

RECYCLE OILS FROM FLUID COKING OF COAL LIQUEFACTION BOTTOMS

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ABSTRACT

A series of nine fluid-coker tars, produced by Lummus-Crest, Inc., from coal liquefaction vacuum bottoms, was characterized to evaluate their use as liquefaction recycle oils. The primary variables in the coking tests were temperature (1000 to 1200°F) and coker feedstock source. The properties of the tars are principally influenced by the coking temperature. Those produced at higher temperature are more aromatic and contain less hydrogen, and are principally unsubstituted and methyl-substituted condensed aromatic compounds. The tars produced at 1000°F are expected to be poor hydrogen donor solvents, whereas those produced at 1200°F are not expected to be hydrogen donor solvents. However, a 1200°F tar was readily hydrotreated to produce a good to excellent donor solvent. Based on these results, it would appear that tars produced from fluid coking of liquefaction vacuum bottoms can be recycled to a catalytic liquefaction reactor to produce additional liquids without adversely affecting process performance.

INTRODUCTION

In the development of processes for the direct liquefaction of coal, the efficient removal of solids from the product has proven to be particularly difficult. Many techniques have been tested and used, including filtration, hydrocyclones, vacuum distillation, Critical Solvent Deashing and antisolvent deashing; however, no truly satisfactory means has been developed. All suffer from high product rejection, high cost or serious engineering difficulties. An alternate method, fluid coking of vacuum bottoms, is being explored by Lummus-Crest, Inc., under subcontract to Burns and Roe Services Corp. through U.S. DOE Contract DE-AC22-84PC72571. The recently completed Lummus experimental program included ten tests in which five different samples of coal liquefaction vacuum bottoms were coked in a 20g/hr (nominal) continuous stirred coking unit (CSCU). The CSCU was used to simulate true fluid coking. The range of operating conditions used in the CSCU tests was chosen based on earlier tests (1,2) with a batch coker. Operating conditions for the CSCU tests are shown in Table 1, as reported by Lummus (3). Ranges of product yields (3) from the ten tests (on a wt % of total product basis) were as follows: gases, 5 to 18; coker distillate, 30 to 81; coke plus ash, 14 to 59. On an ash-free product basis, coke yields (3) ranged from 11 to 52 wt %. Details of the coker tests, the equipment and product yields appear elsewhere (3). The vacuum bottoms that were coked were originally produced in the Advanced Coal Liquefaction Test Facility at Wilsonville, Alabama, and at the Catalytic Two-Stage Liquefaction (CTSL) continuous bench unit, which is operated by Hydrocarbon Research Inc. (HRI) in Lawrenceville, New Jersey. The vacuum bottoms were produced from

Ohio 6, Illinois 6 and Wyodak coals. In the conceptual integration of liquefaction and fluid coking, the coker tars would be processed in the liquefaction plant, ultimately to produce additional distillate products. The tars could be introduced to the liquefaction plant as part of the recycle solvent or as a second stream entering a second-stage reactor. The coke would be gasified to produce hydrogen, burned for power or landfilled.

The coker tars may be quite dissimilar to typical liquefaction oils. If used as a significant part of the recycle oil, the donor-solvent quality of that stream could be altered. Moreover, the ease with which the coker tars can be hydrotreated to finished products is unknown. The objectives of the work reported here are: 1) to characterize the coker tars, 2) to evaluate their properties as donor solvents, and 3) to explore the potential of hydrotreating to improve their characteristics as products and as donor solvents.

EXPERIMENTAL

MATERIAL

Nine coker "distillates" were obtained from Lummus. Lummus uses the term "coker distillate" to describe these materials; however, since they are largely non-distillable, the term "coker tar" will be used here. The feedstock and operating conditions used to produce each of the coker tars are shown in Table 1 (3). Lummus' program consisted of ten tests, but no product was provided from Run CSCU-11. In some cases, the samples we received were total liquid products (TLP). In other cases we received the 650°F⁺ portion from a true boiling point distillation of the TLP. Typically, the 650°F⁺ portion accounted for about 97% of the TLP (4).

ANALYSES

C, H, N and S were determined on the tars with Leco CHN-600 and SC-32 instruments. There was some difficulty obtaining samples containing representative quantities of ash for the CHN-600 instrument and, as a result, C, H, and N results may contain more uncertainty than usual. Ash was determined on the whole samples. The samples were filtered through Whatman #42 filter paper with freshly distilled tetrahydrofuran (THF). The filter cake was dried, weighed and ashed to determine the ash and insoluble organic matter (IOM) content, and to confirm the ash content. The filtrate was rotary evaporated to dryness to remove the THF and to determine the mass of solubles. Complete removal of THF was verified by proton nuclear magnetic resonance (¹H-NMR) spectroscopy. ¹H-NMR spectra were obtained in CDCl₃ solution as previously reported (5). Spectra were obtained on each whole sample and on several of the THF-soluble portions. There was no significant difference between the spectra of the two types of samples. The ¹H-NMR solvent, CDCl₃, dissolved almost, but not quite the entire THF-soluble sample. This did not appreciably affect the ¹H-NMR spectra since spectra obtained on the whole sample in C₅D₅N were essentially the same as the spectra of the THF solubles in CDCl₃. Phenolic -OH contents were determined on the THF solubles by the previously reported Fourier-transform infrared spectroscopic method (6). Gas chromatography/mass spectrometry (GC/MS) analyses were performed by the previously reported method (7).

