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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

QUARTERLY TECHNICAL PROGRESS REPORT FOR THE PERIOD JULY 1 THROUGH SEPTEMBER 30, 1990

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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

ABSTRACT

This is the eighth 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. This includes the evaluation of methods to distinguish between compound classes originating from coal versus those originating from petroleum resid. Techniques being evaluated include carbon isotope ratios and the variations in compound classes in response to changes in the coal/resid ratio in the feed. A final objective of this project is to provide detailed knowledge on the composition of coprocessing products.

This report reviews the use of isotope ratios to determine the source of compound classes (e.g., acids, bases, neutrals, aromatics, saturates, etc.). Selective isotope fractionation is a complicating factor in the use of carbon isotope ratios to determine the source of coprocessing products. Other researchers have shown that through the use of appropriate correction factors to correct for this isotope selectivity, isotope ratios can be used to quantitatively determine the source of coprocessing fractions obtained by distillation. It is concluded in this report that although isotope ratios may provide qualitative information on the source of coprocessing compound classes, that the high degree of isotope selectivity in compound classes originating from a single feed prohibits the quantitative determination of the origin of such compound classes.

INTRODUCTION

One phase of improving our understanding of the fundamental chemistry of coprocessing involves the development of the ability to distinguish between products originating from coal versus those originating from petroleum resid. A primary objective of this project is to develop analytical techniques to determine the source (coal versus resid) of the various compound types found in coprocessing products. A corollary 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.

Two approaches are being evaluated as potential methods to distinguish between products originating from coal and those originating from petroleum resid. 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.

Other researchers using carbon isotope ratios to determine the origin of products have typically examined distillation fractions. This project involves determination of the origin of specific chemical classes (e.g., saturates, neutral-aromatics, acids, bases, etc.) within each boiling range rather than calculation of coal versus resid contributions based on global examination of whole distillation fractions.

Maya resid and Illinois No. 6 coal (with coal feed varying from 2 to 40%) were coprocessed in a batch autoclave to obtain products for detailed analysis. Reaction products were separated into a number of fractions--first by distillation and then by a comprehensive chromatographic separation scheme developed at NIPER (1). Both carbon isotope ratios and the response of product composition to changes in feed composition are being evaluated with respect to their utility in determining the source of compound classes in the product. This report, covering the period July through September, 1990, evaluates the use of isotope ratios in determining the source of particular compound classes in coprocessing products.

In the absence of complications such as isotope fractionation (discussed below), the application of isotope ratios to determine the source of products is simple and straight-forward. If the carbon isotope ratios, represented by $\delta^{13}\text{C}^1$, of two components differ adequately, the amount of each component in a mixture can be determined from $\delta^{13}\text{C}$ for the mixture. Where a product is made up of components A and B, the amount of each component in the product (more strictly, the amount of carbon in the product arising from each component) can be calculated from the relationship

$$(1-x) \delta^{13}\text{C}_A + x \delta^{13}\text{C}_B = \delta^{13}\text{C}_{\text{Product}} \quad \text{Eq. 1}$$

where x = the fraction of the carbon in the product arising from component B.

With mixtures, application of the method is straight forward and has been successfully used, for example, with mixtures of natural gas (2)

¹ Carbon isotope ratios in this work are represented by $\delta^{13}\text{C}$ which by convention is the difference between the sample and a reference material, Peedee Belemnite (PDB), in parts per thousand or parts per mil. Carbon isotope ratio values ($\delta^{13}\text{C}$) are determined by the relation $\delta^{13}\text{C} = 1000(R_{\text{sample}} - R_{\text{ref}})/R_{\text{ref}}$ where R is the ratio $^{13}\text{C}/^{12}\text{C}$ in the sample and reference materials.

For determining the contribution of coal carbon and resid carbon to a coprocessing product, the above relationship (in the absence of necessary corrections) becomes

$$(1-x)\delta^{13}C_{\text{resid}} + x\delta^{13}C_{\text{coal}} = \delta^{13}C_{\text{product}} \quad \text{Eq. 2}$$

where x = the fraction of the product carbon arising from the coal.

