

RHEOLOGICAL CHARACTERISTICS, MOLECULAR WEIGHT AND POLYDISPERSITY AND ANALYTICAL STUDIES OF ASPHALTIC MATERIAL SEPARATED FROM INDIAN CRUDE OIL

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ABSTRACT

Asphaltic components present in crude oil create problems during production & refining processes. In the present paper some of the highlights of the work done at IIP, Dehradun on separation & characterization of asphaltic materials derived from some Indian crude oils viz. Viraj, North Kadi & Santhol crude oil have been summarized & presented. The studies carried out indicated that ethyl acetate and n-pentane are good solvents for precipitation of asphaltic components from Viraj & North Kadi crude oil residues and that yield of asphaltic components is a function of the nature and type of extracting solvent. The study suggests that solvent used for the extraction asphaltic components has an influence on molecular weight and polydispersity of asphaltic components without any definite trend. The number average molecular weight of them determined by VPO and GPC differs greatly. It has been observed that irrespective of the type and nature of the extracting solvents the separated asphaltic components are amorphous in nature. IR and ¹HNMR analysis indicated that the asphaltic components constitute mainly highly substituted aromatics having ether linkages, ketone and pyrolic N-H function and large number of methyl and methylene groups in alkyl chain substituents.

Keywords: Asphaltic Components, Effect of Solvent Analysis.

INTRODUCTION

Asphaltic components present in crude oils create problems during oils production & reeving process. They increases the viscosity resulting in the reduction of the flow of crude oil. They have a tendency to form coke & catalyst deactivation and poisoning during catalytic reeving processes. This paper reports some of the highlights of work done at IIP on separation and analysis of asphaltic materials derived from some Indian crude oils viz Viraj, North Kadi and Santhol [1-6].

MATERIALS AND METHODS

Separation of Asphaltic Components & Their Influence on Rheological Properties:

Viraj, North Kadi & Santhol crude oils of Gujrat region after dehydration were distilled under atmospheric condition upto 200⁰C + and these residues were used for separation of asphaltic components. The extraction of asphaltic components from these residues were carried out independently by two methods namely IP 143/78 (Method A) and Corbet method ASTM – 4124/84 (Method B) using petroleum ether 40-60⁰C, ethyl acetate, n-pentane & n-heptane as the solvents. The characteristics of crude oil residues 200⁰C + used for separation of asphaltic components are given in Table 1.

Table -1. Physical characteristics of crude oil residue 200⁰C

Characteristics	Viraj	North Kadi
Density at 15 ⁰ C	0.9454	0.9665
Viscosity, cSt		
At 40 ⁰ C	1426	2708
At 50 ⁰ C	761	1645
Pour Point ⁰ C	21	15
Carbon Residue, wt%	5.6	5.1

The yield of asphaltic components precipitated with different S/F ration using method A for both the crude oils residues have also been determined & shown in Table -2.

RESULTS AND DISCUSSION

Effect of solvent and solvent dilution ratio on yield of asphaltic components

The asphaltic components in both the crude oil residues increases asymptotically with S/F ratio varying from 5:1 to 50:1 vol/wt using ethyl acetate and petroleum ether as solvent. The yield percentage of asphaltic components beyond 30:1 S/F ration can be presumed to remain practically constant (Table-3, Figure-1). The asphaltic components concentration in both the crude oil residues at all dilution level show lower values in petroleum ether as compared to ethyl acetate. Thus highest values for asphaltic components are obtained when ethyl acetate is used as the extracting solvent.

Table-2. Yield, wt, % of asphaltic components by using different solvents

Solvents S/F Ratio	Viraj Crude Oil Residue 200 ⁰ C		North Kadi Crude Oil Residue 200 ⁰ C	
	Method A	Method B	Method A	Method B
	30:1	100:1	30:1	100:1
Ethyl Acetate	12.12	10.89	5.63	4.22
n-Pentane	6.16	5.02	2.34	1.64
Petroleum ether(40-60 ⁰ C)	4.11	3.78	1.55	1.04
n-Heptane	0.60	0.48	0.43	0.30

Table-3: Effect of S/F ratio on the yield of asphaltic components from crude oil residue using method A

S/F Ratio Vol./wt	Asphaltic components wt %			
	Viraj Crude Oil Residue 200 ⁰ C		North Kadi Crude Oil Residue 200 ⁰ C	
	Ethyl Acetate	Petroleum Ether (40-60 ⁰ C)	Ethyl Acetate	Petroleum Ether (40-60 ⁰ C)
50:1	12.04	3.86	5.34	1.51
35:1	11.93	3.87	5.42	1.53
30:1	12.12	4.04	5.64	1.56
25:1	9.43	3.46	5.48	1.50
20:1	6.83	2.77	4.46	1.08
15:1	3.63	1.56	3.76	0.85
10:1	2.35	0.99	1.93	0.18
5:1	1.08	0.21	0.76	

