THE ORGANIC/MINERAL INTERACTION IN COAL LIQUEFACTION BOTTOMS

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ABSTRACT

Characterization of the organic/mineral matter interactions is central to the problem of solid/liquid separation in the liquefaction of coal. Samples of the vacuum tower bottoms from the liquefaction of Illinois No. 6 coal in the Wilsonville pilot plant have been studied. The techniques include various analyses such as elemental, solvent extraction, STEM, FTIR, XPS, XRD, and XRF. Surface active oxygenates associated with organic/mineral matter interaction appear to consist of both phenolics and carboxylates. The observed characteristics of the organic/mineral interactions were affected by the recycle of mineral matter and unconverted coal as part of the liquefaction feed solvent.

INTRODUCTION

The separation of unconverted coal and mineral matter from heavy coal-derived liquids is difficult. Work was undertaken to determine if an interaction between these components could be demonstrated which could prove useful in the design of efficient mineral removal processes. Specific reference is made to the use of critical solvent deashing (CSD) such as that of the ROSE-SR process of Kerr-McGee Corporation. The polar functionality of clays, carbonates, and other minerals would likely interact with heterofunctional groups in coal asphaltenes and preasphaltenes. Therefore, typical coal-derived resids and unconverted coal solids were characterized, focusing on the loading of organic oxygenates onto mineral matter.

Coal asphaltenes have been shown to have high levels of heterofunctionality(1), and the oxygenate groups are primarily phenolic(2) with low to immeasurable levels of carboxylic groups. In fact, Illinois No. 6 coal, which was used to generate the products tested in this study, was shown to contain about one-tenth(2) or less(3) of its oxygen as carboxylic groups. In addition, it has been shown(4) that coal loses carboxylic groups on heating to elevated temperatures. Therefore, since this functionality was observed in the heavy fractions and CSD operation greatly improved with the recycle of unconverted coal, we extended this study to include the characterization of recycled solids which may have served as catalytic sites for liquid upgrading and/or coking. Reference is made to the work of Wakeley, et al.(5) with respect to the nature of reactor solids accumulating during liquefaction.

EXPERIMENTAL

Samples were obtained from the Advanced Coal Liquefaction R&D Facility at Wilsonville, AL, which has been described by Lamb, et al(6). The Wilsonville pilot plant was operating in a two-stage mode with direct coupling of the thermal and catalytic (hydrotreater) reactors as shown in the schematic, Figure 1. After flashing and vapor recovery, the vacuum tower bottoms (VTB) cut was fed to a critical solvent deashing (CSD) unit to reject an ash concentrate and recover an ash-free resid. The products of two runs were studied. In run 250D, the liquefac-

tion feed solvent consisted of recycled flash distillates plus CSD-derived resid. In run 250H, a portion of the VTB, including unconverted coal and mineral matter, was added to the feed solvent. Both runs were made with Illinois No. 6 coal at essentially the same reaction conditions, and CSD operation was shown (7) to be much smoother in the latter run.

Characterization data for samples of VTB of these two runs are summarized in Table I. GPC analysis of the organic Soxhlet fractions produces identical molecular weight profiles for the two samples. The data document the higher concentration of mineral matter and unconverted coal in run 250H product as a result of recycle. The shift in the Soxhlet characterization data, specifically the decrease in the oils (pentane solubles) content, highlights a significant shift in character as a result of process recycle. Apparently, recycle leads to increased solubilization and reaction of the heavy fractions in the liquefaction reactors resulting in a more refractory resid.

The VTB cuts resids were Soxhlet extracted with tetrahydrofuran (THF) to separate the soluble organic matter from the solids. NMR analysis of the THF extracts is provided in Table II. There are large differences in the aliphatic carbon and ring size (bridgehead carbon) between the two samples. Run 250H VTB is more highly dealkylated (C_{a-s} = 12.2 vs. 18.3%) and condensed (C_{a-i} = 27.2 vs. 18.6%). This is consistent with the lower level of oils found in the VTB upon recycle. FTIR data confirm the observation. FTIR analysis also points to a nearly five-fold increase in the phenolic oxygen content of run 250D product over that of 250H. This difference is largely due to THF extractables.

The physical makeup of the THF insolubles fraction of both runs was examined by Dr. Alan Davis of Pennsylvania State University using petrographic techniques. The results indicate that the organic portion of the fractions were primarily composed of vitroplast (20 vol %), unreacted "inertinite" (9-12 vol %), and unreacted vitrinite (2-8 vol %). The 250D sample contained larger amounts of unreacted inertinite than the 250H sample. The 250H sample also contained masses of larger vitroplast spheres (secondary vitroplast) which were not seen in the 250D sample. No mesophase structures were observed and only very rare particles of coke were noted in the residues. Both samples exhibited large amounts of clays (50-55 vol %) and iron sulfides (6-13 vol %). While the clay concentrations were similar for both fractions, the concentration of iron sulfides in the 250H VTB were twice that in the 250D sample, reflecting the concentration of mineral matter by process recycle. Trace (1-4 vol %) carbonates were also identified. However, the carbonates, present also in the feed coal, were highly crystalline and exhibited none of the structure of the reactor-formed carbonates which are generated during the processing of some carboxylate-rich low-rank coals.

