PYROLYSIS OF WILSONVILLE COAL LIQUEFACTION RESIDUES

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Wilsonville coal liquefaction residues including vacuum tower bottoms (VTB), critical solvent deashing (CSD) product resids, and CSD ash concentrates were pyrolyzed via isothermal thermogravimetric analysis. Pyrolysis yields of gas, liquid, and coke were found to be insensitive to temperature over the range of 800-1200°F. The yields of pyrolysis products generated from the CSD resids indicate that the CSD resids represent the more thermally reactive and volatile portions of the VTB. The tendency of such resids to form coke upon pyrolysis correlates with phenolic hydroxyl content. Unusually low gas plus liquid yields for the relatively hydrogen rich ash concentrates correlates with high heteroatom and mineral matter contents. Differences observed in pyrolysis yields for samples from Wilsonville runs made with and without recycle of unconverted coal and mineral matter further characterize the role of such recycle.

INTRODUCTION

In the development of coal liquefaction processes, the pyrolysis (notably delayed and fluid coking) of coal liquefaction residues (resids) has been incorporated into liquefaction process design to supplement liquid yields. The following report presents an update on the viability of low temperature pyrolysis for the processing of coal liquefaction resids. Specifically, the report examines short contact time pyrolysis yields from various liquefaction resids generated at the Advanced Two-Stage Coal Liquefaction R&D Facility at Wilsonville.

EXPERIMENTAL

Liquefaction resid samples were obtained from the coal liquefaction facility at Wilsonville, AL.[1] The Wilsonville pilot plant was operating in a two-stage mode with direct coupling of the thermal liquefaction and catalytic (hydrotreater) reactors as shown in the schematic, Figure 1. After flashing and vapor recovery, the residual vacuum bottoms (VTB) cut was fed to a critical solvent deashing (CSD) unit (currently designated the ROSE-SR process by Kerr McGee Corp.) to reject an ash concentrate and recover an ash free-resid. The VTB product, CSD resid, and CSD ash concentrate from three Runs were studied. In Run 250D, the liquefaction feed solvent consisted of recycle distillates plus CSD resid. In Runs 250H and 251E, the recycle of VTB resid, including unconverted coal and mineral matter, was added to the feed solvent. In Run 251E, catalyst was also loaded into the thermal liquefaction reactor.

All three runs were made with Illinois No. 6 coal at essentially the same reaction conditions. The relevant characterization data are presented in Table I for the runs of interest.

Thermogravimetric (TGA) was used to screen pyrolysis coke, liquid, and gas yields as a function of temperature. Traditionally operated under an inert atmosphere at a preprogrammed heating rate of 5-50°C/min., an isothermal TGA procedure was developed to mimic the more rapid heating rates characteristics of short contact time pyrolysis processes. Provision was made to collect and weigh the liquids as well as recovered "coke" (residual mineral matter, unconverted coal, and coke). Gas yields were calculated by difference. Although representative process variable effects and product quality data could not be obtained due to the small sample sizes involved, such screening provided a relative measure of pyrolysis yields among samples as a function of temperature.

RESULTS

Preliminary screening of the coke yield of the Wilsonville samples was carried out by standard and isothermal TGA runs. Initial screening of Run 250H VTB indicated that coke yields were insensitive to heating rate, sample size, and purge nitrogen flow rate. Pyrolysis yields for Run 250D and Run 250H VTB products are plotted in Figure 2 as a function of pyrolysis temperature. The insensitivity of the yields to pyrolysis temperature over the range (800-1200°F) investigated suggests that the VTB cuts are highly aromatic and not readily thermally cracked under pyrolysis conditions. Such high aromaticity is due to the condensed structure of the original coal feedstock and the liquefaction and concomitant retrogressive reactions to which it is subjected in the liquefaction process. The decrease in liquid yields with VTB recycle, which is seen in comparing products of Run 250D with those of Run 250H and 251E, is attributed to additional solubilization and reaction of recycled VTB organic matter in the liquefaction reactors. This leads to the formation of more highly condensed resids.

For the key Wilsonville runs on bituminous coal, average pyrolysis liquid yields are plotted versus feed H/C ratio in Figure 3. The liquid yields, despite diminished vapor phase cracking of the volatiles evolved in the TGA experiments, are comparable to average Exxon simulated fluid coking yields for samples of resids from the H-Coal and SRC-I processes.[2-4] Such results support a physical picture in which fluid coking of Wilsonville resids lead primarily to vaporization of remaining volatiles with little concomitant liquids upgrading. Liquid yields obtained from pyrolysis of the CSD resids represent the more volatile fractions of the thermally reactive portion of the CSD feeds. Moreover, considering the high H/C ratio, the CSD ash concentrates yield unusually low quantities of liquid product upon pyrolysis. The organic matter rejected in the ash concentrate represents highly condensed and nonvolatile aromatic structures which are heteroatom rich and exhibit strong interactions (adsorption and/or chemical bonding) with the ash mineral matrix.