This equation may be rearranged to the following by which the percentage of coal carbon (x) in the product may be conveniently calculated. This equation is equivalent to the uncorrected versions of those of Steer, et al. (3) or of Burke, et al. (4).

$$x = \frac{\delta^{13}C_{\text{resid}} - \delta^{13}C_{\text{product}}}{\delta^{13}C_{\text{resid}} - \delta^{13}C_{\text{coal}}} \times 100 \quad \text{Eq. 3}$$

Carbon-13 isotope ratios of coal are typically on the order of -25 per mil (-24.56 for the Illinois No. 6 coal used in this work) and petroleum resids, while more variable, are generally isotopically lighter; i.e., more negative $\delta^{13}C$ (-27.56 for the Maya vacuum resid used in this work). Repeatability of the $\delta^{13}C$ measurement is generally better than 0.1 per mil allowing for good accuracy in the determination of the source of carbon in coprocessing products for properly selected pairs of reactants in the absence of complicating factors.

It is now well established that complicating factors require that various corrections be made in order to use isotope ratios to determine the source of products of coprocessing. Corrections have been used by Steer, et al. (3), and by Ohio Ontario Clean Fuels, Inc. (isotope methods credited to Alberta Research Council and the University of Alberta) (5). Corrections required for the accurate carbon sourcing of coprocessing products have been studied most extensively by Winschel, et al. at Consolidation Coal Co. (6).

The complications in application of isotope ratios to determine the source of coprocessing products arises from the facts that neither coal nor petroleum are isotopically homogeneous and, more importantly, to isotopic fractionation during coprocessing. Carbon-13 heterogeneity has been reported for both coal (7), and petroleum. Carbon isotope ratios for petroleum vary with boiling range (8), and by compound class (9).

Selective isotopic fractionation results from the kinetic isotope effect. Due to differences in bond energies, there is a tendency for certain fractions to become enriched in one of the two stable carbon isotopes during molecular weight reduction. This is most evident in the formation of hydrocarbon gas formed from the decomposition of higher molecular weight hydrocarbons. For example, in the pyrolysis of n-octadecane, there is a substantial enrichment of the methane in ^{12}C (10).

To correct for isotopic fractionation, Winschel et al. (6) developed a correction procedure based on the following three assumptions:

1. the carbon in the gas is formed from the two feedstocks in proportion to the carbon fed to the unit from each feedstock,
2. the difference between $\delta^{13}\text{C}$ for each feedstock and $\delta^{13}\text{C}$ for the gas produced from that feedstock is the same for the coal and the petroleum, and
3. the non-gas producing carbon undergoes no further selective isotopic fractionation.

Although the assumptions are not strictly true, Winschel et al. (6) argued that the likely errors in the assumptions do not dramatically effect results of carbon sourcing based on isotope ratios with corrections based on these assumptions. Note that the primary use of these corrections was in the application of carbon isotope ratios to determine the source of distillation fractions. Discussion of assumptions necessary to determine the source of compound classes through the use of isotope ratios is included in the following section.

RESULTS AND DISCUSSION

The application of isotope ratios for determining the source of coprocessing products separated by distillation was discussed in the prior section. This section will critically review the findings of this project related to the use of isotope ratios for determination of the origin of compound class fractions obtained in coprocessing.

Details of the batch autoclave procedures used in this study were provided previously (11). Carbon isotope ratios were first determined on reactor products with minimal prior separation. Results are summarized in Table 1 and partial results are plotted in Figure 1. $\delta^{13}\text{C}$ values for the

feed materials are included as is the calculated $\delta^{13}\text{C}$ for the feed blend (based on the $\delta^{13}\text{C}$ values for the resid and coal, the fractional amounts of coal and resid used, and the carbon analyses of 84.6 weight percent for the resid and 69.8 weight percent for the coal).

Gaseous products were examined in more detail than has typically been done in isotope studies in coprocessing; in particular, carbon dioxide was separated from the hydrocarbon gases and analyzed separately. The $\delta^{13}\text{C}$ values for carbon dioxide from the various runs are nearly identical as would be expected since it is derived almost exclusively from the coal. The origin of carbon dioxide from coal is, of course, already established and is consistent with the variation of carbon dioxide yields with coal concentration shown in this project (11). The $\delta^{13}\text{C}$ value for carbon dioxide is significantly different from coal or the reaction mix and may indicate that it is formed, at least in part, from mineral decomposition rather than decarboxylation of organic coal components. Carbon dioxide produced by the treatment of coal with hydrochloric acid and trapped as barium carbonate had a $\delta^{13}\text{C}$ of -2.62. The amount of barium carbonate recovered indicated a carbonate content of 0.58 percent CaCO_3 or 0.255 percent CO_2 . If all of the carbonate decomposed during coprocessing, and it is assumed that the balance of the CO_2 was supplied by coal at $\delta^{13}\text{C} = -24.56$, about 25% of the carbon dioxide originated from the coal mineral and the remainder from the organic content of the coal.

