COKE FORMATION MECHANISMS IN SELECTED SLURRY OILS

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Introduction

Results of mesophase formation studies conducted on a variety of hydrocarbon liquids including coal tar pitch, certain fractions of coal tar pitch and various petroleum residues have been reported. (1-8) Only a few investigators have reported on coke formation mechanisms in actual delayed coker feedstocks. White and Price (7) described mesophase microstructures in a number of coker feedstocks ranging from Gilsonite to a decant oil. Whittaker and Grindstaff (6) compared mesophase formations observed in several reduced crudes which are the usual feedstocks for the production of "regular" petroleum (sponge) cokes.

One of the principal feedstocks for the production of premium or needle cokes is clarified slurry oil from fluid catalytic cracking operations. Due to an increasing demand for premium cokes, efforts are being made to provide additional quantities of feedstocks by upgrading certain slurry oils presently unsuited for the production of high quality needle cokes. (9) Some slurry oils contain small amounts of micron-size catalyst fines which remain in suspension despite conventional separation techniques designed to remove them. These catalyst fines, because of their extreme fineness, have a pronounced effect on mesophase formation and thus the resultant needle coke structure. This paper describes mesophase formations and coke structures observed in selected slurry oils before and after removal of catalyst fines by filtration techniques.

Experimental

Materials.

Two slurry oils identified as "A" and "B" were evaluated. Except where indicated, the slurry oils were used as received from the refinery. Pertinent properties of the two feedstocks are summarized below.

	A	B
API @ 60°F	- 2.1	4.6
Viscosity, cps @ 210°F	27	15
Conradson Carbon, Wt. %	10.9	5.2
Carbon, Wt. %	90.30	90.05
Hydrogen, Wt. %	7.22	8.12
Sulfur, Wt. %	1.31	1.15
Aromaticity (NMR)	0.67	0.60

Laboratory Cokings.

Laboratory cokings were made in a 4 liter glass flask equipped with a distilling head and thermocouple well. The materials were heated slowly to a predetermined setting temperature and allowed to remain at this temperature for a time sufficient to harden the coke. To adjust the volatile content of the raw coke to the desired level, final heating was made at a relatively slow rate of temperature increase to a maximum of 550°C.

Smaller samples were conveniently prepared by simulating the above coking operation on a test tube scale in a fluidized sandbath. The maximum operating temperature of the bath was 600°C. Appropriate controls for the fluidizing air and temperature were employed to achieve the desired reproducibility and minimize thermal gradients (±3°C) within the bath at the normal operating temperature of 440-450°C.

Microscopic Studies.

After the desired treatment, the glass test tubes were carefully removed and the residue recovered intact for preparation of polished sections by conventional techniques. The polished sections were microscopically examined with reflected polarized light. Longitudinal cross-sections of the residues were used to observe the effect of time on mesophase formation. To relate pertinent structural characteristics to ash constituents, various polished samples were examined with an Acton Laboratories Model MS64 electron microprobe.

Ultrafiltration.

Filtration was conducted under vacuum at about 120°C in a Buchner funnel using Reeve Angel 984H filter paper which is capable of retaining solids in the range of approximately 0.1 micron diameter. To ensure a perfect seal, a thin layer of high vacuum grease was applied around the edges of the filter paper.

Results and Discussion

A most convenient and rapid means of assessing the potential of a slurry oil as a needle coke feedstock is to observe the mesophase during the early stages of coke formation. During recent evaluation experiments, slurry oil "A" was found to contain micron-size solids, believed to be catalyst fines, which interfered with the orderly growth and coalescence of mesophase spherulites. Solids removed by filtration and analyzed by X-ray fluorescence (XRF) were found to be composed principally of silicon and aluminum which confirmed the presence of catalyst fines. Size analysis by Coulter Counter indicated the fines to be 63% less than 2 microns.

Coke formation in slurry oil "A" is characterized by the following structural variations:

1. a fine disordered structure (i.e. non-coalesced mesophase) during the initial stage.
2. a coarser disordered structure with increasing tendency for coalescence of the irregular spherulites.
3. normal spherulite formation, growth and coalescence.

Slurry oil "B", a known precursor of high quality needle coke, is characterized during the entire coke formation process with no inhibition of normal spherulite formation, growth and coalescence. Removal of the solids from slurry oil "A" resulted in mesophase formation which was essentially equivalent to slurry oil "B".

Certain anomalous structures observed by polarized light microscopy were examined by electron microprobe to determine the nature of the interfering solids. These structures were scanned to detect the presence of aluminum and silicon. The disordered structures which were predominant during the early stages of coke formation were shown to contain concentrations of approximately 5-10% of aluminum and silicon. Areas of high concentrations of catalyst fines which were randomly dispersed throughout the disordered mesophase structure yielded aluminum and silicon contents as high as 15%.

Laboratory cokes were prepared from

1. slurry oils "A" and "B" as received from the refinery;
2. slurry oil "A" after removal of fines by filtration;
3. slurry oil "B" after the addition of small amounts of micron-size alumina.

Evaluation of the laboratory cokes indicated that interference of mesophase formation by catalyst fines or by deliberate additions of finely divided alumina resulted in a more isotropic structure than is desired in high quality needle cokes. Removal of the fines from slurry oil "A" resulted in a suitable needle coke feedstock.

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