

THE CHEMICAL NATURE OF COAL LIQUID RESIDS AND THE IMPLICATIONS FOR PROCESS DEVELOPMENT

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INTRODUCTION

The informational needs for the advancement of direct coal liquefaction process development include the knowledge to choose the appropriate analytical tools. CONSOL Inc. is working with a number of research groups to evaluate various methods for analyzing direct coal liquefaction process-derived samples.¹ Each individual method was applied to process-derived samples and the advantages (and some drawbacks) for each have come to light.²⁻⁸ The large database accumulated in the study may be useful in choosing analytical methods for process development and design of facilities. This paper will explore the usefulness of these data for that purpose by examining a few specific examples.

Close-coupled integrated two-stage direct coal liquefaction, on a pilot plant scale, is a continuous, multi-step operation. The process steps include mixing feed coal with recycled coal liquid to form a slurry; thermal and/or catalytic liquefaction of the coal in the slurry; stripping of the light, high-value products; and recycling of the heavy residues to near extinction. The coal concentration in the feed slurry is typically 30 wt %. The slurry oil consists mostly of relatively high molecular weight material (resids) and some light distillable materials. Each process stream, with the exception of the distillation column overheads, also is comprised of 50% or more of non-distillable (850°F) resid. Because of the preponderance of the resid in the system, and its influence on the overall properties of the process streams, the program described above was directed to the study of these materials.

RESULTS AND DISCUSSION

The results of the analyses of six 850°F distillation resid samples, obtained from two process runs (Run 257⁹ and Run 259¹⁰) conducted at the Wilsonville Advanced Two-Stage Direct Coal Liquefaction facility, will be used to demonstrate the potential usefulness of these data for process development. Each of the samples are composites of many daily samples obtained over the length of the liquefaction test. These tests lasted for a number of months and included numerous changes in operating conditions. The feed to Wilsonville Run 257 was Illinois No. 6 coal from Burning Star No. 2 Mine and the feed to Run 259 was Pittsburgh seam coal from Ireland Mine. The resid from Run 259 was notably more difficult to convert to distillate products, based on Wilsonville operating results. Both runs were carried out with catalyst in both reactors. Both runs operated, for the most part, with the first of the two reactors at a higher temperature than the second reactor. Samples were obtained from three locations in the plant (Figure 1): between the two reactors (Interstage), after the second reactor but before the deasher (2nd Stage Product), and at the vessel used to accumulate different process flows to form the slurry solvent that is recycled back through the system (Recycle). Samples obtained from these different locations during a single run are expected to represent different degrees of coal conversion in the direct liquefaction process. The samples analyzed were the 850°F distillation resids of these three process streams, and, in some cases, the tetrahydrofuran-soluble portion of the resids.

The analyses performed by CONSOL on the samples include elemental analyses, proton NMR (and classification of the proton signal into defined groups), and determination of phenolic -OH by Fourier transform infrared spectroscopy (FTIR). Pyrolysis and subsequent detection and analysis of the pyrolysate by thermogravimetric (TG)-FTIR, fluorescence microscopy, reflectance microscopy, field ionization mass spectrometry (FIMS), and various separation techniques, including liquid chromatography were performed by Advanced Fuel Research,⁷ University of Kentucky,⁴ The Pennsylvania State University,³ SRI International,⁵ and Virginia Polytechnic and State University,² respectively.

Table 1 presents the elemental analyses of the six composite resid samples and the parent coals. It is readily apparent that the hydrogen content is increased and the heteroatom content is decreased in the resid as the coal slurry proceeds through the liquefaction process. Also given in Table 1 are the phenolic -OH contents of the tetrahydrofuran (THF)-soluble portion of each resid. Figure 2 shows that the phenolic -OH contents, determined by FTIR, correlate relatively well with the yield of the most polar liquid chromatography fraction of the THF-soluble portion of resids.² The data presented in Figure 2 were obtained from a number of resids obtained from different liquefaction runs made at different facilities, including Runs 257 and 259 made at Wilsonville.

The TG-FTIR results, presented in Table 2, show a reduction in gas make in the pyrolysis of the resids with a corresponding increase in tar yield as the coal is converted in the liquefaction system. The remaining -2 to -10% of the resid, not accounted for in these analyses, is converted to additional gases (NH₃, COS) and light hydrocarbons, such as C₂H₆ and benzene. It is notable that the resids produced in the Illinois No. 6 coal run generate a much larger proportion of these volatile materials and more tar than the resids produced from the Pittsburgh seam coal resid. The char yields from the distillation resids correlate with the phenolic -OH content of the THF-soluble portion of the resid, which, as discussed above, correlates to the very polar material found in the resid.

