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COAL LIQUEFACTION PROCESS SOLVENT CHARACTERIZATION AND EVALUATION

TECHNICAL PROGRESS REPORT
January 1 through March 31, 1987

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Section 1
INTRODUCTION

This is the Technical Progress Report for the ninth quarter of activities under Contract No. DE-AC22-84PC70018. It covers the period January 1 through March 31, 1987.

OVERVIEW

Consolidation Coal Research and Development is characterizing samples of direct coal liquefaction process oils based on a variety of analytical techniques to provide a detailed description of the chemical composition of the oils, to more fully understand the interrelationship of process oil composition and process operations, to aid in plant operation, and to lead to process improvements. The approach taken is to obtain analyses of a large number of well-defined process oils taken during periods of known operating conditions and known process performance. Close cooperation is maintained with the process developers and with DOE in order to maximize the benefits of the work. Analytical methods used are based on their ability to provide quantitatively valid measures of process oil composition. Particular use is made of methods which provide chemical/molecular information of proven relevance to process performance. All samples are treated using conventional methods of analysis and preparation so that unit performance parameters, such as conversions and yields, can be independently determined to assure sample validity and correlation of analytical results among various plant operations. In addition to this more routine analytical work, specific coal liquefaction research topics are being addressed and specialized analytical methods are being developed under this contract.

CONTRACT ACTIVITIES

Contract activities for this quarter are listed below. Each topic is summarized and discussed in detail under a separate heading in

Section 2, Discussion. Because each topic is summarized, when appropriate, in the corresponding section of the Discussion, no overall Summary section is provided in this report.

- A set of ten oils from Hydrocarbon Research, Inc., (HRI) Run I-19 was analyzed to provide information on the performance of Burning Star No. 2 mine (Illinois 6) bituminous coal, cleaned by four chemical and physical processes, in the Catalytic Two-Stage Liquefaction (CTSL) process.

- A set of eleven oils from HRI Runs I-22 and I-23 was analyzed to provide information on the performance of a NiW and a FeMo catalyst in the CTSL process when using Burning Star No. 2 mine bituminous coal.

- Thirty-two coprocessing products from tests 1 through 16 of the Signal Research/UOP continuous bench unit were analyzed by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy and Fourier-Transform infrared (FTIR) spectroscopy to explore the possibility of using aromaticity and phenolic concentration measurements to determine the contributions of the coal and petroleum to the product. Carbon isotope ratios were previously determined on these samples. The tests were made with Lloydminster resid and either Illinois 6 bituminous or Wyodak subbituminous coal.

- Eight boiling-point fractions of the products from UOP's 2 1/2 month continuous coprocessing test were analyzed by carbon isotope mass spectrometry, ^{1}H-NMR and FTIR to determine the contributions of the two feedstocks (Lloydminster resid and Illinois 6 coal) to each fraction.

- Twelve microautoclave tests were made to "calibrate" the reactivity of our standard coal.

- Two major contract activities were in progress, but not completed this quarter. First, analyses were completed though interpretation is not yet finished on oils from Wilsonville Run 251. Second, we are analyzing products from liquefaction tests being conducted by Energy International. Results of these two activities will appear in a future report.

- Two papers were accepted for the 1987 International Conference on Coal Science. "Coal and Petroleum Reactions in Coal/Oil Coprocessing" concerns the carbon isotope work and appears as Appendix 1. "Similarities in the Structural Units of Different Coals" includes results from the dewaxing work and appears as Appendix 2.

Section 2

DISCUSSION

HRI CTSL RUN I-19

RUN DESCRIPTION

Consol analyzed ten samples from the Hydrocarbon Research Incorporated (HRI) Catalytic Two-Stage Liquefaction (CTSL) process development program. The samples were from bench-unit Run I-19, also called Run 227-39, which was operated for 17 days in November 1986 to test the performance of various cleaned coals in the process (1). The coals tested included conventionally cleaned Burning Star No. 2 mine (Illinois 6 bituminous) coal and the same coal additionally cleaned by the three other methods listed below:

- Bituminous Coal Research (BCR) - heavy media washing at +30 mesh prior to pulverizing/drying for bench unit feed.
- Advanced Energy Dynamics (AED) - electrostatic dry cleaning of pulverized (-70 mesh) coal.
- Resource Engineering, Inc. (REI) - "Ash-Lite" chemical leaching process (details proprietary).

