Characteristic changes of asphaltenes during visbreaking of North Gujarat short residue

I. D. Singh, V. Kothiyal, V. Ramaswamy and R. Krishna
Indian Institute of Petroleum, Dehradun 248 005, India

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The physico-chemical properties and structural parameters of asphaltenes separated from feed (short residue) and visbroken products (+500°C) were estimated using various instrumental analytical techniques. Analysis of the variation of these properties and parameters with varying severity of operation (temperature and residence time in soaker visbreaking), provided information regarding the chemistry of visbreaking, and in particular the structural changes with respect to asphaltenes. The major reactions are dealkylation of aromatic clusters, and, at high severity, dehydrogenation and/or ring opening of naphthenic rings condensed with aromatic clusters. These reactions promote the condensation of aromatic clusters to yield more asphaltenes and coke.

(Keywords: asphaltene; petroleum products; structural properties)

Petroleum residues are rich in asphaltenes, which do not undergo cracking easily and are coke precursors in thermal and catalytic cracking. Asphaltenes also impart undesirable properties to the residues, such as high viscosity. An inexpensive and versatile form of thermal cracking is visbreaking. Visbreaking reduces the viscosity and pour point of the products, thus producing low viscosity fuel oil. Visbroken products boiling in the vacuum gas oil range may be used as feed for catalytic cracking.

A study[1] of the structural changes of asphaltenes during catalytic hydroprocessing was made, based on their physical and chemical properties. The role of asphaltenes in the visbreaking process has been studied[2] through molecular weight and structural changes of asphaltenes under laboratory and pilot plant pyrolysis of atmospheric residues and vacuum gas oil. The characteristic and structural changes of asphaltenes during visbreaking and catalytic hydroprocessing have been the subject of several papers[3–8]. The variation in distributions of heavy metals and heteroatoms in the asphaltenes and maltenes with varying severity of vacuum residue visbreaking has also been reported[9].

In all these studies, only one of the two operating variables (either temperature or residence/contact time) was varied under coil visbreaking or pyrolysis operations. This paper reports on structural changes accompanying visbreaking in both coil and soaker drum. The structural changes were also monitored at different severity levels, obtained by variation of both temperature and residence time.

EXPERIMENTAL

The soaker visbreaking pilot plant included six stainless steel coils (total volume 530.1 ml including interconnections): the first three were used for preheating, and the last three were used for cracking. Further cracking was performed in a soaker drum (length 25 cm, i.d. 10 cm). To overcome the heat losses from the surface as well as those due to the endothermic nature of the cracking reactions, the soaker drum was heated from the outside to maintain a proper temperature difference between inlet and outlet. The outlet temperatures of the three cracking coils were maintained at 455–460°C, and the inlet and outlet temperatures of the soaker drum were 433–440°C and 426–434°C respectively. The feed flow rates were varied from 7.5 to 18.0 l/h^{-1} in different experiments. In all the experiments, the soaker outlet pressure was maintained at 1.8 MPa, and water injection was 1 vol%. The short residue (+500°C) was prepared from the liquid products on a vacuum distillation unit.

Asphaltene separation

The nC_5-asphaltenes from feed as well as products were separated as reported previously[10]. As the maltenes were to be further separated by column chromatography, n-pentane was chosen as the precipitating solvent to avoid material loss due to permanent adsorption of n-heptane soluble asphaltenes and resins[11]. To estimate the stable asphaltenes, nC_5-asphaltenes were Soxhlet extracted with n-heptane and then with toluene. The insolubles in toluene were assumed to be the coke formed during visbreaking.

