

THE CHARACTERIZATION OF PRODUCTS FROM COAL/RESID CO-COKING

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Introduction

Co-coking is a novel process that incorporates the fundamentals of coal liquefaction and coal pyrolysis. The main motivation behind this novel process was to obtain coal-derived liquid products and carbon-rich solid products, by introducing coal and petroleum resid into a delayed coking operation and simultaneously upgrading them. The liquid products obtained would contain coal-derived material that is desirable because it would include cyclic structures, which when hydrotreated would produce a product that may have higher thermal stability than petroleum-based fuels in advanced aircraft applications. This is important since the next generation of aviation fuel may use the fuel as a heat sink, requiring the fuels to withstand the higher operating temperatures of high Mach aircraft.

In the past direct coal liquefaction processes satisfied the need for producing a feedstock for coal-derived jet fuel, that was a high yield of low-boiling aromatic hydrocarbons, which can be upgraded to hydroaromatic and cycloalkane compounds [1]. Coal liquefaction at present is not an economically viable solution. Coal pyrolysis is also a process that yields these coal-derived products using mild operating conditions. However, the main products obtained from coal pyrolysis are water, carbon oxides and light hydrocarbon gases while the desired coal-derived liquids are produced in low quantities [2]. In our approach to this study we wanted to see how we could adapt a well known and extensively used process for the production of coal-derived feedstocks for advanced jet fuel production. To this end we chose to study how we could utilize the delayed coking process.

Delayed coking is a process used commercially to obtain quality coke and light hydrocarbon fractions from low value petroleum resids and decant oil. This process typically operates in the temperature range of 450-500 °C [3]. Martin and co-workers researched the effects of simulating delayed coking conditions with the co-processing of resid and coal, on the overall products formed [4].

The work presented here represents a continuation of previous studies of co-coking [4,5,6], while focusing in on the characterization of the coal-derived products from this novel co-coking process.

Experimental

Three coals were selected from the Penn State Coal Sample Bank and Database based on their high fluidity, high volatile content and relatively low ash values. Two of the coals were high volatile bituminous coals from Virginia, while the third was a high volatile bituminous coal from the Pittsburgh seam. Table 1, displays the main characteristics of the three coals selected for co-coking. The samples were ground to a -60 mesh and vacuum dried at 110 °C for 2 hours prior to each of the experiments to remove excess moisture. The petroleum vacuum resid used was a coker feed supplied by BP America and was used as received.

Table 1. Properties of the coals used in this study

| RANK | POWELLTON | EAGLE | PITTSBURGH #8 |
|------------------------|-----------|--------|---------------|
| | hVAb | hVAb | hVAb |
| MOISTURE | 6.5 | 6.8 | 2.4 |
| ASH | 5.0 | 5.5 | 10.0 |
| %C | 87.6 | 87.3 | 83.3 |
| %H | 5.8 | 5.6 | 5.7 |
| %N | 1.6 | 1.6 | 1.4 |
| %S | 0.9 | - | 1.3 |
| %O | 3.9 | - | 8.4 |
| TEMP. MAX FLUIDITY (C) | 448.0 | 437.0 | 438.0 |
| FLUIDITY (DDPM) | 30000+ | 30000+ | 20002 |

The reactions were carried out in vertical 25 ml microautoclave sealed reactors with *ca* 6 grams of coker feed and 3 grams of coal (resid/coal ratio of 2:1 by weight) at four temperatures (450, 465, 475, and 500 °C). The reaction length was 2 hours. The reactors were purged with nitrogen to remove any air within the reactors and left at ambient pressure. Once the reaction was complete, the reactors were cooled and the gases that evolved were vented. Any pourable liquid was collected through the stem and later included in the oils (hexane soluble fraction). The products were then removed from the reactor and subjected to a Soxhlet extraction using hexane to remove the oils, toluene to remove the asphaltenes, and finally THF to remove the preasphaltenes. The THF insolubles were then dried in a vacuum oven for 2 hours at 30 °C to remove any excess solvent so the coke product yield could be recorded on a dry weight basis.

