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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

SUMMARY

A series of coprocessing products prepared from Maya crude >1000° F resid and Illinois No. 6 coal were produced for the study of the contributions of the reactants to the specific chemical classes and components of the products. Descriptions and results of separations, composition studies, and carbon isotope ratio measurements have been presented in previous reports.

The composition of neutral aliphatic and aromatic fractions of the distillates has been determined by high resolution mass spectrometry. A broad range of acyclic and cycloalkyl aliphatic and aromatic compounds were detected. Aromatic classes through tetraaromatic were determined in the higher boiling distillates. Sulfur compounds, particularly dibenzothiophene derivatives, were present in larger amounts in the 2 percent coal products than in the other samples.

Residual products of the coprocessing reactions were carried through liquid chromatographic separations to allow further analyses of compositions.

Elemental analysis of the various fractions previously reported has been carried out. These results were related to carbon isotope ratios of the fractions by a regression method. A relationship was shown to exist between heteroatom content of the fractions and their isotopic shift. This was particularly obvious for the acid and base samples and may indicate that heteroatom content is as important as relative contributions of residue and coal in determining carbon isotope ratio values of the products.

INTRODUCTION

The chemistry of coprocessing reactions includes both the processes of coal liquefaction and of petroleum resid upgrading along with possible interactions between the two materials. Because of this, coprocessing products show a more complex composition and less well defined origin of the components than usually encountered in coal liquefaction or petroleum resid upgrading. This study is intended to improve the understanding of the effects of resid and coal reactants and the reaction conditions on composition and source of coprocessing products. Maya crude resid (bp >1000° F) and

Illinois No. 6 coal were the materials used as reactants in this study and were combined in several ratios in reactions carried out for study of coprocessing products.

A primary objective of this project has been development of an understanding of the contribution of resid and coal individually to specific product classes and distillates. Earlier results in this project have shown that a clear selectivity relationship could be determined for neutral, acid, and base classes of the distillates on the basis of product yields. This was accomplished through detailed separation and component analysis of coprocessing products formed over a range of resid and coal reactant ratios. The information on product composition and contribution of resid and coal may help in improvement of reaction conditions and in selection of resid and coal reactants. It may also provide a better understanding of the reaction chemistry contributing to the coprocessing product.

This project began with preparation of a series of coprocessing products to provide material for composition studies. The amount of coal used in these reactions varied from 2 to 40 percent of the total fraction mix. As far as possible, the reaction conditions of time, temperature, catalyst level, and hydrogen pressure were held constant during these coprocessing procedures. Details on the reaction conditions and sample workup have been provided in previous reports. The details on separations and compositional analysis have been provided along with selectivity estimates.

The usefulness of carbon isotope analysis in determining the origin of class fractions is being examined in this project. The resid and coal used in these studies have a difference of 3.00 $\delta^{13}\text{C}$ units. If the products can be shown to have a relationship in isotope ratios to the reactant composition, this analysis can be important in determining the origin of the coprocessing products. In addition, efforts are being made to determine if any other relation exists between isotope ratios and composition besides the relative contribution of residue and coal.

This report presents some details on compound class compositions, elemental analysis, and isotope ratios.

EXPERIMENTAL

Neutral aromatic fractions of the 350-538° C (662-1000° F) distillates and the whole neutral fractions of the 175-350° C (347-662° F) distillates were analyzed in detail by mass spectrometry (MS). The procedure used was based on the Teeter (1) method. This determines 18 saturate and aromatic hydrocarbon types and four aromatic sulfur containing species.

Samples of coprocessing resids were separated into neutral, acid, and base fractions by preparative liquid chromatographic methods. Both the acid and base fractions were further resolved to strong and weak subfractions. The procedure is based on nonaqueous ion exchange chromatography and is similar to the procedure described in earlier reports for isolation of neutral and polar fractions from distillate cuts. However, solubility limitations of the resid samples require that a first pass of these samples through the ion exchange columns be carried out in a mixture of ethanol, tetrahydrofuran, and benzene (1:4.5:4.5). In this solvent mixture only the strong acids and bases are retained. Acids are recovered by Soxhlet extraction of the anion resin with benzene containing formic acid while bases are recovered by Soxhlet extraction of the cation resin with 1-propylamine in benzene. The eluant from the first pass of the residue samples contains neutrals, weak acids, and weak bases. It is soluble in less polar solvents than the original residue and therefore is redissolved in a mixture of benzene and cyclohexane (1:3) for a second pass through the column system. Acids and bases are recovered as before. The ion exchange column system consists of the BioRad Laboratories resins MP-1 (anion) in the first position, followed by MP-50 (cation). Because of this arrangement, amphoteric components would be retained in the acid fractions.

