

CO-COKING OF COAL AND PETROLEUM RESID MIXTURES FOR PRODUCTION OF COAL-BASED JET FUEL

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Introduction

The next generation of high Mach aircraft will utilize jet fuel to serve two main purposes. First the fuel will be used as a propellant. The second function of the fuel will be to serve as a heat sink for the aircraft's subsystem. As a result the fuel will be exposed to thermally stressing temperatures that exceed 450 °C, where pyrolytic degradation can occur. If solid deposits form in the fuel as a result of this degradation, plugging of the fuel lines can result. The presently used petroleum-derived jet fuel, JP-8, lacks the necessary hydroaromatic compounds that increase the thermal stability of the fuel. Fuel containing coal-derived components, however, would contain 2-3 ring hydroaromatics that increase the thermal stability of the fuel. However, past methods for obtaining coal-derived liquids are not economical.

There are two main processes for production of coal-derived liquids, coal liquefaction and coal pyrolysis [1,2]. Coal liquefaction produces desired low-boiling aromatic hydrocarbons, which are then upgraded. However the process involves high hydrogen pressures, which pose economic concerns [1]. At the other end of the spectrum, coal pyrolysis is a process that yields coal-derived liquids 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 quantity [2].

In our search for an alternative pathway for producing coal-derived liquids, the desire to incorporate a well-established industrial process became our driving force. Since oil refineries utilize delayed cokers to convert low-valued feedstocks into useful products such as low boiling distillates, it was decided to examine such a process to see if it could be modified to produce coal-derived liquids.

Delayed coking is a commercially used process to obtain quality coke and light hydrocarbon fractions from a low value petroleum resid [3]. This process typically operates in the temperature range of 450-500 °C [3]. For the purpose of this research we decided to incorporate coal into a simulated delayed coking process and termed this novel process co-coking. The intent of this novel process was to obtain liquid products that possess coal-derived structures which, when hydrotreated, would produce a product with higher thermal stability than petroleum-based fuels.

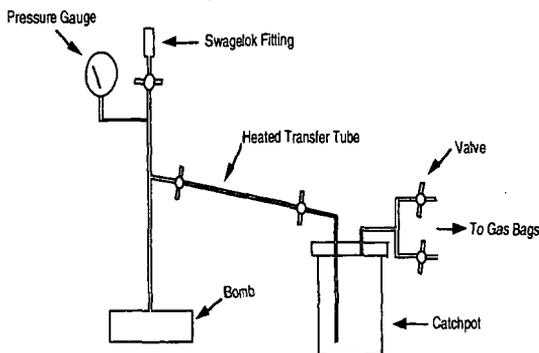
The work presented here focuses on the effects of different feed ratios and reaction length effects for various co-coking reactions. This work represents a continuation of previous studies of co-coking [4,5,6,7].

Experimental

Three coals were originally selected based on their high fluidity, high volatile content and relatively low ash values [7]. This paper, however, will focus on an in-depth study of the Powellton seam coal, to determine effects of reaction conditions, such as feed ratio and reaction length. The trends obtained from this particular coal can then be related to the other two coals based on previous research [6,7]. The coal was ground to a -60 mesh and vacuum dried at 110 °C for 2 hours prior to each experiment to remove excess moisture. Two different petroleum resids were employed. The first was a coker feed supplied by BP America. The second was a decant oil supplied by Marathon Oil Company. Both resids were used as received.

These coking reactions were carried out in a constructed vented reactor system. Figure 1 displays a schematic of reactor system utilized. This system consisted of a modified microautoclave reactor (tubing bomb) that was attached to a catchpot system immersed in an ice bath. The reactor system was developed to model aspects of delayed coking in the laboratory. The bomb portion of the system was intended to model a coking drum, while the catchpot was used to catch volatiles, which were then, re-condense into liquids. Before each reaction, the reactants were placed in the bomb portion of the reactor system in various feed ratios. The bomb portion, piping and catchpot were then purged with nitrogen to remove any air within the reactor system and finally left at ambient pressure. The bomb portion of the reactor system was then placed in a fluidized sand bath at a temperature of 465°C, while the

Figure 1: The vented reactor system



catchpot portion was placed in an ice bath. This temperature proved from previous work [6,7] to produce desirable liquid and solid product yields. Reaction length was varied.