As noted in the Introduction, any isotope fractionation complicates interpretation of isotope ratio data. The severity of isotope fractionation which can occur in coprocessing is evident even in these initial results (Figure 1). The hydrocarbon gas samples were much lighter isotopically (more negative $\delta^{13}\text{C}$ values) than the feed or the condensed products. Differences in $\delta^{13}\text{C}$ between the hydrocarbon gas and the feed were 7.5 to 10.5 per mil. This is true even at the lowest coal concentration (2 weight percent) where nearly all of the gas must have arisen from the petroleum resid. This difference is similar to that reported by other workers. For example, Winschel et al. (6) reported that forced isotope balances indicated that the gases from petroleum pyrolysis must have isotope ratios 6 to 8 per mil lighter than the respective feedstocks (although analysis indicated that the gases were isotopically heavier than the respective feedstocks). The separation of carbon dioxide in this work directionally contributes to a larger difference between the gas and the feedstock but this effect, although measurable, is minor (due to the low carbon dioxide yield) compared to the overall isotope fractionation.

TABLE 1. - Carbon Isotope Ratios for Reactor Products

Coal, percent	$\delta^{13}\text{C}$			
	2	20	30	40
Feed blend	-27.51	-27.05	-26.79	-26.51
CO ₂	ND	-18.87	-18.88	-19.13
Hydrocarbon gas	-36.32	-37.60	-34.31	-34.46
Filtrate	-26.44	-26.17	-26.18	-26.00
THF solubles	-27.53	-26.89	-26.50	-26.05
THF insolubles	-27.50	-26.38	-25.58	25.70
Feed components	$\delta^{13}\text{C}$			
Maya resid		-27.56		
Illinois No. 6 coal		-24.56		

Figure 1. Carbon Isotope Ratios for Reactor Products

As is evident in Figure 1, there is not a regular trend in $\delta^{13}\text{C}$ for the hydrocarbon gases with varying coal concentration in the feed. The random variations in $\delta^{13}\text{C}$ for the hydrocarbon gases reported in this work are likely to be related to difficulties in transfer of $\text{C}_2\text{-C}_5$ from the charcoal trap to the pressurized sample vessel. At the two higher coal concentrations, $\delta^{13}\text{C}$ for the hydrocarbon gases is less negative (more coal like) but the very large isotope fractionation effect negates any possibility of determining the source of the hydrocarbon gases by isotope ratios.

The more negative $\delta^{13}\text{C}$ values for the hydrocarbon gases (depleted in ^{13}C) are balanced by the sum of the liquid and solid products having $\delta^{13}\text{C}$ values less negative (enriched in ^{13}C) than the feed. In contrast to the hydrocarbon gases, trends in carbon isotope ratios for the remainder of the reactor products more-less paralleled those of the reactor feed (Figure 1).

In the workup of the reactor products, after removal of gas and light hydrocarbons, the liquid phase was filtered in a pressure filter to obtain a solids-free filtrate and a filter cake. The filter cake was then washed with THF to obtain THF soluble and insoluble fractions. The THF soluble phase isolated from the filter cake tended to be significantly higher boiling than the filtrate (11). The insoluble phase includes ash and insoluble organic matter.

$\delta^{13}\text{C}$ for the filtrate (the primary reactor product) tended to follow that of the reactor feed but the overall range in $\delta^{13}\text{C}$ was quite small--varying only from -26.4 to -26.0. Due to isotope fractionation leaving the condensed products enriched in carbon-13, the filtrate appears to be more coal-like than the feed blend. The obvious need for correction for isotope fractionation can be shown by application of Eq. 3 to the 2 percent coal run without an isotope fractionation correction. The uncorrected application of Eq. 3 indicates that 37 percent of the filtrate arose from coal--a meaningless conclusion since the feed contained only 2 percent coal. With an increase in coal concentration from 2 to 40 percent, the contribution of coal to the filtrate has to have increased substantially based on mass balance considerations; this magnitude of increase is not shown by the small change in $\delta^{13}\text{C}$.

