaromatics		7.61	
Naphthalenes			2.40
Acenaphthenes			2.55
Fluorenes			2.66
Triaromatics		3.52	
Phenanthrenes			2.29
Naphthenephenanthrenes			1.23
Tetraaromatics		1.08	
Pyrenes			0.63
Chrysenes			0.45
Pentaaromatics		0.53	
Perylenes			0.34
Dibenzanthracenes			0.19
Thiophenearomatics		1.02	
Benzothiophene			0.70
Dibenzothiophene			0.32
Naphthobenzothiophene			0.00
Unidentified compounds		4.09	

is to be made with alumina chromatography, the concentrations of benzothiophene, dibenzothiophene and unidentified compounds in mass spectrometric analysis are to be included, respectively, with the mono-, di- and polyaromatic compositional data. Further, the distributions of mono- and diaromatics show the dominance of naphthenes condensed with benzene and naphthalene rings respectively. The comparison of these data with BH VGO (Fig.1) shows that although both the VGOs contain nearly the same amount of saturates and aromatics, their compound type distributions are different, especially in saturates. While the NGM VGO saturate is dominated by naphthenes, paraffins are dominant in BH VGO. Out of the total paraffins present nearly 71% and 76% are *n*-paraffins in NGM VGO and BH VGO saturates respectively. Thus, although the total amount of paraffins are very different in the two VGOs, the ratio of normal to isoparaffins is nearly constant. The comparison of aromatic data reveals that naphthenebenzenes are in maximum concentration in NGM monoaromatics while the maximum concentration in BH monoaromatics is that of alkylbenzenes. The distribution of rest of the compound types are nearly same.

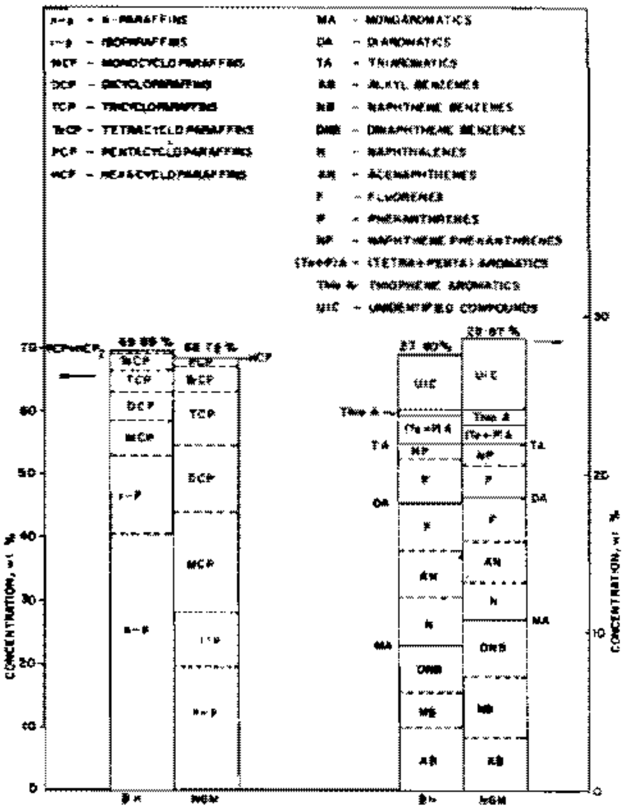

Fig. 1 — Comparison of the distribution of compound types in the saturate and aromatic fractions of vacuum gas oils from Bombay High and North Gujarat mix crudes

Table 4 presents the proton NMR data of saturates and aromatics of NGM VGO. The lower value of branchiness index (0.31) for saturates as compared to CH_3/CH_2 ratio (0.40) may be due to some contribution of methyl groups attached with naphthene rings to H_β. The relatively small value of the percentage of aromatic hydrogen atoms (H_{ar} = 9.82%) indicates that the aromatics contain substantial amount of naphthenes and alkyl groups as substituents. This is also corroborated by the presence of 67.1% of saturated carbons in aromatics (Table 5). Table 5 also reveals that the aromatic carbons are dominated by protonated ones followed by $C_{ar,alk}$, $C_{ar,br}$ and C_{ar,CH_3}. The value of H/C computed from ^{13}C NMR data for aromatic fraction is comparable with those obtained by elemental analysis. Considering the assumptions involved in the computation of f_a, H_{aru}/C_{ar} and σ from ^{1}H NMR data, the values determined/obtained by ^{13}C- and ^{1}H NMR data are in fair agreement. The carbon distribution in saturates and aromatics obtained from ^{13}C NMR spectra in the aliphatic region are presented in Table 6. The ratio of *n*-paraffinic, isoparaffinic and naphthenic carbons in saturate is 1:0.44:0.69 whereas that of respective compound types (Table 3, Fig.1) is 1:0.42:2.02. This indicates that the

Table 4 — Proton NMR Data on Saturates and Aromatics from North Gujarat Mix Vacuum Gas Oil

%H	Saturates	Aromatics
H_{ar}	0.00	9.82
H_{sat}	100.00	90.18
H_β	76.38	49.61
H_γ	23.62	20.73
H_α	0.00	19.84
$H_{\alpha-CH_3}$	0.00	7.24
$H_{\alpha-alk}$	0.00	12.60*
Branchiness index	0.31	0.42

*computed from $C_{ar,alk}$

Table 5 — ^{13}C NMR Data in the Aromatic Region and Structural Parameters of Aromatics from North Gujarat Vacuum Gas Oil Fractions