Consol's analyses of the four feed coals are shown in Tables 2 and 3. BCR and AED achieved approximately equal ash reductions, although the coal recovery was considerably higher for the BCR case (>70% vs >50%). REI achieved a lower ash product and substantially changed the ash composition. High carbon recoveries (>90%) were claimed, although this is not supportable by the bulk quantities shipped from and received by HRI (1).

The operating conditions (1) for Run I-19 are summarized in Table 1. All operating conditions were constant for the entire run except for catalyst age and the choice of feed coal. Because of the different ash contents of the four feed coals, the feed rate of the whole coal was adjusted in conditions 2, 3 and 4 to give constant coal feed rate, coal space velocity and solvent/coal ratio on an MAF basis. Process flows in the CTSL bench unit are shown schematically in Figure 1 (2). The nominal throughput of the bench unit is 50 lbs/day (3), and each reactor has a capacity of 2000 cm^3 (2).

Except for the use of the three specially prepared coals, the operating conditions used for the entirety of Run I-19 were identical to those used during condition 1 of Run I-18. Portions of four earlier runs were also made at similar operating conditions but with different catalysts. Run I-13 was made with Amocat 1C (1/16-inch extrudates) produced by Cyanamid. Run I-15 simulated catalyst "cascading" with the same catalyst. In catalyst cascading, spent first-stage catalyst is charged to the higher temperature second stage in order to reduce the required catalyst replacement rate. Run I-16 was made with Amocat 1C (1/32-inch extrudates) produced by Davison and Run I-17 was made with UOP RCM-4 spherical catalyst. Consol's analyses of oils produced in Runs I-13 and I-15 (4), and Runs I-16, I-17 and I-18 (5) were presented earlier and are also discussed here in relation to Run I-19.

HRI reported (1) that the BCR and AED coals gave marginal (1-3%) increases in coal conversion, with the additional MAF distillate yields approximately in line with the additional conversion, when corrected for catalyst deactivation. When the REI coal feed was introduced, operating problems were experienced almost immediately, including low coal conversion and agglomeration of the first-stage catalyst, which eventually required a shutdown (1,6).

SUMMARY

The major conclusions of this work are summarized below. Detailed results are presented and discussed later.

- The BCR and AED cleaning processes substantially reduced the ash and pyritic and sulfatic sulfur contents of the coal. The REI cleaning process made the greatest reductions in ash and sulfatic sulfur, but significantly increased the chlorine and nitrogen contents of the coal. On a mineral matter-free basis, the four coals have very similar petrographic analyses.

- Condition 1 of Runs I-18 and I-19 were ostensibly identical. However, the oils produced in Run I-19 at condition 1 are less highly upgraded. The difference is significant analytically, though relatively small. Its cause is unknown, though it may merely reflect the reproducibility in the operation of the bench unit.

- No representative product sample was obtained from the REI coal. Differences in oil properties resulting from the use of the other three coals are small in comparison to catalyst aging effects. Any differences must be small.

SAMPLE DESCRIPTION

We obtained a set of ten samples (30g to 40g each) from Mr. J. B. McLean of HRI. The set included pressure-filter liquid (PFL) samples from the first three conditions, first-stage reactor inventory samples from conditions 2 and 3, a filtered charge-pot sample from condition 4 and the four feed coals. No first-stage oil was withdrawn by HRI at condition 1 because it was assumed that it would be identical to the sample from condition 1 of Run I-18.

Operation with the REI coal (Condition 4) did not last long enough to allow representative samples to be taken. The last available material collected was the filtered charge-pot sample from period 17A (initiation of shutdown). This material, a second-stage product, was contaminated with distillate flush oil (start-up oil) (1). Though this is the closest available material to a definable product from the REI coal, our analyses suggest that even the resid portion of this sample may not be a representative product. For example, it contains significantly fewer preasphaltenes and is significantly less aromatic than the PFL resids made earlier in the run. Though these differences may have resulted from the properties of the feed coal, or because very little converted coal reported to this sample, it is impossible to be certain. Therefore, this sample will not be further discussed here.

