Carbonization of Coker Feedstocks and their Fractions

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Introduction

Delayed coking is commonly used to produce a mixture of gases, distillate liquids and carbonaceous solids by the thermal treatment of high-boiling petroleum feedstocks.[1] The formation of carbonaceous solids is of interest in this study. Apart from the production of premium graphitizable cokes (needle cokes) from selected aromatic feeds, the cokes usually produced are porous solids ('sponge' cokes). A less desirable form of solid carbon, occasionally co-produced with sponge coke, is known as 'shot' coke and consists of small hard spherules of low porosity, typically about 5 mm diameter which can aggregate into large clusters and can occur dispersed with sponge coke to varying extents.[2] The studies described in this paper were conducted in order to obtain clearer indications of the factors which contribute to shot coke formation.

Experimental

Two vacuum distillation residua VR1, VR2, a coker feed comprising VR2 mixed with 5-10% coker recycle oil and a clarified slurry oil (CSO) from catalytic cracking were used as basic feedstocks. The residua were further separated into pentane-soluble and pentane-insoluble fractions using the procedure suggested by Mima et al.[3]

The vacuum residua, their solvent separated fractions and the clarified slurry-oil were carbonized individually and in different combinations using conventional tubing bomb apparatus. Reactions were conducted isothermally at temperatures of 400-500°C for up to 8 h under an atmosphere of nitrogen (2 atm cold pressure). The extent of semi-coke formation during carbonization was determined by Soxhlet extraction of the reaction products with pyridine. The experimental procedures have been described in detail elsewhere.[4] The microstructures of the semi-cokes produced in the carbonization experiments and samples of sponge coke and shot coke produced in commercial units were examined by optical microscopy in reflectance using polarized-light. The vacuum residua and their fractions and the clarified slurry oil were analyzed for elemental composition.

Results and Discussion

Elemental Analysis

Elemental analyses of VR1, VR2, their solvent fractions and the clarified slurry-oil are given in Table 1. The pentane insoluble fraction constitutes 33% w and 43% w of VR2 and VR1, respectively.

Table 1. Elemental Analysis of Selected Materials; PtI: Pentane Insolubles, PtS: Pentane Solubles.

Material	C	H	% Weight O	S	N
VR1	82.9	9.6	1.1	5.6	0.7
VR1 PtI	82.5	8.0	1.5	7.0	1.2
VR2	83.8	9.8	0.7	4.8	0.5
VR2 PtS	84.2	10.8	0.7	3.6	0.4
VR2 PtI	83.5	7.9	1.0	6.5	1.0
CSO	90.4	7.8	0.5	1.3	0.2

The carbon contents of the two residues and their solvent fractions are similar and significantly lower than that of the clarified slurry-oil. It should be noted that the pentane insoluble fractions of both VR1 and VR2 contain more heteroatoms (O, S, N) and less hydrogen compared to the respective parent residues and the pentane soluble fraction of VR2. The low heteroatom contents and H/C ratio of the CSO are consistent with this material possessing a greater proportion of aromatic components than the residual oils.

Optical Texture of Cokes

The appearances of the sponge and shot coke samples and of the cokes produced by carbonization of the various precursors are summarized in Table 2.

The differences in optical texture and the long-established dependence of coke properties upon the chemical nature of the precursor (5) indicate that the co-production of sponge and shot cokes arises from the carbonization of species which differ substantially in their carbonization reactivity and chemical structure (6).

Table 2. Optical Texture of Cokes Obtained by Carbonization of Vacuum Residua and Their Fractions; WR: Whole Residuum, (PtI: Pentane Insolubles, PtS: Pentane Solubles, RO: Recycle Oil).