%C	
C_{sat}	67.10
C_{ar}	32.90
$C_{ar,H}$	15.34
C_{ar,CH_3}	3.77
$C_{ar,alk}$	9.84
$C_{ar,br}$	3.95
Structural Parameters	
H/C	1.667
H_{sat}/C_{sat}	2.101
f_a	0.329 (0.380*)
H_{aru}/C_{ar}	0.890 (0.729*)
σ	0.470 (0.447*)

*computed from ^{1}H NMR data

Table 6 — ^{13}C NMR Data in the Aliphatic Region of Saturates and Aromatics from Vacuum Gas Oil Fractions

% C	Saturates	Aromatics
C_{sat}	100.00	67.10
C_{n-p}	46.86	18.90
C_{i-p}	20.72	11.12
C_N	32.42	37.08
$C_{29.7}$	4.38	2.25
$C_{40.0}$	29.01	7.79
$C_{14.1}$	3.99	2.31
$C_{22.7}$	5.41	4.02
$C_{32.0}$	4.07	2.52
n	17.30	8.20

naphthenic compounds contain sufficient quantity of *n*- and isoalkyl chains as substituents. The average chain length computed[6] from ^{13}C NMR data of saturates (17.3) is lower than that obtained from GC analysis of urea-adductables from NGM VGO (26.9). This discrepancy may be due to the presence of large amount of naphthenic compounds which are taken into consideration while computing *n*, thus reducing the average number of methyl groups per chain. Relatively higher amount of naphthenic carbon in aromatics indicates the presence of naphthenes condensed with aromatics in larger amount.

The comparison of different types of carbons in saturates and aromatics of NGM and BH VGOs are shown in Fig.2. It reveals that naphthenic and isoparaffinic carbons are higher in NGM while paraffinic carbons are higher in BH saturate. The comparison of saturated carbons in aromatics shows dominance of naphthenic carbons in NGM and isoparaffinic ones in BH VGO. The distribution of aromatic carbons shows higher amount of $C_{ar,alk}$ and $C_{ar,br}$ in NGM and $C_{ar,H}$ and C_{ar,CH_3} in BH aromatics. Thus the aromatics from NGM VGO contain more condensed structures (aromatic-aromatic and aromatic-naphthenic).

Conclusion

NGM VGO is found to be rich in saturated hydrocarbons, predominantly naphthene structures. The aromatic compounds are rich in monoaromatics with naphthene substituents being predominant. The major portions of aromatic carbons are alkyl substituted and bridgehead indicating higher condensation of structures (aromatic-aromatic and aromatic-naphthenic).

The comparison of the data on NGM VGO with those of BH VGO reveals that although both the samples show nearly equal concentration of saturates, aromatics and polars, the distribution of various types of hydrocarbons is entirely different.

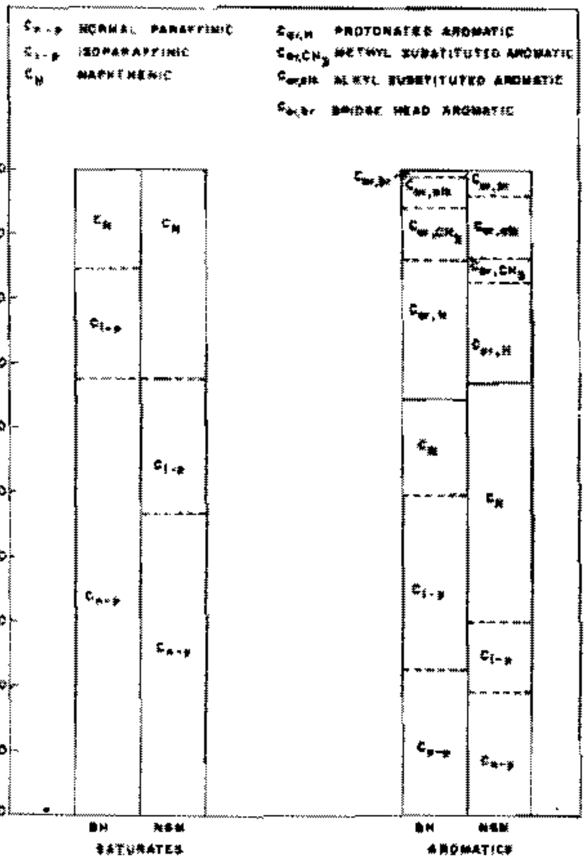

Fig. 2 — Comparison of the distribution of different types of carbons in the saturate and aromatic fractions of vacuum gas oils from Bombay High and North Gujarat mix crudes

Though these two VGOs contain different paraffinic concentrations, the ratio of *n*- to isoparaffins is the same in the two cases. The aromatics also reveal a predominance of naphthene structures on aromatic rings in NGM and alkylbenzenes in BH.

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References

1 White P J, *Oil Gas J*, **66** (1968) 112.
2 Hinds (Jr) G P, *Proc Am Petrol Inst, Div Refining*, **49** (1969) 147.
3 Nilsson P & Otterstedt J E, *J Appl Catal*, **33** (1987) 145.
4 Ramaswamy V, Sarowha S L S, Singh I D & Krishna R, *Indian J Technol*, **26** (1988) 374.
5 Ramaswamy V, Kumar P & Gupta P L, *Fresenius Z Anal Chem*, **317** (1984) 37.
6 Ramaswamy V, Sarowha S L S & Singh I D, *Indian J Technol*, **25** (1987) 486.