Characterization

Detailed characterization studies were carried out on the nC_5-asphaltenes. The elemental compositions were determined with a CHN elemental analyser and a Perkin-Elmer ICP-6500 system, and the average molecular weights were determined in toluene at 37°C, with a vapour pressure osmometer (VPO). The proton n.m.r. spectra were recorded in $CDCl_3$ solution at a frequency of 80.13 MHz. The spectra were obtained using 32 scans with a 60 s interpulse interval. I.r. spectra were recorded on a FT-i.r. spectrometer in CS_2 and C_2Cl_4 solutions by co-adding 32 scans and subtracting the

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Table 1 Yields and physicochemical data for asphaltenes from feed and for visbroken products

Conversion (wt%)	0	5.3	5.6	6.6	7.2	9.1
Yield (wt% on residue basis)						
nC_5-asphaltenes	13.9	32.0	31.1	36.8	32.7	45.9
nC_7-asphaltenes	3.0	25.3	23.6	25.0	24.9	29.0
Molecular weight						
nC_5-asphaltenes	2510	2436	2688	2100	2614	3357
nC_7-asphaltenes	3190	8375	6700	8221	7791	7283
CCR (wt%)						
nC_5-asphaltenes	35.3	57.5	62.7	77.6	63.6	70.4
Elemental composition of nC_5-asphaltenes						
C (wt%)	84.7	85.1	86.2	86.6	88.6	87.5
H (wt%)	8.2	7.7	7.4	7.6	7.9	7.1
N (wt%)	0.8	1.0	1.2	1.2	1.3	1.3
S (wt%)	1.8	1.3	1.1	0.4	0.9	0.1
O (wt%)[a]	4.5	4.9	4.1	4.1	1.3	4.0
V (ppm)	41.9	48.5	48.6	43.4	48.0	45.2
Ni (ppm)	857.5	984.6	956.8	795.0	994.7	803.0
Fe (ppm)	76.5	125.9	68.3	34.3	140.0	66.0
Atomic ratio						
H/C	1.16	1.08	1.03	1.05	1.07	0.97
$N/C \times 10^3$	8.38	10.33	11.43	11.94	12.32	12.22
$S/C \times 10^3$	8.06	5.68	4.87	1.90	3.90	0.47

[a] Obtained by difference

solvent spectra from the sample. Thermogravimetric studies of the asphaltenes were carried out up to 850°C in argon atmosphere (flow rate 25 ml min^{-1}) with 10°C min^{-1} heating rate.

RESULTS AND DISCUSSION

The conversion to products boiling below 150°C increased with increasing severity, and this conversion can therefore be used as a consolidated measure of the operation severity. The yield and physicochemical data of asphaltenes from the feed, as well as products, at different conversion levels, are reported in *Table 1*. The nC_5-asphaltenes yield, their molecular weight and Conradson carbon residue (CCR) contents increase with increasing conversion. Similar trends in the nC_7-asphaltene and coke (toluene insolubles) yields are observed (*Figure 1*). These trends are attributable to cracking of resins (which disturbs the equilibrium or reduces the peptizing power of the maltenes) as well as dealkylation of polyaromatic rings, which permits the aggregation of these rings into bigger molecules and hence yields higher molecular weights and CCR values. The asphaltenes polymerize by condensation, which can be facilitated by increasing dealkylation. This polymerization is reduced by the association of asphaltenes with resins present in maltenes[12]. At high conversion, there is a significant increase in coke yield (*Figure 1*). This is due to severe dealkylation, which enhances aggregation of asphaltene sheets, and possibly due to dehydrogenation and/or splitting of naphthenic rings condensed with aromatic clusters. The evidence for the presence of significant amounts of naphthene-aromatics in the feed can be obtained from the data on vacuum gas oil (VGO) and short residue from the same origin[13,14].