Elemental analyses of all distillates, residues, and fractions derived from them were completed during this quarter. To conserve material in cases where fractions were quite small and to provide a uniform basis for all sample analyses, nitrogen and sulfur were determined by the Antek chemiluminescence method and the microcoulimetric procedures, respectively. Oxygen values are reported as the net difference from 100 percent based on the reported values of carbon, hydrogen, nitrogen, and sulfur.

Carbon isotope ratio values were determined at the School of Geology and Geophysics (Univ. of Oklahoma) under the direction of Dr. Micheal Engle.

RESULTS AND DISCUSSION

Neutral Class Analysis

The yields of neutral fractions obtained from the ABN separations of coprocessing distillates have been shown in previous reports. The neutral fractions were further resolved to saturate and aromatic subfractions by adsorption and charge transfer chromatography. The MS analysis of both saturate and aromatic subfractions of the 175-350° C products and the saturate subfraction of the 350-538° C products have been reported in the Oct-Dec, 1989 report of this series (2).

The subfraction from the 175-350° C coprocessing neutral materials proved to be somewhat unsatisfactory for compositional analysis because of loss of volatile components and contamination by residual solvent. Because of this, the MS analysis was repeated for determination of the hydrocarbon composition in the original neutral fractions. The Teeter mass spectrometry method determines the major saturate and aromatic hydrocarbons as well as several sulfur classes commonly present in petroleum products. These include a series of cycloalkyl saturates and aromatics and di- and polyaromatic hydrocarbons. It is suitable for olefin-free distillates boiling in the range 120-566° C containing less than 5 percent oxygen, nitrogen, or sulfur. It is based on high resolution electron impact spectra.

Table 1 shows the results of analysis for the 175-350° C neutral samples. No composition trends with coal content are evident for the saturate and monoaromatic compounds. The diaromatics and triaromatics as well as total aromatics show increased levels with increasing coal content. The sulfur compounds are higher in the 2 percent coal product than in the other samples. In the July-September, 1989 quarterly report (3) the reduced effectiveness of the coprocessing procedure in removing nitrogen and sulfur from the 2 percent coal reaction product was noted. This may have been due to poorer dispersion of the catalyst. The calculated elemental compositions of the neutral samples are shown at the bottom of the table.

TABLE 1
Neutral Fractions, 175-350° C. Wt %

Coal, %	2	20	30	40
Saturates				
Paraffins	18.5	20.2	20.1	18.7
Monocyclo	13.7	14.5	13.8	12.8
Dicyclo	7.6	7.5	7.8	6.2
Tricyclo	4.6	5.4	4.9	4.7
Tetracyclo	0.0	0.0	0.0	0.0
Total Saturates	44.4	47.6	46.6	42.3
Monoaromatics				
Alkylbenzenes	6.1	6.3	6.6	5.3
Benzocycloparaffins	7.8	8.6	9.1	7.1
Benzodicycloparaffins	1.5	1.9	1.9	1.9
Diaromatics				
Naphthalenes (Z= -12)	6.6	6.8	8.3	9.5
(Z= -14)	3.6	4.5	5.0	6.2
(Z= -16)	4.4	4.9	5.3	6.3
Polynucleararomatics				
(Z= -18)	2.1	2.4	2.5	3.2
(Z= -22)	0.8	0.7	0.5	0.5
Total Aromatics	32.8	36.3	39.2	40.1
Sulfur Compounds				
Thiophenes	0.2	0.0	0.0	0.0
Benzothiophenes	20.6	13.9	12.4	16.0
Dibenzothiophenes	2.0	2.2	1.7	1.7
Naphthobenzothiophenes	0.0	0.0	0.0	0.0
Total Sulfur Comps.	22.8	16.1	14.1	17.7
Calculated % C	85.2	85.9	86.2	86.0
% H	11.7	12.0	12.0	11.6
% S	3.07	2.08	1.84	2.32

