

# **ANALYSIS OF COPROCESSING PRODUCTS**

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## ABSTRACT

One phase of improving understanding of the fundamental chemistry of coprocessing involves development of the ability to distinguish between products originating from coal versus those originating from petroleum resid. A primary objective of this project was to develop analytical techniques to determine the source (coal versus resid) of the various compound classes found in coprocessing products. A corollary objective was 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 were evaluated for distinguishing between products originating from coal and those originating from petroleum resid. One was based on the use of carbon isotope ratios and the other was based on variations in compound classes 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 involved determination of the origin of chemical classes (e.g., saturates, neutral aromatics, phenols, indoles, etc.) rather than distillate classes. Maya resid and Illinois No. 6 coal (with coal feed varying from 2 to 40 percent) were coprocessed in a batch autoclave to obtain products for detailed analysis.

Coprocessing products were separated into a number of fractions--first by distillation and then by a comprehensive chromatographic separation scheme developed at NIPER. The use of carbon isotope ratios to determine the source of particular compound classes was made more difficult by substantial isotope fractionation between compound classes. For example it was found that acid and base fractions are strongly enriched in the carbon-13 isotope -- even in a completely petroleum derived product. Relationships between concentrations of particular compound classes and the ratio of coal and resid in the feed were established. As an example, it was shown that coal was clearly the dominant source of both acids and bases. The acid fraction consisted primarily of phenols and, to a lesser extent, pyrrolic nitrogen compounds (indole-carbazoles) while bases were primarily aromatic amines and pyridine types (quinolines, benzoquinolines, etc.).

Similar techniques were used for analysis of coprocessing products produced by another DOE contractor using a continuous product development unit. Emphasis was placed on determination of the composition of the coprocessing resid; composition of this material is of interest as it is the material which failed to be converted to the desired distillate range material.

## I. BATCH AUTOCLAVE RUNS

Most of the analyses in this project were conducted on coprocessing products made in a series of batch autoclave runs. Maya vacuum resid ( $>538^{\circ}\text{C}$ ,  $1000^{\circ}\text{F}$ ) and Illinois No. 6 coal were used as reactants. After establishing satisfactory conditions for the desired conversion levels, a series of runs was made in which the only variable was the ratio of coal to resid in the feed. Coal concentration ranged from 2 percent to 40 percent. Products from these runs were used for both carbon isotope ratio and detailed composition studies. Analyses of the reactants are shown in Table 1, processing conditions are shown in Table 2, and the workup procedure is shown in Figure 1. A filtration step was included so that the insoluble organic matter (IOM) and soluble resid could be analyzed independently. At the end of the filtration, the filter cake was found to contain a viscous material which differed from the bulk filtrate. Thus the filter cake was washed with tetrahydrofuran (THF) to provide a THF soluble fraction in addition to the THF insolubles (ash and insoluble organic matter [IOM]). As the THF soluble fraction was found to contain significantly more nondistillable material than the filtrate, the filtrate and THF solubles were analyzed independently.

Gross reactor yields (except for gases) are shown in Figure 2. Filtrate is, of course, the predominant reactor product and its extensive separation and analysis is discussed later. At this point, discussion of trends with changing coal concentration will be limited to the THF insolubles (or insoluble organic matter [IOM] since results are presented on an ash free basis). IOM increases with increasing coal content for the 20, 30 and 40 percent coal runs indicating coal as the primary source of this product. However, the highest IOM yield was obtained with the 2 percent coal run. The original Maya vacuum resid is free of THF insolubles so the IOM in the 2 percent coal run was formed via retrogressive runs. Such reactions may have been promoted by a poorer catalyst distribution with the low coal concentration.

Table 3 shows the H/C molar ratios for the reactants, filtrate, THF solubles, and THF insolubles (IOM). As anticipated, the filtrate is enriched in hydrogen compared to the reactants. The H/C ratios of the filtrate samples show only a small decline with increasing coal content. The THF solubles fractions are quite hydrogen deficient compared to the filtrate. A fraction comparable to this THF soluble fraction, which is distinctly different from the filtrate, is not found in conventional coal liquefaction. This fraction, soluble in THF but insoluble in the coprocessing filtrate, presumably results from the lower solvency of the petroleum coprocessing product compared to more aromatic coal liquefaction products. As anticipated, the THF insolubles (IOM) are quite deficient in hydrogen compared to the other products.

Overall coprocessing yields are summarized in Table 4. Overall yields are relatively consistent over the range of coal concentrations investigated; the largest changes in yields occurred between 30 and 40 percent coal. Conversion to  $>538^{\circ}\text{C}$  ( $1000^{\circ}\text{F}$ ) products [100 - ( $>538^{\circ}\text{C}$  resid + IOM)] range from 76 to 69 percent with the lowest conversion obtained at the highest coal concentration. The decreased conversion is, of course, reflected in a decreased total distillate yield and increased  $>538^{\circ}\text{C}$  ( $1000^{\circ}\text{F}$ ) resid yield. The yield of light distillate ( $<175^{\circ}\text{C}$ ,  $347^{\circ}\text{F}$ ) decreased with increasing coal concentration while the yields of middle ( $175\text{-}350^{\circ}\text{C}$ ,  $347\text{-}662^{\circ}\text{F}$ ) and heavy ( $350\text{-}538^{\circ}\text{C}$ ,  $662\text{-}1000^{\circ}\text{F}$ ) distillates remained relatively constant.

## II. DETAILED COMPOSITION STUDIES

Methods for the exhaustive analysis of complex petroleum products have been developed at NIPER and are described in detail in a two-volume report (1). An overall schematic of the methods which are available for application to a wide variety of fossil fuel products is shown in figure 3.

Emphasis was placed on analysis of polar compounds. These types of compounds are typically present in significantly higher concentrations in coal liquefaction products than in conventional petroleum products. Particular emphasis was placed on analysis of acid fractions; acid compounds have been found to be particularly troublesome with regard to both upgrading and product quality.

Where possible, concentrations of various compound types were related to concentration of coal in the feed. This included the determination of selectivity factors which provide a numerical estimation of the contributions of coal or resid to the compound class of interest.

### Analysis Light Distillates

Analysis of light distillates (boiling below  $175^{\circ}\text{C}$ ,  $347^{\circ}\text{F}$ ) was limited to a high resolution gas chromatographic method known as PIANJ analysis. In this method, individual hydrocarbons up to about C-12 are quantitated. Compound classes (Paraffins, Isoparaffins, Aromatics, Naphthenes, Olefins) are reported based on the summation of the individual compounds. Table 5 summarizes results for the light distillate samples from the four batch autoclave runs.