HYDROTREATING

A sample of the coker tar from Run CSCU-1 (5g) was hydrotreated (750°F, 60 min) in a 45 mL shaking microautoclave in the presence of 5g of

Amocat 1A catalyst and 1600 psig H₂ (cold). The total H₂ charged was about 0.34 g. Its initial pressure at 750°F would be about 3700 psig. The micro-autoclave was agitated at 1000 half-inch strokes/min. The catalyst was supplied by Hydrocarbon Research, Inc., and was removed from the first-stage reactor early in Run O-1 of their Catalytic Two-Stage Liquefaction program. The product was freed of solids and analyzed as described above. The overall recovery of charged material (excluding gases) was 97.8 wt %. The THF-soluble hydrotreated product accounted for 88.5 wt % of the feed, or 101.9 wt % of the THF-solubles in the feed.

DISCUSSION

CHARACTERISTICS OF COKER TAR

The elemental analyses and ash and IOM contents of the coker tars are shown in Table 2. Table 3 shows the proton distributions of the chloroform solubles and the concentrations of phenolic -OH in the THF solubles. All the coker tars contained substantial quantities of ash and IOM. The ash appeared to be a mixture of coal ash and alumina particles that reported with the tars through entrainment. It appears that the alumina "seed" used as the bed in the coker (3) was the source of the alumina particles in the coker tar ash. The IOM in the coker tars may have also originated from entrainment, though some portion of it may derive from retrogressive reactions among the tar components.

The characteristics of the hydrocarbon portion of the tars are clearly influenced heavily by coking temperature. Averages (\pm std dev) of selected properties are shown below as a function of temperature.

Coking T, °F	wt %, ash free		Proton Types, % in CCl ₄ Solution		
	C	H	Aromatic	Cyclic Beta	Paraffinic
1000	91.2 \pm 0.4	6.6 \pm 0.5	36.8 \pm 7.5	12.2 \pm 2.7	25.0 \pm 0.5
1100	91.8 \pm 0.4	5.0 \pm 0.3	53.2 \pm 2.3	6.7 \pm 0.8	12.4 \pm 0.2
1200	94.8 \pm 0.4	4.6 \pm 0.1	68.0 \pm 1.6	3.1 \pm 0.3	4.7 \pm 0.8

Aromatic protons consist of the sum of condensed and uncondensed aromatic protons. Paraffinic protons consist of the sum of alkyl beta plus gamma protons. Cyclic beta protons provide an indication of the donatable (hydroaromatic) hydrogen content. Though Lummus did not use a complete factorial experimental design, the above table clearly demonstrates that the properties of the hydrocarbon portion of the tar are most affected by coking temperature. With increasing coking temperature, the tars became much more aromatic and contained much lower concentrations of hydroaromatic, paraffinic and total hydrogen. Over the range tested, the other variables had a less significant impact on the properties of the hydrocarbon portion of the tars.

In fluid coking, material can report to the tar product through a combination of cracking and devolatilization. Additional material is carried out of the coker by simple steam distillation and entrainment. The characteristics of the tars indicate that the former mechanism is relatively more important at 1200°F and that the latter mechanisms are relatively more important at 1000°F. However, cracking reactions are important even at 1000°F, as evidenced by the proton distributions of, for example, the feedstock and tar product from CSCU Run 8. Though the exact feedstock used in Run CSCU-8 was not available for analysis, numerous other second-stage vacuum bottoms samples from Wilsonville Run 254 were analyzed (8). Ranges of their properties are shown below.

Proton Type	Proton Distributions, %	
	Vacuum Resid, Range From Wilsonville Run 254	Run CSCU-8 Coker Tar
Aromatic	22.4 - 35.4	42.1
Cyclic Beta	14.1 - 18.2	10.3
Paraffinic	20.5 - 32.6	21.4

The lower concentrations of paraffinic and cyclic beta protons in the tars produced at 1200°F indicate that pyrolysis reactions have cracked most of the alkyl substituents longer than methyl from the aromatic nuclei.