Significant isotopic fractionation also occurred between the filtrate and THF soluble phase. The largest difference was in the run with 2 percent coal--an unexpected difference since both of these fractions must be derived almost entirely from the petroleum resid. The difference decreased with increasing coal concentration to almost nil in the 40 percent coal run. $\delta^{13}\text{C}$ for the THF solubles followed that of the feed--becoming more coal-like with increasing coal concentration.

The most pronounced increase (becoming less negative) in $\delta^{13}\text{C}$ with changing coal concentration occurred in the THF insolubles which qualitatively indicated coal to be the primary source of this fraction.

Each filtrate was distilled to produce two distillate cuts and a resid. Isotope ratio data for the distillation fractions are summarized in Table 2 and are plotted in Figure 2. Isotope fractionation is apparent in the 2% coal run with the light distillate ($< 175^\circ\text{C}$) isotopically lighter than the filtrate (-27.08 per mil for the $< 175^\circ\text{C}$ distillate versus -26.44 for the filtrate). This trend holds for the other runs also with $\delta^{13}\text{C}$ for the $< 175^\circ\text{C}$ distillate 1.08, 1.22, and 1.05 per mil lighter than the corresponding filtrate for the 20, 30 and 40% coal runs, respectively. As is apparent in Figure 2, there is not a regular trend in $\delta^{13}\text{C}$ for the $< 175^\circ\text{C}$ distillate with both the 2 and 40 percent coal runs having essentially identical $\delta^{13}\text{C}$ values (-27.08 and -27.05, respectively). Similarly, the range in $\delta^{13}\text{C}$ for the $175\text{-}350^\circ\text{C}$ distillate is small and the trend is irregular varying only from -26.16 to -26.45. Except for the $< 175^\circ\text{C}$ distillate, there is a general correlation between $\delta^{13}\text{C}$ for the feed blend and the distillation products for the 20, 30 and 40 percent coal runs.

Table 2 includes a comparison of the measured values of $\delta^{13}\text{C}$ for the filtrate with those recalculated from the yields of the distillation fractions and their measured $\delta^{13}\text{C}$ values. The average absolute difference between the measured and calculated values is 0.10 per mil indicating good accuracy for the carbon isotope measurements and distillation mass balance.

Each of the distillates were separated into acid, base and neutral fractions by standard NIPER methods (1) and isotope ratios were determined for each fraction. Results are summarized in Table 3 and are plotted in Figures 3 and 4. Isotopic fractionation is apparent throughout including the run with only 2 percent coal. The neutral materials show depletion in ^{13}C while polar materials are enriched (less negative $\delta^{13}\text{C}$). The significant range of isotope ratios in products from the 2 percent coal run demonstrates the substantial isotope fractionation occurring during reaction of petroleum resid itself. For example, in the $175\text{-}350^\circ\text{C}$ distillate, the base fraction is 1.61 per mil isotopically heavier than the neutral fraction while in the $350\text{-}538^\circ\text{C}$ distillate, the difference is 1.01 per mil. The $\delta^{13}\text{C}$ value for the base fraction from the 2 percent coal run $175\text{-}350^\circ\text{C}$ distillate approaches the value for coal (-24.56).

The acids and bases from the runs with higher coal concentrations are more coal-like (less negative $\delta^{13}\text{C}$). This is qualitatively in agreement with studies of changes in product composition with changing coal concentration which indicated that coal was the primary source of acid and base

TABLE 2. - Carbon Isotope Ratio Values for Distillation Fractions

Coal, percent	$\delta^{13}\text{C}$			
	2	20	30	40
Total filtrate, measured	-26.44	-26.17	-26.18	-26.00
Total filtrate, recalculated	-26.55	-26.38	-26.22	-25.96
Difference ^a	0.11	0.21	0.04	-0.04
>175° C (<347° F)	-27.08	-27.25	-27.40	-27.05
175-350° C (347-662° F)	-26.38	-26.45	-26.38	-26.16
350-538° C (662-1000° F)	-26.24	-26.05	25.92	25.75
>538° C (>1000° F)	-26.94	26.14	-25.92	25.71

^a measured-recalculated

Figure 2. Carbon Isotope Ratios for Distillation Fractions

Figure 3. Carbon Isotope Ratios for Acid-Base-Neutral Fractions of 175-350° C Distillate

Figure 4. Carbon Isotope Ratios for Acid-Base-Neutral Fractions of 350-538° C Distillate

fractions. However, the large isotope fractionation seen in the 2 percent coal run makes a quantitative assessment of the source of the acids or bases in coprocessing problematic.