Correlations between compound classes and coal concentration, although not strong, are evident for paraffins, isoparaffins and aromatics. Normal paraffins decrease with increasing coal concentration while isoparaffins and aromatics increase with increasing coal content.

#### **Analysis of 175-350 (347-662) and 350-538 ° C(1000° F) Distillates**

Separation into Acid, Base and Neutral Fractions.

The 175-350 and 350-538° C distillates were processed by nonaqueous ion exchange chromatography to produce acid, base and neutral fractions. This procedure was developed at NIPER for application to high boiling and residual materials (1). Figure 4 shows the percentage yields of these fractions from the 175 - 350 ° C distillates. Behavior for the heavier distillate was similar but with higher concentrations of polar materials.

Both acid and base levels show a relationship to coal content of the coprocessing feed. The formation of product classes from the coprocessing feed may be represented by a relation for the linear combination of petroleum residuum and coal products.

$$\text{Prod} = a \cdot \text{Res} + b \cdot \text{Coal}$$

The terms a and b represent the fraction of residuum and coal converted to the particular component or product class. If Res and Coal are the weight fractions of residuum and coal in the reaction feed and Prod is the percentage of a product class in a distillate class, the values of a and b may be determined by graphical means as intercepts at Res and Coal = 0. This is illustrated in Figure 5 in which the concentrations of a hypothetical product are plotted against the coprocessing feed composition. The four points represent concentrations of the product at coal concentrations of 2, 20, 30 and 40 wt percent. However, more reliable determinations may be made by the least squares method. The a and b values may be converted to terms for selectivity in residue and coal formation of products by the relations:

$$S_R = a/(a+b) ; S_C = b/(a+b).$$

The yield of a product class may be represented as relative product yield (RPY) by the relation:

$$\text{RPY} = (a+b)/2.$$

Table 6 shows values of selectivities  $S_R$  and  $S_C$  and RPY for the product classes contained in the distillates. The selectivities may be considered to show the relative contributions of resid and coal to the product in a reaction mix of equal amounts of residue and coal. Data in Table 6 indicate that for a coprocessing run in which the feed consisted of equal concentrations of coal and petroleum resid, 9 percent of the acids in the 175-350° C distillate would have arisen from the petroleum resid and 91 percent from the coal. Similarly, 59 percent of the neutral fraction would have arisen from the resid and 41 percent from the coal. The selectivity values show that coal is clearly the dominant source of acid and base components in the products. The selectivity for these classes to be formed from coal is less pronounced in the higher boiling distillate. In a similar manner, RPY is the magnitude of that product in the distillate from the same reaction mix. The RPY values show the higher concentrations of acids and bases in the higher boiling fraction.

#### Chemical Derivatization/Gas Chromatography/Mass Spectrometry of the Acid Fraction

Detailed analysis of the acids of the 175-350° C distillate of the 20 percent coal processing product was conducted by derivatization with methyl iodide followed by gas chromatography/mass spectrometry (GC/MS). The alkylation procedure for derivatizing acid fractions is described elsewhere (2).

Table 7 shows a list of the compound classes identified and the amount of each class present. It is clear that the phenols predominate with all classes of phenols summing to 82.9 percent. These amounts are approximate only since it was necessary to assume uniform ionization yield of the parent ions.

Several interesting structural details were determined in this study. The molecular weight of the first cycloalkylphenols (M.W. = 134, two isomers) clearly indicates the hydroxyindane (cyclopenta) form. In addition, of the nine isomers at M.W. = 148, only one lacked a distinct methyl loss peak further indicating cyclopenta form. It should be noted that hydroxytetralin (M.W. = 148, cyclohexa) would have only two isomers. In addition, the bis(cycloalkyl)phenols at M.W. = 174 should have two cyclopenta groups and at M.W. = 188 should have at least one. From this it may be assumed that a large part of the cycloalkyl function in coprocessing acids must be cyclopenta.

The acidic nitrogen compounds are a minor but significant part of the coprocessing acids. The three-ring systems, carbazoles and benzimidoles, are the dominant types in this class.

## Nuclear Magnetic Resonance (NMR) Analysis of Methylated Acid Fractions

The acid fractions were derivatized with  $^{12}\text{CCH}_3\text{I}$  and  $^{13}\text{CCH}_3\text{I}$  and the methylated acids were analyzed by 2-dimensional NMR and other NMR techniques which are described elsewhere (2).

Three general types of acids are present in the coprocessing products--all of which are determined by the NMR techniques. These include oxygen acids (phenols, hindered phenols, and much less prominently, carboxylic acids), nitrogen acids (indoles and carbazoles), and benzylic or sulfur containing acids. Figures 6 and 7 show graphically the number of functional groups of each type (oxygen acids, nitrogen acids and benzylic/sulfur acids) in the 175-350 and 350-538° C acid fractions, respectively.

Figure 6 and 7 show that phenols increase in prominence with increasing coal concentration while nitrogen acids are much more prominent in the run with 98 percent petroleum resid; generally, nitrogen acids diminish with increasing coal reactant content. Benzylic/sulfur acids are minor contributors in all cases but are also much more prominent in the 98 percent petroleum resid run. Both nitrogen acids and benzylic/sulfur acids are more prominent in the higher boiling distillates.

## Analysis Base Fractions

The base fractions isolated from the coprocessing distillates were analyzed by nonaqueous titration. The solvents used were acetonitrile and acetic anhydride and the titrations were monitored by special glass electrodes. This procedure determines bases in strong and weak basic strength classes. Strong bases include azaarenes (e.g., pyridine, quinoline, etc.) and arylamines (e.g., aniline, etc.). Titration in  $\text{CH}_3\text{CN}$  determines both of these together while titration in acetic anhydride detects azaarenes alone because arylamines are acetylated in this solvent. Weak bases determined by this procedure include sulfoxides, diarylamines, amides, and carbonyl classes.

No weak bases were detected in any of the coprocessing base samples. This contrasts with the composition of petroleum fractions in which weak bases are often significant. It is possible that the coprocessing reaction converts these components to neutral or strong base materials.