The analysis of the 350-538° C neutral aromatic subfractions is shown in Table 2. Results for the neutral class subfractionations into saturates and aromatics were presented in the October-December, 1989 quarterly report (2). The polynuclear aromatic species Z=-22 and the total aromatic hydrocarbon content show an increasing trend with increasing coal content. The Z=-22 group is also the largest single species in these samples. Compound types with Z=-22 include dinaphthenophenanthrenes, dinaphthenoanthracenes, pyrenes, and fluoranthenes. Sulfur compounds (particularly the dibenzothiophenes and naphthobenzothiophenes) are again high in the 2 percent coal sample.

Resid Fractionation and Analysis

Samples of the 2%, 20%, and 40% coal coprocessing resids (bp >1000° F) were separated into neutral, acid, and base class fractions. Separation is based on nonaqueous ion exchange techniques. The procedure developed for separation of resid samples further resolves the acid and base materials into strong and weak subfractions.

Table 3 shows the yields of fractions obtained from the coprocessing resid samples. These samples showed poorer solubility in the solvent system than do the petroleum resids for which the procedure was developed. This caused total recovery to fall in the range 82-90 percent. Strong correlations between coal concentration and resid compositions were not apparent. The strong acid content was lower in the resid from the 2% coal run.

In a similar separation procedure, a set of fractions were prepared from Maya >1000° F resid. Special effort was made to remove traces of solvent from these fractions. Table 4 shows the yields and carbon isotope ratio results.

Comparison of fraction yields in Tables 3 and 4 show the coprocessing residues to contain less neutral and more polar compound classes. However, the coprocessing resids contain much less of the weak bases which are usually prominent in petroleum distillates and residues. Results of base titrations reported in the January-March, 1990 quarterly report (4) showed that weak bases could not be detected in the coprocessing distillates. Weak bases that may be found in petroleum products include such compounds as sulfoxides, diarylamines, amides, and carbonyl classes. It is possible that the weak bases most prominent in petroleum fractions are destroyed in the coprocessing reactions.

TABLE 2
Aromatic Neutral Subfractions, 350-538° C. Wt %

Coal, %	2	20	30	40
Saturates				
Paraffins	1.3	1.8	1.5	0.2
Monocyclo	2.1	2.8	2.7	0.8
Dicyclo	1.0	2.0	1.7	0.7
Tricyclo	1.1	1.5	1.0	0.6
Total Saturates	<u>5.5</u>	<u>8.1</u>	<u>6.8</u>	<u>2.4</u>
Monoaromatics				
Alkylbenzenes	2.7	3.5	3.5	2.7
Benzocycloparaffins	2.4	3.4	3.5	2.4
Benzodicycloparaffins	1.7	1.7	1.5	1.4
Diaromatics				
Naphthalenes (Z= -12)	2.1	2.8	2.7	2.3
(Z= -14)	2.3	2.6	3.0	2.3
(Z= -16)	6.9	6.6	7.8	6.7
Polynucleararomatics				
(Z= -18)	6.8	8.2	7.9	7.1
(Z= -22)	14.9	16.1	18.7	25.4
(Z= -24)	9.5	9.1	9.4	10.0
(Z= -28)	11.1	9.2	9.1	9.9
Total Aromatics	<u>60.4</u>	<u>63.3</u>	<u>67.1</u>	<u>70.3</u>
Sulfur Compounds				
Thiophenes	0.4	0.8	0.6	0.8
Benzothiophenes	7.6	7.5	7.9	7.6
Dibenzothiophenes	18.1	13.7	12.0	12.6
Naphthobenzothiophenes	8.0	6.6	5.6	6.4
Total Sulfur Comps.	<u>34.1</u>	<u>28.6</u>	<u>26.1</u>	<u>27.3</u>
Calculated % C	87.2	87.5	87.8	88.1
% H	9.6	9.8	9.8	9.2
% S	3.18	2.71	2.43	2.65