The proton NMR data for the THF-soluble portions of the resids (Table 3) are divided into five spectral regions corresponding to five proton types. These types are condensed aromatics, uncondensed aromatics, alpha protons, beta protons, and gamma protons. The condensed aromatic component of the Run 257 resids decreases from interstage to second-stage product samples and is relatively unchanged in the recycle stream by partial deashing. The increase in aromaticity from recycle to interstage samples comes about from the addition of fresh feed coal to the slurry which is then liquefied in the first reactor. The conversion of the 850°F resid in each stage of the liquefaction process is not the same; it was approximately two times greater in the first stage than in the second stage for Run 257, and about 1.5 times greater in the first stage than the second stage in Run 259. Nonetheless, it is concluded that for Run 257, the aromatic coal structure is broken down in the first stage of the liquefaction system with little additional change of aromaticity in the second reactor. The liquefaction process conditions in Run 259 were more severe than in Run 257 (higher temperature, lower space velocity) and the rejection of resid in the deasher was lower. This accounts for the total aromaticity being higher in the Run 259 samples. However, within Run 259, an interesting trend is seen. The percent of condensed aromatic protons decreases and that of the uncondensed aromatic materials increases sequentially from the interstage to second stage product to recycle resid. This indicates that the process stream (which is mostly resid) is being converted to less-condensed aromatic moieties, but the unconverted resid is not being saturated. This is supported by a number of other analyses. For example, total volatile material of the resids (100% char) determined from the TG-FTIR experiment is essentially the same as the percentage of uncondensed aromatic protons for each sample from Run 257. However, for the Run 259 samples, there is

a large increase observed for total volatiles and uncondensed aromatic protons in the recycle sample.

Microscopy proved to be a useful technique in the examination of the resids, which are solid at room temperature. It was possible to distinguish different petrographic components in the samples that are related to the extent that the coal slurry had reacted. Point counts and mean random reflectance measurement were made of three components: the high-reflecting vitroplast, the partially reacted vitrinite, and the low-reflecting vitroplast. Values for the interstage and recycle materials in this example data set are given in Table 4. The concentration of low-reflecting vitroplast is higher for the interstage samples than the recycle samples in both Runs 257 and 259. However, for the recycle samples, its concentration is considerably lower in Run 259 than in Run 257. This indicates that across the second stage reactor and deasher, the Pittsburgh coal resid is less upgraded than the Illinois coal-derived materials, and may, in fact, be undergoing retrogressive reactions. This supports the NMR results described above.

Fluorescence microscopy^{4,11} provides a great deal of qualitative information and some quantifiable values including the wavelength of maximum fluorescence (L_{max}) and the fluorescence intensity at L_{max} . It is possible to relate the intensity and the wavelength at L_{max} to the relative degree of aromaticity, and thus to the relative reactivity of the material; the lower the intensity and the longer the wavelength, the higher the aromatic concentration and therefore the lower the reactivity. Resids from Run 257 were found to contain two distinct populations; values of L_{max} and intensity are given in Table 5 for both. Comparison of samples from Run 257 (either population) and Run 259 (Table 5) shows the intensity of the Run 259 interstage sample is relatively low and the L_{max} is high (approaching 700nm). This suggests that the interstage resid from Run 259 is comprised of a more-condensed aromatic structure than the Illinois No. 6 interstage resid and it is thus inferred to be less reactive. The recycle resid samples follow the same trend; the Run 259 sample is also more aromatic and is inferred to be less reactive. Another quantifiable value is the quotient of the fluorescence intensities measured at 700nm (red) and 525nm (green). These red:green quotients (Q) can be used to assess the variability of the fluorescence properties within a heterogeneous sample. A shift to longer wavelengths (red) indicates a more extended pi-bond conjugation or a larger proportion of condensed aromatics. The red:green quotients usually are reported as histograms. Figure 3 shows the histograms for the Runs 257 and 259 interstage and recycle resid samples. The Run 259 samples exhibit much higher proportion of the material at higher Q values than the Run 257 samples. This is consistent with the ¹H-NMR data where ~20% of all protons are aromatic in the Run 257 recycle sample and ~32% are aromatic in the Run 259 recycle sample. Across the second-stage reactor (and including the part of the process stream that has been deashed), there is a considerable shift of the fluorescence of the material to the green (or shorter wavelength, lower aromaticity) in Run 257, but not in Run 259. This may help explain the greater propensity of the Run 259 resids to form char in the TG-FTIR experiments.

