

SULFUR RETENTION DURING CARBONIZATION OF DECANT OIL AND CALCINATION OF SEMI-COKE

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Introduction

FCC (Fluidized Catalytic Cracking) decant oils are the primary feedstock to the delayed coker to produce highly graphitizable precursor—the needle coke. The quality of needle coke is determined, in essence, by the development of mesophase formation in the early stages of liquid-phase carbonization that, in turn, closely relates to the chemical composition of coker feedstock [1,2]. The coexistence of heteroatom compounds with polyaromatic hydrocarbons in the decant oils will become a major concern considering the ever heavier and more sour crudes introduced to the refineries [3].

The objective of this study was to identify the sulfur compounds in four decant oil samples and to monitor sulfur retention in the corresponding semi-coke and calcined coke. Mesophase development during the carbonization of the decant was also examined.

Experimental

Carbonization of Decant Oils

Four decant oil samples with different sulfur contents were used in this study. Carbonization experiments were conducted in tubing bomb reactors (15 mL) at 500°C for 3 hours under autogenous pressure. The reactors were heated in a fluidized-sand bath. After reaction, the reactors were quenched in cold water. The semi-coke product was recovered as whole piece for microscopic examination. The liquid product was also collected for analysis.

Calcination of Semi-coke

About 3 grams of semi-coke was placed in a horizontal quartz tube reactor. The heating profile consists of three stages: the sample was heated from room temperature to 450°C at 25°C/min, from 450°C to 1000°C at 10°C/min and maintained at the final temperature for one hour. Calcination experiments were carried out under nitrogen flow to prevent oxidation.

Optical Characterization of Semi-coke

Each semi-coke sample was mounted in a pellet of epoxy resin, then cut into two sections. The polished pellets were examined under a polarized light microscope (Nikon-Microphoto_FXAI). We used a 1.1 mm X 1.1 mm mask and 10X object lens to acquire the surface images. At least 150 images were examined for a pellet. The extent of mesophase development was determined in terms of an Optical Texture Index (OTI) of semi-coke [4].

Analysis of Liquids

The sulfur compounds in decant oils and in the liquid products from carbonization and calcination were analyzed by Gas Chromatography with Flame Photometric Detector (GC/FPD) and Gas Chromatography with Mass Spectrometry (Shimadzu GC-17A, MS-OP-5000). Total sulfur in the samples was determined on a sulfur analyzer (Leco-SC-132). The elemental analysis was performed on a CHN determinator (Leco-CHN 600).

All the data reported are results from triplicate measurements.

Results and Discussion

Composition of Decant Oils

Table 1 lists the elemental composition for each decant oil sample used in this study. The GC amenable group distribution is illustrated in Figure 1. Table 2 presents the concentrations of the three major sulfur compounds present in the decant oil samples, as determined by GC/MS: dibenzothiophene (DBT), methyl dibenzothiophenes (MDBDT), and dimethyl dibenzothiophenes (DMDBT). The FPD chromatogram of the decant oil F3 along with those of carbonization/ calcination liquid products are shown in Figure 2, indicating the presence of dibenzothiophene (DBT), polymethylated DBT, and benzonaphthothiophenes in high concentrations. Decant oils F3 and F4 have higher sulfur contents than the other two samples, and F3 has the lowest hydrogen content among the four samples. Relatively high concentrations

of dimethyldibenzothiophenes in F2 and F3 should also be noted.

Mesophase Development

A comparison of semi-coke textures from mesophase development is given in Table 3 in terms of optical texture indices (OTI). F3 produced a semi-coke with the lowest OTI that is significantly lower than those of the other semi-cokes, indicating a much lower degree of mesophase development during the carbonization of this sample. In contrast, F1 produced the most anisotropic semi-coke followed by F2 and F4 that produced comparable textures in the semi-cokes. The lowest degree of mesophase development seen with F3 can be attributed more to the differences in its hydrocarbon distribution (e.g., high phenanthrene to pyrene ratio with relatively low concentrations of n-alkanes) than its high sulfur content [1].

Sulfur Distribution in the Products of Carbonization and Calcination

Figure 2 compares the GC-amenable sulfur compounds present in the original decant oil and in the liquid products obtained from carbonization and calcination experiments. It can be seen that both liquids contain relatively high concentrations of DBT and sulfur compounds with low degree of methyl substitution. It appears that sulfur compounds with a high degree of methyl substitution have been incorporated in the semi-coke.

