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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

ABSTRACT

This is the tenth quarterly report under DOE Contract No. DE-AC22-88PC88810, Development of Analytical Procedures for Coprocessing. The overall objective of the contract is to improve our understanding of the fundamental chemistry of coprocessing. A primary objective is to evaluate methods to distinguish between compound classes originating from coal versus those originating from petroleum resid while a corollary objective is to provide detailed knowledge on the composition of coprocessing products.

This report summarizes work conducted in support of the latter objective in which process development unit samples produced by HRI, Inc. are being subjected to detailed analysis. Coprocessing resid samples selected for detailed analysis were made under constant conditions except for variations in coal concentration or in the coal (New Mexico subbituminous or Texas lignite). The soluble material was separated into strong and weak acids, strong and weak bases, and neutrals. The predominant fraction from the ABN separations was the neutral fraction (67-81%). All of the polar fractions increase with increasing coal concentration. The concentration of saturates in the neutrals is high in a run with 33% subbituminous coal but drops substantially with either increasing coal concentration or the substitution of lignite for subbituminous coal. High temperature gas chromatography showed that both the neutral aromatics fractions and saturates fractions from all of the runs are extremely similar regardless of the coal concentration or coal type. The neutral aromatics fractions were further separated by ring number separation. Chromatograms were again very similar regardless of the initial coal concentration or coal type with most material eluting in the 3-ring to 6-ring region.

INTRODUCTION

Earlier phases of this project have been involved with improving our understanding of the fundamental chemistry of coprocessing through the development of the ability to distinguish between compound classes originating from coal versus those originating from petroleum resid. Two approaches have been evaluated as potential methods to accomplish this objective. One is based on the use of carbon isotope ratios and the other is based on variations in compound classes in the coprocessing products in response to changes in the ratio of coal to resid in the coprocessing feed. Results of these studies have been summarized in the prior two quarterlies (1)(2).

An additional objective is to develop an expanded knowledge of the detailed composition of coprocessing products. This knowledge will aid in the development of improvements in coprocessing, guide development of refining methods for coprocessing liquids and provide information on the quality of coprocessing products. Studies of the detailed composition of coprocessing products made over a range of coal concentration in a batch autoclave have been reported in previous quarterlies.

This quarterly report addresses the detailed analysis of coprocessing process development unit (PDU) samples obtained from HRI, Inc. Emphasis is being placed on resid samples; detailed knowledge of the composition of the resid fractions is of interest as this is material which failed to be converted to distillate range materials.

RESULTS AND DISCUSSION

A set of eight coprocessing samples was received from HRI, Inc. Based on run conditions and preliminary analyses, a set of vacuum still bottoms samples was selected for detailed analysis. The samples were selected so that processing conditions were constant except for variations in feed composition. The samples selected allowed a determination of the effect of changing coal concentration and a comparison of results with subbituminous coal versus lignite.

Samples were selected from run 238; in all cases reaction temperature was 810° F, relative space velocity was 1 and the petroleum resid was Hondo. Variable conditions are as follows:

<u>Sample, wt %</u>	<u>Coal</u>	<u>Coal Concentration, %</u>	<u>Resid Conversion</u>
238-8-5	New Mexico*	33	93
238-8-9	New Mexico	50	90
238-10-8	Texas Lignite	33	93

*Subbituminous coal from the McKinley Mine

Thus, 238-8-5 and 238-8-9 vary only in coal concentration and 238-8-5 and 238-10-8 vary only in the coal feedstock. In all cases the samples further analyzed were vacuum still bottoms (VSB). Elemental and solubility analyses of the samples provided by HRI are shown in Table 1. Note from these data that the difference between the quinoline insolubles and the toluene insolubles is quite small (0.2 to 1.7 weight percent); thus the amount of material in the "preasphaltene" category is quite small. The difference between the toluene insolubles and the cyclohexane insolubles is larger but also small (2.5 to 5.4 weight percent).

Table 1. Elemental and Solubility Analyses of Vacuum Still Bottoms Samples (HRI, Inc.)