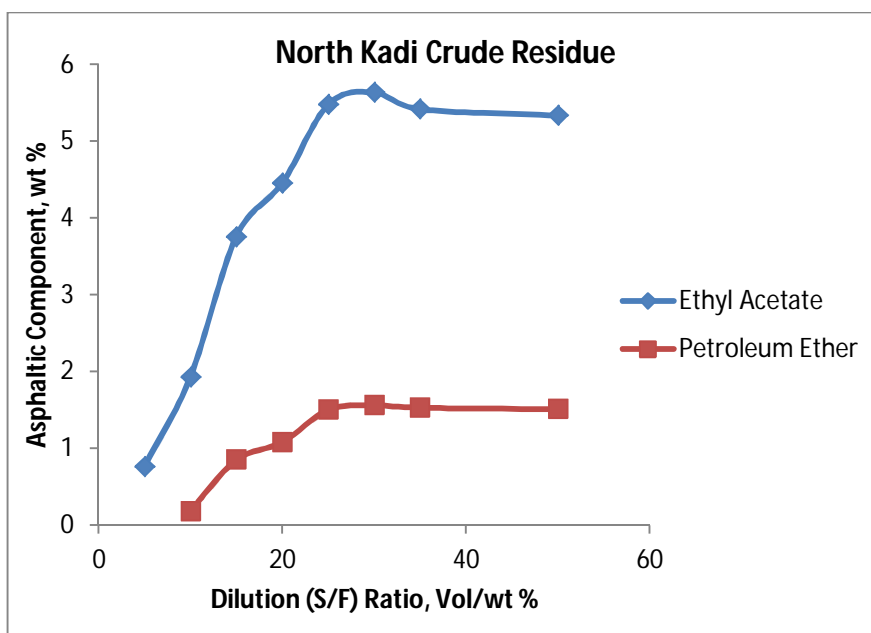
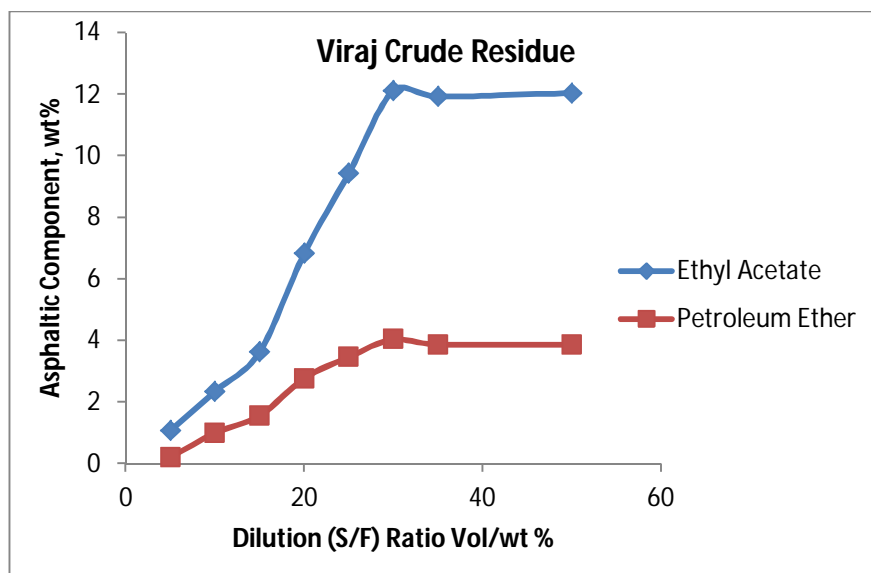


Fig. 1 Effect of dilution on the separation of asphaltic component from residue of crude oils

It is observed from Table -2&3 that the yield of asphaltic component is dependent on the physical properties particularly molecular weight and surface tension of the solvent. Effect of the physical properties of the solvent on the yield of asphaltic components is shown in Figure-2. These data indicated that in general with increasing boiling point, surface tension and molecular weight of the solvent the yield of asphaltic components decreases. Table-2 further indicated that

among paraffinic solvents n-pentane gives the highest yield of asphaltic component followed by petroleum ether while lowest yield is with n-heptane. This trend is observed with both crude oils. These observations confirms that asphaltic components yield is a function of the physical properties of the solvents viz. surface tension, molecular weight and solubility parameters.

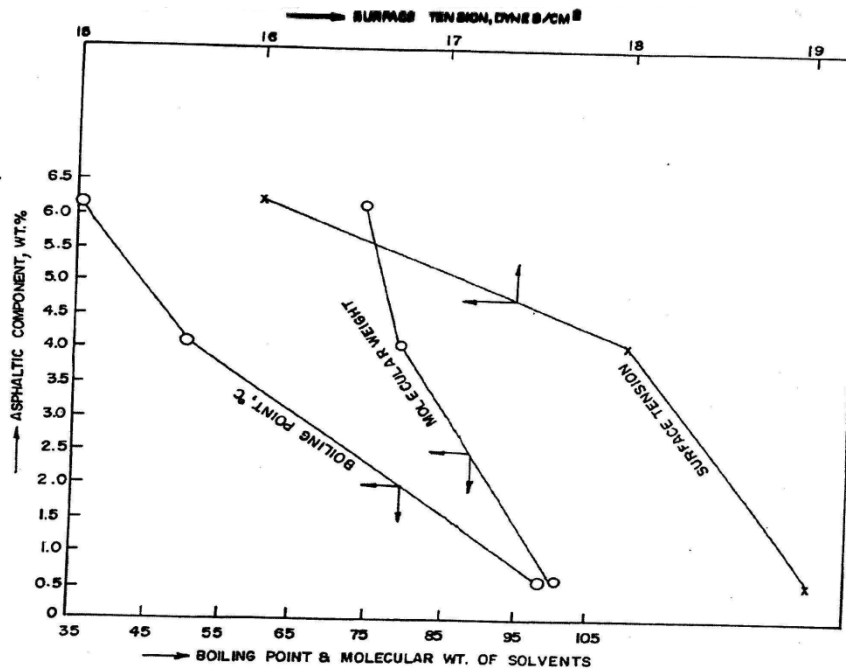


Figure-2 : Relationship between characteristics of solvent and wt% of asphaltic components