Upon carbonization of the decant oils under the conditions described, approximately 50% of sulfur in the decant oil samples were retained in the semi-coke. Table 4 gives the sulfur contents and calcined coke yields of the semi-cokes from carbonization. Linear correlations between the sulfur content of the decant oils and those of the resulting semi-coke and calcined coke are shown in Figure 3.

Conclusions

GC-amenable sulfur compounds in decant oils with high degree of methyl substitution tend to be more readily incorporated in the semi-coke. This results in the abundant presence of dibenzothiophene and naphthobenzothiophenes in the carbonization liquids. Upon carbonization, about 50 wt% of sulfur is incorporated into the semi-coke. There appears to be a linear relationship between the sulfur content of the

decant oil feedstock and sulfur contents of the corresponding semi-coke and calcined-coke products.

Acknowledgements

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References

1. Eser, S. in Supercarbon: Synthesis, Properties and Applications, ed. By Yoshimura, S. and Chang, R.P.H., Springer-Verlag, Berlin, 1998, p147.
2. Mochida, I., Fujimoto, K. and Oyama, T. in Chemistry and Physics of Carbon, Vol 24, ed. By Thrower, P. A., Marcel Dekker Inc., New York, 1994, p111.
3. Filley, R.M. and Eser, S., Energy & Fuels, 1997, 11, 623.
4. Yang, M-G, Wang, G. and Eser, S., Eurocarbon 2000, International Conference on Carbon, pp. 163-164.

Table 1. Elemental composition of decant oils

	C, wt%	H, wt%	S, wt%	N, wt%
F1	89.4	8.0	2.6	0.5
F2	88.9	8.4	2.8	0.3
F3	88.0	7.5	4.9	0.4
F4	88.2	8.2	4.0	0.3

Table 2. Sulfur compounds in decant oils, wt%

	DBT	MDBT	DMDBT
F1	0.02	0.12	0.17
F2	0.06	0.20	0.86
F3	0.08	0.22	1.40
F4	0.08	0.21	0.49

Table 3. Semi-coke microscopy analysis results

Sample	FD *	D*	SD*	M*	OTI
F1 (I)	109	59	3	2	77
F1 (II)	107	57	5	1	78
F2 (I)	63	51	1	0	72
F2(II)	77	73	5	0	73
F3(I)	27	66	28	4	49
F3 (II)	29	66	27	3	50
F4 (I)	61	82	4	1	69
F4 (II)	70	86	4	1	70

Note: FD: flow domain, D: domain, SD: small domain, M: mosaic.

Table 4. Sulfur retention in calcined cokes, wt%

	Sulfur, Semi-coke,	Sulfur, Calcined coke,	Calcined coke yield,	Sulfur retention
F1	2.17	1.77	89	73
F2	2.36	1.95	88	74
F3	3.73	3.01	87	71
F4	3.16	2.62	88	73