To examine the coking tendencies of the Wilsonville Streams, selected CSD feed and product resids were fractionated by sequential Soxhlet extraction with n-pentane, toluene, and tetrahydrofuran (THF) to oil (pentane soluble), asphaltene (pentane insoluble, toluene soluble), preasphaltene (toluene insoluble, THF soluble), and lumped ash/unconverted coal/coke (THF-insoluble) fractions. Although arbitrary in measure, such a fractionation scheme permits a finer resolution of the chemistry involved in terms traditionally applied to coal-derived products. The fractions in turn were pyrolyzed at 1100°F to examine the propensity of each to form coke. The results are summarized in Table II for VTB and CSD resids.

Comparison of the results of Table II shows that all three VTB cuts are similar in character. Coke yields from CSD feed oils, asphaltenes, preasphaltenes, and THF-insoluble residues average about 4, 47, 67, and 89 wt%, respectively, seemingly independent of the actual feed contents of each fraction. Given Soxhlet extraction data of a Wilsonville CSD feed, linear weighting of the above ratios by concentration results in a prediction of actual coke make accurate to ± 3%. Deviations from the cited averages and resultant yield predictions coincide with shifts in phenolic hydroxyl activity measured by FTIR. Decreasing coke make in the pyrolysis of 250D, 250H, and 251E VTB organic fractions (oils, asphaltenes, and preasphaltenes) parallels decreasing phenolics content of the whole resid (Figure 4). Quick calculations show that this simple ratio approach also predicts well the coke make of the CSD ash concentrates, underpredicting coke yield by only 1%. As with the VTB cuts, the deviations can be correlated with phenolic hydroxyl content via FTIR.

Attempts to correlate the CSD product resid fractions of Table II proved less successful. The material which is recovered as product resid represents the more volatile and thermally reactive components of the VTB cuts. As the nature of such material varies with liquefaction severity and subsequent CSD unit operation, the tendency of the various CSD resid fractions (oils, asphaltenes, etc.) to form coke appears to vary greatly with coal feedstock and process configuration. The CSD resid oil fraction makes up the bulk of the VTB oil fraction recovered by extraction and solidification. The CSD resid asphaltene and preasphaltene fractions form less coke than their VTB product counterparts; thus they appear to represent the more volatile fractions and cracked products of the parent VTB resid fractions. Among the three CSD resids studied, like results are obtained for coke yields from the Soxhlet fractions for Runs 250D and 251E. Again, the increased coke make of Run 250H asphaltene and preasphaltene fractions relative to the corresponding fractions of 250D and 251E CSD resids coincides with an increase in the phenolic hydroxyl content of the whole resids.

CONCLUSIONS

Despite an increase of liquid yields due to the development of two-stage liquefaction processes, Wilsonville liquefaction resids are similar to those obtained from older liquefaction processes in that they give similar yields when subjected to thermal pyrolysis. The resids are highly aromatic and hence resistant to thermal cracking, leading to a pyrolysis in which liquid recovery is effected by limited cracking and extensive vaporization of lighter oil and asphaltenic fractions. Heteroratom content and retrogressive reactions[5] partially masked by poorly understood organic-inorganic interactions with the mineral matter play a dominant role in determining the nature of the liquefaction resids.

ACKNOWLEDGEMENT

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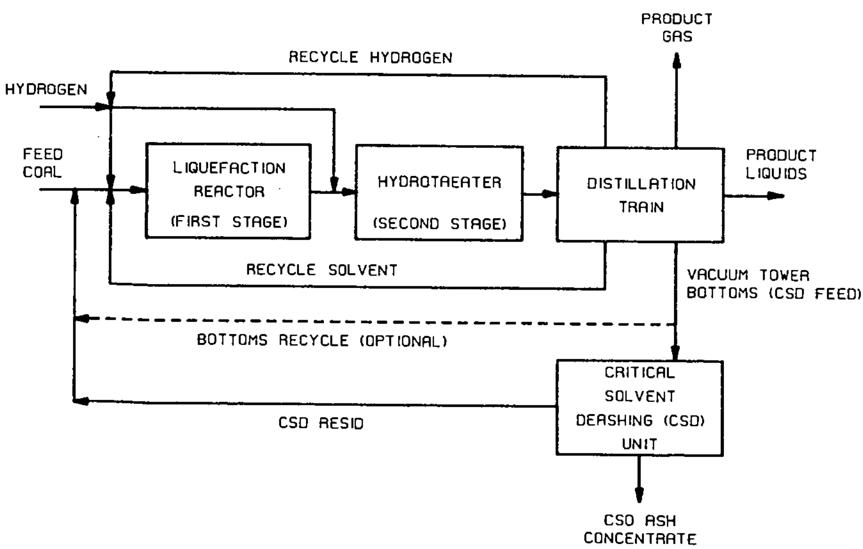

Figure 1. Wilsonville flowsheet.

