CO-COKING: AN ALTERNATIVE PROCESS FOR COAL DERIVED JET FUEL PRODUCTION

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Introduction

It has been found that coal-derived aviation fuels are more thermally stable than petroleum-derived fuels. This is mainly due to the presence of 2 to 3 ringed aromatic components in the oil fractions, which on further processing yield cycloalkane rich fuels [1,2]. Conventionally, coal-derived fuels were produced via coal liquefaction [3,4]. But due to economic market trends a more viable path to obtain these ringed aromatic components is through co-coking. Co-coking is a thermal process used to upgrade and convert petroleum resid and coal simultaneously. Co-coking involves simulating a delayed coker unit in a refinery while adding coal, so that petroleum resids are upgraded to yield a distribution of products that include oils, gases, and coke. Coal is added to increase oil yields as well as produce the coal-derived aromatic components that make a thermally stable jet fuel.

The delayed coking process involves subjecting a petroleum resid to temperatures of 450 - 500 °C [5,6]. A constant pressure of 10-20 psig within the coke drum is maintained due to the evolution of gaseous products. This process not only produces useful oil products, but also quality coke products depending on the initial feedstock. These conditions produce product yields of 70% liquids, 10% gas, and 20% coke. However, since this process was simulated in batch reactors, the product distribution will vary.

The work presented here represents a continuation of previous studies of co-processing [7].

Experimental

Three high volatile bituminous coals were obtained for the Penn State Coal Sample Bank and Database. The coals were chosen for their extremely high fluidity, as well as their low moisture, and sulfur content. These properties are displayed in Table 1. The samples were ground to a <60 mesh to ensure good contact qualities and then vacuum dried at 110 °C for 2 hours prior to each of the experiments. The petroleum vacuum resid used was a coker feed supplied by BP America.

The reactions were carried out in vertical 25 ml microautoclave 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 by the GC, GC-MS, and the Sim Dis GC. Ultimate analysis was performed on the coke products using a LECO 600 for C, H, and N, and a LECO MAC 400 for proximate analysis to obtain the ash and moisture content to determine the chemical interactions between the coals and the resid. Optical microscopy was also performed to determine how the coal and the resids contributed towards the coke product.

Results and Discussion

Figure 2 shows the GC traces for the four different temperatures for one of the coals used, Powellton coal. By examining this figure the trends described below can be seen. Table 2 shows the percentage yields for the various fractions from co-coking experiments using Powellton, Eagle, and Pittsburgh coal at temperatures between 450 - 500 °C.

The results for the coals and coker feed mixed together at 450 °C, showed high oil yields with relatively high coke yields. However, GC traces showed that the oils contained long-chain paraffins, and not the 2-3 ring aromatics that are precursors to thermally stable jet fuel. The results of the coker feed and the coal at temperatures of 465-475 °C showed an increase in coke production with a decrease in oil yield. GC traces further showed that the oils produced contained the 3-5 ringed aromatic components that could be further processed to desirable precursors. The results of the resid and coal at 500 °C showed a heightened effect of an increase in coke production with a decrease in the oil yield. However, when the GC traces were examined the 1-3 ringed aromatics were the major components, suggesting that the reaction conditions were too severe.

Figure 1 shows the changes in the yield of the solvent fractions for co-coking experiments with Powellton coal. Similar trends for the changes in product yields were observed for the Eagle and Pittsburgh coals. The product yields showed that the coke yield increased with decreasing oil yield. This resulted because the reactors were not vented during the reaction, which caused the volatile gases to build up inside. The higher pressure and sealed environment within the reactor, as well as the longer contact time between the volatile constituents at reaction temperature caused the coke yield to increase to the detriment of the oil yield. This effect was noted previously by Hossain and co-workers [8]. This may be why the yields of the products differ from delayed coking operation yields. Delayed coking is a system that allows the volatiles to be vented off on production, which in turns leads to high oil yields (~70%) and lower coke yields (~20%).