Table 8 shows the base class composition on a whole distillate basis. For reference, the values for the amount of base in the distillates are included. The yields are shown in terms of milliequivalents per gram of distillate. Trends in content of both azaarenes and arylamines with coal content are similar to that of yields of base fractions described previously. It appears that the levels of azaarenes increase and arylamines decrease in the higher boiling distillates.

### Neutral Class Analysis

The neutral class fractions were further separated into saturate and aromatic subfractions; results are summarized in Table 9. Separations were carried out on charge transfer and adsorption type liquid chromatography columns (1). Yields of 175-350° C subfractions were less satisfactory than those of higher boiling range because of volatility of some of the components. To avoid excess loss of sample, the solvent content was left at about 5 to 7 percent in each sample, as determined by gas chromatographic analysis.

The trends in saturate and aromatic composition of the 175-350° C neutral fraction appear somewhat erratic, possibly because of the effect of loss of sample in the 20 and 30 percent coal products. In both distillate ranges, the 2 percent coal product appears to have less saturate and more aromatic content than might be expected from the trends shown by the other samples. This may indicate that the reaction mechanisms controlling product distribution may differ somewhat in the absence of substantial amounts of coal. The distribution of saturate and aromatic products in the 350-538° C distillate for the 20-40 percent coal runs appears quite constant.

### Conclusions

Coprocessing products made under constant conditions with the exception of ratio of coal to resid in the feed were subjected to extensive separation and analysis. Changes in product compositions with changing feed ratio have allowed a determination of the source of particular compound classes.

In the light distillates (boiling below 175° C, 347° F), correlations between compound classes and coal concentration, although not strong, are evident. Normal paraffins decrease with increasing coal concentration while isoparaffins and aromatics increase



In the middle (175-350° C, 347-662° F) and heavy (350-538° C, 662-1000°F) distillates, both acids and bases increase with increasing coal concentration. Selectivity factors, which are an expression showing the fraction of a particular compound class which is derived from coal or resid, were determined. These factors indicate that coal is clearly the dominant source of both acids and bases.

Two-dimensional NMR analysis of the middle and heavy distillates showed that phenols increase in concentration with increasing coal content while nitrogen acids are much more prominent in the run with 98 percent petroleum resid. Generally, nitrogen acids decreased in concentration with increasing coal content. Benzylic or sulfur acids were minor contributors in all cases but were much more prominent in the run with 98 percent petroleum resid. Nitrogen acids and benzylic or sulfur acids were more prominent in the higher boiling distillates.

Analysis of basic fractions by nonaqueous titration techniques showed increases in both azarenes (e.g., pyridines, quinolines, etc.) and arylamines (e.g., anilines, etc.) with increasing coal content. Compared to middle distillates (175-350° C), heavy distillates (350-538°C) contain increased levels of azarenes and decreased levels of arylamines.

Subfractionation of the middle distillate (175-350° C) neutrals into saturates and aromatics showed a general trend for an increase in aromatics with increasing coal content. However, the run with 98 percent resid was high in aromatics. This may indicate somewhat differing reaction mechanisms in the absence of substantial amounts of coal. In the heavy distillate, saturate/aromatic ratios were relatively independent of coal concentration. Selectivity values indicate that in the heavy distillate, 56 percent of the aromatics would originate from the coal and 44 percent from the petroleum resid (with a 1:1 ratio of coal:resid in the feed). The contribution of aromatic materials by coal is greater than that indicated by the selectivity values since the larger part of the acids and bases (almost entirely aromatic) arise from the coal.

### III. CARBON ISOTOPE STUDIES

This section reviews the use of isotope ratios to determine the source of compound classes (e.g., acids, bases, neutrals, aromatics, saturates, etc.) in coprocessing products. 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 section 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.

Materials used in the carbon isotope studies were produced in the batch autoclave runs discussed in Section I and were separated into compound classes as discussed in Section II. Carbon isotope ratios were first determined on reactor products with minimal prior separation. Partial results are plotted in Figure 8.  $\delta^{13}\text{C}$  values for the feed materials are included as is the calculated  $\delta^{13}\text{C}$  for the feed blend. 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 8). 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. (3) 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).

As is evident in Figure 8, 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  $^{13}\text{C}$ ) are balanced by the sum of the liquid and solid products having  $\delta^{13}\text{C}$  values less negative (enriched in  $^{13}\text{C}$ ) 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 8).

$\delta^{13}\text{C}$  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. 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 three distillate cuts and a resid. Isotope ratio data for the distillation fractions are plotted in Figure 9. Isotope fractionation is apparent in the 2 percent coal run with the light distillate (< 175° C) isotopically lighter than the filtrate (-27.08 per mil for the <175° C distillate versus -26.44 for the filtrate). This trend holds for the other runs also with  $\delta^{13}\text{C}$  for the <175° C distillate 1.08, 1.22, and 1.05 per mil lighter than the corresponding filtrate for the 20, 30 and 40 percent coal runs, respectively. As is apparent in Figure 9, there is not a regular trend in  $\delta^{13}\text{C}$  for the < 175° 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 175-350° C distillate is small and the trend is irregular varying only from -26.16 to -26.45. Except for the <175° 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.

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 showed an average absolute difference between the measured and calculated values of 0.10 per mil indicating good accuracy for the carbon isotope measurements and distillation mass balance. Good carbon-13 mass balances were also obtained for compound type separations discussed below (2).

Each of the distillates were separated into acid, base and neutral fractions by standard NIPER methods and isotope ratios were determined for each fraction. Representative results are shown in Figure 10. Isotopic fractionation is apparent throughout including the run with only 2

percent coal. The neutral materials show depletion in  $^{13}\text{C}$  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.

Neutral fractions were separated by NIPER techniques into saturate and aromatic fractions. Representative results for isotope ratio measurements for the whole neutrals and saturate and aromatic subfractions are shown in Figure 11. The largest differences between  $\delta^{13}\text{C}$  for the saturate and aromatic fractions were observed for 2 percent 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  $\delta^{13}\text{C}$  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.

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.

## 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,  $<17^\circ\text{C}$  distillate) being depleted in  $^{13}\text{C}$ . Polar materials are significantly enriched in  $^{13}\text{C}$ --to such an extent that  $\delta^{13}\text{C}$  for one of the polar fractions from the 2 percent 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.

### III. ANALYSIS HRI SAMPLES

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 Fondo. 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). The benzene soluble fractions of 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 shown in Figure 12. The predominant fraction (67-81 percent) 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.