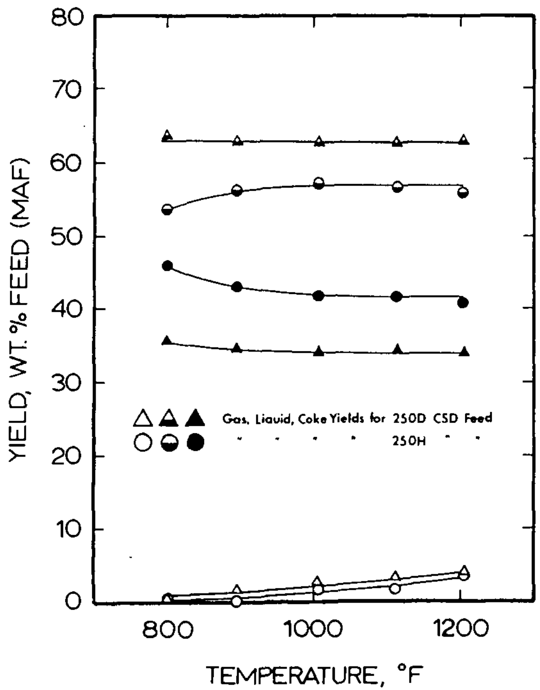

Figure 2. TGA pyrolysis yields for Wilsonville Run 250D and 250H VTB's.

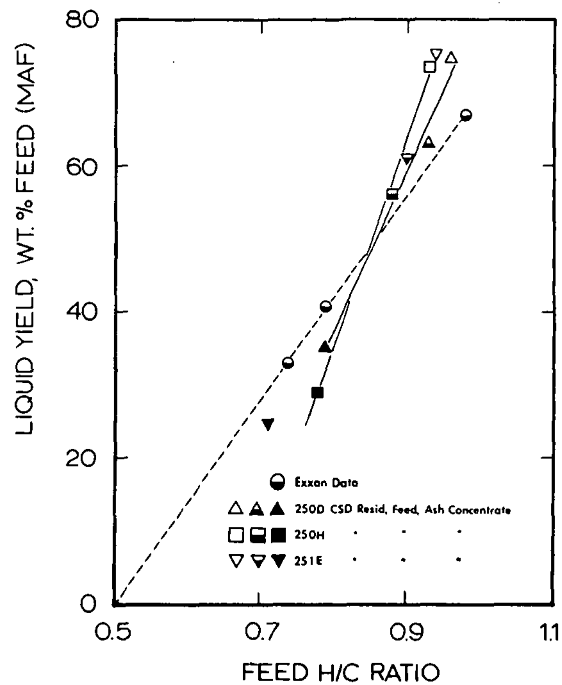

Figure 3. Average liquid yield vs. feed H/C ratio for pyrolysis of Wilsonville resids.