Once the reaction was complete, the reactor system was left to cool. The liquids that accumulated in the catchpot portion of the reactor system were collected and subjected to a hexane extraction to obtain the oil products. The products were then removed from the bomb portion of the reactor system and subjected to a tetrahydrofuran (THF) Soxhlet extraction and finally a hexane extraction to obtain hexane-solubles. The THF-insoluble products were then collected and dried to obtain the coke product on a dry weight basis.

The hexane-soluble fractions from both the catchpot and bomb portion were subject to semi-quantitative analysis using a Shimadzu GC 17A GC-MS, to identify the composition of oils produced, and a HP 5890 II instrument with an FID high temperature simulation distillation GC, to obtain the various boiling cut points. Ultimate analysis and proximate analysis was performed on the coke products using a LECO 600 CHN analyzer and a LECO MAC 400 respectively. Optical microscopy was also performed on the coke products to determine if any interactions were occurring between the coal and petroleum resids.

Results and Discussion

Table 1 shows the overall distribution of the liquid and solid products obtained from co-coking reactions at 465°C for various feed ratios and reaction lengths. We know from previous research that the product distribution from these vented co-coking reactions is unaffected by temperature effects [7]. During the co-coking reactions, partial vaporization and mild thermal cracking, occurs causing both gas and light boiling distillates to flash distillate into the cooled catchpot [8]. The remaining heavy liquids in the bomb portion of the reactor are further subjected to cracking and polymerization reactions, which produce more gas. These gases are also re-condensed in the catchpot [8]. Along with the gases, a solid coke product is formed as a result of cracking reactions. This effect was evident when we examine the product distribution effect versus reaction duration. As the reaction length was increased for a particular feed ratio, the overall liquid yield decreased, while the solid product yield increased. The decrease in overall liquid product yield was mainly a result of the drastic decrease in the THF soluble liquid products as reaction time increased. This occurred because the liquids were exposed to further cracking reactions. The catchpot liquids, however, were unaffected by reaction length, since most of the liquids were flashed off very early in the reaction.

Table 1 also shows the feed ratio effect on the product distribution of co-coking reactions at 465°C. As the amount of petroleum resid was increased in these co-coking reactions for a particular reaction length, the overall liquid products increased, while the overall solid products decreased. Generally the increase in overall liquid product results from an increase in liquid products collected in the catchpot portion of the reactor system. This concurs with logic, since an increase in the amount of paraffinic liquid results in an increase in volatiles, which are easily re-condensed. This present reactor system was not designed to accommodate for adequate gas collection. However, the amount of gas most likely produced from these co-coking reactions, according to mass balances, would be negligible.

The addition of coal from previous studies [6,7] has been shown to decrease the overall liquid product yield when compared to a heat-treated petroleum resid alone. The coal seems to contain highly reactive components that initiate radical reactions that result in retrogressive polymerization reactions.

Overall these liquid and solid yields are comparable to an industrial delayed coking process product distribution of 70% liquids, 10% gas, and 20% coke [3,8]. The product distribution results verify that simplified delayed coking was being simulated by the vented reactor system.

However, our primary goal of this research was to produce low-boiling distillates that can be hydrotreated to produce a thermally stable coal-derived jet fuel. To determine the extent of suitability of the liquid products produced from these co-coking reactions for jet fuel, high temperature simulation distillation GC was performed on the hexane-soluble fractions. For this research, the desired boiling range for the hexane-soluble fraction was 180-330°C. This boiling distribution was defined as the jet fuel range. Figure 2 shows the effect of feed ratio on the liquid yield that fell within the jet fuel boiling range for various co-coking reactions at 465 °C for two hours. The general trend observed was that as more coal was added to these co-coking reactions, the greater the liquid yield, from the catchpot, that distills in the jet fuel boiling range. However, process conditions limit the amount of coal that can be added to a delayed coker. Although the jet fuel boiling yield from the 1:1 ratio of Powellton coal and decant oil in Figure 2 demonstrates a desirable yield of distillates, the ability to process this feed mixture through connective piping in an industrial delayed coker becomes a concern.