FIMS data and their interpretation for these samples have been presented elsewhere.¹² Because of a distinct bimodality, the FIMS profiles of the distillation resids were deconvoluted into two overlapping components, A and B. Component A represents a molecular weight (m/e) range centered at approximately 350 Da, component B is centered around 600 Da. The relative weight fractions of A and B were used to compare the resid samples. Table 6 presents the weight percent of component A for each of the six samples obtained from both the even- and odd-mass FIMS profiles. In agreement with the data discussed above, the concentration of component A in the Run 257 resid almost doubles as the coal slurry passes through the first-stage reactor indicating that the molecular weight of the resid was

reduced in the first-stage reactor. As discussed above, conversion of the resid in the first-stage reactor was approximately twice that of the second-stage reactor for Run 257, and correspondingly the concentration of component A in the second-stage product sample increases from the interstage sample, but is only about 1.5 times that of the interstage sample. In comparison, Run 259 interstage and second-stage samples are less enriched with lower molecular weight material. The concentration of low molecular weight material decreases across both the first-stage and second-stage reactors. It increases in the recycle sample only after part of the second-stage product stream passes through the deasher where high molecular weight materials are rejected along with the ash.

SUMMARY AND CONCLUSION

To briefly summarize the information presented above; relative to the Illinois No. 6 resids, the Pittsburgh seam resids are less hydrogenated, higher molecular weight, less fluorescent and they produce fewer volatiles upon pyrolysis. In addition, the Pittsburgh seam resids are more phenolic, more aromatic and contain more nitrogen. These characteristics are consistent with the lower observed reactivity of the Pittsburgh seam resids, which must have arisen from a combination of the coal and operating conditions. The NMR, FIMS and TG-FTIR data indicate that in Run 257, the upgrading of Illinois No. 6 coal to lower molecular weight, more volatile, less aromatic materials was primarily achieved in the first stage of the two-stage system. Additionally, reflectance microscopy data show that the resid derived from the Illinois No. 6 coal in the first-stage reactor is more upgraded in passing through the second-stage reactor and deasher than the Pittsburgh seam coal first-stage resid. Phenolic -OH determinations made on the THF-soluble portion of the distillation resids correlate with the amount of very polar fraction isolated from the resids by liquid chromatography and also with the char yield from the TG experiments. Fluorescence microscopic examination of the resids leads to inferences of resid reactivity. These inferences are supported by the other data. It is apparent that no single method fully describes process derived materials; however, the trends observed by any one method are generally mimicked in the response of the other methods. The implication for process development is that the choice of methodology for analytical use, among these methods tested, can be determined by the requirements of the process developer based on such factors as cost, time, or frequency of measurement.

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REFERENCES

1. Brandes, S. D.; Winschel, R. A.; Burke, F. P. "The Application of Advanced Analytical Techniques to Direct Coal Liquefaction," Am. Chem. Soc., Div. Fuel Chem. Preprints, 1991, 36(3), 1172.
2. Taylor, L. T.; Hellgeth, J. W.; Sequeira, A. "Coal Liquefaction Process Streams Characterization and Evaluation; Analysis of Coal Liquefaction Process Streams by Chromatographic and Spectroscopic Techniques, Topical Report," DOE/PC 89883-41, January 1992.
3. Mitchell, G.; Davis, A. "Coal Liquefaction Process Streams Characterization and Evaluation; Gold Tube Carbonization and Reflectance Microscopy, Topical Report," DOE/PC 89883-37, December 1991.
4. Rathbone, R. F.; Hower, J. C.; Derbyshire, F. J. "Coal Liquefaction Process Streams Characterization and Evaluation; Novel Analytical Techniques for Coal Liquefaction: Fluorescence Microscopy, Topical Report," DOE/PC 89883-30, October 1991.

5. Malhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation; Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization, Topical Report," DOE/PC 89883-39, January 1992.
6. Miknis, F. P. "Coal Liquefaction Process Streams Characterization and Evaluation; Solid-State NMR Characterization of Coal Liquefaction Products, Topical Report," DOE/PC 89883-36, November 1991.
7. Serio, M. A.; Hsisheng, T.; Bassilakis, R.; Solomon, P. R. "Coal Liquefaction Process Streams Characterization and Evaluation; FT-IR Methods for Characterization of Coal Liquefaction Products, Topical Report," DOE/PC 89883-45, April 1992.
8. Green, J. B.; Pearson, C. D.; Young, L. L.; Green, J. A. "Coal Liquefaction Process Streams Characterization and Evaluation; Application of Liquid Chromatographic Separation Methods to THF-Soluble Portions of Integrated Two-Stage Coal Liquefaction Resids, Topical Report," DOE/PC89883-47, May 1992.
9. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report July 1 through Sept. 30, 1988," DOE/PC 70018-68, July 1989.
10. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report April 1 through June 30, 1990," DOE/PC 89883-22, July 1991.
11. Rathbone, R. F.; Hower, J. C.; Derbyshire, F. J. "Application of Fluorescence Microscopy to Coal-Derived Resid Characterization," Am. Chem. Soc., Div. Fuel Chem. Preprints, 1991, 36(3), 1164.
12. Malhotra, R.; McMillen, D. F., Huestis, D. L. "Characterization of Coal Liquefaction Resids by Field Ionization Mass Spectrometry: Correlation Spectral Features with Processing Parameters," Am. Chem. Soc., Div. Fuel Chem. Preprints, 1992, 37 (2), 908.

TABLE I
ELEMENTAL ANALYSES AND PHENOLIC -OH CONTENTS OF 850°F^a
DISTILLATION RESIDS AND PARENT COALS^{9,10}

	Run 257				Run 259			
	Feed Coal	Inter-stage Resid	2nd Stage Resid	Recycle Resid	Feed Coal	Inter-stage Resid	2nd Stage Resid	Recycle Resid
wt % of 850°F ^a Resid in Process Stream	-	81.9	77.5	79.8	-	72.3	67.9	73.1
Ash wt % as det.	11.76	12.52	13.49	9.28	4.68	8.74	10.21	8.51
C wt % MAF	79.52	88.05	87.99	88.64	81.24	90.12	90.24	91.01
H wt % MAF	5.51	7.70	7.87	8.08	5.97	6.19	6.39	6.50
N wt % MAF	1.53	0.86	0.77	0.78	1.37	1.15	1.05	1.04
S wt % MAF	3.68	1.34	1.20	0.79	3.28	1.50	1.49	1.25
O wt % (by diff) MAF	9.58	2.05	2.16	1.71	8.07	1.04	0.83	0.20
Phenolic -OH, meq/g ^(a)	-	0.68	0.57	0.50	-	0.92	0.70	0.69

(a) determined on the THF-soluble portion of the resid

TABLE 2
TG-FTIR ANALYSES OF 850°F⁺ DISTILLATION RESIDS⁷

TG Yield (wt % daf)	Run 257			Run 259		
	Interstage	2nd Stage	Recycle	Interstage	2nd Stage	Recycle
Tar	70.48	69.90	73.49	65.00	65.56	67.07
Gas ^(a)	4.85	4.32	3.71	5.59	3.89	3.61
Char	17.50	15.88	14.15	27.80	28.39	22.88
Unaccounted	7.17	9.90	8.65	1.61	2.16	6.44

(a) Gas = CH₄+CO+CO₂+SO₂

TABLE 3
PROTON NMR ANALYSES OF THF-SOLUBLE PORTION OF 850°F⁺ RESIDS^{9,10}

Proton Type (wt %)	Run 257			Run 259		
	Interstage	2nd Stage	Recycle	Interstage	2nd Stage	Recycle
Condensed Aromatic	18.1	16.9	16.8	30.7	27.8	26.1
Uncondensed Aromatic	3.7	3.4	3.1	2.6	3.8	5.4
Alpha	28.8	28.6	28.0	31.1	30.8	28.3
Beta	39.1	40.5	41.4	27.2	28.9	30.4
Gamma	10.4	10.7	10.6	8.4	8.7	10.8

TABLE 4
NORMALIZED CONCENTRATION OF PETROGRAPHIC COMPONENTS^(a)
OF 850°F⁺ DISTILLATION RESIDS³

Component, %	Run 257		Run 259	
	Interstage	Recycle	Interstage	Recycle
Low-Reflecting Vitroplast	78.0	73.5	79.0	63.5
Partially Reacted Vitrinite ^(b)	0.5	0.0	0.5	0.5
High-Reflecting Vitroplast	21.5	26.5	20.0	36.0

(a) 200 reflectance measurements made on each sample

(b) unreacted coal

TABLE 5
WAVELENGTH AND INTENSITY OF MAXIMUM FLUORESCENCE
OF 850°F⁺ DISTILLATION RESIDS⁴

	Run 257		Run 259	
	Interstage	Recycle	Interstage	Recycle
Fluorescence Spectrum Maximum, L_{max} , nm	646 ^(a) /604 ^(b)	633 ^(a) /585 ^(b)	696	696
Intensity at L_{max} , counts	6714/12666	9284/32108	6658	8497