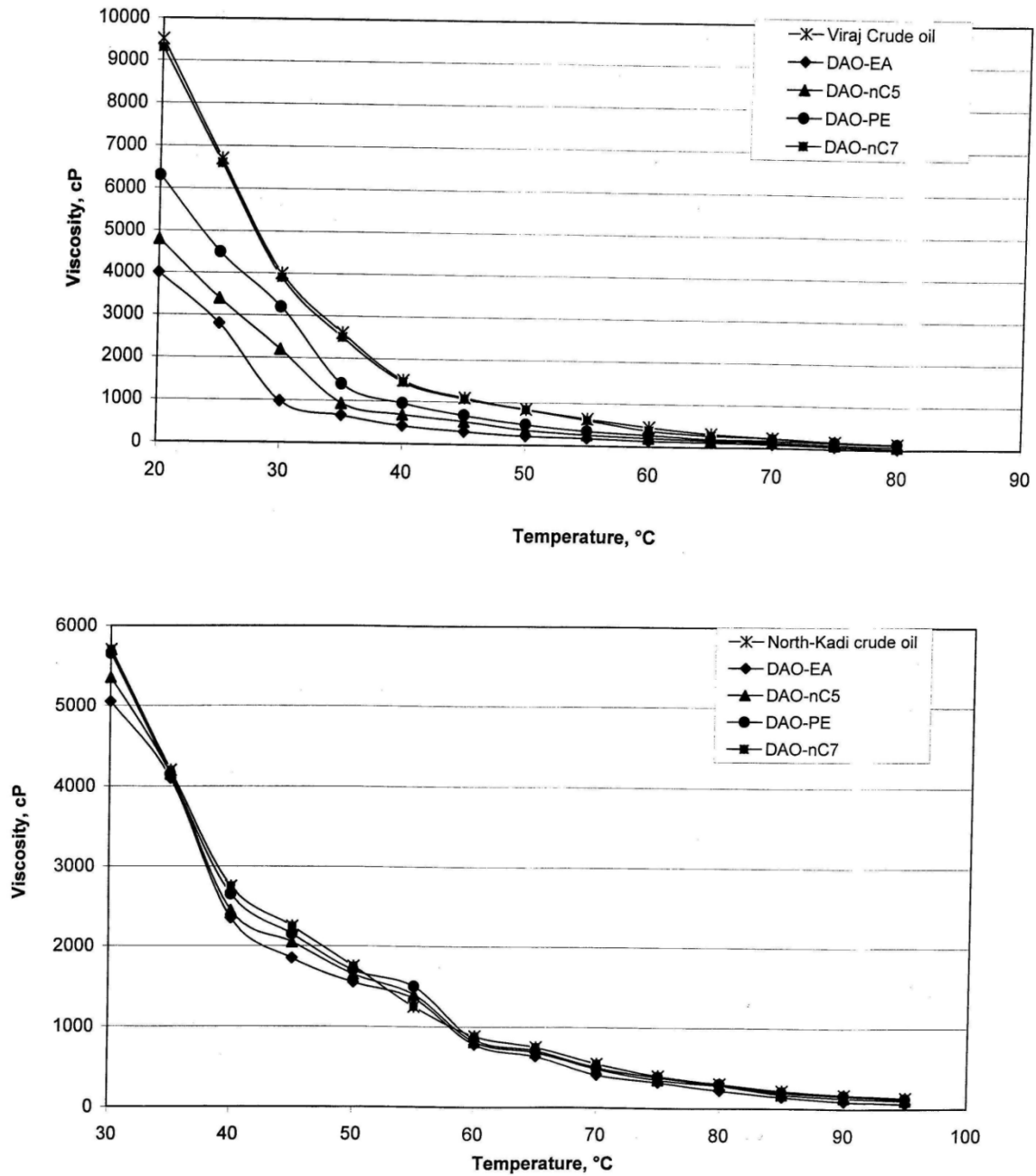


Figure-3: Effect of asphaltic component on viscosity – temperature behavior (A) Viraj crude residue 200⁰C+ (B) North Kadi crude residue 200⁰C+

Viscosity temperature behavior:

The viscosity/shear stress-temp behavior of 200⁰C + residues from crude oils before & after removal of asphaltic components have been determined by AIMIL-EMILA rheometer. Measurement were made at decreasing temp. in step 5⁰C from 95⁰ C/ 80⁰C to 20⁰C.

From Fig. 3 the viscosity increases with decrease in temperature and this trend is quite independent of the composition of the sample. These data further indicate that increase in viscosity from higher to a particular lower temperature levels viscosity increases abruptly. The magnitude of this temperature level at which abrupt increase in viscosity in observed however, depends upon the type and nature of the crude oil (Figure-3).With parent crude oil residues the change in temperature is obtained at high temperature levels and when the asphaltic materials are removed, these temperature levels also shifted towards the lower side.

Analysis of asphaltic components: VPO & GPC analysis

Number average molecular weight (Mn) of the samples (asphaltic components separated from Viraj & North Kadi crude oil residue 200⁰C+) were measured by using vapour pressure osmometer (VPO-KNAUR) as ASTM-D-2503 procedure (Table-5). The different average molecular weight and polydispersity of the asphaltic components samples were determined by GPC. Two mixed bed column (Jordi Gel Mixed ‘C’ 5μ and PL-GEL Mixed ‘C’ 5μ) arranged in series and dichloromethane (HPLC grade) was used as mobile phase in GPC analysis. For the calibration of the column system mono – disperse polystyrene polymer mixtures were used.