In contrast to the hydrocarbon moieties, the heteroatom contents and phenolic -OH concentrations in the tars show no clear temperature dependence and may primarily reflect the characteristics of the liquefaction bottoms used as the coker feed.

EVALUATION OF TARS AS DONOR SOLVENTS

Conceptually, the coker tars could be introduced to the liquefaction plant as a portion of the recycle oil. If the tars were to comprise a significant portion of the recycle oil, their properties as donor solvents could be important to the performance of the overall process.

None of the tars was directly tested for donor solvent quality. However, a previously developed correlation (5) between proton distributions and donor solvent quality was used for their evaluation. The original correlation was developed for distillate coal liquefaction recycle oils. Though the correlation was not developed for coker tars, it should provide a good indication of their donor solvent quality. The solvent quality index shown in Table 3 was calculated from Equation 4 of Reference 5. These data are summarized below by coking temperature.

Coker Temp., °F	Calculated Solvent Quality Index
1000	74.0 ±7.4
1100	67.4 ±6.9
1200	52.5 ±4.1

With increasing coker temperature, donor solvent quality is substantially reduced. Based on our experience in evaluating solvent quality, we would conclude that the tars produced at 1000°F are poor donors, those produced at 1100°F are even poorer donors and those produced at 1200°F are essentially non-donors.

In those situations in which donor solvent properties are important, for example in a non-catalytic first-stage reactor, it would be expected that the tars would deleteriously affect liquefaction performance if used as a substantial portion of the recycle oil. Of course, any deleterious effect would be reduced as the tar became a smaller portion of the recycle oil. In catalytic liquefaction, such as the H-Coal or catalytic two-stage liquefaction processes, the solvent quality of the recycle oil may be less important. If the tars can be rapidly hydrogenated to produce hydroaromatics (donors), then they may actually improve the donor solvent quality in the reactor inventory. The low concentration of alkyl groups longer than methyl would be beneficial to the donor solvent quality of the hydrogenated tars.

HYDROTREATING OF COKER TAR

All advanced liquefaction processes being developed employ at least one catalytic reactor to maximize distillate production by converting the solubilized coal to distillable products. If fluid coking is to be successfully combined with liquefaction, it must be possible to hydroprocess the coker tars to produce suitable products and an acceptable recycle oil. If the tars are refractory to hydrotreating, coking will provide very little additional liquids yield to the liquefaction process.

One experiment was performed with a coker tar produced at 1200°F to explore the potential of hydrotreating to upgrade the coker tar. Procedural details are presented in the Experimental section. Analyses of the feed and product are presented in Table 4. The data show that even this simple batch hydrotreating was quite successful in hydrogenating the coker tar and removing heteroatoms. ¹H-NMR spectra of the feed coker tar and the hydrotreated product, which are shown in Figures 1A and 1B, respectively, show that a substantial portion of the aromatics were converted to hydroaromatics. The calculated solvent quality index (5) increased from 51.3 to 85.9, i.e., the tar was converted from an essentially non-donor solvent to a high quality solvent.

GC/MS analyses were performed on both materials. Only the portion boiling below about 500°C was detected by the procedure used. The only identified components in the coker tar were four-ring condensed aromatics containing 0 to 2 alkyl carbons (most alkylation was methyl and dimethyl). The hydrotreated product contained compounds with a range of from two to six rings, most of which were partially hydrogenated and contained 2 or fewer alkyl carbons. Examples include methyl tetralins, octahydrophenanthrene, decahydrophyrene and tetrahydrochrysene, all of which are good donors.

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TABLE 1
 COKER FEEDSTOCKS AND OPERATING CONDITIONS (3)

CSCU Run	Vacuum Bottoms Feedstock Source			Operating Conditions				
				T, °F	P, psig	Inject Steam to Feed, wt Ratio	Approx. Res. Time, sec.	
	Coal	Plant (Run No.)	Sample				Liquid	Vapor
8	Ohio 6	W'ville (254)	3587	1000	10	0.40	7.7	4.0
11	Ohio 6	W'ville (254)	3587	1100	10	0.40	7.9	4.3
9	Ohio 6	W'ville (254)	3587	1200	10	0.40	7.3	3.6
1	Ohio 6	W'ville (254)	3587	1200	2	0.31	8.2	5.2
2	Ill. 6	W'ville (250-D,E)	3567	1200	10	0.28	10.2	5.9
4	Ill. 6	W'ville (250-D,E)	3567	1200	10	0.33	7.8	4.6
12	Ill. 6	W'ville (253)	3584	1100	10	0.40	7.4	3.9
7	Ill. 6	HRI (1-25)	3576	1000	10	0.35	9.6	5.8
6	Ill. 6	HRI (1-25)	3576	1200	10	0.37	8.4	5.5
13	Wyodak	W'ville (251)	3566	1100	10	0.4	7.4	3.9

