Effects of Molecular Composition and Carbonization Reactivity of FCC Decant Oil and its Derivatives on Mesophase Development

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Introduction

FCC decant oil is the primary feedstock to delayed coker to produce needle coke, a premium carbon precursor to synthetic graphite electrodes. Mesophase development during coking, determines the graphitizability of the needle coke product. Mesophase development, in turn, depends on the molecular composition of the feedstocks [1,2].

In a commercial delayed coking unit, liquid-phase carbonization (coking) takes place in insulated coke drums as the feed, heated in a tubular furnace, flows upward in the drums [3]. Liquid products from delayed coking are separated into light and heavy oils by distillation in a fractionator. Fresh feed (typically decant oil) is also fed to the fractionator. The furnace charge (coker feed) comes from the bottom of the fractionator that includes the heavy ends of both fresh feed and liquid products from coking.

Most studies on delayed coking have used FCC decant oil as the feedstock material, although the actual coker feed may have a very different composition from that of the parent decant oil. The objective of this study is to analyze the molecular composition of the coker feeds as compared to the parent decant oils. Laboratory carbonization experiments were carried out on the decant oil and coker feed samples as well as on the bottom and top fraction (gas oil) of the decant oils separated by vacuum distillation. Samples of hydrotreated gas oil were also carbonized under comparable conditions. Semi-coke and asphaltene yields from the carbonization experiments were determined to compare the carbonization reactivity of different samples. Mesophase development was monitored by polarized-light microscopy of semi-coke samples.

Experimental

The samples used for both analysis and carbonization experiments include two sets of decant oils (DO3-1 and DO3-3), coker feed (CF3-1 and CF3-3), and gas oil (GO3-1 and GO3-3). Samples of hydrotreated gas oil (HYD3-1 and HYD3-3) and vacuum tower bottoms (VTB3-1 and VTB 3-3) were used only in the carbonization experiments.

Gas Chromatography/Mass Spectrometry (GC/MS), was used to determine the concentrations of GC-amenable aromatic compounds, using a method reported elsewhere [4].

Carbonization experiments were carried out in 15 mL tubing bomb reactors under autogenous pressure at two different temperatures using a sample size of 4 g. A lower temperature (450°C) was used to determine the product yield from the carbonization of individual samples for 15 min to 180 min. Carbonization at higher temperature (500°C) for 4 – 6 h was carried out to examine the optical texture of semi-coke products to monitor mesophase development.

Semi-coke samples were prepared in epoxy resin pellets, and the polished pellets were examined using a polarized light microscope. We used a 1.1 mm X 1.1 mm mask and 10X object lens to acquire surface images. At least 150 images were examined for each sample. The extent of mesophase development that produced the semi-coke texture was expressed in terms of an Optical Texture Index (OTI) [1] as a measure of structural anisotropy. Higher OTI, higher is the degree of anisotropy in terms of the shape and size of optical units observed under a polarized-light microscope. The desired needle coke anisotropy will consist mostly of the flow domain texture that represents elongated regions of liquid crystalline (mesophase) structures. Domains, and small domains represent a decreasing extent of anisotropy in this order.

Products from low temperature (450°C) carbonization were separated into semi-coke (dichloromethane insoluble), asphaltenes (dichloromethane soluble and pentane insoluble), and maltenes (pentane solubles) to determine the semi-coke and asphaltene yields.

Results and Discussion

Table 1 shows the OTI of semi-cokes obtained from carbonization of different samples. The two decant oil samples produced semi-cokes with very different OTI under the same experimental conditions: 83 for DO3-1 and 66 for DO3-3. A similar trend was observed when comparing the semi-coke textures for the respective derivatives (except HYD), although the differences were not as significant as that obtained with the DO samples. In contrast, HYD03-1 gave a lower value of OTI than that of HYD03-3. Within each sample set, CF produced more developed textures than the parent DO. This difference was particularly pronounced for sample Set 03-3 where CF OTI (82) is much higher than DO OTI (66), indicating a substantially improved mesophase development from CF03-3 compared to DO03-3. GO produced the worst optical texture within each sample set. GO3-1 produced a better texture than GO3-3, whereas HYD03-1 produced a worse texture than HYD03-3. This reversal in the trend of texture development suggests that hydrotreatment can very significantly change the resulting optical texture obtained from the carbonization of the hydrotreated products compared to the starting GO. VTB produced better textures than DO and CF in both sample sets. While VTB produced the most developed texture in Set 03-1 (OTT:95), HYD gave the most developed texture in Set 03-3 (OTT: 94).

Table 1. Optical Texture Indices for semi-cokes produced by carbonization at 500°C, for 4 h and 6 h (GO and HYD).