TABLE 3
Separation of Resid (>1000° F) Fractions

Coal, %	2	20	40
Neutral	32.18	39.32	27.52
Strong Acid	20.28	27.04	28.28
Weak Acid	11.68	9.73	9.87
Strong Base	15.43	12.31	14.54
Weak Base	<u>1.94</u>	<u>1.72</u>	<u>1.73</u>
Total	81.51	90.12	82.82

TABLE 4
Maya Resid (>1000° F) Fractions and Carbon Isotope Ratios

	Yield, %	δ^{13}
Whole Residue	-	-27.60
Neutral	54.3	-27.68
Strong Acid	17.8	-27.75
Weak Acid	8.1	-27.36
Strong Base	10.3	-27.58
Weak Base	8.4	-27.53
Total Yield	98.9	
Mean $\delta^{13}\text{C}$		-27.64

Results of carbon isotope ratio analysis of the coprocessing resid fractions are shown in Table 5. The last row of the table shows isotope ratio values calculated for the original coprocessing resids based on isotope ratios of the fractions and the yield values from Table 3. These values are all depleted in ^{13}C by 0.3 to 0.5 $\delta^{13}\text{C}$ units relative to the measured values for the whole resid. These differences are probably caused by retention of solvent in the fractions. The results shown in Table 4 for the Maya residue fractions differed by only 0.04 $\delta^{13}\text{C}$ units from the whole residue. Those Maya residue fractions were dried rigorously to eliminate solvent. The severe drying conditions may degrade the samples and were not applied to the coprocessing fractions.

Light Distillate Analysis

Distillates boiling below 175° C from the 20 and 30 percent coal coprocessing products by the PIANO method. This procedure is a capillary gas chromatographic method developed for light hydrocarbon fractions of petroleum products. It was described in the January-March, 1990 quarterly report (4) along with results for the 2 and 40 percent coal distillates. Table 6 shows results for these samples by hydrocarbon class on the distillate and whole product filtrate basis. Estimated mean molecular weights are shown for each hydrocarbon class.

Figures 1 and 2 show the distribution of hydrocarbon classes with molecular weight. These show a trend of increasing isoparaffin and aromatic concentration with increasing coal content. These trends are consistent with those reported earlier for the 2 and 40 percent coal products.

Elemental Analysis and Carbon Isotope Ratio

Elemental analyses of the coprocessing distillates, resids, and class fractions are shown in Table 7. Direct analysis was carried out for carbon, hydrogen, nitrogen, and sulfur with all results given in weight percent. Oxygen was estimated by difference, that is, 100 minus the sum of the analyzed elements.

The elemental data show fairly consistent trends with sample type. Nitrogen and oxygen are most concentrated in the acid and base samples with

TABLE 5
Isotope Ratios ($\delta^{13}\text{C}$) of Coprocessing Residue Fractions

Coal, %	2	20	40
Whole Residue	-26.90	-26.13	-25.76
Neutral	-27.19	-26.64	-26.51
Strong Acid	-27.37	-26.88	-25.90
Weak Acid	-27.46	-26.75	-26.49
Strong Base	-26.94	-26.07	-25.65
<u>Weak Base</u>	<u>-26.96</u>	<u>-26.22</u>	<u>-26.39</u>
Recalc. Residue	-27.22	-26.64	-26.14

TABLE 6
PIANO Analysis of <175° C Distillates

	Distillate wt%	Filtrate wt%	Mean M.W.
20% Coal			
Paraffins	22.94	3.212	118.8
Isoparaffins	31.30	4.383	130.0
Aromatics	15.61	2.186	118.2
Naphthenes	23.42	3.278	118.4
Olefins	4.51	0.632	116.7
Unknown	2.21	0.310	-
30% Coal			
Paraffins	21.13	2.092	123.0
Isoparaffins	31.63	3.131	133.7
Aromatics	16.93	1.676	116.9
Naphthenes	23.96	2.372	122.7
Olefins	4.11	0.407	119.6
Unknown	2.24	0.222	-