Another general trend observed from Figure 2 was that the addition of coal decreases the overall yield of products that distill in the jet fuel boiling range when compared to reaction with heat-treated resid only. The exception that occurred here was with the coker feed. The addition of coal to the coker feed seemed to enhance the yield of jet fuel distillates. This most likely occurred because both the coal and coker feed were acting as hydrogen donors toward the more aromatic components produced in these reactions. This enhancement of the jet fuel boiling distribution yield did not occur when the Powellton coal and decant oil are co-coked, since the decant oil does not appear to act as a hydrogen donor. This explanation was supported by the results obtained when a mixture of the two resids was coked in the presence of the coal. We saw an increase in the yield for the 180-330 °C boiling range when the coker feed was incorporated into the co-coking reactions with decant oil and Powellton coal. The results seem to show that both Powellton coal and the coker feed act as hydrogen donors during these coking reactions, while the decant oil acts as an initiator of radical reactions.

Figure 3 shows the effect of reaction length and feed ratio on the liquid yield from the catchpot that fell within the jet fuel boiling distribution. The general trend observed was that, as reaction length increased, an increase in the jet boiling distribution range occurred. However, an important note was that although the percent yield in the jet fuel range increased as reaction length increased, the overall liquid product being produced decreased. This was mostly likely due to secondary cracking reactions of the heavy liquid, producing more volatiles. Another trend observed involved jet fuel yields from co-coking reactions involving the coker feed, decant oil and the Powellton coal. These yields fell exactly in between the Powellton/coker results and the Powellton/decant results for corresponding reaction lengths and feed ratios.

Ultimate analysis was performed on the hexane-soluble fractions produced from co-coking reactions at 465°C to determine the quality of products being produced. Table 2 shows the H/C ratio for the hexane-soluble products. The results showed the liquid H/C ratio obtained from reactions with a 1:2 feed ratio (coal:resid) in the catchpot were unaffected by reaction length. These results further indicated the liquids obtained in the catchpot had undergone flash pyrolysis. Table 2 also shows that as the feed ratio was increased to 1:4 (coal:resid) there was no real significant effect in the catchpot H/C ratio. While the liquid H/C ratios from the bomb portion showed a decrease in the H/C ratio as reaction length was increased. This occurred because of further liquid decomposition in the bomb portion of the reactor during longer co-coking reactions. When the feed ratio was increased to 1:4 (coal:resid) a higher bomb H/C ratio occurred as a result of the increased concentration of paraffinic compounds.

Ultimate analysis and optical microscopy were performed on the THF-insoluble products to give an indication of the quality of the coke being produced. Figure 4 illustrates that as reaction length was increased, the H/C ratio of the coke product decreased, indicating a more carbon-rich product. This trend was a result of cracking and polymerization reactions that occur in the co-coking reactions. The effect of feed ratio was negligible on the solid H/C ratio.

Optical microscopy indicated enhancement of coal particles when Powellton coal and decant oil was co-coked. However, when the coke products from the coker feed and Powellton coal were examined, no interactions were observed. Varying the feed ratio had no effect on this reaction matrix. Results from co-coking of the three reactants showed that the influence of the decant oil on the coal particles diminished as compared to the coal and decant oil interaction. The influence of the decant oil in this tri-coking proved to be quite variable throughout the

sample. As a result some coal particles were fully enhanced, and some remained unaffected, but most coal particles fell somewhere in between the two extremes.

Conclusions

From work to date we can adequately conclude that we are upgrading these heavy petroleum resid by producing a coke product that is more carbon and liquids with increased H/C ratios. It was found that by increasing the feed ratio to favor the addition of a petroleum resid, the overall liquid product yield increased, but a decrease in the jet fuel boiling distribution yield was observed. While little effect was observed on the H/C ratio of the liquids obtained when the feed ratio was increased, an increase in reaction length resulted in a decrease of the overall liquid products and an increase in the jet fuel boiling distribution yield. In conclusion this process seems to be simulating the delayed coking process on a laboratory scale.