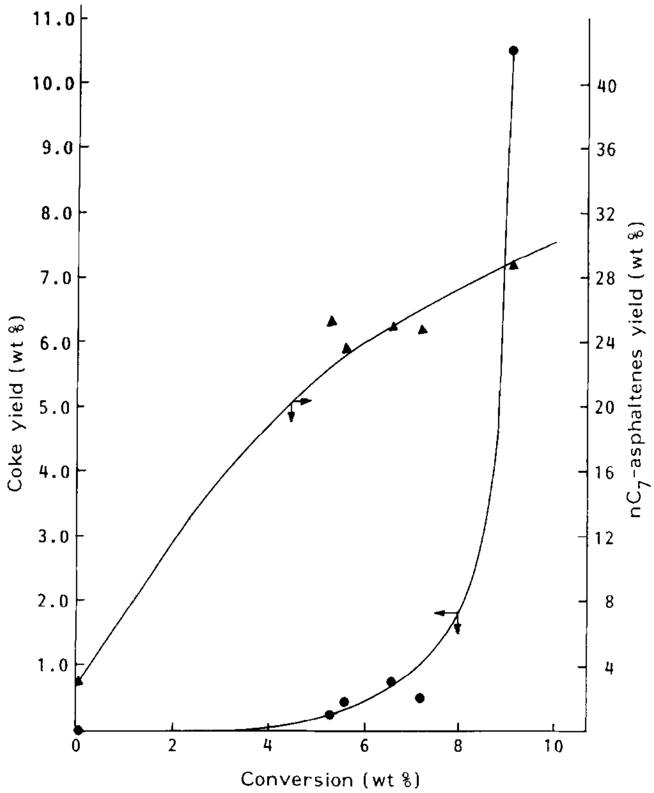

Figure 1 Variation in yields of: ●, coke; and ▲, nC_7-asphaltenes with conversion

The variations of H/C, S/C and N/C atomic ratios of nC_5-asphaltenes with increasing conversion are presented in *Table 1*. The H/C and S/C ratios decrease with increasing conversion, while an increasing trend is observed in the N/C ratio. This indicates that nitrogen

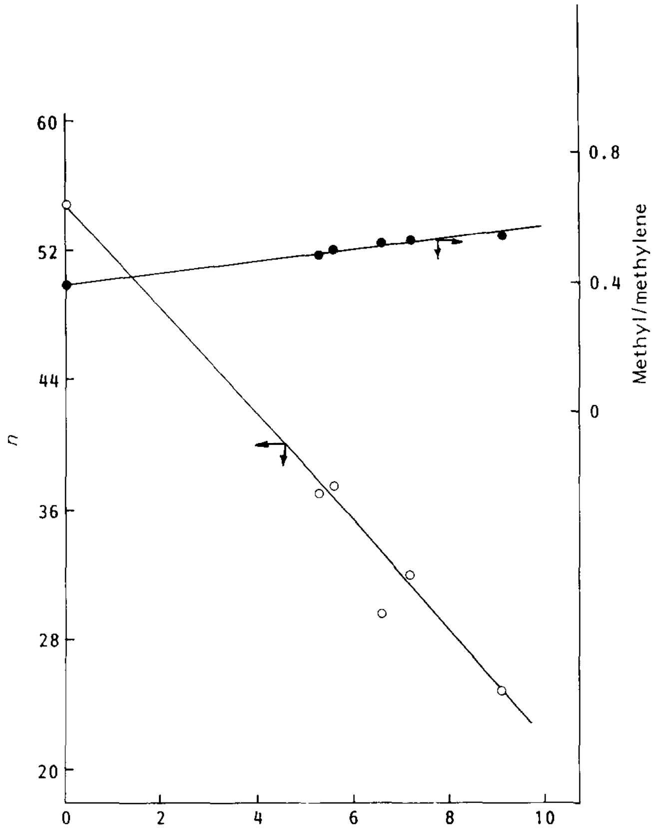

Figure 2 Variation in number of paraffinic methylene groups per average molecule, n, and methyl/methylene ratio of nC_5-asphaltenes with conversion

atoms are present as a part of the complex condensed aromatics that concentrate in the asphaltenes. The relatively steeper decrease of S/C ratio with conversion is due to weaker C—S bonds that break more readily than C—C bonds in dealkylation, thus reducing the H/C ratio.