All of the polar fractions increase with increasing coal concentration. Comparing runs 238-8-5 and 238-10-8, (subbituminous coal versus lignite), there is a significantly larger strong acid fraction from the lignite run. 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 for separation of the neutral fraction into saturates and neutral aromatics are shown in Figure 13. The concentration of saturates is high (70 percent) in the neutrals from run 238-8-5 (33 percent subbituminous coal, 67 percent Hondo resid) and drops markedly (to 26 percent) with an increase in coal concentration to 50 percent (238-8-9). This suggests that the resid is the source of the saturates--not a surprising suggestion. However, the run with 33 percent lignite and 67 percent Hondo resid (238-10-8) contains a much lower level of saturates (32 percent) 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.

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 fraction from each sample was 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 (1). 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.

The hydrocarbon skeletons of saturated hydrocarbons in the HRI coprocessing resids appear to be fundamentally different than those of aromatic species. The average molecular weights of various compound types in a given resid are similar to one another; the overall average molecular weights for Hondo: subbituminous coal products are somewhat lower than those for the Hondo:

lignite product. The average molecular weights determined for these resids ( $\leq 650$ ) are well below those of typical straight-run petroleum  $>1000^\circ\text{F}$  resids ( $\geq 900$ ) (1). Base fractions contain predominantly single nitrogen compounds of azarone or aminoaromatic type. Acid fractions contain appreciable quantities of pyrrolic benzologs, but surprisingly low concentrations of compounds with a free OH group. Neutral-aromatic fractions contain minor levels of sulfur compounds, an unknown proportion of ether or other oxygen-containing species, and major concentrations of aromatic hydrocarbons containing from 3 to 6 aromatic rings.

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TABLE 4. - Overall coprocessing yields

Coal, Percent	2	20	30	40
Normalized Yields, Wt Percent*				
Gases (C <sub>1</sub> -C <sub>7</sub> , CO <sub>2</sub> , H <sub>2</sub> S)	8.5	6.2	7.2	10.7
Distillates				
<175° C (347° F)	20.5	15.5	15.8	7.9
175-350° C (347-662° F)	27.0	28.3	26.4	27.6
350-538° C (662-1000° F)	20.1	22.2	25.5	22.8
Total	57.6	66.0	67.7	58.3
Nondistillable				
>538° C (1000° F) resid	17.8	24.9	22.2	26.7
THF Insolubles (OM)	6.9	2.9	2.9	4.3
Total	23.6	27.8	25.1	31.0
Total	100.0	100.0	100.0	100.0
538° C+ (1000° F) conversion	76.4	72.2	74.9	69.0

\* Based on petroleum resid plus MAF coal. Yields are normalized to 100 percent

TABLE 5. - PIANO analysis of light distillates (<175° C) (347° F)

Coal, Percent	2	20	30	40
Paraffins	25.60	22.94	21.13	20.50
Isoparaffins	31.28	31.30	31.63	34.60
Aromatics	15.72	15.61	16.93	22.26
Naphthenes	21.85	23.42	23.96	16.92
Olefins	4.90	4.51	4.11	3.28
Unknown	0.66	2.21	2.24	2.45

TABLE 6. - Selectivity and RPY values of distillate subfractions

	S <sub>R</sub>	S <sub>C</sub>	RPY
175-350° C			
Acids	0.09	0.91	11.58
Bases	0.12	0.88	5.67
Neutral	0.59	0.41	79.18
350-538° C			
Acids	0.25	0.75	20.07
Bases	0.32	0.68	7.24
Neutral	0.56	0.44	75.82

TABLE 7. - Acids of 175-350° C (347-662° F), 20 percent coal product, analyzed by GC/MS

Compound Class	Amount, %	First M.W.	Max. M.W.
Alkylphenols	43.9	108	122
Cycloalkylphenols	21.9	134	162
Bis(cycloalkyl)phenols	3.2	174	188
Phenylphenols	10.6	170	198
Cycloalkylphenylphenols	1.0	196	224
Bisphenols	2.4	186	200
Indoles	2.2	117	145
Carbazoles/benzoindoles	14.4	167	195

TABLE 8 - Base class composition of coprocessing distillates

Coal, percent	2	20	30	40
<b>175-350° C</b>				
Base Content, %	1.5	2.5	5.3	4.0
Azaarenes*	0.0563	0.0848	0.1034	0.1144
Arylamines*	0.0153	0.0395	0.0668	0.0584
<b>350-538° C</b>				
Base Content, %	4.8	5.0	7.2	6.3
Azaarenes*	0.1195	0.1300	0.1598	0.1676
Arylamines*	0.0173	0.0250	0.0346	0.0334

\*Meq per gram of distillate

TABLE 9. - Neutral class fractionation

Coal, percent	2	20	30	40
<b>175-350° C</b>				
Saturates	48.0	55.3	38.9	30.0
Aromatics	53.2	39.6	55.5	68.0
Recovery	101.2	94.9	94.4	98.0
<b>350-538° C</b>				
Saturates	26.8	31.2	29.4	29.9
Aromatics	74.0	70.7	69.8	69.8
Recovery	100.7	101.8	99.2	99.8