The hexane-soluble fractions were subject to analysis using GC-MS and SimDis GC. Semi-quantitative analysis was performed using a Shimadzu GC 17A linked to a QP5000 MS and fitted with a Restek XTI-5 30 meter column. Boiling point distributions were measured using an HP 5890 II plus instrument with and FID and fitted with a 6 meter Restek MXT-500 SimDis column. Ultimate analysis was performed on the coke products using a LECO 600 CHN analyzer and a LECO MAC 400 was used for proximate analysis. Optical microscopy was also performed to determine how the coal and the resids interacted in the coke products.

Results and Discussion

Table 2 shows the overall distribution of the liquid and solid products obtained from co-coking experiments at temperatures of 450, 465, 475 and 500 °C respectively. From these results we can conclude the general trend that as the temperature increases the coke yield increases while the liquid products decreases. Similar conclusions were shown in the work carried out by Hossain and co-workers [7], in that the higher the internal pressures in the tubing bomb reactor the higher the solid carbon yield. In our system the higher temperatures promotes greater decomposition of the liquid phase to gaseous products, which in turn leads to higher internal pressure, and thus higher coke yields.

Table 2: Percent yields for the solvent fractions from co-coking experiments using Eagle, Powellton, and Pittsburgh coal plus coker feed at 450, 465, 475, and 500 °C

| PERCENT YIELDS | | | | | | |
|----------------|----------------|------|------|-------------|----------------|-------|
| TEMP (°C) | FEED | GAS | OILS | ASPHALTENES | PREASPHALTENES | COKE |
| 450 | CO-EAGLE | 14.0 | 24.7 | 3.5 | 2.5 | 42.1 |
| | CO-POWELLTON | 12.1 | 32.2 | 17.2 | 4.0 | 37.1 |
| | CO-PITTSBURGH | 12.2 | 19.5 | 4.3 | 3.9 | 44.5 |
| | COKER ONLY | 16.9 | 52.5 | 5.0 | 1.6 | 21.2 |
| | POWELLTON ONLY | 19.2 | 2.3 | 1.1 | 20.0 | 86.2 |
| 465 | CO-EAGLE | 22.3 | 13.2 | 2.7 | 4.7 | 50.4 |
| | CO-POWELLTON | 22.5 | 7.1 | 0.3 | 0.8 | 25.91 |
| | CO-PITTSBURGH | 18.0 | 16.9 | 1.8 | 1.1 | 49.1 |
| | COKER | 16.1 | 47.7 | 7.9 | 1.9 | 14.5 |
| 475 | CO-EAGLE | 18.3 | 6.5 | 8.0 | 2.3 | 47.6 |
| | CO-POWELLTON | 9.1 | 7.7 | 0.6 | 2.4 | 36.5 |
| | CO-PITTSBURGH | 24.9 | 12.5 | 1.4 | 4.5 | 51.2 |
| | COKER | 37.2 | 28.2 | 1.6 | 6.9 | 25.9 |
| 500 | CO-EAGLE | 17.0 | 5.4 | 0.3 | 4.4 | 48.5 |
| | CO-POWELLTON | 28.3 | 6.7 | 0.3 | 2.2 | 50.6 |
| | CO-PITTSBURGH | 28.6 | 6.3 | 0.5 | 2.7 | 50.9 |
| | COKER | 47.1 | 16.9 | 0.4 | 6.0 | 35.3 |

Reactions preceded by a Co- indicates co-coking experiments.

GC-MS was performed on the hexane soluble fractions to obtain the specific compound distribution of the products from these experiments. The major peaks and volume percents were identified and based on the total area under the peaks. From Table 3, we can see that as the temperature of the reaction is increased, the presence of aromatic compounds increased. This would indicate that the coal conversion and the inclusion of coal derived material in the products was increasing. The coker feed on the other hand consisted of mainly saturated alkanes, which we see contributed to the high content of alkanes for the co-coking reactions at lower temperatures. It is also worth noting that the different coals produced coal-derived compounds at similar reaction temperatures. For example, co-coking experiments performed at 465 °C with Eagle produced high quantities of naphthenes, Pittsburgh produced high quantities of pyrenes, and Powellton had compounds that averaged out across the range of those identified. In addition we can see that in the identified products from co-coking, with the exception of Eagle at 465 °C, that no phenols have been identified. This suggests that their numbers have been sufficiently reduced under the reaction conditions, possibly due to their inclusion in the propagation reactions that lead to coke formation, and thus, their removal from liquid products. These compound distributions obtained from co-coking experiments showed similarities with the products derived from flash pyrolysis experiments by Nip *et al* [7].