Table-4: Elemental Analysis of Asphaltic Components present in Crude Residue

Solvents	Vijay			North Kadi		
	C%	H%	C/H	C%	H%	C/H
Ethyl Acetate	86.91	10.35	0.69	86.62	10.32	0.68
n-Pentane	85.75	10.03	0.71	87.14	10.21	0.71
Petroleum ether 40-60 ⁰ C	86.17	11.65	0.62	86.88	10.58	0.68
n-Heptane	-	-	-	86.12	10.22	0.70

Table-5: Average molecular weights & polydispersity of asphaltic components present in Viraj & North Kadi crude residue 200⁰C

Asphaltic Components separated using different solvent (S/F ratio 30:1)	Avg Mole cular Wt.(VPO)	Different average molecular wt. (GPC)					Polydispersity			
		Mn1	Mn2	Mw3	Mz4	Mz+1(5)	Mv(6)	Mn1 Mn2	Mw(3) Mn(2)	Mz(4) Mw(3)
Viraj Crude Residue										
Ethyl Acetate	5880	2099	28712	197685	340750	28711	2.88	13.7	6.9	1.7
n-Pentane	4440	1704	61303	343065	499257	61302	2060	36.0	5.6	1.5
Petroleum Ether (40-60°C)	3650	2265	51373	306848	474317	51372	1.60	22.6	6.0	1.5
North Kadi Crude Residue										
Ethyl Acetate	5274	1531	47139	293052	459752	47135	3.44	30.8	6.2	1.6
n.pentane	6414	1315	42452	314236	474511	42452	4.48	32.2	7.4	1.5
Petroleum Ether (40-60°C)	4945	1189	39320	320015	482178	39319	4.16	32.9	8.1	1.5

Table-5 summarizes the molecular weight obtained by vapor pressure osmometry and Gel permeation chromatography. Analysis of the data reveals a mix response of the effect of solvents used for extraction of asphaltic material on the number average molecular molecular weight (Mn) measured by VPO. For Viraj crude residue the highest (5880) and lowest (3650) number average molecular weight of asphaltic components are achieved when ethyl acetate and petroleum ether (40-60°C) respectively have been used as the extracting solvent. Similar trend has also been observed for North Kadi crude indicating that ethyl acetate extracted asphaltic components has higher agglomeration compared to those extracted by petroleum ether (40-60°C). The Mn value measured by Gel permeation chromatography are found to be substantially lower to those determined by VPO for all the asphaltic samples irrespective of the nature of extracting solvent. The apparent reason for low molecular wt values by GPC may be that all asphaltic samples have again been extracted in dichloromethane (the solvent used as mobile phase in GPC) and filtered through a fine filter to remove any particulate material and getting a clear solution ready to inject in GPC system. This process might have removed some insoluble

components having high molecular weights. It seems that M_n values determined by GPC pertain to those components of asphaltic components which are soluble in dichloromethane and do not represent the whole product as in case of VPO. Therefore the M_n values obtained by GPC could not be correlated with those obtained by VPO.

For asphaltic components derived from Viraj crude, the M_n (VPO) and M_n (GPC) ratio varies from 1.61 to 2.88 where as in case of asphaltic components derived from North Kadi crude residue, this ratio varies from 3.44 to 4.88. This ratio did not show a definite trend as regard to the nature and type of extracting solvent.

In GPC analysis the sample components have got resolved according to molecular weight and thus yielded a molecular mass distribution pattern as well as the averaged out values of M_n , M_w , M_n and M_z+1 , and also polydispersity among them (Table-5).