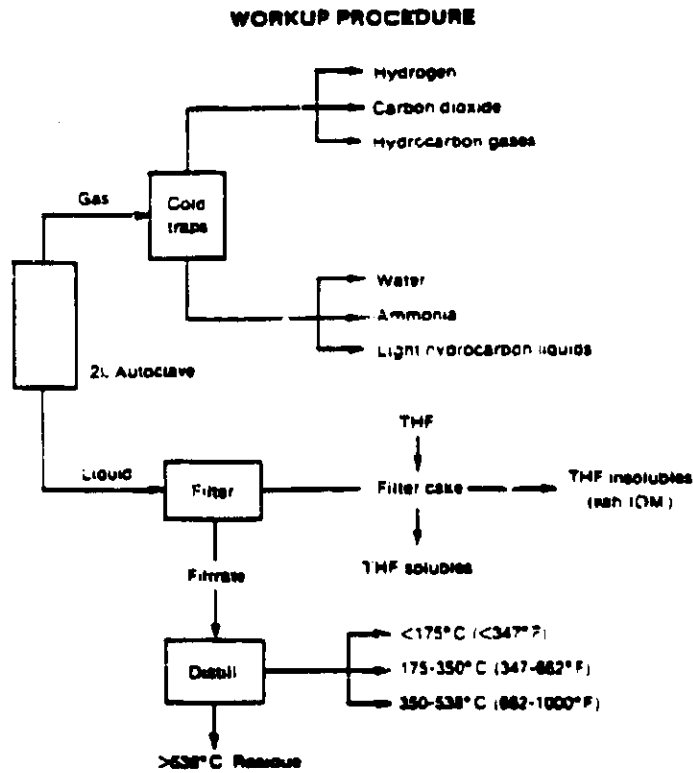


FIGURE 1. - Workup procedure for coprocessing runs

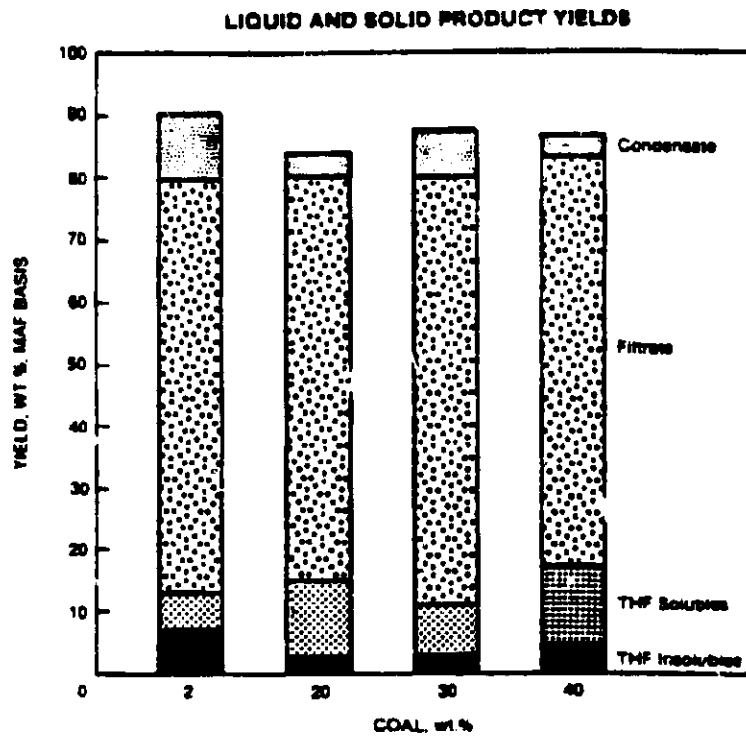


FIGURE 2. - Yields of reactor products versus coal concentration

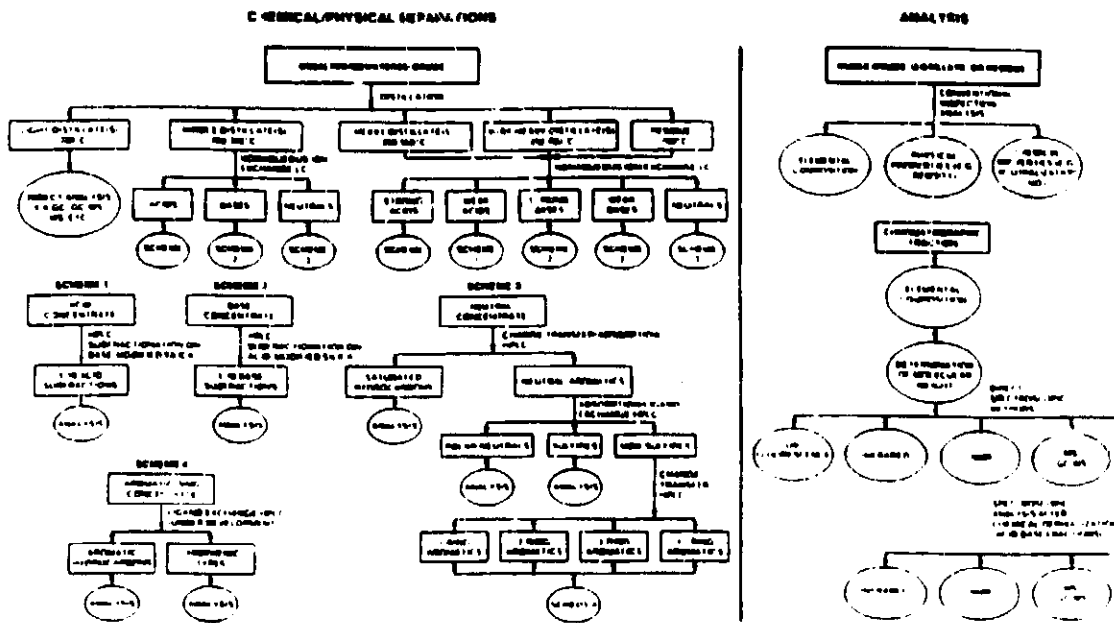


FIGURE 3. - Schematic for separation and analysis of conventional, heavy, or synthetic crudes and their products

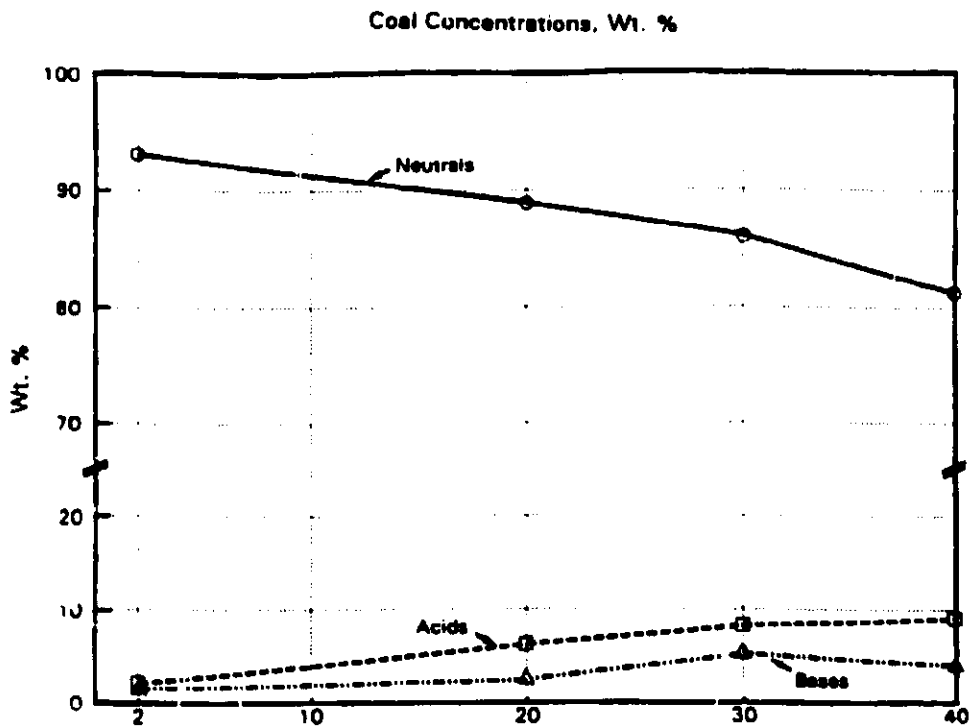


FIGURE 4. - Acid-base-neutral classes in 175-350°C (347-662°F) distillate versus coal concentration

