

EARLY CARBONIZATION CHEMISTRY OF FCC DECANT OILS HEATED IN A FLOW REACTOR

*Richard P. Dutta, Kevin Kelleher, and Semih Eser
The Energy Institute, Penn State University
209 Academic Projects Bldg, University Pk, PA 16802*

Introduction

Delayed coking of FCC decant oils is used to produce high quality needle cokes for manufacturing graphite electrodes [1]. Mesophase development during delayed coking affects the coke texture and related properties of the needle cokes, such as the coefficient of thermal expansion [2]. Some important chemical reactions that influence the mesophase development can occur in the heater section of the delayed coker. Here we report the results of an initial study directed towards understanding the changes that occur in the molecular composition of a decant oil sample as it flows through a heater tube.

Experimental

Figure 1 shows a schematic representation of the flow reactor used to heat decant oil to 480°C for various residence times (depending on the flow rate and heater length). The reactor comprised of a 1/8" SS tube of various lengths (7-16 in.) which was heated by a heating tape controlled at the outlet of the tube by a temperature controller. Samples were taken at various times during a run and analyzed by GC/MS using selective ion monitoring, as reported previously by Filley and Eser [3]. Additional carbonization experiments were carried out in 15 mL tubing-bomb reactors for longer residence times (10-30 minutes). Asphaltene and coke yields were measured by extracting the products sequentially with methylene chloride and hexane.

Results and Discussion

Alkane Distribution

Figure 2a shows the alkane distribution in a decant oil heated to 480°C for various residence times up to 2.5 min. Alkane cracking starts after 0.5 min residence time in the heater tube. As the extent of cracking increases the concentration of the long chain alkanes C21-31 is reduced by 40% (see Figure 2b). Alkane cracking could play an important role in mesophase development because of the generation of reactive radicals that can initiate further H-abstraction reactions (from aromatics). Thermal cracking of alkanes also generates hydrocarbon gases that

can shear the liquid domains to produce anisotropic coke texture in the late stages of coking.

Naphthalene (C1-C3) Distribution

Figures 3a and b show the naphthalene and substituted naphthalene product distribution vs. residence time. Fig 3b shows the early product distribution in the heater section of the coker. Increases in the concentrations of naphthalenes can be attributed to several reactions, including dealkylation of substituted naphthalenes, alkylation of naphthalene, and enrichment of naphthalene due to the loss of heavy ends via production of asphaltenic material during carbonization. One method to examine the possible reactions is to quantitatively determine how the concentration of isomers changes. In this case, the concentration of 1- and 2-methylnaphthalene (1-, 2-MNaph) was examined and the ratio of 2-MNaph to 1-MNaph is shown in Table 1. The 2-MNaph is more stable than 1-MNaph, therefore if dealkylation was a significant mechanism early in the carbonization, the ratio of these two compounds should increase with residence time. Table 1 shows the concentration of both isomers increasing with residence time but the ratio stays relatively constant for the first 2.5 min in the heater. Only after longer reaction times in the batch reactor does the ratio start to significantly increase. This result suggests that the early increase in naphthalene concentration is due to enrichment and not due to thermal dealkylation of substituted aromatics. However, the initial decrease in C3-naphthalene concentration is probably due to cracking of the side chain to produce methylnaphthalenes.

Phenanthrene (C1-C3) Distribution

Using the same methodology used for naphthalene and its substituted compounds, the concentration of phenanthrene and its alkyl derivatives (C1-C3) was followed during heating and for longer reaction times in the batch reactor (see Figures 4a and b). Concentration of phenanthrene stays relatively constant in the heating stage and then increases with the residence time in the batch reactor. The C1 and C2 phenanthrene concentration increases steadily in both reactor systems and C3-phenanthrene concentration drops during preheating, increases for the next 10 minutes residence time and then starts to decline again up to 30 minutes residence time. In order to determine possible mechanisms

for this trend in product distribution, quantitative analysis of the concentration of the four isomers of methyl phenanthrene (2-, 3-, 9- and 10-MPhen) was undertaken. Table 2 shows the concentration of these isomers and the ratio of 2+3 to 9+10- MPhen and how they vary with residence time in the heater and in the batch reactor. The data suggests that initially there is a decrease in the ratio of 2+3/9+10 isomers which suggests there may be alkylation of the reactive 9- and 10- position on the phenanthrene ring system. As the reaction progresses, there is also dealkylation of the reactive 9- and 10- methyl isomers. Coupling of the reactive isomers could also account for a reduction in their concentration. The subsequent increase in the ratio of stable to unstable isomers could also be due to formation of stable isomers by cracking of the side chain in C3-MPhen. The chemistry becomes more complex as the ring size increases from 2 to 3 with the increasing number of possible isomers of the various substituted aromatics. What is evident is the existence of alkylation, dealkylation and enrichment (by loss of light and heavy ends) in the chemistry of phenanthrenes during the early stages of carbonization.