These results indicate that we have a flexibility in our process. Depending on the temperature of operation we can manipulate the product yields and compositions to produce precursors for thermally stable jet fuel. That is, for products with 3-5 ringed aromatics an upgrading/hydrogenation process under severe conditions will produce cycloalkanes in the desired boiling fractions which could be used as thermally stable jet fuels. However, it may be desired that a less severe upgrading process be utilized and therefore a product with 1-3 ringed aromatics would be more advantageous.

Elemental analysis of the coke products has produced some interesting and, as yet, not fully understood results. The general trend noted is that when coal and resid are co-coked, we obtain a product that has a lower H/C ratio (more carbon rich) than when resid is coked alone. This, however, does not unequivocally indicate that the product is of a higher quality. Optical microscopy studies tend to suggest that the presence of the coal changes the way resid eoke is formed. Interactions between coal and resid have been noted, which may indicate some dissolution. Initial studies have shown that the optical texture of the cokes produced at 450 °C during co-coking have similar properties of cokes produced from the coking of the resid alone, at temperatures above 475 °C. As to why this is occurring is unclear at present and needs further study.

From the work performed so far in the batch reactor systems, we believe that 465 °C is the best temperature to produce the best quality oil fraction at reasonable yields. Further study will include feed ratio studies, and the effects of reaction length on yields. Alternative feeds, such as decant oil, will also be investigated, with the hope that greater dissolution of the coal will occur while producing different coke products.

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Table 1: Properties of the Coals

	POWELLTON	EAGLE	PITTSBURGH #8
RANK	hVAb	hVAb	hVAb
MOISTURE	6.5	6.8	2.4
ASH	5.0	5.5	10..
%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

Table 2: Percent yields for the Eagle, Powellton, and Pittsburgh coal at 450, 465, 475, and 500°C

		PERCENT YIELDS						
TEMP (C)	COAL	GAS	OILS	ASPHALTINES	PRE-ASPHALTINES	COKE	TOTAL	LOSSES
450	EAGLE	14.0	24.7	3.5	2.5	42.1	86.8	13.2
	POWELLTON	12.1	32.2	17.2	4.0	37.1	102.5	-2.5
	PITTSBURGH	12.2	19.5	4.3	3.8	44.5	84.4	15.6
465	EAGLE	22.3	13.2	2.7	4.7	50.4	93.3	6.7
	POWELLTON	23.6	12.5	0.7	1.6	51.8	90.1	9.9
	PITTSBURGH	18.0	16.9	1.8	1.0	49.1	86.9	13.1
475	EAGLE	18.3	6.5	8.0	2.3	47.6	82.7	17.3
	POWELLTON	9.1	7.7	0.6	2.4	36.5	56.4	43.6
	PITTSBURGH	24.9	12.5	1.4	4.5	51.2	94.4	5.6
500	EAGLE	17.0	5.4	0.3	4.4	48.5	75.6	24.4
	POWELLTON	28.3	6.7	0.3	2.2	50.5	87.9	12.1
	PITTSBURGH	28.5	6.3	0.5	2.7	50.9	89.0	11.0

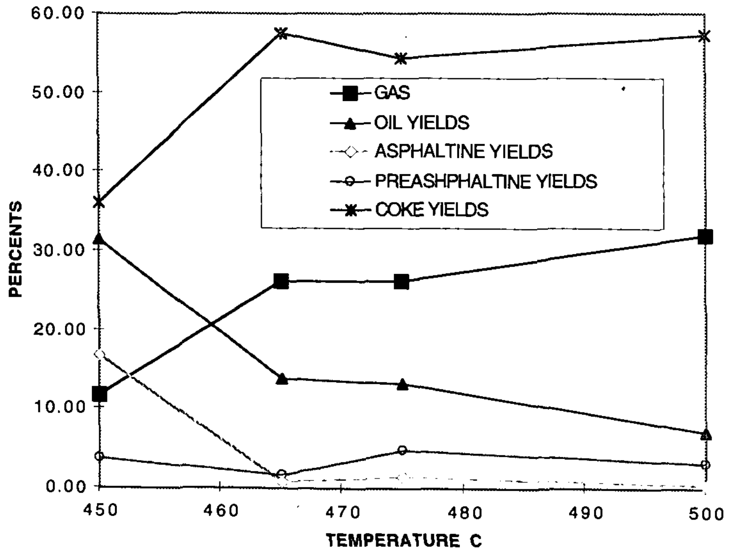

Figure 1: The product yield trends for the Powellton coal at the four temperatures