The $\delta^{13}\text{C}$ values for the whole distillates can be recalculated from the $\delta^{13}\text{C}$ values for the separated components and the yields of the fractions. The recalculated values and the differences between the measured and recalculated values are included in Table 3. The excellent agreement between the measured and calculated values confirms the quality of the product fractions and the quality of the $\delta^{13}\text{C}$ measurements. Significant contamination of the fractions with solvents used in the separations would result in poor ^{13}C balances. Average absolute variations between the measured and calculated values are 0.04 per mil for the 175 - 350 ° C distillate and 0.09 per mil for the 350 - 538° C distillates.

Neutral fractions were separated by NIPER techniques (1) into saturate and aromatic fractions. Isotope ratios for the whole neutrals and saturate and aromatic subfractions are included in Table 4 and are plotted in Figures 5 and 6. Again, measured $\delta^{13}\text{C}$ values for the whole fraction are compared with that recalculated from the yields and $\delta^{13}\text{C}$ values for the subfractions. The calculated $\delta^{13}\text{C}$ values would include effects of errors in yield determination, isotope ratio measurement, solvent content of the fractions and any other contamination. Agreement is again excellent with the average absolute differences being 0.05 per mil for the 175 - 350° C fractions and 0.02 for the 350 - 538° C fractions.

Differences between $\delta^{13}\text{C}$ for the saturate and aromatic fractions are included in Table 4. The largest differences were observed for 2% coal run. As noted previously, essentially all of the neutral compounds in this product must have originated from the Maya resid alone; thus the difference in $\delta^{13}\text{C}$ (0.98 per mil for the 175 - 350° fraction and 1.13 for the 350 - 538° C fraction) is reflecting the selective nature of isotope distribution in products originating from the petroleum resid.

Interestingly, carbon isotope ratios for saturate fractions from products where 20 to 40 percent coal was added are more negative than those from the corresponding 2 percent coal run. The trend opposes that of the acid and base fractions as well as that for the coal versus resid. This may result from isotopic fractionation within the coal or a shift in isotopic fractionation within saturates from the resid in the presence of coal. Furthermore, differences between $\delta^{13}\text{C}$ for the aromatic and distillate fractions decreases strongly although somewhat erratically with increasing coal content.

Table 3. - Carbon Isotope Ratios for Distillate Acid-Base-Neutral Fractions

Coal, percent	$\delta^{13}\text{C}$			
	2	20	30	40
<u>175-350° C fractions</u>				
Whole distillate, measured	-26.38	-26.45	-26.38	-26.16
Whole distillate, recalculated	-26.37	-26.48	-26.42	-26.09
Difference ^a	-0.01	0.02	0.04	-0.07
Acids	-25.88	-24.51	-24.83	-24.33
Bases	-24.80	-24.19	-24.84	-23.94
Neutrals	-26.41	-26.68	-26.67	-26.39
<u>350-538° C fractions</u>				
Whole distillate, measured	-26.24	-26.05	-25.92	-25.75
Whole distillate, recalculated	-26.30	-26.15	-26.07	-25.79
Difference ^a	0.06	0.10	0.15	-0.04
Acids	-25.64	-25.54	-25.15	-24.50
Bases	-25.42	-24.77	-24.74	-24.41
Neutrals	-26.43	-26.34	-26.39	-26.19

^a measured-recalculated

TABLE 4. - Carbon Isotope Ratios for Neutral Subfractions

Coal, percent	$\delta^{13}\text{C}$			
	2	20	30	40
<u>175-350° C</u>				
Neutrals, measured	-26.41	-26.68	-26.67	-26.39
Neutrals, recalculated	-26.47	-26.67	-26.70	-26.50
Difference ^a	0.06	-0.01	0.03	0.11
Saturate subfraction	-25.95	-26.40	-26.54	-26.32
Aromatic subfraction	-26.93	-27.05	-26.82	-26.59
Difference (sat-aromatic)	0.98	0.65	0.28	0.27
<u>350-538° C</u>				
Neutrals, measured	-26.43	-26.34	-26.39	-26.19
Neutrals, recalculated	-26.44	-26.39	-26.37	-26.19
Difference ^a	0.01	0.05	-0.02	0.00
Saturate subfraction	-25.61	-26.11	-26.28	-26.01
Aromatic subfraction	-26.74	-26.52	-26.40	-26.27
Difference (sat-aromatic)	1.13	0.41	0.12	0.26

^a measured-recalculated

Figure 5. Carbon Isotope Ratios for Neutral Subfractions 175-350° C Distillate

Figure 6. Carbon Isotope Ratios for Neutral Subfractions 350-538° C Distillate

This suggests that coal-derived neutral products differ from petroleum resid-derived materials in selective isotope distribution. A possible explanation consistent with this observation is that saturates derived from coal may be more naphthenic, having been derived from aromatics by hydrogenation.