Pyrene (C1-C3) Distribution

Pyrene and substituted pyrenes showed interesting chemistry that could have a significant impact on needle coke texture. Figures 5a and b show the concentration of pyrenes vs. residence time for both flow and batch reactor. Pyrene concentration increases steadily with the residence time. Methylpyrene concentration drops initially and then increases steadily after about 30 s residence time. C2-pyrene concentration drops with residence time initially and then increases, while C3 pyrene concentration decreases in both the flow and the batch reactor. The ratio of stable to unstable methylpyrenes (2-Mpy / 4-Mpy + 1-Mpy) shows a slight increase initially followed by a larger increase when the reactions are done in the batch reactor (Table 3). It appears that there is some dealkylation early in the heater, followed by enrichment because of light end removal and further dealkylation of the unstable methylpyrenes later in the reaction. Coupling of these reactive isomers could also account for the increasing ratio.

Asphaltene and Coke Yields

Figure 6 shows the asphaltene and coke yields as a function of residence time in the preheater and the batch reactor. Initially, asphaltenic material is produced, reaches a maximum at 18wt% and then the asphaltenes reach a concentration level that phase separation can occur to produce coke. In order to determine which compounds are producing the asphaltenes in the heater, an analysis of total concentration of PAH's with residence time was undertaken (Figure 7). The data shows a continual increase for naphthalenes, a slight decrease initially for

phenanthrenes and a significant decrease for pyrenes. This suggests that it is the primarily pyrenes (and larger ring systems) that are condensing to produce asphaltenic materials which are the coke precursors. Therefore, the substitution pattern of these condensing pyrenes could have a significant impact on the final coke texture.

Conclusions

Substantial changes have been observed in the molecular composition of an FCC decant oil flowing through a tube heater with residence times from 0.5 to 2.5 min. The concentrations of n-alkanes and 2-4 ring PAH depend strongly on the residence time. As expected, the initial carbonization reactions are complex, including dealkylation, alkylation, enrichment by removal of light ends and formation of asphaltenic material by oligomerization reactions. It appears from the data in this study that naphthalene (C1-C3) concentration is primarily governed by enrichment although there is evidence of dealkylation of highly substituted aromatics (e.g., C3 naphthalenes). Changes in the concentrations of phenanthrenes can be explained by alkylation, dealkylation, and enrichment due to loss of light ends. Pyrene and substituted pyrene show some dealkylation early in the heater followed by oligomerization of aromatics to produce asphaltenic material (coke precursors). Overall, the data suggests that the chemical reactions that take place during the very early stages of carbonization i.e., in the heater of delayed coker, can significantly influence the mesophase development, and, thus, the final coke texture.

References

- [1] Mochida, I., Fujimoto, K. and Oyama, T., in Chemistry and Physics of Carbon, Vol. 24, Marcel Dekker, New York. 1994, 111-213.
- [2] White, J.L. and Price, R.J. *Carbon*, 1974, **12**, 321-333.
- [3] Filley, R.M. and Eser, S. *Energy Fuels.*, 1997, **11**, 623-630.

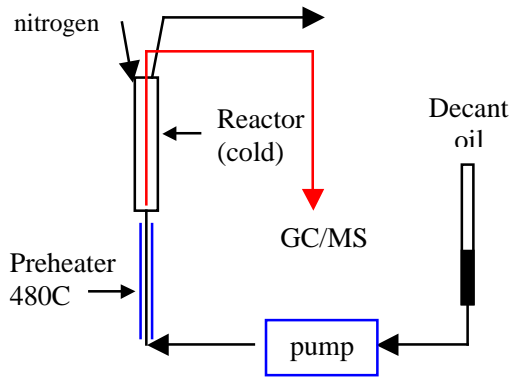


Figure 1. Schematic of flow reactor

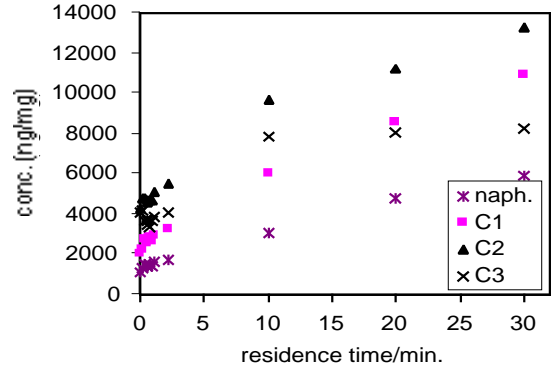


Figure 3a. Naphthalene (C1-C3) distribution for various residence times (0 – 30 min).