Feedstock	Fraction	Description
VR1	WR	Domains, 25 μm
	PtI	Domains, 15 μm
	PtS	Domains, 30 μm
VR2	WR	Mosaics, 5 μm
	PtI	Fine Mosaics, 1.5 μm
	PtS	Domains, 30 μm
CSO		Elongated flow domains, 200 μm
VR1 + 10% wt CSO		Flow domains, 60 μm
VR2 + 5-10% wt RO		Mosaics, 10 μm
Sponge Coke		Extensive flow-type coalescence
Shot Coke		Mosaics, 5 μm

The appearances of the cokes produced from the solvent fractions of VR1 and VR2 further emphasize the dependence of coke structure upon the feedstock composition. For both feedstocks the most developed mesophase was observed for the pentane solubles, followed by the whole feed, followed by the pentane insolubles. The principal differences between VR1 and VR2 were seen in the cokes produced from their pentane-insoluble fractions. These observations strongly suggest that shot coke is produced from reactions involving the asphaltenic portion of the feedstock.

The spherical morphology of shot coke may be due to the segregation of a rapidly hardening (i.e., rapidly carbonizing) phase of high viscosity and high surface tension under the dynamic conditions prevailing in the coker drum. The random incorporation of shot coke in the sponge coke matrix along with the uniformity in the size of individual shots support this suggestion.

Kinetics of Semi-coke Formation

The relative rates of carbonization of the different feedstocks were determined by measuring the amount of pyridine insolubles (PI) formed (at 450°C) as a function of time, Figure 1. A cross-examination of Figure 1 and Table 2 indicates that the
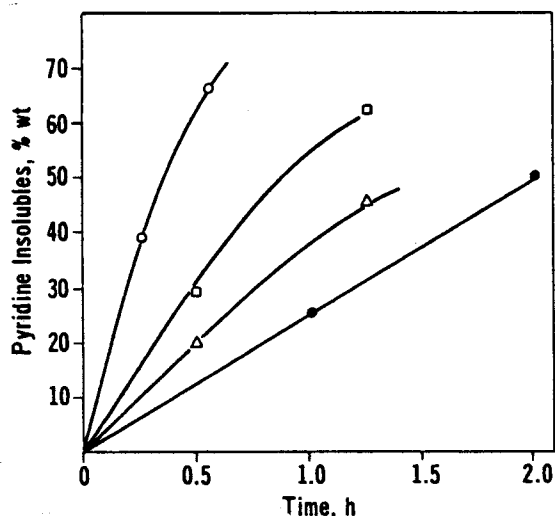

Figure 1. Relative rates of carbonization of petroleum feedstocks; HTT:723 K, ○ VR2 pentane insolubles, □ VR1, △ VR1 + CSO (15% w), ● VR2 pentane solubles.

rate of PI formation during carbonization is inversely related to the average size of anisotropic structures observed in the resulting semi-cokes. The beneficial effects of CSO addition to VR1 in enhancing mesophase development are seen to be commensurate with its lowering the rate of carbonization. For wide ranges of conversion (up to 70% PI) an apparent first-order kinetic behavior was observed for semi-coke formation from VR2 and its pentane insoluble fraction. The calculated rate constants together with the associated activation energies and pre-exponential factors are presented in Table 3, and compared to those obtained for Ashland 240 pitch which forms flow-domain anisotropy (> 200 μm in length) in cokes (7). The acti-

Table 3. Calculated Rate Parameters for Carbonization of VR2 and Its Pentane Insoluble Fraction

Material	T,K	$k \times 10^4$, s^{-1}	Ea, kJ/mole	A, s^{-1}
VR2	698	0.472		
	723	1.568	195	2.1×10^{10}
	748	4.498		
VR2 PtI	673	0.469		
	701	1.920	182	8.0×10^9
	723	4.459		
A 240	723	0.427	167	5.9×10^7

vation energies calculated for VR2 and its pentane insoluble fraction are higher than that obtained for A 240 pitch. It should be noted, however, that both VR2 and its pentane insoluble fraction carbonize more rapidly than A 240 pitch does, as can be inferred from the reported rate constants at 723 K. This indicates that a consideration of the activation energies alone, without taking into consideration the pre-exponential factors, can be misleading in comparing relative rates of carbonization.

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