The mineral matter concentrated in the THF insolubles was analyzed by XRF and XRD. Analysis by XRF shows that the mineral matter of the two samples to be similar in composition (Table III), with large amounts of silicon, alumina, and iron present. XRD analysis shows the latter three components to be in the form of α-quartz, iron sulfide minerals (predominantely pyrrhotite), and aluminosilicates (principally kaolinite). Both samples exhibit traces of carbonates as noted earlier.

Ground particles of VTB before and after THF extraction were characterized by STEM and XPS. STEM analysis points to the agglomeration of iron sulfide and calcium mineral particles upon THF extraction. XPS data for mineral matter for both resids

before and after THF extraction are summarized in Table IV. The data indicate high levels of physical adsorption of organic matter on the silicate and aluminosilicate mineral surfaces in that the organic coating is removed by THF extraction. However, the iron sulfide surface exhibits significant irreversible adsorption or coking on the surface, because organics are not removed by THF extraction. A similar situation exists for calcium carbonate surfaces, but to a lesser extent than that of iron sulfide.

Elemental analysis of the organic matter in the THF insolubles fractions of the VTB cuts is given in Table V. The THF insolubles fractions of both VTB cuts are similar with significant concentrations of heteroatoms in the THF insolubles. Much of the organic oxygen shows up as strong phenolic oxygen absorption in the OH/NH stretch region of the FTIR spectrum (Figure 2). Comparison of ratios of normalized integrals and normalized intensities of the second derivatives by deconvolution shows that like amounts and types of phenolics are concentrated in the THF insolubles fractions of the two VTB cuts. The FTIR spectra also exhibit small but marked residual carboxylic acid absorption at around 1700 wavenumbers and a carboxylate band around 1530 (Figure 3). In comparison to the very weak carboxylic signal in the whole VTB, the data indicate that the carboxylate functional groups are preferentially attached to the THF insolubles portion of the resids. Acidification of the THF insolubles with 6N HCl followed by extraction with $CHCl_3$ leads to a 44% reduction in the intensity of the carboxylic acid band in the insolubles, so there is interaction with the minerals that are removed by acid treatment.

CONCLUSIONS

The separation of unconverted coal and mineral matter at Wilsonville was shown to be better when a portion of these solids were recycled with the feed solvent to the liquefaction reactor. Our analysis of the VTB feed to the separation unit indicates that such recycle leads to increased solubilization of the heavy fractions and a more refractory (condensed) resid. We also observed that some carboxylic acid functionality is retained in the heavy coal-derived fractions after coal liquefaction. This appears to be due to an interaction of these groups with the mineral matter. It has also been observed that much of the carbonaceous deposits formed on the silica and aluminosilicate clays can be removed by extraction with a polar solvent, but the organic matter deposited on the iron sulfides and carbonates are more coke-like and not readily removed.

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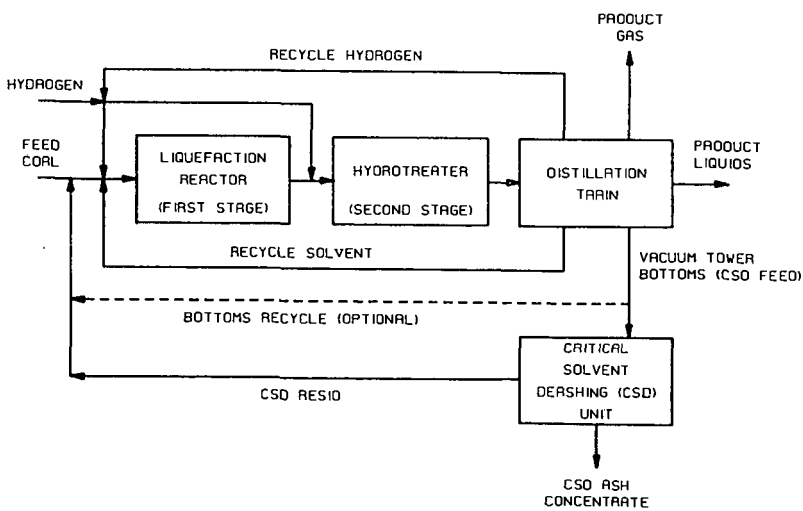

Figure 1. Wilsonville flowsheet.