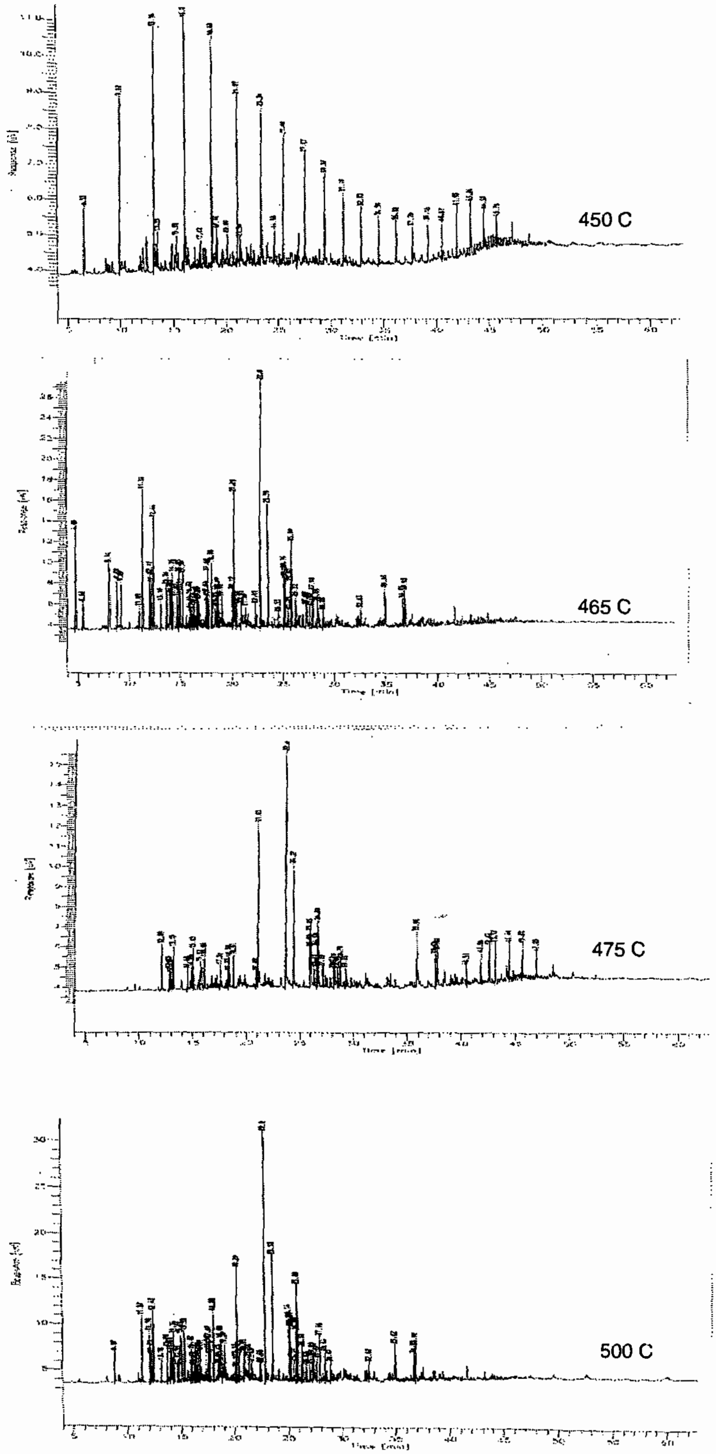

Figure 2: GC Traces for the Powellton coal and coker feed at the four various temperatures [X Axis: *time (min)* Y Axis: *Response (uV)*]