I.r. spectroscopy has been used to estimate[15] the number of paraffinic methylene groups per average molecule (n) as well as the methyl/methylene (CH_3/CH_2) ratio of nC_5-asphaltenes. The estimation of n involves the average number molecular weight, which is artificially very high because of strong inter-molecular association in the solvent. At the temperature used in VPO measurement, the values of n are thus not absolute, but their relative variation can be used to establish trends. The variation of these two parameters with conversion is shown in *Figure 2*. A significant decrease in n with severity indicates removal of longer alkyl chains from condensed aromatics in asphaltenes. The increasing trend of the CH_3/CH_2 ratio indicates that longer alkyl chains are converted into shorter ones. The slow variation of CH_3/CH_2 with severity can be rationalized by considering the contribution of naphthenic methylene groups at 1462 cm^{-1}, which was used to compute CH_3/CH_2 ratio. The reduction of naphthenic methylene is much slower than that of paraffinic methylene, as dehydrogenation and/or ring opening of naphthenic rings is found to be pronounced only at higher severity.

Proton n.m.r. spectrometry was used to estimate some average structural parameters[16] of the asphaltenes, and the variations with conversion are shown in *Figure 3*. The ratio of aliphatic to aromatic hydrogens (H_{al}/H_{ar}) decreases with increase of conversion, due to the increase in removal of aliphatic chains from aromatic clusters of asphaltenes. The increase in aromaticity (f_a) with conversion is very slow compared with the decrease of H_{al}/H_{ar}. This is because of the presence of a large amount of aromatic carbon (due to higher condensation) and aliphatic hydrogens (mostly present as alkyl groups) in asphaltenes as compared with aliphatic carbons and aromatic hydrogens. Therefore, dealkylation affects H_{al}/H_{ar} more significantly than aromaticity. The increase in fraction of substitutable aromatic carbons (H_{aru}/C_{ar}) after a certain conversion value is due to either dehydrogenation to aromatics or ring opening of naphthenes condensed with aromatic clusters at these conversion levels. This is contrary to the data of Favre and Boulet[4], who estimated H_{aru}/C_{ar} for asphaltenes from feed and product obtained at a single severity, which may not have been sufficient to dehydrogenate or split open the naphthene rings. In this study also, at lower conversion where dealkylation is predominant (*Figure 3*), little decrease was observed, which may be due to polymerization of aromatic clusters. The degree of substitution in substitutable aromatic carbons (σ) decreases to a constant level. A significant decrease of H_{aru}/C_{ar} and increase of σ values at very high conversion (9.1 wt%) could be due to a high level of condensation of aromatic clusters, which increases bridgehead carbons. As the total peripheral aromatic carbons are decreased, the fraction of substituted aromatic carbons will increase, even if the substitution is of the same order. This is corroborated by the high value of coke at this conversion (*Figure 1*).

Thermogravimetric (TGA) studies of asphaltenes were carried out to corroborate the inferences obtained from aggregation (molecular weight), CCR and coke data. In TGA, distillation normally takes place up to 400°C, and above 400°C cracking occurs. In the case of asphaltenes distillation is not possible, but nearly 5–10 wt% loss is

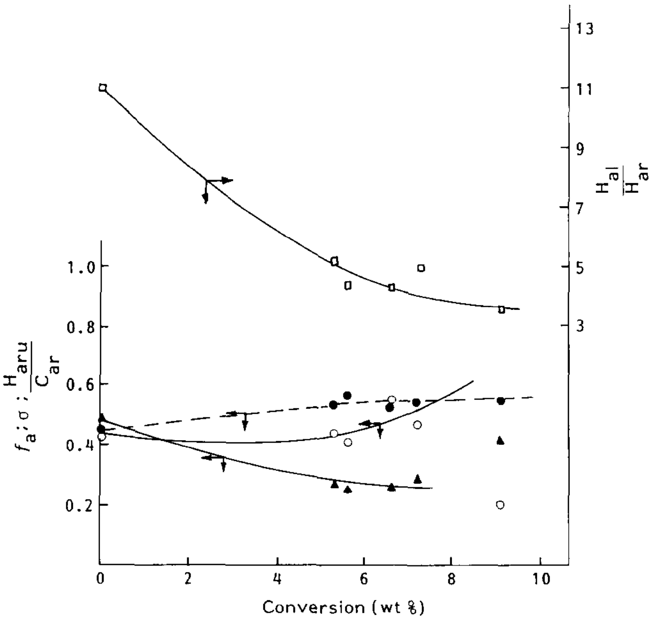

Figure 3 Variation of average structural parameters derived from ^1H n.m.r. spectra of nC_5-asphaltenes with conversion: ●, aromaticity (f_a); ○, fraction of substitutable aromatic carbons (H_{aru}/C_{ar}); ▲, degree of substitution of aromatic carbons (σ); □, ratio of aliphatic protons to aromatic protons (H_{al}/H_{ar})