Resid fractions were separated into five fractions (strong acids, weak acids, strong bases, weak bases and neutrals) rather than the three fractions produced from the distillates. The samples showed poorer solubility in the solvents used in the LC separation than is typical for petroleum samples and recoveries fell in the range of 82 to 90 percent. Results for the carbon isotope ratio measurements for the resid fractions are shown in Table 5. Again, a comparison of the measured values for the whole resids with the values recalculated from the fraction yields and the fraction $\delta^{13}\text{C}$ measurements are included. In contrast to all of the earlier results, the recalculated values are significantly more negative (isotopically lighter) by 0.3 to 0.5 per mil relative to the measured values for the whole resid. The differences are probably caused by retention of solvent in the subfractions.

Isotope fractionation in resid from the 2% coal run is apparent, but it differs from that of the distillate fractions. For the distillate fractions, $\delta^{13}\text{C}$ for the acids was 0.5 to 0.6 less negative than for the neutrals while for the resid, $\delta^{13}\text{C}$ for the weak and strong acid fractions were slightly more negative (probably within experimental error considering the poorer ^{13}C balance for the resid fractionation) than $\delta^{13}\text{C}$ for the neutrals. The bases in the resid fractions were isotopically heavier (less negative $\delta^{13}\text{C}$) than the neutrals as was observed for the distillates but the effect was less pronounced. The difference between $\delta^{13}\text{C}$ for the neutrals and bases decline with increasing boiling point as shown below:

	$\Delta\delta^{13}\text{C}^*$
175 - 350° C distillate	-1.61
350 - 538° C distillate	-1.01
>538° C resid	-0.24

* $\delta^{13}\text{C}_{\text{neutrals}} - \delta^{13}\text{C}_{\text{bases}}$; used average of strong and weak bases for the resid fractions

As boiling point is increased, the polar fraction of the molecule which caused it to segregate into the acid or base fraction becomes a smaller part of the overall molecule. As the carbon isotope heterogeneity is presumably associated with the polar segment of the molecule, this is probably the reason for the decreased difference in $\delta^{13}\text{C}$ values between polar and neutral fractions with increasing boiling point.

TABLE 5. - Carbon Isotope Ratios for Coprocessing Resid Subfractions

Coal, percent	$\delta^{13}\text{C}$		
	2	20	40
Whole resid, measured	-26.90	-26.13	-25.76
Whole resid, recalculated	-27.22	-26.64	-26.14
Difference ^a	0.32	0.51	0.38
Neutrals	-27.19	-26.64	-26.51
Strong acids	-27.37	-26.88	-25.90
Weak acids	-27.46	-26.75	-26.49
Strong bases	-26.94	-26.07	-25.65
Weak bases	-26.96	-26.22	-26.39

^a measured-recalculated

Figure 7 shows the carbon isotope ratios of the resid fractions from the various coprocessing runs. Although there are some irregularities, $\delta^{13}\text{C}$ for all of the fractions tend to follow that of the feed blend qualitatively indicating the expected increase in coal-like character with increasing feed level of coal.

Because of the variations in $\delta^{13}\text{C}$ for the various fractions from the 2 percent coal run demonstrating isotope fractionation, an analogous set of measurements was made on Maya crude. These fractions were prepared directly from the crude oil without application of hydrogenation or any other processing chemistry. Carbon isotope ratios for the Maya crude fractions are provided in Table 6. Differences in $\delta^{13}\text{C}$ for the various boiling range fractions are much smaller than for the coprocessing products from the 2 percent coal run. For example, in the 2 percent coal run the difference between the $<175^\circ\text{C}$ distillate and the whole filtrate was 0.64 per mil while for the unprocessed crude, the difference between the $<175^\circ\text{F}$ fraction and the whole crude was only 0.05 per mil. In fact, the whole range in distillation cuts for the Maya crude was only 0.12 per mil.