Acknowledgements

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Table 1: Feed ratio and reaction length effects on product yields from co-coking reactions with Powellton coal and the two petroleum resids at 465 °C

RESID	TIME	PRODUCT YIELDS			
		Feed Ratio 1:2		Feed Ratio 1:4	
		Liquid %	Solid %	Liquid %	Solid %
Coker	30 minutes	83.61	24.78	69.19	26.71
Coker	2 hours	38.84	40.74	61.54	30.98
Coker	4 hours	48.71	38.87	55.78	30.20
Decant	30 minutes	73.09	28.57	78.23	13.78
Decant	2 hours	55.47	37.67	56.88	34.03
Decant	4 hours	39.68	43.12	49.24	49.24
Decant/Coker	30 minutes	53.86	30.50	*	*
Decant/Coker	2 hours	44.64	39.88	60.59	26.50
Decant/Coker	4 hours	52.97	40.49	62.01	26.53

* Data Missing

Table 2: Feed ratio and reaction length effects on hexane-soluble product H/C ratios from co-coking reactions with Powellton coal and various petroleum resids at 465 °C

COAL	RESID	TIME	HEXANE SOLUBLE H/C RATIOS			
			Feed Ratio (1:2)		Feed Ratio (1:4)	
			CATCHPOT	BOMB	CATCHPOT	BOMB
Powellton	Coker	30 minutes	2.30	1.64	2.49	2.01
Powellton	Coker	2 hours	1.86	1.36	2.30	1.36
Powellton	Coker	4 hours	2.30	0.87	2.47	1.03
Powellton	Decant	30 minutes	1.30	1.05	1.23	0.90
Powellton	Decant	2 hours	1.40	0.70	1.45	0.82
Powellton	Decant	4 hours	*	0.90	1.59	0.76
Powellton	Decant/Coker	30 minutes	1.60	0.98	*	*
Powellton	Decant/Coker	2 hours	1.51	1.16	1.74	1.46
Powellton	Decant/Coker	4 hours	1.67	1.82	1.78	1.04

* Data missing

Figure 2: Feed ratio effects on the jet fuel boiling distribution (180-330°C) for the hexane-soluble fractions from co-coking reactions at 465°C for two hours

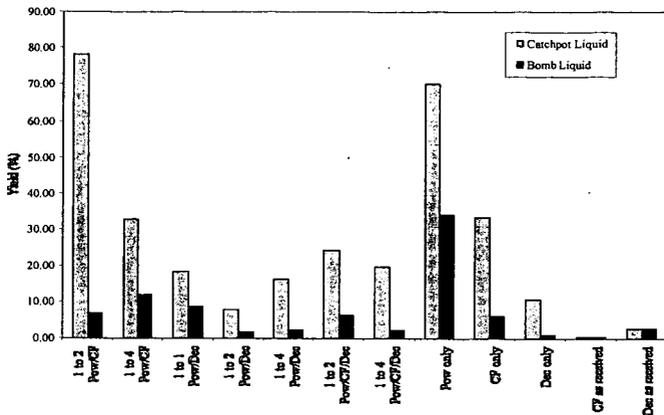


Figure 3: Reaction Length effects and feed ratio effects on the jet fuel boiling distribution of the catchpot hexane-soluble fraction from co-coking experiments at 465 °C.

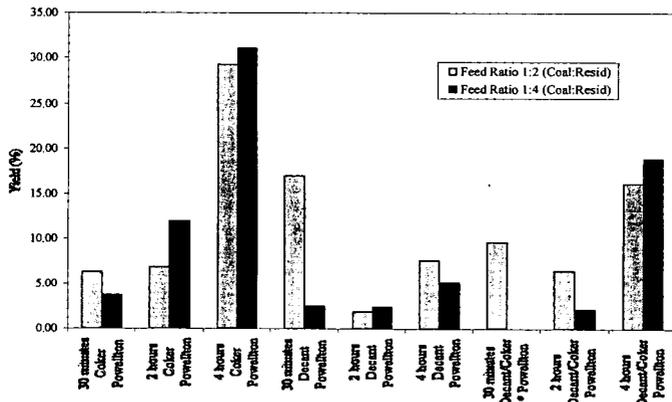


Figure 4: Reaction length and feed ratio effects on the solid coke products formed from co-coking reactions at 465 °C with Powellton coal and the two petroleum resids