TABLE 7
Elemental Composition of Coprocessing Fractions

	C	H	N	S	O
2% Coal Products					
Distillate, <175° C	85.10	14.66	0.050	0.212	-0.47
Distillate, 175-350° C	83.92	12.10	0.210	2.083	1.69
Neutral	84.01	12.28	<0.01	1.999	1.71
Acid	72.49	7.76	3.171	2.996	13.58
Base	78.58	8.22	6.691	1.370	5.14
Distillate, 350-538° C	85.10	9.81	0.734	2.759	1.60
Neutral	84.78	10.32	0.080	2.768	2.05
Acid	82.51	7.14	3.163	1.748	5.44
Base	82.56	7.55	3.830	2.373	3.69
Residue, >538° C	86.01	6.24	1.400	3.926	2.42
Neutral	85.64	7.48	0.134	4.831	1.92
Strong Acid	82.68	5.88	1.674	2.952	6.81
Weak Acid	82.74	6.30	1.072	3.054	6.83
Strong Base	78.84	5.93	1.194	3.725	10.31
20% Coal Products					
Distillate, <175° C	85.16	14.00	0.084	0.063	0.69
Distillate, 175-350° C	84.38	11.64	0.260	1.396	2.32
Neutral	84.08	11.96	<0.01	1.452	2.51
Acid	78.24	8.21	1.362	0.548	11.64
Base	80.14	8.34	6.898	0.769	3.85
Distillate, 350-538° C	85.77	10.22	0.692	1.782	1.54
Neutral	86.06	10.85	0.064	1.873	1.15
Acid	81.98	7.32	2.301	0.758	7.64
Base	84.20	7.80	4.186	1.231	2.58
Residue, >538° C	87.11	7.24	1.224	2.662	1.76
Neutral	86.66	8.83	0.132	3.102	1.28
Strong Acid	81.39	6.29	0.997	1.565	9.76
Weak Acid	83.60	6.62	1.068	2.133	6.58
Strong Base	80.32	6.30	2.802	2.323	8.26

TABLE 7 (Cont'd)
Elemental Composition of Coprocessing Fractions

	C	H	N	S	O
30% Coal Products					
Distillate, <175° C	83.09	13.50	0.080	0.125	3.21
Distillate, 175-350° C	84.60	11.72	0.448	1.230	2.00
Neutral	84.86	12.14	0.026	1.343	1.63
Acid	76.74	8.43	0.572	0.299	13.96
Base	77.70	9.02	5.074	0.267	7.94
Distillate 350-538° C	85.30	10.10	0.724	1.449	2.43
Neutral	85.18	10.84	0.073	1.667	2.24
Acid	80.48	7.54	2.200	0.606	9.17
Base	82.63	7.83	3.888	0.971	4.68
Residue, >538° C	87.58	6.72	0.856	2.138	2.71
40% Coal Products					
Distillate, <175° C	85.26	13.42	0.102	0.082	1.14
Distillate, 175-350° C	84.92	11.36	0.477	1.350	1.89
Neutral	85.35	11.76	0.026	1.494	1.37
Acid	78.12	8.12	0.532	0.480	12.75
Base	79.22	8.08	6.278	0.622	5.80
Distillate, 350-538° C	86.25	9.93	0.842	1.598	1.38
Neutral	85.82	10.68	0.084	1.771	1.65
Acid	82.85	7.12	2.222	0.674	7.13
Base	82.59	7.34	4.660	1.031	4.38
Residue, >538° C	87.98	6.48	1.030	2.061	2.45
Neutral	86.26	8.46	0.084	3.049	2.15
Strong Acid	83.92	5.89	1.256	0.976	7.96
Weak Acid	84.61	6.34	0.798	2.148	6.10
Strong Base	85.00	5.93	1.642	1.590	5.84

nitrogen being most prominent in the bases and oxygen in the acids. Sulfur appears to be concentrated in the neutral fractions somewhat preferentially over the acid and base fractions.

The distribution and amounts of heteroatoms (nitrogen, sulfur, oxygen) somewhat parallel the trends in carbon isotope ratio values that have been reported previously. In past reports it has been shown that acid and base fractions are strongly enriched in the ^{13}C isotope (i.e., $\delta^{13}\text{C}$ is less negative). The extent of enrichment in some cases was greater than the isotope ratio of the coal reactant and it was impossible to determine reactant contributions to these fractions. Enrichment of those fractions at about the same magnitude was also observed for the 2 percent coal product and for the unprocessed Maya crude fractions. Selectivity values based on yield data can show the relative contribution of resid and coal to specific products but no quantitative relation of selectivity to isotope ratio has been established.