TABLE 2
 ANALYSES OF COKER TARS

Sample	wt %, Ash Free					wt %, As Determined	
	C	H	N	S	O (diff)	Ash	IOM
CSCU-8, TLP	91.0	6.3	1.0	0.1	1.6	2.5	0.6
CSCU-9, TLP	92.1	4.7	1.0	0.2	2.0	4.7	4.0
CSCU-1, 650°F ⁺	95.0	4.7	1.1	0.2	-1.0	10.7	6.9
CSCU-2, 650°F ⁺	94.3	4.5	1.2	0.2	-0.2	9.8	8.8
CSCU-4, 650°F ⁺	94.9	4.6	1.0	0.2	-0.7	12.7	8.2
CSCU-12, TLP	91.3	5.3	1.0	0.3	2.1	4.4	3.3
CSCU-7, 650°F ⁺	91.5	7.0	0.6	<0.1	0.9	1.2	1.0
CSCU-6, 650°F ⁺	95.1	4.7	0.9	0.1	-0.8	19.0	7.3
CSCU-13, TLP	92.0	4.9	1.0	0.7	1.6	26.9	13.6

TABLE 3
 PROTON DISTRIBUTIONS AND PHENOLIC -OH CONCENTRATIONS OF COKER TARS

Sample	Proton Distributions, %							Conc. of Phenolic -OH in THF-Sols., meq/g	Calculated Solvent Quality Index
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma		
	CSCU-8, TLP	28.2	13.9	12.7	13.5	10.3	14.1	7.3	0.65
CSCU-9, TLP	54.7	10.9	14.9	10.7	3.5	3.5	1.8	0.60	59.3
CSCU-1, 650°F ⁺	57.6	11.1	13.6	10.9	2.7	3.2	1.0	0.53	51.7
CSCU-2, 650°F ⁺	54.8	12.4	12.2	11.6	3.3	3.7	2.1	0.53	49.5
CSCU-4, 650°F ⁺	56.7	11.9	13.6	11.0	3.0	2.4	1.4	0.51	52.8
CSCU-12, TLP	41.2	10.3	16.6	12.3	7.3	7.8	4.4	0.64	72.3
CSCU-7, 650°F ⁺	25.6	5.9	16.1	9.6	14.1	19.3	9.4	0.23	79.2
CSCU-6, 650°F ⁺	60.0	9.9	12.9	10.3	2.8	2.8	1.4	0.30	49.1
CSCU-13, TLP	42.6	12.2	13.5	13.1	6.1	9.0	3.5	0.52	62.6

TABLE 4
HYDROTREATING RESULTS

<u>Analysis, wt % Ash Free</u>	<u>Feed (CSCU-1) (a)</u>	<u>THF Soluble Hydro Product</u>
C	92.3	91.7
H	5.1	6.7
N	1.3	0.9
O (Diff)	1.2	0.6
S	0.2	<0.1
<u>Conc. of Phenolic -OH in THF Solubles, meq/g</u>	0.55	0.31
<u>H-Aromaticity of CDCl₃ Solubles, %</u>	68	41

(a) This is a different sample of the 650°F⁺ fraction from Run CSCU-1 than appears in Tables 2 and 3. Differences in analytical data from Tables 2 and 3 may be real or may reflect uncertainty.

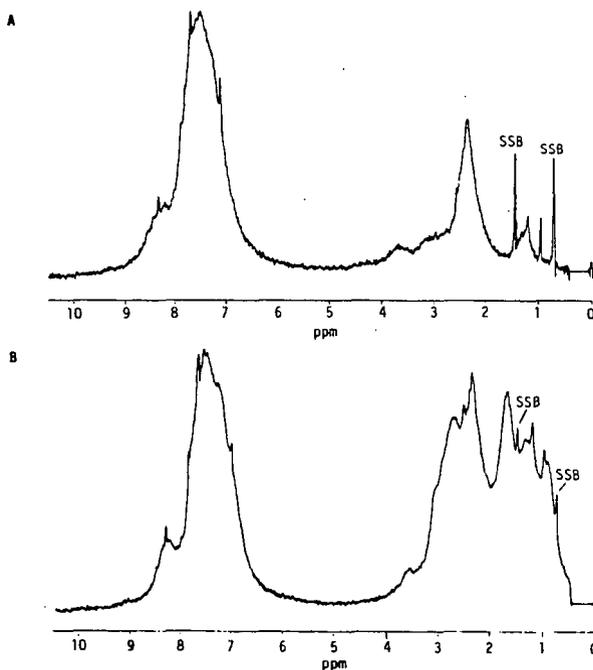


Figure 1. ¹H-NMR Spectra in CDCl₃ of A) Coker Tar from Run CSCU-1 and B) of Hydrotreated Product (SSB = Spinning Side Bands).