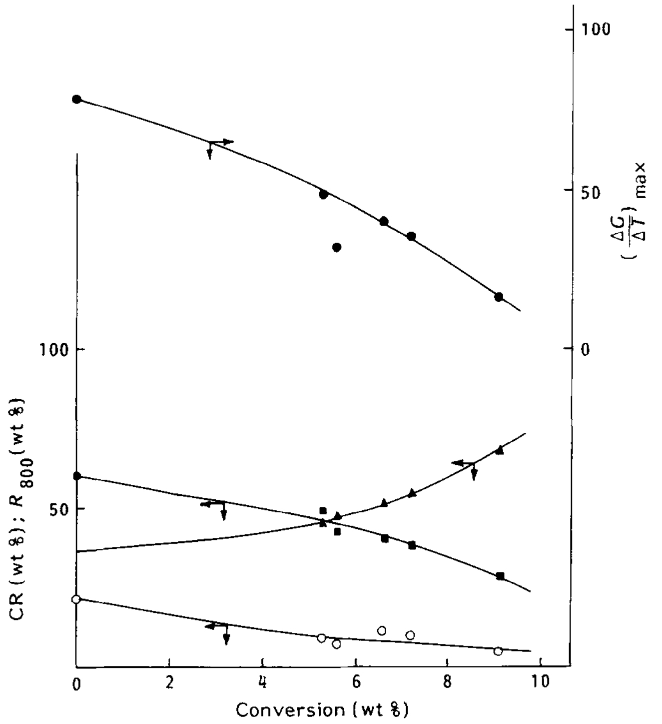

Figure 4 Variation of some characteristic parameters derived from thermal analysis of nC_5-asphaltenes with conversion: ■, wt% of asphaltene that can be cracked at 800°C (CR_{800}); ○, wt% of asphaltene that can be cracked at 450°C (CR_{450}); ▲, residue (wt%) at 800°C (R_{800}); ●, maximum reaction rate related to initial weight $(\Delta G/\Delta T)_{max}$

observed up to 400°C. This may be due to moisture adsorbed by asphaltenes, which also supports the higher yield of oxygen (*Table 1*). This is corroborated by the temperature at the start of distillation, which is nearly constant for all the asphaltenes. The weight of residue obtained at 800°C (R_{800}) from asphaltenes was found to increase with increasing conversion (*Figure 4*). This agrees with trends observed in CCR and coke yields. *Figure 4* also indicates that that part which can still be cracked at 450 and 800°C decreases with increasing conversion ($CR = 100 - \Delta G_{400} - R_{450}$ (or R_{800})). The maximum reaction rate for all samples is in the temperature range of cracking (>450°C). The height of the maxima decrease with increased conversion (*Figure 4*), which indicates that easily cracked components are already cracked. This is supported by the observed trend in the values of CR.

CONCLUSIONS

In the soaker visbreaking of short residue, the following characteristic changes in asphaltenes are considered to have occurred with increasing conversion: dealkylation of asphaltene sheets, mainly by reduction in size of alkyl chains; dehydrogenation and/or split opening of naphthenic rings condensed with aromatic clusters at higher conversion. These two reactions enhance the polarity of asphaltene sheets, which facilitates their aggregation. At very high conversion, stripping of aromatic clusters is pronounced; this can be attributed to removal of even shorter chains, yielding highly condensed aromatic structures (coke). The reduction (with conversion) in the amount that can still be cracked shows that short alkyl chains (mainly methyls) and/or naphthenic rings are still present in asphaltene sheets.

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