(a) Population 1
(b) Population 2

TABLE 6
wt % COMPONENT A OF 850°F⁺ RESIDS
FROM EVEN- AND ODD-MASS PROFILES⁵

Weight %	Run 257			Run 259		
	Interstage	2nd Stage	Recycle	Interstage	2nd Stage	Recycle
A Even	22.4	32.0	13.1	13.7	9.2	18.5
A Odd	7.9	12.9	4.3	4.0	2.2	6.3

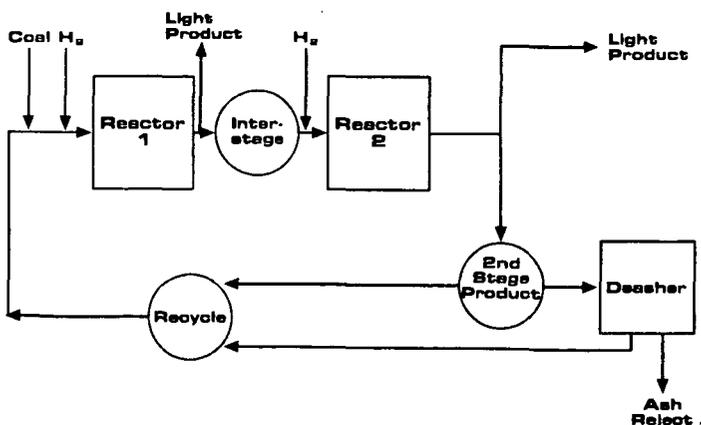


Figure 1. Simplified Flow Scheme Generic Integrated Two-Stage Direct Coal Liquefaction Unit.

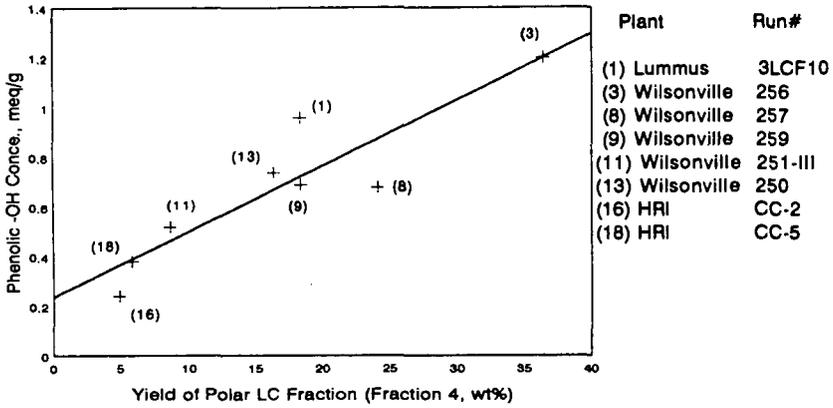


Figure 2. Phenolic -OH Concentration vs Yield of Liquid Chromatography Polar Fraction (F4).²

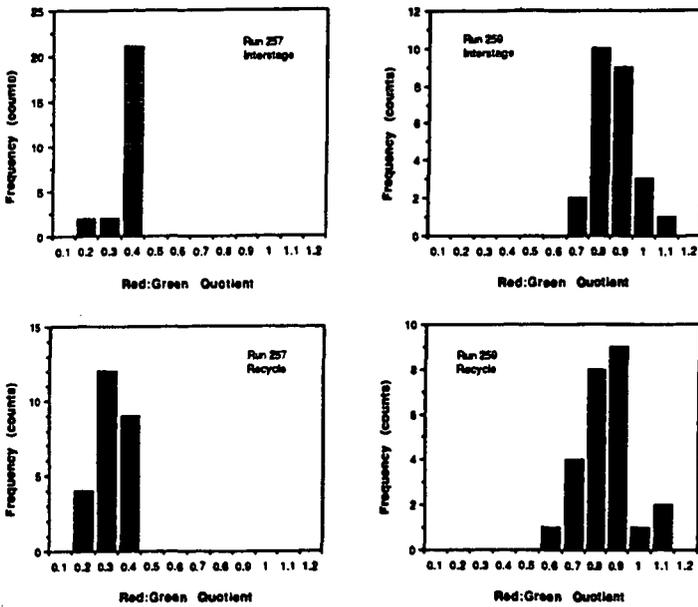


Figure 3. Red: Green Quotient Histograms for Run 257 and Run 259.⁴