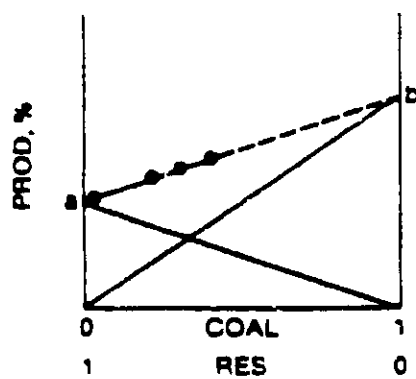


FIGURE 5. - Hypothetical yield structure for coprocessing

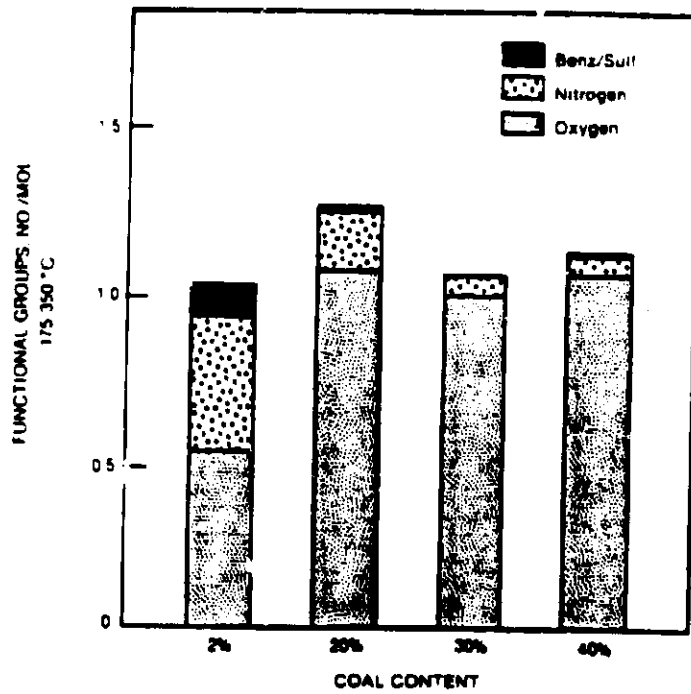


FIGURE 6. - Number of functional groups per molecule for the 175-350°C (347-662°F) products

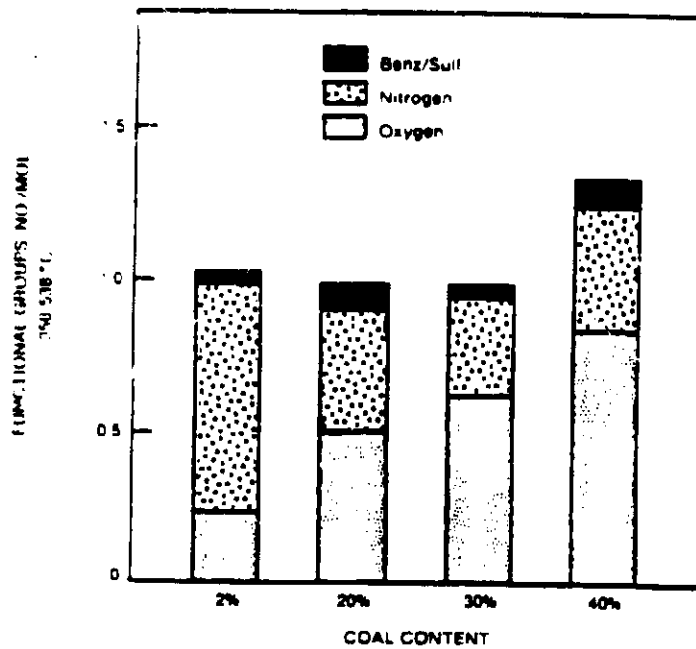


FIGURE 7. - Number of functional groups per molecule for the 350-538°C (662-1000°F) products