The pressure-filter liquid is the major second-stage product and, in most cases discussed in this report, it was the only component of the recycle oil. It is obtained by filtering the atmospheric-still bottoms (Figure 1). First-stage oils, which are samples of the first-stage reactor inventory, were filtered by HRI prior to shipment. The sampling procedure used by HRI (6) is to take the PFL sample first, then to take the first-stage sample while maintaining constant operating conditions. As a result, any first-stage sample corresponds most closely to the PFL sample taken one period earlier (7). Where possible, we have chosen to illustrate the discussion of the data using PFL samples instead of first-stage samples. The first-stage samples and the data collected on them are generally less reliable than the PFL samples and data because the first-stage samples are instantaneous reactor inventories.

OBJECTIVES

The objectives of Consol's work with these samples were to 1) analyze the four feed coals, 2) compare the properties of oils produced at ostensibly identical conditions in Runs I-18 and I-19, and 3) define any observable effects on oil properties from the use of the deeply cleaned coals.

ANALYSES

Proton distributions were obtained by ^{1}H-NMR for each whole sample (Table 6). Each whole sample was tested in the microautoclave at the modified equilibrium conditions (Table 10). Each sample was distilled (Table 4) to 320°C pot/270°C column/5 torr (850°F/atm). Each 850°F$^+$ resid was analyzed by solubility fractionation (Table 5), ^{1}H-NMR (Table 8), and FTIR for phenolic content (Table 9). Each 850°F$^-$ distillate was analyzed by ^{1}H-NMR (Table 7) and FTIR (Table 9). Microautoclave coal conversions are calculated assuming that the oil is solids-free.

Similar analyses of other HRI CTSL runs have been reported by Consol including bituminous coal Runs 227-18, 227-20 (I-11) (8), I-12 through I-15 (4), I-16 through I-17 (5), and subbituminous coal Runs 227-22 (9), 227-25 (10), 227-26 (11), and 227-27 (12).

PROPERTIES OF THE FEED COALS

Proximate and chemical analyses of the four coals are shown in Table 2. It is worth noting that the conventionally cleaned coal, which was the feedstock for the three deep cleaning processes, has a sulfatic sulfur content of 0.65% MAF indicating that the coal was moderately oxidized. Since sulfatic sulfur is relatively easy to remove, total sulfur reductions by the deep cleaning processes would probably be lower using a fresh coal.

The BCR and AED processes reduced the ash and pyritic and sulfatic sulfur contents of the coal, but made only relatively minor differences in other properties. The REI process reduced the ash and sulfatic sulfur contents to lower levels than the other processes, but left the coal with a greatly increased chlorine content, an increased nitrogen content, and a greatly altered ash composition.

Petrographic analyses of the four coals are shown in Table 3. The major difference between the four coals is the mineral matter content. On a mineral matter-free basis, the four coals have very similar petrographic analyses.

COMPARISON OF RUNS I-18 AND I-19

Though the operating conditions used during condition 1 of Runs I-18 (periods 5 and 9) and I-19 (period 6) were ostensibly identical, the properties of the oils differ by more than analytical error. For example, Figures 2 through 9 show that the PFL from period 6 of Run I-18 contains somewhat more resid, preasphaltenes and phenolics, and is more aromatic than expected based on the data from Run I-18. The oils compared here were made with the same catalyst and feed coal. Slightly poorer performance during the first six days of Run I-19 was also noted by HRI (6). For many of these properties, the PFL from period 6 of Run I-19 is more similar to oils produced in Run I-13. The catalyst used in Run I-13 was noted earlier (5) to give poorer performance than the catalyst used in Run I-18. Though the origin of the differences between oils produced in Runs I-18 and I-19 is uncertain, they are relatively small and may merely reflect the reproducibility in the operation of the bench unit including such factors as catalyst preparation, start-up procedure and the operation of the atmospheric still.

Though the oils produced during period 6 of Run I-19 have poorer qualities than expected, those made with the more deeply cleaned coals (periods 10 and 15) have properties that are very similar to those expected based on an extrapolation of the data from Run I-18.

TESTS WITH DEEPLY CLEANED COALS

Since only a single charge of catalyst was used in Run I-19, each of the four feed coals tested was processed at a different catalyst age.