	238-8-5	238-8-9	238-10-8
	-----weight percent-----		
<975° F	13.8	10.9	16.2
C	64.26	63.62	61.02
H	6.43	5.84	6.05
N	0.48	0.65	0.56
S	0.71	0.47	1.07
Ash	27.63	28.56	30.04
Quinoline Insolubles	43.09	44.41	50.99
Toluene Insolubles	44.10	46.15	51.14
Cyclohexane Insolubles	48.92	48.68	56.55

The vacuum still bottoms samples were separated by nonaqueous ion exchange liquid chromatography into five fractions: strong acids, weak acids, strong bases, weak bases, and neutrals; results are summarized in Table 2. The separation scheme is applicable only to soluble materials so the samples (~ 35g samples) were first Soxhlet extracted with benzene. As noted above, there is a relatively small difference in quinoline versus toluene or cyclohexane insolubles. The quinoline insolubles (including ash and what is typically termed "IOM" or insoluble organic matter) would typically not be material which would be capable of undergoing further reaction and thus its composition is of limited information anyway. The benzene solubles/insolubles are shown on the first two rows of Table 2.

This preparative extraction indicates a higher percentage of benzene insolubles than anticipated from Table 1. Note that recovery from the acid-base-neutral separation is greater than 100 weight % by 6 to 10%. This is due to retention of some of the separation solvents by the resid fractions.

The predominant fraction (67-81%) from the ABN separation is the neutral fraction. Unless there is a predominance of highly condensed aromatics, this type of material would be expected to be relatively easily converted into distillate range materials. Separation of the neutral fraction into saturates and neutral aromatics is discussed below.

Table 2. Liquid Chromatographic Fractionation of HRI Resids

Fraction	238-8-5	238-8-9	238-10-8
---Vacuum Still Bottoms Basis, wt%---			
A. Separation of Benzene Solubles			
Benzene Solubles	47.2	44.7	29.8
Benzene Insolubles	53.8	55.3	70.2
----Benzene Solubles Basis, wt%----			
B. ABN Separation			
Strong Acids	12.2	17.4	21.0
Weak Acids	7.0	13.2	14.2
Total Acids	19.2	30.6	35.2
Strong Bases	5.5	9.3	6.8
Weak Bases	0.8	1.2	1.0
Total Bases	6.3	10.5	7.8
Neutrals	80.8	67.3	67.4
Total	106.3	108.4	110.4

Comparing runs 238-8-5 and 238-8-9, all of the polar fractions increase with increasing coal concentration. This is not wholly consistent with the earlier work at NIPER in which only the strong acids (in the resid fraction) showed a strong increase with an increase in coal concentration. This variation may be due to differences in composition of the resids used (Maya at NIPER vs Hondo at HRI), the coal used (bituminous at NIPER versus subbituminous at HRI), or the more effective heteroatom removal at HRI.

Comparing runs 238-8-5 and 238-10-8, (subbituminous coal versus lignite), there is a significantly higher strong acid fraction from the lignite run (consistent with the higher concentration of phenolic functional groups in lignite). Weak acids (generally indole/carbazole type structures) are also significantly higher in the resid from the lignite. There are, however, only relatively small differences in the concentrations of the basic fractions from the two different coals.

Results of infrared analyses of fractions will be reported in the next quarterly report

As noted above, the predominant fraction in the resid in all cases is the neutrals. Results for separation of the neutral fraction into saturates and neutral aromatics are presented in Table 3. Recoveries were 97.5 to 100.4 percent. The concentration of saturates is high (70%) in the neutrals from run 238-8-5 (33% subbituminous coal, 67% Hondo resid) and drops markedly (to 26%) with an increase in coal concentration to 50% (238-8-9). This suggests that the resid is the source of the saturates--not a surprising

Table 3. Liquid Chromatographic Separation of Neutrals into Saturates and Neutral Aromatics

Fraction	238-8-5	238-8-9	238-10-8
-----VSB Benzene Solubles Basis ^a , wt%-----			
Saturates	55.5(69.8)	17.4(25.7)	20.8(31.7)
Neutral Aromatics	24.0(30.2)	50.2(74.3)	44.9(68.3)
Total	79.5	67.6	65.7
Recovery, %	98.4	100.4	97.5

^a Values within parentheses are on a normalized neutrals basis

suggestion. However, the run with 33% lignite and 67% Hondo resid (238-10-8) contains a much lower level of saturates (32%) than the run with the same level of subbituminous coal indicating a role of the coal (or an unrecognized variable) in controlling the level of saturates in the neutral resid fraction.