Differences in fractions separated by polarity were much larger than differences in the fractions separated by boiling point. The carbon isotope ratios for the Maya crude acid-base-neutral fractions for the distillate fractions generally paralleled those of the coprocessing products. These comparisons are shown in Table 6. In comparison to a range in $\delta^{13}\text{C}$ of only 0.12 for the boiling point range fractions, the difference between the neutrals and bases in the $175 - 350^\circ\text{C}$ distillate was 2.06 per mil or 1.39 per mil for the $350 - 538^\circ\text{C}$ distillate. The products from the coprocessing runs are enriched in ^{13}C ($\delta^{13}\text{C}$ is less negative) due to the loss of gas which is depleted in ^{13}C .

The initial results for the acid-base-neutral fractions of the resid were inconsistent with the trends for the distillate fractions. It was suspected that the problem was due to contamination from the solvents used in the separation so an additional separation of Maya + 538°C resid was carried out with rigorous drying to eliminate solvent. The severe conditions may degrade the samples so such vigorous conditions were not used with the coprocessing fractions. Carbon isotope measurements for these fractions are shown in Table 7. The calculated $\delta^{13}\text{C}$ for the whole resid based on the fraction yields and their $\delta^{13}\text{C}$ differed by only 0.04 per mil. In this case, there is only a minimal range in $\delta^{13}\text{C}$ for the various fractions.

Figure 7. Carbon Isotope Ratios for Resid Fractions

TABLE 6. - Carbon Isotope Ratios of Acid-Base-Neutral Fractions of Maya Crude and Coprocessing Fractions

	$\delta^{13}\text{C}$		
	Maya Crude	2% Coal	20% Coal
<175° C ^a	-27.72	-27.08	-27.25
175-350° C ^a fractions			
Whole distillate	-27.77	-26.38	26.45
Acids	-26.14	-25.88	-24.51
Bases	-25.73	-24.80	-24.19
Neutrals	-27.79	-26.41	-26.68
350-538° C ^a fractions			
Whole distillate	-27.71	-26.24	-26.05
Acids	-26.58	-25.64	-25.54
Bases	-26.36	-25.42	-24.77
Neutrals	-27.75	-26.43	-26.34
Whole resid, >538° C	-27.60	-26.94	-26.14

a) Nominal boiling point ranges.

TABLE 7. - Carbon Isotope Ratios for Maya Crude >538° C Resid Fractions

	$\delta^{13}\text{C}$
Whole resid, measured	-27.60
Whole resid, recalculated	-27.64
Difference	0.04
Neutrals	-27.68
Strong Acids	-27.75
Weak Acids	-27.36
Strong Bases	-27.58
Weak Bases	-27.53

CONCLUSIONS

The isotope measurements were shown to be of high quality and generally consistent trends were observed. Isotope ratios can be used to provide qualitative indications of the source of various coprocessing compound class fractions. Isotope fractionation during coprocessing is significant with lighter materials (notably hydrocarbon gases but also, to a lesser extent, <175° C distillate) being depleted in ^{13}C . Polar materials are significantly enriched in ^{13}C --to such an extent that $\delta^{13}\text{C}$ for one of the polar fractions from the 2% coal run (where the contribution from coal would be nearly insignificant) approached that of coal.

There appears to be no solid basis for making corrections to allow accurate determination of the origin of compound classes in coprocessing products through the use of carbon isotope ratios. Even within whole distillate classes from the 2 percent coal run, isotopic fractionation makes the light distillate appear more petroleum-like and the heavier distillate appear more coal-like. Selective isotopic fractionation between compound classes all derived primarily from a single feed (2 percent coal run) was substantial (e.g., difference in $\delta^{13}\text{C}$ of 1.6 per mil for bases versus neutrals in the 175 - 350° C distillate). The difference in $\delta^{13}\text{C}$ for similar classes varies with boiling range of the fraction. There is no basis to assume that this isotopic fractionation would be constant for variable feeds (resid versus coal or even for different resids or different coals). Although isotope ratios are qualitatively useful for determining the source of compound classes and for understanding other facets of coprocessing chemistry, the use of isotope ratios for accurate and quantitative determination of the source of compound classes does not appear feasible. If the difference between isotope ratios for the coal and resid were increased significantly, the situation could be improved.

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