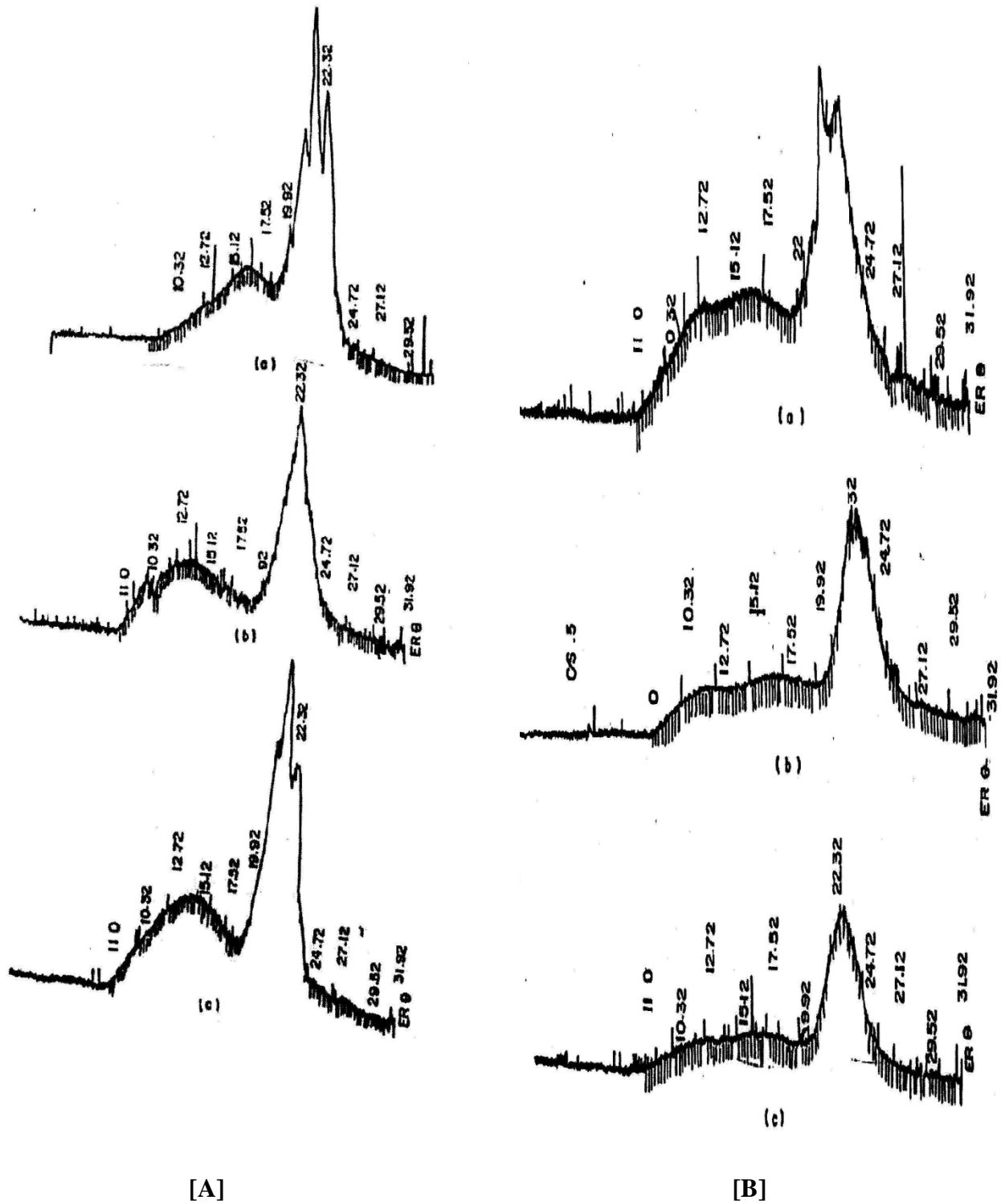


Fig-4: GPC Chromatograms for asphaltic components drive from (A) Viraj crude residue 200⁰C+ (B) North Kadi crude residue 200⁰C

X-ray Diffraction Analysis:

The X-ray diffractograms of the asphaltic samples of Viraj, North Kadi & Santhol crude oil were recorded on a GE XRD -6 diffractometer equipped with XRD -900 detector. A few diffractograms showing the variation of d' values with 2θ from ~ 2 to 36° are shown in Figure-6.

The X-ray diffractograms of asphaltic components separated from Viraj and North Kadi crude residue does not give any sharp peaks for 2θ variation upto 36° . Similar to diffractograms as shown in Figure -5, the peaks are hallow in all cases. This indicates that the asphaltic components derived from both the crude oil residues are quite amorphous in nature and do not show any crystallinity for the entire range of 2θ .

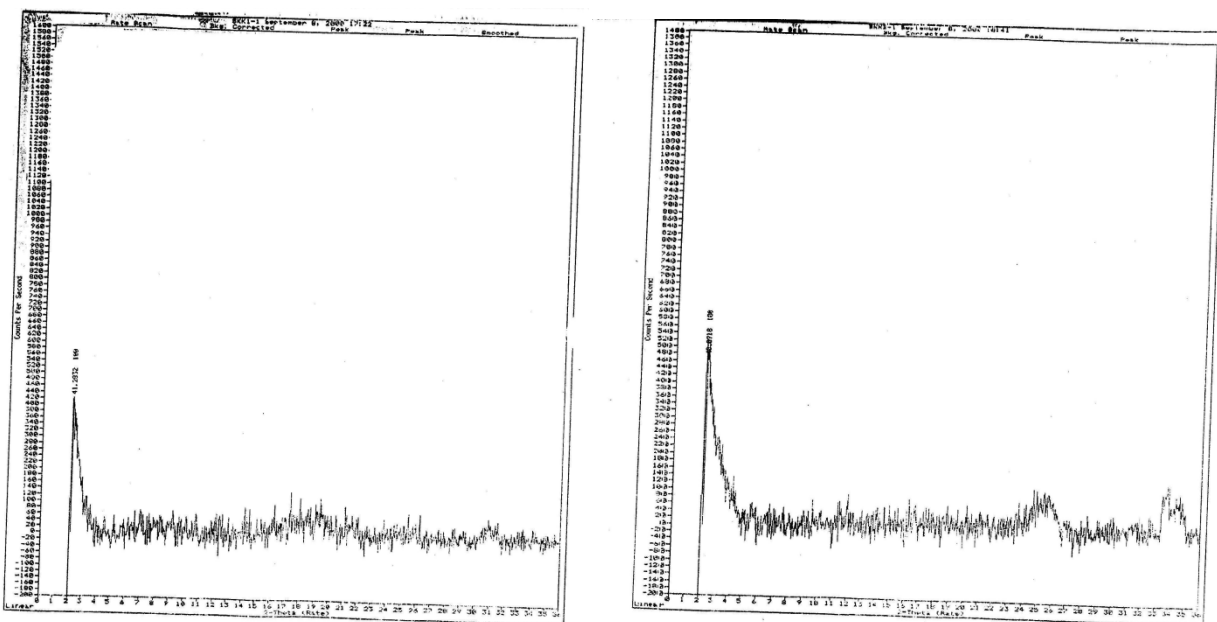


Figure-5: X-ray diffractogram of asphaltic components [A] Viraj crude oil residue 200⁰C+ [B] North Kadi crude oil residue 200⁰C+

Thermal Gravimetric Analysis (TGA):

For studying the thermal behavior viz wt% loss with temperature/time, the thermal analyzer (TA9900) was used for asphaltic components of Viraj, North Kadi & Santhol crude oils. The loss of weight obtained for the samples under different condition of temperature were recorded.