Tables 4 shows the percentage yields of methyl substituted compounds that were identified in the oil fraction from co-coking experiments. C1, C2, C3, etc. correspond to mono, di, and tri substituted compound, respectively. It is clear to see that heat-treated coker feed does not contribute any significant quantities of substituted aromatic compounds to the oil fraction (see Table 3). Therefore all the aromatics identified come from coal-derived material.

Once again it can be seen that the different coals produced compounds with differing levels of substitution. Thus indicating the differences in the molecular composition of the coals, even though they are of the same rank classification. The most likely reason for this would be in the subtle structural differences in the reactive macerals, although this is difficult to prove. The increases in temperature are exemplified in the series of tests performed on Powellton coal between

450-500 °C. The general trend shown is that with an increase in temperature, there is a decrease in the amount of substitution in the compounds after the reaction is complete. This is due to the increased cleavage of the methyl groups from the ring at elevated temperatures, with formation of gaseous products. Although not reported, this does also contribute to a reduction in the H/C ratio in the products at higher temperature.

Ultimate analysis and optical microscopy was performed on the THF-insoluble to give an indication of the quality of the coke products being formed. Figure 1 shows that the H/C ratio for the products from co-coking have a lower value than the individual heat-treated feeds. If we calculated the H/C ratios for the products from co-coking from the results of the feeds coked individually, the estimated value is higher than the actual result from the co-coking experiments. This suggests that in co-coking we are enhancing coke formation and the formation of a more carbon-rich product. This is different from what other researchers, such as Tanabe and Gray [8], have seen. In their study the presence of fine particles such as clays, inhibited coke formation during the heat-treatment of vacuum resid.

The optical microscopy results indicated that the coal was contributing more to the mass of the coke product than the petroleum resid. The optical microscopy results also concluded that good mixing was occurring in the reactor between the resid and coal. Which was also a conclusion we gained from fluidity studies which were performed on the feeds and mixtures, that showed both the coals and coker feed were fluid over the same temperature range, and underwent devolatilization at the same rate. In addition optical microscopy gave a good indication of the fine mosaic structures formed during the co-coking conditions. Although there was little evidence to support the homogenizing of the two phases – coal and resid – the analyses showed interesting features. Amongst them were the influences of coal particle size on the degree mesophase formation and the elongated fluid structures from the coal, which were produced during the reactions.

Simulation distillation GC was performed on the hexane soluble fractions produced, to obtain boiling point distributions. For this research, the primary temperature range that was desired for the hexane soluble fraction to fall within was the jet fuel range. The jet fuel range is defined as liquids falling within the 200-260 °C temperature ranges. Figure 2, shows the boiling range for the three different coals with the coker feed, as well as the coker feed and heat-treated coals only, reacted at 465 °C. We can see the effect of combining both the coker feed and the coal lowers the yield of the jet fuels fraction by about half. It seems that the coal is acting as a catalyst for decomposition. When coal is present there is both an increase in gas and coke yields. Couple this with a decrease in liquids yields, we can assume the extra coke and gas come from the decomposition of the coker feed. One reason for this decomposition may be due to the presence of relatively high quantities of phenols being produced from the coal under the reaction conditions. Phenols are known to be good sources of radicals, which in turn can initiate retrogressive polymerization reactions, and the increased yield of coke.

Conclusions

From the work performed so far in the sealed batch reactor systems, we believe that 465 °C is the best temperature to produce the best quality oil fraction and carbon-rich product at reasonable yields. Further study will include feed ratio studies, alternative feeds and the effects of reaction length on yields. Future investigation of product characterization from this co-coking process will include the use of a vented reactor to increase the yield of liquid products at the optimum operating temperature of 465 °C, while still maintaining a relatively high yield of carbon-rich coke.