Elemental analysis data for the 20, 30, and 40 percent coal products selected from Table 7 have been related to carbon isotope ratios by a multivariate regression procedure. The relation fitted to the data has the form:

$$(1) \quad \delta^{13}\text{C} = a + b(\text{coal}\%) + c(\text{N}\%) + d(\text{S}\%) + e(\text{O}\%).$$

The values a, b, c, d, and e were determined in the regression procedure. Other terms in (1) are $\delta^{13}\text{C}$ - calculated carbon isotope ratio; coal% - percent reactant coal; N%, S%, O% - weight percent nitrogen, sulfur, and oxygen. Values for elemental analysis and isotope ratios of the resid fractions were not included in this calculation because the ratios had shown poor balance with the parent resid material as shown in Table 5. Data values for the 2 percent coal products did not fit well with the other values in the regression procedure and were processed in a separate regression analysis. The values determined are:

a	-28.02
b	+ 0.0183
c	+ 0.3376
d	+ 0.4630
e	+ 0.1744

Observed and calculated values are shown in Table 8.

TABLE 8
Observed and Calculated Carbon Isotope Ratios

	20% Coal		30% Coal		40% Coal	
	Obs	Calc	Obs	Calc	Obs	Calc
Distillate, <175° C	-27.25	-27.47	-27.40	-26.83	-27.05	-27.02
Distillate, 175-350° C	-26.45	-26.51	-26.38	26.40	-26.16	-26.17
Neutral	-26.68	-26.54	-26.67	-26.56	-26.39	-26.35
Acid	-24.51	-24.91	-24.83	-24.70	-24.33	-24.66
Base	-24.19	-24.30	-24.84	-24.25	-23.94	-23.87
Distillate, 350-538° C	-26.05	-26.33	-25.92	-26.13	-25.75	-26.02
Neutral	-26.34	-26.56	-26.39	-26.28	-26.19	-26.15
Acid	-25.54	-25.19	-25.15	-24.85	-24.50	-24.98
Base	-24.77	-25.22	-24.74	-24.89	-24.41	-24.47
Residue, >538° C	-26.14	-25.70	-25.92	-25.72	-25.71	-25.56

The agreement of the observed and calculated values is reasonably good. The average difference between the observed and calculated values is $0.22 \delta^{13}\text{C}$ units. Figure 3 shows the plot of observed against calculated values. The line shown on the plot represents equivalence values; that is, $\delta^{13}\text{C}(\text{Calc}) = \delta^{13}\text{C}(\text{Obs})$. The scatter shown in this plot appears to be somewhat greater in the region representing acid and base samples (δ below 26) than in the remainder of the plot. However, the overall fit of calculated and observed values is sufficient to indicate that a relationship between isotopic composition and heteroatom content is probable. The failure of the regression method to include values from the 2 percent coal products in a satisfactory manner and some of the scatter shown in the data and plot may be related to the limitation of equation 1 in not including the effect of reaction selectivity of resid and coal contributions to isotopic shifts. In this circumstance, the agreement shown in the data and plot would indicate that heteroatom content may have as much or more importance in isotopic shift as reaction selectivity.

The c, d, and e terms listed above all show positive values which indicate that the nitrogen, sulfur, and oxygen are all associated with enriched ^{13}C levels. If the relation of isotopic enrichment to heteroatom content is correct, it is likely that the ^{13}C atoms are adjacent to or directly bonded to the heteroatoms since an effect of this type at a distance is improbable. This effect may have originated in the biochemistry of the algae and plant matter from which the petroleum and coal were formed. Although molecular rearrangements and other processes during maturation would have diminished the association, the effect could still be present. The fact that similar isotopic fractionation is found in the Maya crude fractions (Table 12, January-March, 1990 report) indicate that the effect is not related to the hydroprocessing conditions of the coprocessing procedure.

A similar regression procedure was applied to the data of the 2 percent coal reaction product. In this procedure equation (1) was modified by the elimination of the b(coal%) term. The values determined are:

a	-26.59
c	+ 0.2726
d	- 0.0338
e	+ 0.0055

Observed and calculated values are shown in Table 9. Figure 4 shows a plot of observed and calculated δ values. Agreement of these values is somewhat poorer than that for the previous set with an average difference of 0.25 $\delta^{13}\text{C}$ units.