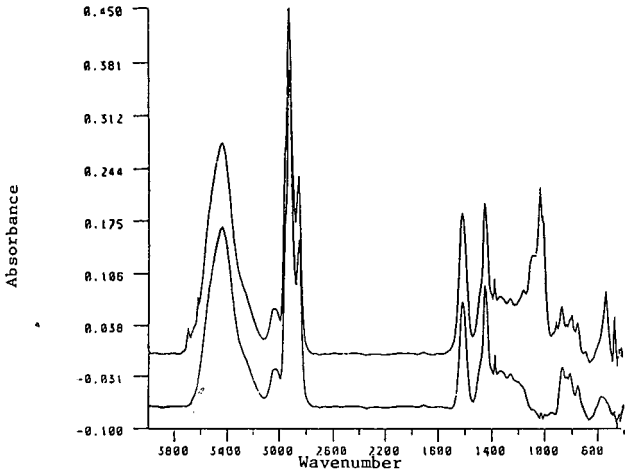

Figure 2 FTIR Spectra of Run 250D VTB and the $HCl/CHCl_3$ Insolubles from the VTB/THF Insolubles

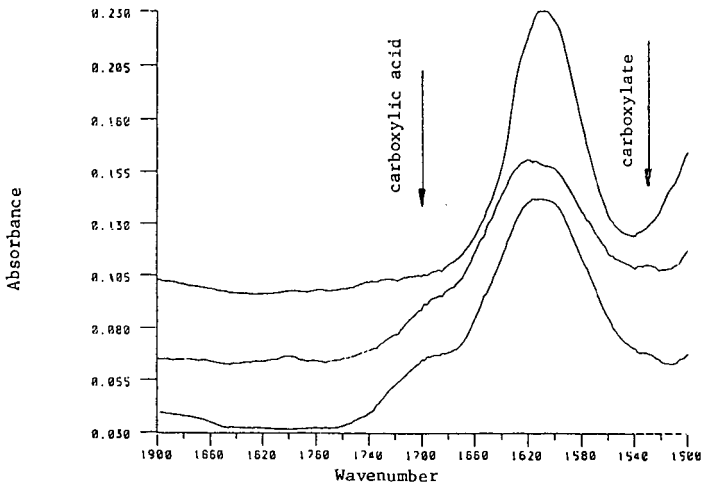

Figure 3 FTIR Spectra of Run 250H VTB (A), its THF Insolubles (B), and its $HCl/CHCl_3$ Insolubles

TABLE I

CHARACTERIZATION OF WILSONVILLE VACUUM TOWER BOTTOMS STREAMS

	Run 250D	Run 250H
Proximate Analysis (wt%)		
Moisture	0.09	0.10
Volatiles	67.8	58.1
Fixed Carbon (by diff.)	22.3	24.9
Ash	9.8	16.9
Elemental Analysis[1] (wt%)		
Carbon	81.2	74.2
Hydrogen	6.29	5.43
Nitrogen	1.26	1.24
Sulfur	0.98	1.58
Oxygen	2.09	3.66
Atomic H/C	0.93	0.88
Soxhlet Extraction[2] (wt%)		
Oils	46.4	29.3
Asphaltenes	24.0	21.4
Preasphaltenes	8.8	13.1
Coke & Unconverted Coal & Mineral Matter	20.8	36.2

[1] Uncorrected for mineral matter.

[2] Sequential extraction with n-pentane, toluene, and tetrahydrofuran.

TABLE II

NMR ANALYSIS OF THF EXTRACTS[1]

	Run 250D	Run 250H
Ha, H on aromatic C	24.1	31.1
Hα, H on a C α to ring	35.4	25.6
Hsat, H on a C β or further to ring ($=CH_2-$)	31.3	35.4
Hme, H on CH_3 γ or further to ring	9.2	7.8
Ca, aromatic C	60.6	67.3
Cat. aromatic C bearing a H	23.7	28.0
Ca-s, aromatic C bearing an alkyl C	18.3	12.2
Ca-i, aromatic C at bridgehead position	18.6	27.2
Average number of rings[2]	6	9

[1] Analyses based on combined ^1H and ^{13}C-NMR. Data is expressed as % of total C or H.

[2] Average number of aromatic rings was calculated using a number average MW of 740 (VPO).

TABLE III

METAL COMPOSITIONS OF THF INSOLUBLES BY XRF

	Run 250D	Run 250H
Al	6.3	6.5
Na	<0.1	<0.1
Mg	0.18	0.22
Si	14.3	14.3
S	1.24	1.26
K	0.97	1.07
Ca	3.2	2.0
Ti	0.25	0.31
Fe	7.4	7.8
Ba	0.03	0.03
Mn	0.04	0.02
Total Metals	34.0	33.5
Oxide Ash	63.8	62.8

TABLE IV

ATOMIC RATIOS ON PARTICLE SURFACES AT RESIDS CALCULATED FROM XPS DATA[1]

	Run 250D		Run 250H	
Atomic Ratio	Whole Resid	THF Insol	Whole Resid	THF Insol
Si/100C	1.0	11	0.8	10
Al/100C	0.0	7.3	0.6	7.1
Fe/100C	0.0	0.5	0.0	0.5
Ca/100C	0.0	1.0	0.0	1.5

[1]Adjusted to THF insolubles content basis.

TABLE V

ELEMENTAL ANALYSIS OF THF INSOLUBES[1]

	Run 250D	Run 250H
Carbon	29.5	29.8
Hydrogen	2.0	1.8
Nitrogen	0.5	0.8
Sulfur	4.4	4.3
Oxygen	6.5	5.9
Atomic H/C	0.83	0.73

[1] Uncorrected for mineral matter.