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Table 3. Compound Distribution Yield in the Hexane Soluble Fraction

| Feed | Oil Yield | Benzenes | Phenols | Alkanes | Naphthenes | Fluorenes | Anthracenes/ Phenanthrenes | Pyrenes |
|-------------|-----------|----------|---------|---------|------------|-----------|-------------------------------|---------|
| Eagle 450 | 4.4 | - | 0.30 | 0.31 | 0.53 | - | 0.17 | - |
| Pow 450 | 2.3 | 0.20 | 0.13 | 0.27 | 0.02 | 0.11 | - | - |
| Coker 465 | 47.7 | - | - | 18.28 | 0.97 | - | - | - |
| CoEagle 465 | 13.2 | 0.19 | 0.16 | 1.30 | 2.99 | 0.19 | 0.75 | 0.08 |
| CoPitts 465 | 16.9 | - | - | 2.06 | 1.89 | - | 0.35 | 4.63 |
| CoPow 450 | 32.2 | - | - | 11.34 | - | - | - | - |
| CoPow 465 | 14.1 | 0.13 | - | 0.47 | 2.62 | 0.11 | 0.97 | 0.18 |
| CoPow 475 | 7.7 | 0.32 | - | - | 1.84 | 0.11 | 0.77 | 0.13 |
| CoPow 500 | 6.7 | - | - | - | 1.52 | 0.11 | 0.91 | 0.29 |

Table 4. Yield of substituted compounds in hexane soluble fractions from co-coking studies.

| REACTION | Benzene | | | Phenols | | | Naphthenes | | | Fluorene | Anthracene/ Phenanthrene | | Pyrene |
|-------------|---------|------|------|---------|------|------|------------|------|------|----------|-----------------------------|------|--------|
| | C1 | C3 | C4 | C1 | C2 | C3 | C1 | C2 | C3 | C1 | C1 | C2 | C1 |
| Pow 450 | - | - | - | 0.07 | 0.09 | 0.04 | 0.08 | 0.14 | 0.06 | 0.02 | 0.09 | - | - |
| Eagle 450 | - | - | - | - | 0.21 | 0.09 | 0.21 | 0.25 | - | - | 0.11 | - | - |
| CoEagle 465 | - | - | 0.15 | 0.05 | 0.11 | - | 0.76 | 1.21 | 0.88 | 0.19 | 0.53 | 0.09 | 0.04 |
| CoPitts 465 | - | - | - | - | - | - | 0.56 | 0.98 | 0.35 | - | 0.20 | - | - |
| CoPow 450 | - | - | - | - | - | - | - | - | - | - | - | - | - |
| CoPow 465 | 0.11 | - | - | - | - | - | 0.78 | 1.17 | 0.48 | 0.11 | 0.49 | 0.30 | - |
| CoPow 475 | - | 0.04 | 0.27 | - | - | - | 0.61 | 0.74 | 0.29 | 0.11 | 0.45 | 0.15 | 0.05 |
| CoPow 500 | - | - | - | - | - | - | 0.59 | 0.60 | 0.15 | 0.05 | 0.50 | 0.12 | 0.08 |

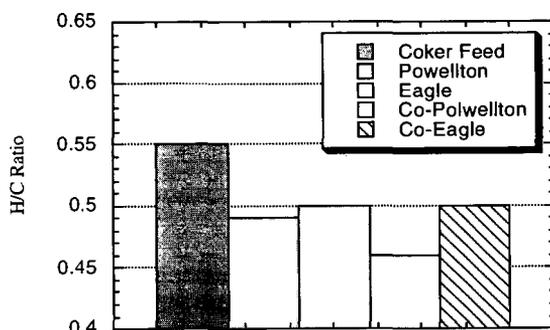


Figure 1. H/C ratios of THF insoluble products from coking experiments performed at 450 °C.

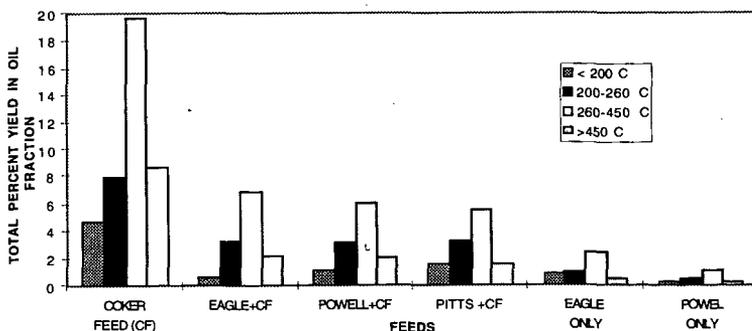


Figure 2. Boiling point distribution analysis of hexane soluble fraction from select co-coking experiments at 465 °C.