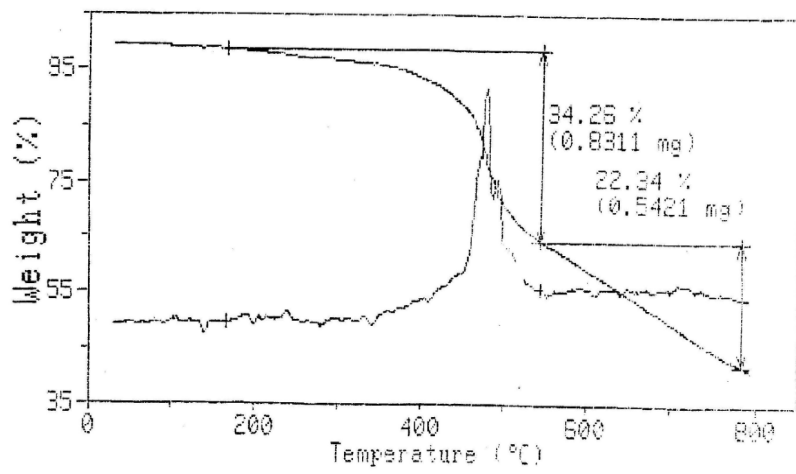
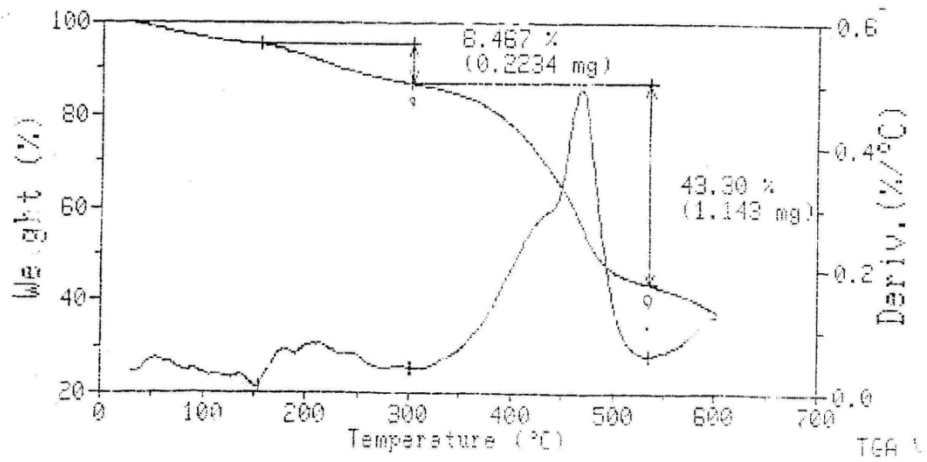


Fig-6: Thermal behavior of asphaltic components derived from (A) Viraj crude oil residue 200⁰C+ (B) North Kadi crude oil residue 200⁰C+

The data on thermal behavior of the asphaltic components as presented in Figure-6 for typical samples indicated that initially irrespective of the nature of the extracting solvent the wt% loss upto about 250-300⁰C is slow but beyond that upto about 500-600⁰C decreases very sharply. The maximum loss in wt% in majority of cases is obtained between 450-500⁰C. Thus these asphaltic components seems to be quite amorphous in nature.

IR Analysis:

The asphaltic materials obtained from Viraj (V), North Kadi (NK) and Santhol (S) crude oil residues 200⁰C+ by employing n-pentane (C5), n-heptane (C7), petroleum ether (PE)(40-60⁰C) & ethyl acetate (EA) as extracting solvents was finally dried in an oven. These insolubles have been accordingly abbreviated as V-C5-1, V-C7-1, V-PE-1, V-EA-1, NK-C5-1, NK-C7-1, NK-PE-1, NK-EA-1, S-C5-1, S-C7-1, S-PE-1 & S-EA-1.

Infrared absorption spectrum of each insoluble sample was obtained by the halide disk method by taking about 2 mg sample mixed with 200mg of spectroscopic grade KBr powder. IR absorption spectra were recorded on this wafer by coadding 9 consecutive scans in the 4000-650 cm⁻¹ range, using a Perkin Elmer 1760XFTIR spectrophotometer equipped with DTGS detector and IRDM software for data processing. Thus recorded spectrum was divided by the concentration of sample in the wafer (weight per unit area of wafer, mg/cm²) to obtain the sample spectrum in normalized absorption units to enable quantitative comparison among various samples. The probable assignments of significant IR absorption bands found in the spectra of insolubles. A typical IR spectrum of S-PE-1 fraction is shown in Figure-8 and is compared with corresponding in-solubles of Viraj and North Kadi crude oils. Assuming that each solvent insoluble fraction may be represented by a hypothetical 'average molecule', we have derived typical average molecular parameters of the hypothetical asphaltic "molecule" from IR spectral data (Table-6).