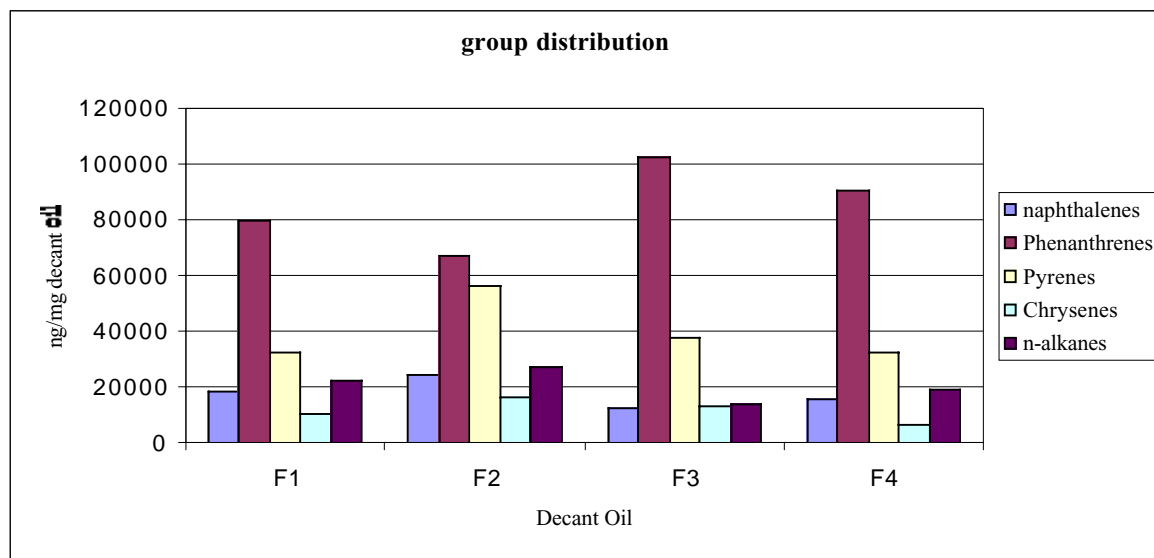


Figure 1. Group composition of decant oils

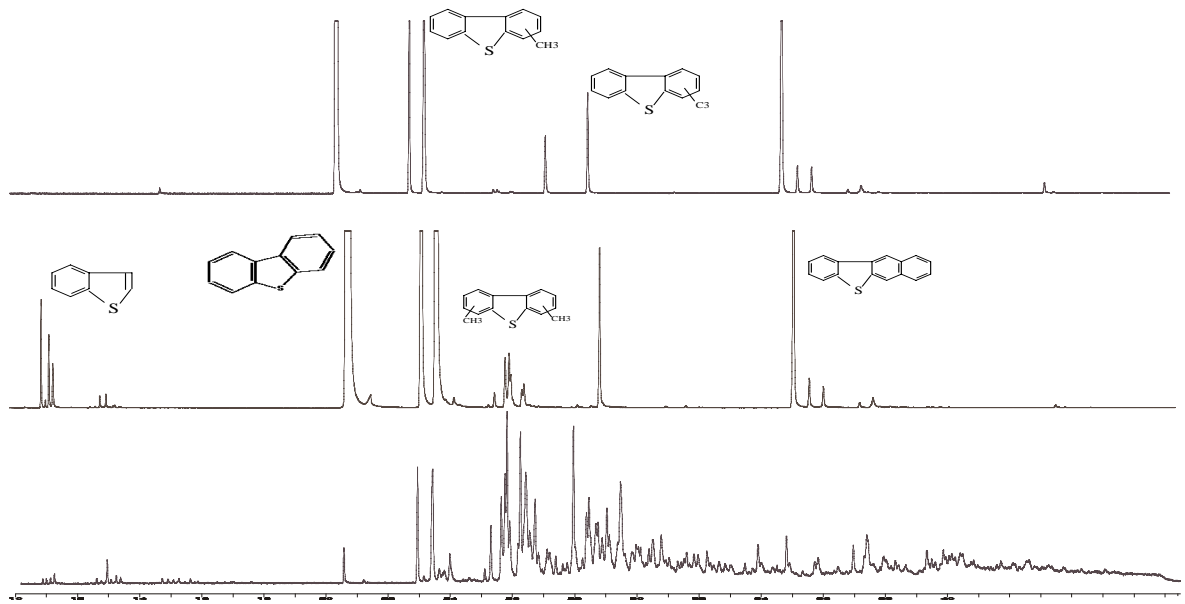


Figure 2. Sulfur compounds in decant oil F3 (bottom), carbonization liquid (middle) and calcination liquid (top)

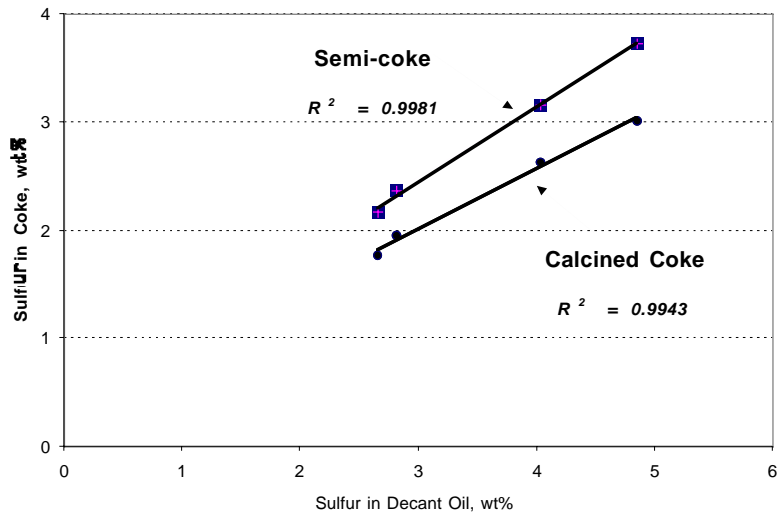


Figure 3. Correlations between sulfur contents of decant oils and resulting cokes.