Both the saturates and neutral aromatic fractions were analyzed by high temperature gas chromatography. While normal simulated distillation techniques can determine boiling point distributions up to only about 1000° F, high temperature simulated distillation can determine distributions to over 1300° F or up to a carbon number of about C-120. By use of an internal standard, the amount of material not eluted from the column is also determined. Chromatograms of the saturate fractions are shown in Figure 1. The regularly spaced sharp peaks represent n-paraffins. Chromatograms of the two runs with 33 or 50% subbituminous coal are virtually indistinguishable while the run with lignite is similar with a slightly higher boiling range distribution. Similarly, the chromatograms for the aromatic fractions (Figure 2) for the 33 and 50% subbituminous runs are nearly indistinguishable. The chromatogram for the lignite shows some differences but many of the same major peaks predominate. Figures 3 and 4 show the cumulative percent of saturates and aromatics eluted as a function of apparent carbon number with the carbon number scale based on n-paraffin elution times. In all cases, the saturates are essentially completely eluted with a maximum apparent carbon number of just over 80. Nearly all of the aromatics (95-97%) were also eluted from the column. Boiling point distributions are summarized in Table 4.

The neutral-aromatics fraction from each sample was further characterized by high performance liquid chromatography (HPLC) using a separation system that gives an aromatic ring-number distribution. An analytical-size column packed with a charge-transfer bonded phase (dinitroanilinopropyl silica or DNAP) was used to study the ring number distribution. Figure 5 is a chromatogram of a mixture of 1 through 5-ring unsubstituted aromatic hydrocarbons separated on the DNAP column. These compounds are benzene, naphthalene, phenanthrene, benz(a)anthracene and dibenz(a,c)anthracene.

Figures 6 - 8 are chromatograms of the neutral-aromatic fractions of samples 238-8-5 (33% New Mexico subbituminous coal), 238-8-9 (50% New Mexico subbituminous coal) and 238-10-8 (33% Texas lignite) run under the same conditions. The sharp spike at 5.5 min. is due to benzene from the acid-base-neutral fractionation procedure. Then there is a low level of mono and diaromatic compounds, and at 15 min. a large broad mass begins to elute. The front of this mass coincides with the retention time of the 3 fused-ring compound in the calibration run.

Table 4. High Temperature Simulated Distillation

% Distilled	°F					
	Saturates			Aromatics		
	238-8-5 33% sub.	238-8-9 50% sub.	238-10-8 33% lig.	238-8-5 33% sub.	238-8-9 50% sub.	238-10-8 33% lig.
1	598	552	598	795	808	853
5	812	807	859	854	860	901
10	859	860	914	882	885	931
20	900	901	950	923	926	966
30	926	927	974	957	959	998
40	950	951	997	986	990	1022
50	971	972	1018	1015	1021	1046
60	995	996	1038	1042	1052	1073
70	1020	1021	1065	1079	1092	1104
80	1052	1053	1097	1127	1147	1147
90	1104	1108	1145	1204	1235	1219
95	1154	1157	1181	1281	1299	1308
99	1234	1233	1239	1321 (97%)	1329 (97%)	-

The broad mass elutes for 30 min. or more before returning completely to the baseline. At approximately 30 min. each sample has a peak that rises significantly above the baseline. Based on its retention time, it is probably a six fused-ring aromatic compound.

The concentration of neutral-aromatics increased with increasing coal concentration suggesting coal as the primary source of this fraction. The chromatograms are remarkably similar indicating the production of very similar materials (even in the resid fraction) from either subbituminous coal or lignite.

REFERENCES

1. Anderson, R. P. Quarterly Technical Report, Analytical Procedures for Coprocessing, DOE/PC88810-8. May, 1991
2. Anderson, R. P. Quarterly Technical Report, Analytical Procedures for Coprocessing, DOE/PC88810-9. June, 1991.

Figure 1. HTGC chromatograms of saturate fractions from HRI coprocessing resids.

Figure 2. HTGC chromatograms of neutral-aromatic fractions from HRI coprocessing resids.

Figure 3. Cumulative percent of saturates eluted as a function of apparent carbon number (carbon number scale based on n -paraffin elution times). Results calculated from GC chromatograms in figure 1.

Figure 4. Cumulative percent of neutral-aromatics eluted as a function of apparent carbon number (carbon number scale based on n-paraffin elution times). Results calculated from GC chromatograms in figure 2.

Figure 5. Chromatogram of known compounds on DNAP-silica.

Figure 6. Chromatogram of 238-8-5 neutral aromatics on DNAP-silica.

Figure 7. Chromatogram of 238-8-9 neutral aromatics on DNAP-silica.

Figure 8. Chromatogram of 238-10-8 neutral aromatics on DNAP-silica.

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