IR spectra have shown following general trends for all insolubles. There is a broad envelop of peaks in the XH stretching region (3700-3100cm⁻¹) showing, instead of any sharp absorption, a maximum near 3400-3430 cm⁻¹. Only the spectrum of NK-PE-1 showed a partially resolved shoulder band at 3465 cm⁻¹ assigned to pyrrollic free ν (N-H) is assignment to ν(O-H) vibrations of free carboxylic or phenol functionally is least probable because other associated absorption bands are not detected unambiguously in other regions of the spectra. The broadening of this band towards lower frequencies is suggestive of the strong hydrogen bonding of these functional groups that could be anticipated in the solid asphaltene samples. The area under this envelope indicated substantial concentration of heteroatomic functional groups in the insolubles, the largest being in fractions of North Kadi asphaltenes, and lowest in Viraj fractions. The species containing these functional

groups appear to be extracted more into the solvent phase with ethyl acetate; in case of Viraj fractions the trend is not clear. The strong absorption due to alkyl $\nu(\text{C-H})$ stretching in 3000-2800 cm^{-1} region shows that all insolubles contain a large number of methyl and methyl groups.

Table-6: Structural parameters of solvent-insoluble fractions of asphaltic components estimated from their IR absorption spectra

Insolubels		Viraj				North Kadi			Santhol			
Parameter		C5-I	PE-I	C7-I	EA-I	C5-I	PE-I	EA-I	C5-I	PE-I	C7-I	EA-I
$\nu(\text{C}=\text{C})$ $\nu(\text{CH}_3+\text{CH}_2)$	$\frac{A_{1605}}{A_{2920}}$	0.11	0.33	0.32	0.33	0.57	0.58	0.80	0.62	0.46	0.49	0.70
$\nu(\text{C}=\text{C})$ $\nu(\text{CH}_3+\text{CH}_2)$	$\frac{A_{1605}}{A_{2850}}$	0.18	0.44	0.44	0.46	0.78	0.80	0.97	0.80	0.52	0.62	1.03
$\overline{\nu}(\text{CH}_2)_{n>4}$ $\nu(\text{CH}_3+\text{CH}_2)$	$\frac{A_{721}}{A_{2920}}$	0.04	0.06	0.06	0.03	0.03	0.04	0.06	0.04	0.08	0.05	0.03
$\overline{\nu}(\text{CH}_2)_n$ $\delta(\text{CH}_3+\text{CH}_2)$	$\frac{A_{721}}{A_{1450}}$	0.18	0.12	0.16	0.07	0.05	0.08	0.08	0.06	0.17	0.11	-
$\delta(\text{CH}_2)_n$ $\delta(\text{CH}_3+\text{CH}_2)$	$\frac{A_{1375}}{A_{1450}}$	0.58	0.79	0.78	0.67	0.84	0.84	0.92	0.51	0.79	0.83	0.87
$\gamma(\text{CH}_{ar4})$ $\gamma(\text{CH}_{ar1})$	$\frac{A_{745}}{A_{870}}$	0.63	0.57	0.67	0.38	0.75	1.20	0.75	0.78	0.50	0.64	0.80
$\gamma(\text{CH}_{ar2,3})$ $\gamma(\text{CH}_{ar1})$	$\frac{A_{815}}{A_{870}}$	0.88	1.14	1.11	-	0.88	1.00	1.23	0.78	0.88	0.79	1.0
$\gamma(\text{CH}_{ar2,3})$ $\gamma(\text{CH}_{ar4})$	$\frac{A_{814}}{A_{747}}$	1.40	-	1.43	-	1.17	0.83	1.08	1.00	1.75	1.22	1.25

The absorption at 3030-3060 cm^{-1} , though not well resolved from neighboring strong alkyl and broad XH bands, shows the presence of unsaturated carbons. These are assigned to $\nu(\text{C-H})$ since there are corresponding strong to medium intensity absorptions of aromatics observed at lower frequencies (1600 and 900-650 cm^{-1}). The absorption due to allene and alkyne type functions is absent or very weak. The trends in the values of both A_{1600} aromatic $\nu(\text{C}=\text{C})$ and aromatic to aliphatic ratio $[\nu(\text{C}=\text{C})/(\text{CH}_3+\text{CH}_2)]$ show that, for corresponding solvent insolubles, the aromaticity increases in the order Viraj>North Kadi>Santhol except S-EA-I. The elemental analysis results (C/H ratio) reported suggest that the aromaticity of insolubles should decrease in the order C5-I>C7-I>EA-I>PE-I. No such common trend could be established from present IR data. The aromaticity of all fractions of North Kadi, for which the variation in C/H ratio was small, however appears from IR data to remain more or less the same. The multiplicity of bands in 1850-650 cm^{-1} region, particularly those of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ linkages, appear to mask the aromatic and all other bands making it difficult to measure their true intentions. Therefore, all parameters in Table -6 should be treated as approximate and the interpreted

trend in chemical composition of average asphaltic molecule as tentative pending further detailed investigations. The spectral features in 900-700 cm^{-1} region indicated that all kinds of substituents on aromatics are present albeit with a marginal difference in their relative abundance depending upon the solvent employed for separation of asphaltene components, Viraj insolubles contain aromatics with the highest degree of substitution and North Kadi insolubles the lowest. The concentration of 1,2 substituted aromatics in a given solvent insoluble fraction seems to be lower than that of mono or 2,3 substituted aromatics in the same fraction. These features suggest also the presence of condensed ring aromatic structures in insolubles, which is further supported by observed very weak overtone bands of highly aromatic compounds (PAH) in 2000-1800 cm^{-1} region.