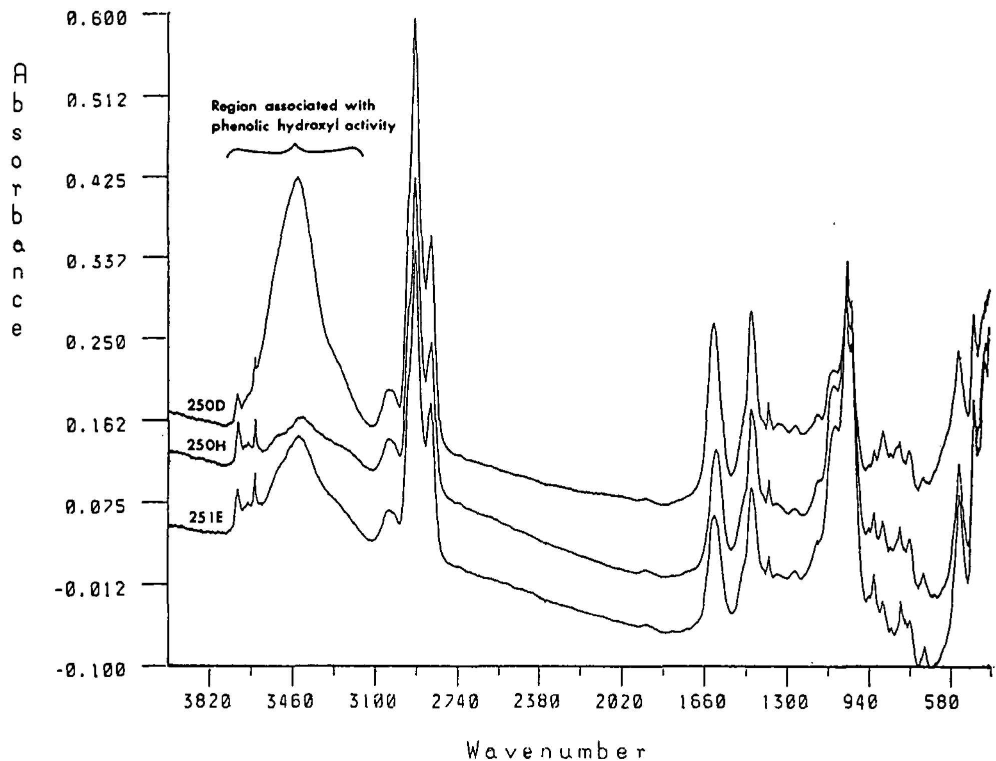

Figure 4. FTIR spectra of VTB's.

TABLE I

ANALYTICAL CHARACTERIZATION OF WILSONVILLE COAL LIQUEFACTION RESIDS FOR KEY RUNS ON ILLINOIS NO. 6 BITUMINOUS COAL

	Run Number and Date								
	250D (020586)			250H (031786)			251E (060586)		
	VTB	CSD Resid	CSD Ash Concentrate	VTB	CSD Resid	CSD Ash Concentrate	VTB	CSD Resid	CSD Ash Concentrate
Proximate Analysis									
Moisture, wt%	0.09	0.05	0.31	0.10	0.05	0.39	0.08	0.20	0.40
Volatiles, wt%	67.8	84.4	28.7	58.1	86.5	18.6	56.9	82.9	22.6
Fixed Carbon, wt% (by diff.)	22.3	14.8	35.2	24.9	13.5	35.3	20.0	16.7	30.9
Ash, wt%	9.8	0.8	35.8	16.9	0.0	45.7	23.6	0.24	46.2
Ultimate Analysis(1)									
C, wt%	81.2	90.2	56.3	74.2	90.3	46.3	69.5	88.9	46.4
H, wt%	6.29	7.25	3.72	5.43	7.04	3.03	5.20	6.95	2.75
N, wt%	1.26	1.10	1.07	1.24	1.45	1.21	1.13	1.16	1.01
S, wt%	0.98	0.27	2.86	1.58	0.34	4.10	1.85	0.31	3.58
O, wt%	2.09	1.54	4.65	3.66	1.80	5.78	3.29	2.63	5.27
Atomic H/C	0.93	0.96	0.79	0.88	0.93	0.78	0.90	0.94	0.69
Soxhlet Extraction									
Oils, wt%	46.4	22.2	3.1	29.3	39.8	0.8	33.2	39.8	1.5
Asphaltenes, wt%	24.0	49.7	18.7	21.4	27.2	3.0	17.7	34.3	4.1
Preasphaltene, wt%	8.8	27.0	8.5	13.1	33.0	12.9	9.4	25.5	12.2
Ash + Coke + Unconverted Coal, wt%	20.8	1.2	69.7	36.2	0.0	83.3	39.7	0.3	82.2

(1) Uncorrected for mineral matter.

TABLE II

PYROLYSIS YIELDS OF WILSONVILLE RESID FRACTIONS AT 1100°F

Wilsonville Run No.	Extracted Fraction	Feed Composition, Wt%	Pyrolysis Coke Yield, Wt% Feed Sample
		I. VTB FRACTIONS	
250D	Oils	46.4	7
	Asphaltenes	24.0	52
	Preasphaltenes	8.8	74
	Ash + Unconverted Coal + Coke	20.8	88
250H	Oils	29.3	4.5
	Asphaltenes	21.4	49
	Preasphaltenes	13.1	68
	Ash + Unconverted Coal + Coke	36.2	91
251E	Oils	33.2	1.9
	Asphaltenes	17.7	46
	Preasphaltenes	9.4	58
	Ash + Unconverted Coal + Coke	39.7	89
		II. CSD PRODUCT RESID FRACTIONS	
250D	Oils	22.2	8
	Asphaltenes	49.7	26
	Preasphaltenes	27.0	40
	Ash + Unconverted Coal + Coke	1.2	76
250H	Oils	39.8	4.5 ± 0.7
	Asphaltenes	27.2	49 ± 2.3
	Preasphaltenes	33.0	58 ± 3.5
	Ash + Unconverted Coal + Coke	0.0	--
251E	Oils	39.8	3.7
	Asphaltenes	34.4	37
	Preasphaltenes	25.5	51
	Ash + Unconverted Coal + Coke	0.3	86