No strong significance can be assigned to the values of c, d, and e other than that they are the result of the best fit determinations in the least squares procedure. Evaluation of the standard errors of coefficients showed the errors for d, the term related to sulfur content, was substantially greater than the errors for the other coefficients. This may indicate that inclusion of the sulfur values in equation (1) may do little for the overall fit of the isotope ratio values. The value for a should represent the carbon isotope ratio for carbon not associated with heteroatoms for the Maya residue products in the coprocessing product. The combination $a + b(\text{coal}\%)$ represents this same carbon for the 20, 30, and 40 percent coal products. If the coal contributed to polar and non-polar products in the same proportion as the residue, the value of b would be expected to be 0.03. However, since relatively more of the carbon of coal goes to polar fractions and less to non-polar, the value $b = 0.0183$ is reasonable.

The only elemental data available for the Maya crude fractions (Table 12, January-March, 1990 report) was that for the 650-1050° F distillate and its fractions. This is shown in Table 10. Both sets of regression constants were applied to this elemental data and the results are shown in Figure 5. The calculated values obtained from the first set of coefficients (20, 30, and 40 percent coal) are shown by squares and the other values (2 percent coal coefficients) are shown as circles. The slope of plotted points is roughly parallel to the equivalence line but the calculated values are about 1.0 $\delta^{13}\text{C}$ units more positive than expected. This might reflect some effect of hydroprocessing chemistry on isotopic composition but the data set is insufficient for worthwhile speculation.

Several sources of error may be considered in relation to the calculated carbon isotope ratio values. The observed isotope ratio values are considered to be quite reliable and are not expected to contribute any significant error in the regression procedure. Calculated values for isotope ratio values of the distillates based on yields and isotope ratios of the fractions have shown good agreement. This agreement has established the validity of the carbon

TABLE 9

Observed and Calculate Carbon Isotope Ratios, 2 Percent Coal

	Obs	Calc
Distillate, <175° C	-27.08	-26.59
Distillate, 175-350° C	-26.38	-26.60
Neutral	-26.41	-26.65
Acid	-25.88	-25.76
Base	-24.80	-24.79
Distillate, 350-538° C	-26.24	-26.48
Neutral	-26.43	-26.65
Acid	-25.64	-25.76
Base	-25.42	-25.61
Residue, >538° C	-26.94	-26.33

TABLE 10

Elemental Composition of Maya Crude Distillate
and Fractions, 650-1050° F

	C	H	N	S	O
Distillate	84.73	11.87	0.202	2.94	0.26
Neutral	85.50	12.73	0.011	2.50	-0.74
Acid	79.88	8.23	2.66	1.69	7.54
Base	80.38	9.92	2.98	3.68	3.04

isotope ratio values. Somewhat greater error is thought to be present in the elemental analysis data. This error is mostly in the oxygen values since these are actually net difference numbers. As such, they contain the error of carbon, hydrogen, nitrogen, and sulfur analyses.

The greatest source of error is contained in the model used for relating isotope ratios to composition. The equation (1) contains a minimum number of factors that can be expected to account for the effect and each of them is included only as a first order term. No interaction or higher order terms are included. However, without a better understanding of the possible relationship of elemental composition to isotopic fractionation, no other terms are justified. The most important error is lack of any terms relating selectivity of residue and coal in contributions to the various fractions. In previous reports, yield based selectivities have shown the significance of contributions of both reactants. Unfortunately, the heteroatom related calculation of isotope ratios does not seem to provide corrected values by which selectivity values may be determined.

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FIGURE 1. - Hydrocarbon distribution of the <175° C distillate of 20 percent coal coprocessing product.

FIGURE 2. - Hydrocarbon distribution of the <175° C distillate of 30 percent coal coprocessing product.

Figure 3. - Plot of calculated vs. observed carbon isotope ratios for the 20, 30, and 40 percent coal coprocessing products.

Figure 4. - Plot of calculated vs. observed carbon isotope ratios for the 2 percent coal coprocessing products.

Figure 5. - Plot of calculated vs. observed carbon isotope ratios for Maya 650-1050° F products.

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