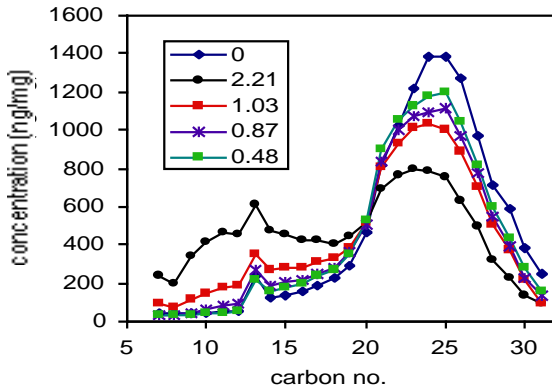


Figure 2a. Alkane carbon no. distribution for various residence times in the preheater

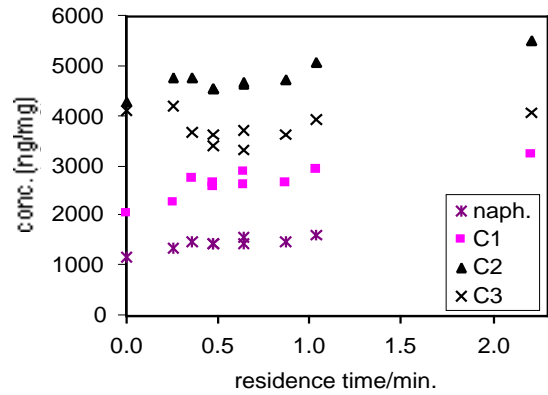


Figure 3b. Naphthalene (C1-C3) distribution for various residence times (0 – 2.5 min).

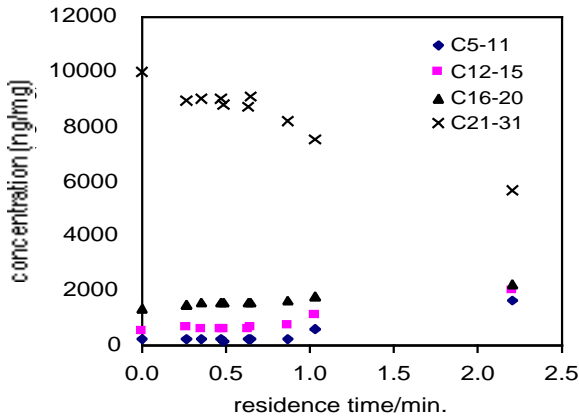


Figure 2b. Concentration of alkanes for various residence times in the preheater

Table 1. 1-, and 2-methylnaphthalene concentration vs residence time (* batch reactor)

Residence time/min	2-MNaph	1-Mnaph	2-/10-Mnaph
0.00	1300	760	1.71
0.26	1437	843	1.70
0.47	1685	992	1.70
0.48	1629	958	1.70
0.64	1653	966	1.71
0.87	1694	997	1.70
1.03	1863	1058	1.76
2.21	2071	1190	1.74
10.00*	4002	1992	2.01
20.00*	6289	2330	2.70
30.00*	8150	2749	2.96

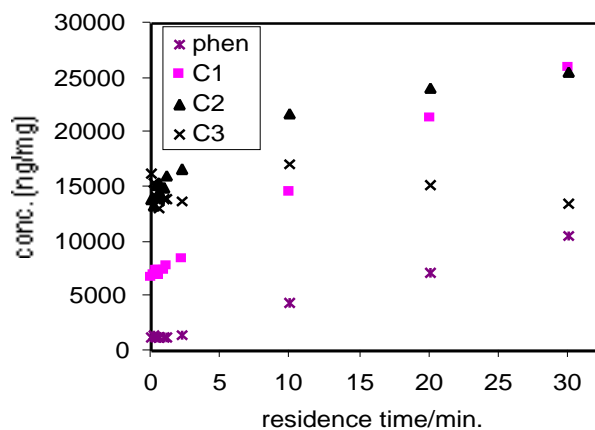


Figure 4a. Phenanthrene (C1-C3) distribution for various residence times (0 – 30 min).

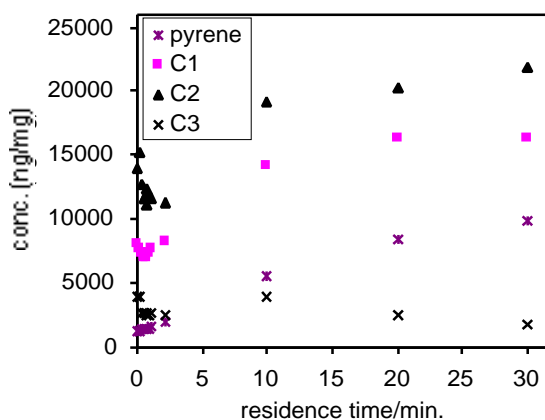


Figure 5a. Pyrene (C1-C3) distribution for various residence times (0 – 30 min).