<table>
<thead>
<tr>
<th></th>
<th>Set 03-1</th>
<th>Set 03-3</th>
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<tbody>
<tr>
<td>DO</td>
<td>83</td>
<td>66</td>
</tr>
<tr>
<td>CF</td>
<td>88</td>
<td>82</td>
</tr>
<tr>
<td>GO</td>
<td>61</td>
<td>54</td>
</tr>
<tr>
<td>HYD</td>
<td>87</td>
<td>94</td>
</tr>
<tr>
<td>VTB</td>
<td>95</td>
<td>86</td>
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Figures 1-4 present the concentrations of polyaromatic hydrocarbons in DO, CF, and GO and n-alkanes in DO in both sample sets. It is shown in Figure 1 that DO3-1 has a higher overall pyrenes/phenanthrenes (py/ph) ratio compared to DO3-3. Figure 2 compares the n-alkanes distributions in DO samples. The DO3-3 has higher concentrations of large n-alkanes (>20 carbon atoms) than DO3-1. These differences in the composition of the aromatic compounds and n-alkanes in the two DO samples can be related to the difference observed in the semi-coke textures between DO3-1 and DO3-3 semi-cokes. It has been reported that higher py/ph ratios and lower concentrations of large alkanes in decant oils lead to higher degrees of mesophase development upon carbonization [1].

A comparison of Figure 1 and Figure 3 shows that CF samples have much higher py/ph ratios than the corresponding DO samples. Again, this difference can explain the more developed textures.
obtained from CF compared to the corresponding DO. It is noted, however, that CF3-3 has a higher py/ph ratio than CF3-1, although the semi-coke texture from CF3-1 is slightly worse than CF3-3. This discrepancy may be attributed to the difference in the composition of the heavy ends that cannot be resolved by GC/MS. The fact that VTB3-1 produced a much better texture than VTB3-3 (Table 1) suggests a significant difference in the molecular composition of the heavy ends of the two samples. It should be noted that VTB constitutes a significant fraction of CF. Laser Desorption/Mass Spectrometry and High-Pressure Liquid Chromatography results indicated that five-ring aromatics (benzopyrene and benzopyrenes) are more abundant in CF and VTB [5].

Figures 5-7 present the semi-coke and asphaltene yields from carbonization at 450°C. Figure 5 shows that DO03-3 has the highest semi-coke yield among the samples after relatively long reaction times (>120 min). In contrast, HYD03-3 gave the lowest semi-coke yields, as expected. A sharp increase was observed in the semi-coke yield from GO during the very early stages of carbonization between 15 and 30 minutes, CF03-3, on the other hand, showed a slow and steady increase in the semi-coke yield throughout the reaction time period. Figure 6 shows the asphaltene yields. Among the samples, CF03-3 stands out with much higher asphaltene yields than the other samples throughout the whole reaction time period. HYD03-3, on the other hand, gave the lowest asphaltene yields among the samples (with the exception of GO after 3 h). GO shows comparable asphaltene yield to those of HYD and DO during the early stages.

A comparison of coke and asphaltene yields shows that the conversion of asphaltenes to semi-coke proceeds most slowly during the carbonization of CF03-3. A very rapid initial increase in asphaltene yields from CF03-3 does not translate into a rapid build-up of semi-coke yield, indicating a prolonged presence of a fluid phase that would promote mesophase development. In direct contrast, GO03-3 shows a very fast conversion of asphaltenes to semi-coke during the early (<60 min) and, particularly later stages (>120 min) of carbonization. DO also shows a relatively fast formation of semi-coke from the asphaltenes. GO03-3 and DO03-3
gave the least developed textures in the sample set, as shown in Table 1.

The asphaltene and semi-coke yields from VTB03-3 show a different trend from that of the other samples. A very rapid initial increase in asphaltene yield is followed by a rapid conversion of asphaltenes to semi-coke, as shown in Figure 7. Relatively well-developed mesophase from VTB03-3 despite a fast conversion of asphaltenes into semi-coke may be attributed to a favorable interaction between the evolution of volatiles and the carbonizing viscous phase (with high asphaltene contents) to form elongated anisotropic domains.

Conclusions
Significant differences were observed between the molecular composition of FCC decant oil and its derivatives in two different sample sets. Coker feeds have higher concentrations of aromatic compounds and possess higher pyrenes/phenanthrenes ratios compared to the parent decant oils. Differences in the extent of mesophase development from decant oil, coker feed, gas oil, hydrotreated gas oil, and vacuum tower bottoms can be explained by differences in their molecular composition that is closely related to their carbonization reactivity. In general, slower conversion of asphaltenes into semi-coke favors a high degree of mesophase development. Conversely, at high asphaltene levels during carbonization, effective deformation of viscous anisotropic domains during conversion to semi-coke also promotes mesophase development.

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References