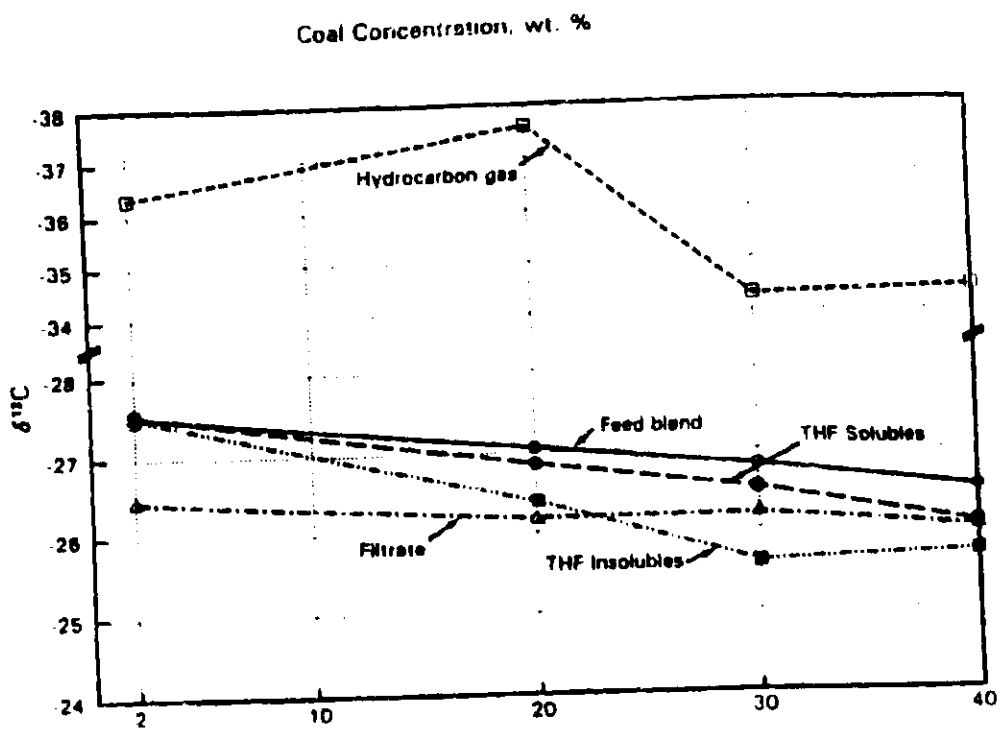


FIGURE 8. - Carbon isotope ratios for reactor products

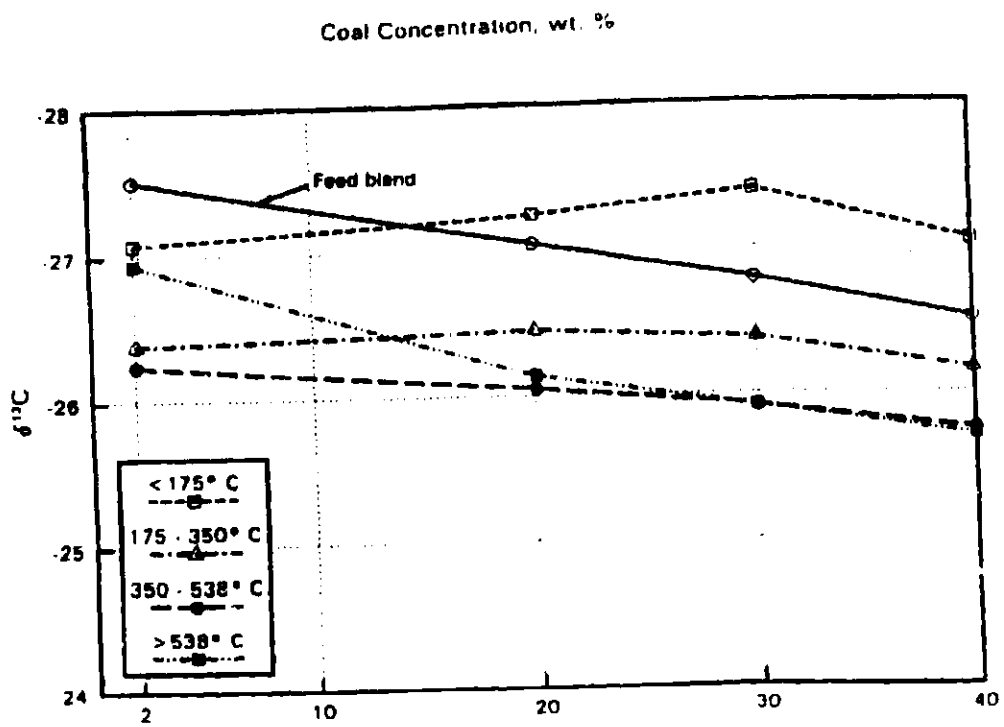


FIGURE 9. - Carbon isotope ratios for distillation fractions



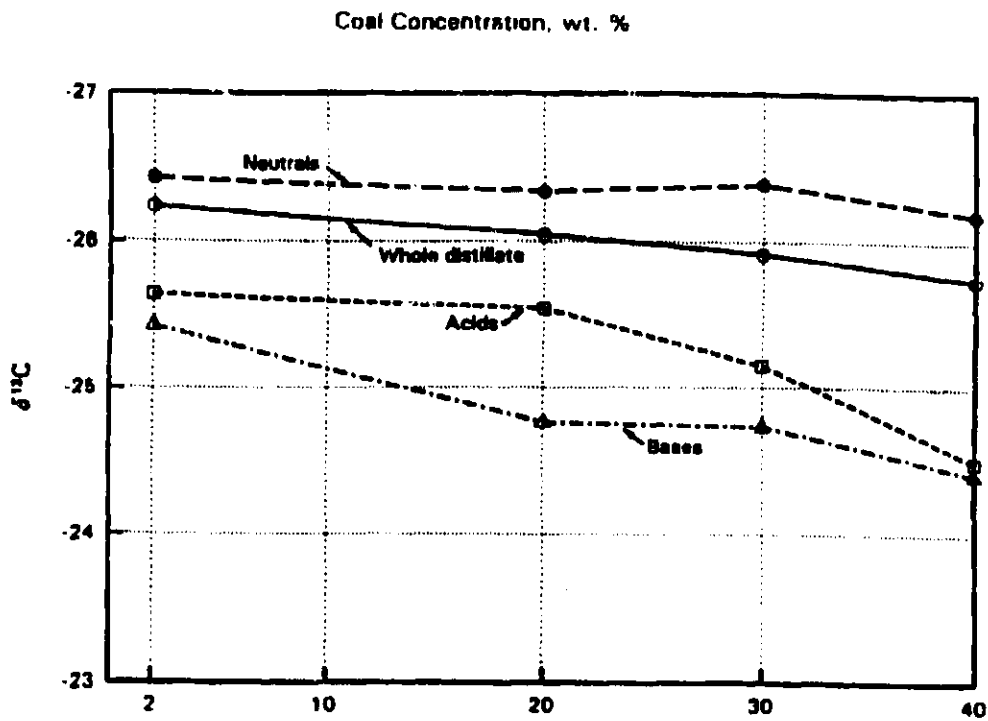


FIGURE 10. - Carbon isotope ratios for acid-base-neutral fractions of 350-538°C (662-1000°F) distillate