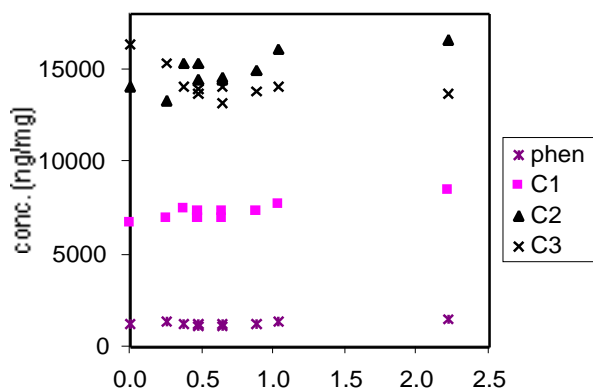


Figure 4b. Phenanthrene (C1-C3) distribution for various residence times (0 – 2.5 min).

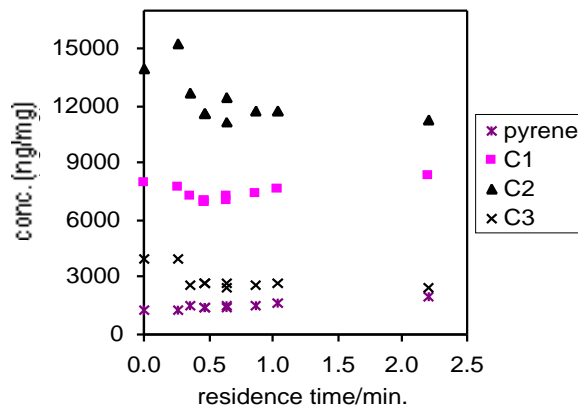


Figure 5b. Pyrene (C1-C3) distribution for various residence times (0 – 2.5 min).

Table 2. Methylphenanthrene isomer concentration vs residence time (* batch reactor)

Residence time/min	2+3-MPhen	9+1-MPhen	2+3/9+1-Mphen
0.00	4083	2239	1.82
0.26	4194	2325	1.80
0.47	4137	2379	1.74
0.48	4329	2498	1.73
0.64	4373	2488	1.76
0.87	4397	2493	1.76
1.03	4541	2584	1.76
2.21	5036	2731	1.84
10*	10598	3934	2.69
20*	17058	4221	4.04
30*	21702	4366	4.97

Table 3. Methylpyrene isomer concentration vs residence time (* batch reactor)

Residence time/min	2-Mpy	4-Mpy	1-Mpy	2-/ (4+1-) MPy
0.00	2560	2980	2443	0.47
0.26	2500	2879	2354	0.48
0.47	2296	2677	2118	0.48
0.48	2269	2620	2050	0.49
0.64	2316	2667	2072	0.49
0.87	2379	2817	2153	0.48
1.03	2512	2959	2195	0.49
2.21	2954	3091	2251	0.55
10*	7490	3927	2096	1.24
20*	10002	3971	1542	1.81
30*	10935	3154	1382	2.41

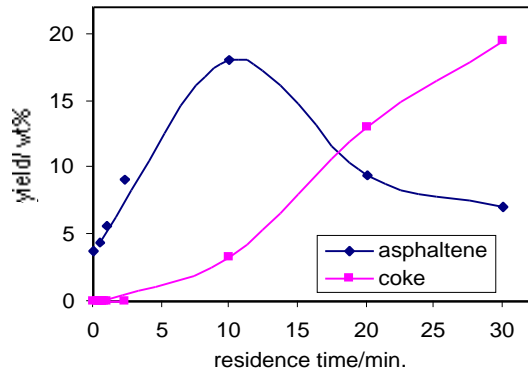


Figure 6. Asphaltene and coke yield from carbonization of decant oil (0-30 min)

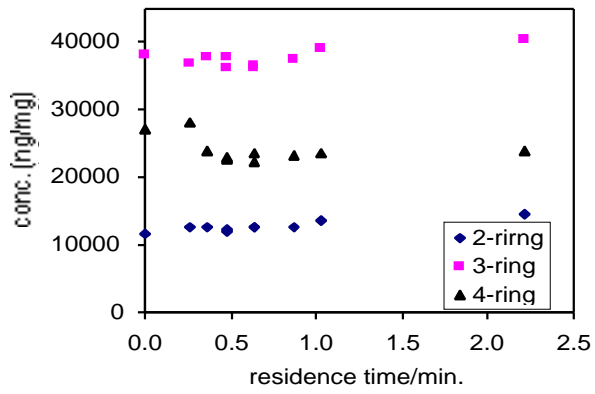


Figure 7. Total PAH concentration (2-4 ring) vs residence time in the preheater