There are several bands in 1300-1100 cm^{-1} region assigned to $\nu(\text{C-O})$ and $\delta(\text{O-H})$ vibrations in phenoxy compounds, and those in 1100-1000 cm^{-1} region to $\nu(\text{C-O})$ of aliphatic ethers. It is thus guessed that aromatic condensed rings may be linked via ether functions. The weak absorption near 1655 cm^{-1} shows the presence of conjugated aromatic ketones. It is not possible to speculate further about the nature of carbonyl groups in any insoluble since, even if there is a hidden absorption due to it, it is inseparable from the broad-based peak in 1850-1550 cm^{-1} region. Such functionality however may be responsible for strong hydrogen bonding and broadening of the 3700-3100 cm^{-1} band. As there is no detectable absorption of $\nu(\text{CH}_2)_{n<4}$ vibration observed at 784 cm^{-1} the alkyl chains present in the insolubles seem to be longer than four carbon atoms, but their numbers appear to be small due to weak intensity of the absorption of $\nu(\text{CH}_2)_{n<4}$ vibration at 721 cm^{-1} . This together with high degree of aromatic substitution indicates that these alkyl chains are part of branched paraffin or are attached to aromatic rings.

¹HNMR Analysis:

The ¹HNMR spectra were recorded with a Bruker model DRX-300 NMR spectrometer. The sample solution were prepared in CDCl₃ using TMS as an internal standard. The frequencies and assignments of various peaks observed in the ¹HNMR spectra of select insolubles studied are given in Table-7 which also includes the values of different structural parameters derived from the NMR data.

¹HNMR spectral data shows North Kadi residue to contain, as compared to Viraj residue, a slightly lower concentration of paraffin species but 2-3 times higher concentration of aromatics (Table-7). Among aromatic, the mono aromatics are about 18-20%, polyaromatics 16-17% and di-substituted aromatics 63-70%. The 16-24% of the alkyl chain protons is located at a position, 60—65% and b position and 16-19% at g or further away positions from the aromatics ring. Interestingly, the proportion of polyaromatics in total aromatics and that of

protons γ to aromatic ring in paraffin chains remained almost constant in all insolubles. This is also reflected in the branchiness index remaining fairly within a narrow range (0.27-0.30).

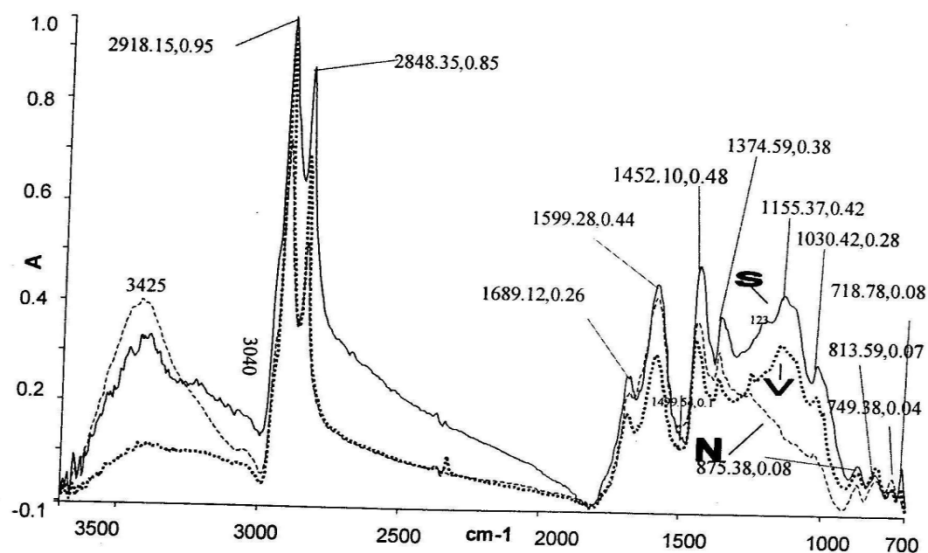


Figure-8 : Comparison of IR spectra of PE-I insoluble fractions of components of Viraj (V), North Kadi (NK) and Santhol (S) crude oil. Absorbance (A) is per mg of sample per cm^2 of halide pellet

Table-7: ^1H NMR data of select solvent-insoluble fractions of Viraj and North Kadi crude oil residues

Parameter		δ, ppm	V-C5-I	V-EA-I	NK-C5-I	NK-PE-I
HS_α	% alkyl protons α to aromatic ring	4.0-2.0	15.78	14.94	15.51	19.81
HS_β	% alkyl protons β to farther to aromatic ring	2.0-1.0	59.75	61.35	54.13	49.51
HS_γ	% alkyl protons γ to farther to aromatic ring	1.0-0.5	17.21	17.90	16.34	13.50
$\text{H}_{\text{ar-mono}}$	% mono substituted aromatics	7.1-6.0	0.95	1.06	2.87	2.23
$\text{H}_{\text{ar-di}}$	% di-substituted aromatics	8.2-7.1	5.06	3.73	8.89	12.13
$\text{H}_{\text{ar-poly}}$	% poly-substituted aromatics	9.0-8.2	1.25	1.02	2.26	2.82
HS_{total}	total paraffinic hydrogens	4.0-0.0	92.74	94.19	85.98	82.82
HA_{total}	total paraffinic hydrogens	9.0-6.0	7.26	5.81	14.02	17.18
BI	Branchiness index	$\text{HS}_\beta / \text{HS}_\alpha$	0.28	0.29	0.30	0.27

CONCLUSION:

The studies thus indicated that these asphaltene components constitute mainly aromatic species (substituted) and condensed aromatic ring structures having ether linkages ketone and pyrolic (N-H) functions and a large number of methyl and methylene groups in their alkyl substituents. Presence of some hetero aromatic functionality involving O, N and S are also indicated.

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