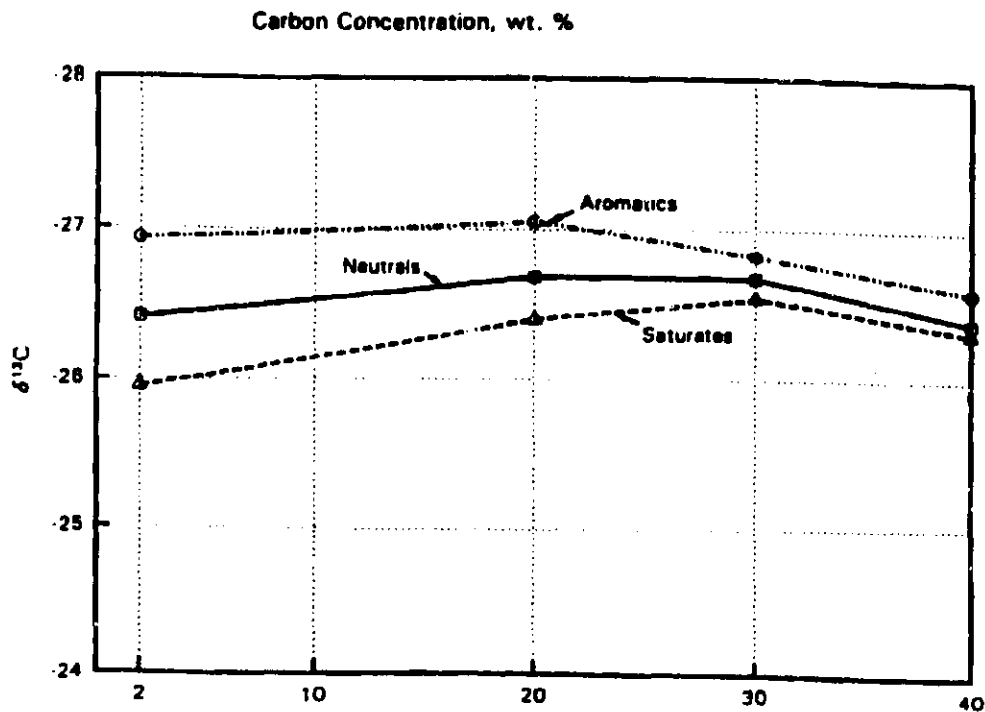


FIGURE 11. - Carbon isotope ratios for neutral subfractions of 175-350°C (347-662°F) distillate

**Acid-Base-Neutral Separations  
HRI VSB Samples  
Benzene Solubles Basis**

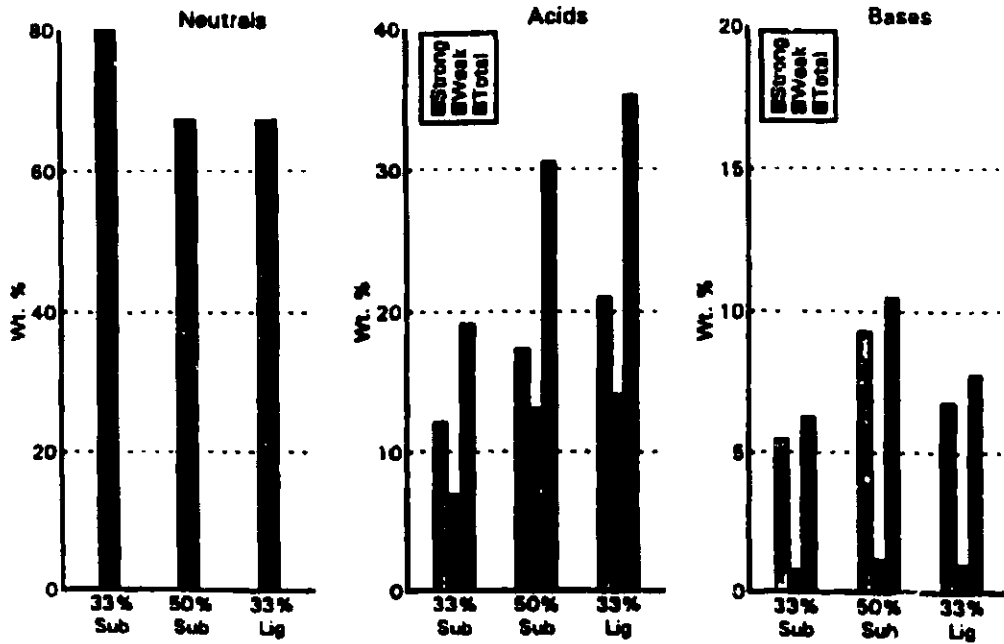


FIGURE 12. - Acid-base-neutral separations of HRI vacuum still bottoms samples

**Neutrals Subfractionations  
HRI VSB Samples**

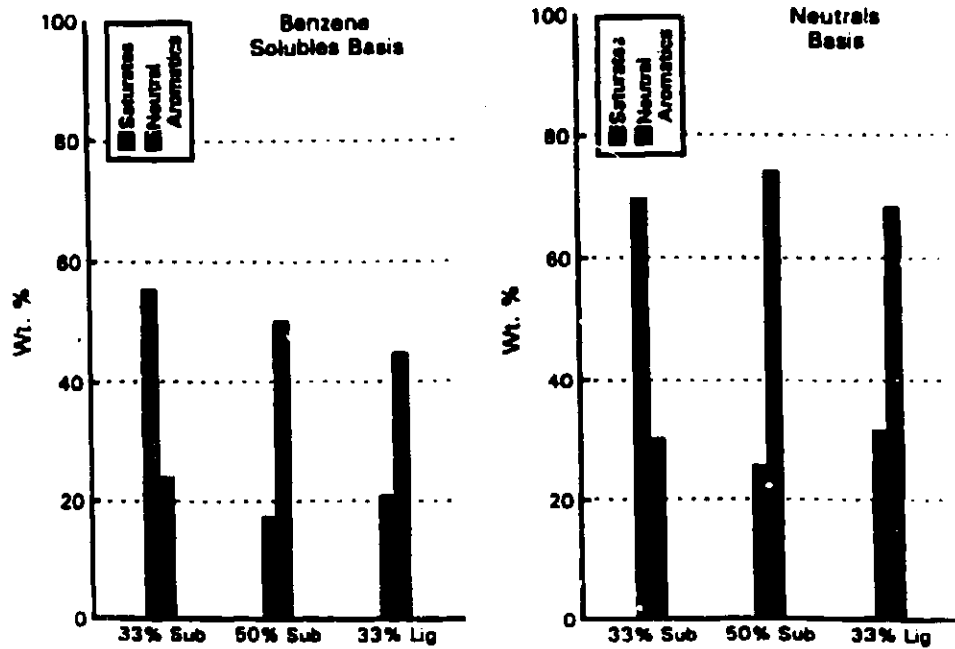


FIGURE 13. - Subfractionation of HRI vacuum still bottoms neutrals fraction