The effects of catalyst aging must be considered to compare the yields or oil properties obtained with the different coals. Our previous work with CTSL oils (4,5,8-12) shows that catalyst aging results in continuous changes in oil properties consisting of increasing concentrations of resid, preasphaltenes and phenolics and increasing aromaticity. The major differences in oils produced with the three feed coals (no representative oil sample was obtained from the REI coal) are consistent with catalyst aging effects.

Figures 2 through 9 show that a linear extrapolation of the data from Run I-18 approximates the data from Run I-19 obtained with the deeply cleaned coals (periods 10 and 15). Therefore, it appears that any differences in oil properties resulting from the use of either the conventionally cleaned, the BCR or the AED coal are small in comparison to catalyst aging effects. Clearly, any differences are small.

HRI CTSL RUNS I-22 and I-23

RUN DESCRIPTION

Consol R&D analyzed eleven oils from HRI's Catalytic Two-Stage Liquefaction (CTSL) development program. The samples analyzed were from bench unit Runs I-22 and I-23, also called Runs 227-42 and 227-43. Each runs was a "process variable" run in which several operating conditions were changed to determine their effects on process performance. Run I-22 was performed during 12 days of March 1987. Run I-23 was performed during 13 days of April 1987. The primary purpose of the two runs was to determine the relative effectiveness of two alumina supported catalysts. For any one run, both reactors were charged with the same catalyst. The two catalysts tested were a NiW catalyst, UOP RCM-1-2202/2203 (1/20-inch spheres), and a FeMo catalyst (1/20-inch extrudates) produced by Ketjen. Operating conditions are summarized in Table 11 (13).

Portions of five earlier runs were made with various NiMo on alumina catalysts at similar operating conditions. Run I-13 was made with Amocat 1C (1/16-inch extrudates) produced by Cyanamid. Run I-15 simulated catalyst "cascading" with the same catalyst. In catalyst cascading, spent first-stage catalyst is charged to the higher temperature second stage in order to reduce the required catalyst replacement rate. Run I-16 tested Amocat 1C (1/32-inch extrudates) produced by Davison. Run I-17 tested UOP RCM-4 (ca. 1/20-inch diameter spheres). Run I-18 tested Shell S-317 (1/32-inch extrudates). Consol R&D's analyses of oils produced from Runs I-13 and I-15 (4) and Runs I-16, 17 and 18 (5) were presented earlier and are also discussed here in relation to Runs I-22 and I-23.

Coal mass feed rate (lbs/hr) and therefore coal space velocity (on a reactor volume basis) were the same for the seven runs. The spherical catalysts used in Runs I-17 and I-22 gave improved ebullation performance and allowed a 10 vol % greater charge of settled catalyst. On a settled catalyst basis, coal space velocity was 45 lbs MF/hr/ft^3 for Runs I-13, 15, 16, 18 and 23 and about 40 lbs MF/hr/ft^3 for Runs I-17 and I-22. In addition, the catalyst charge (on a mass basis) for each run differed because each catalyst had a different bulk density.

The first nine days of Runs I-13, 15-18, 22 and 23 were all operated at similar conditions (Condition 1) except that different catalysts were used. More severe reaction conditions were used beginning on day 10 (Condition 2) in Runs I-16, 17, 18 and 23 to improve conversion. Condition 2 of Run I-22 differed from the other runs. In Run I-22, poor performance during the first nine days led HRI (6) to modify Condition 2. Operating conditions were kept the same as Condition 1 except that spent catalyst (Shell S-317, NiMo) from Run I-19 was ground and added at about 0.5 wt % (equivalent to fresh catalyst, on a coal basis) to the feed slurry to see if an incentive for such a practice existed. No improvement was observed by HRI (6).

Commercially cleaned Burning Star #2 (Illinois 6) bituminous coal was used for each run discussed here. Process flows in the CTSL bench unit are shown schematically in Figure 1 (2). The nominal throughput of the bench unit is 50 lbs/day (3) and each reactor has a capacity of 2000 cc (2).

HRI reported (6) that the overall performances of the two catalysts tested in Runs I-22 and I-23 were generally poorer than the catalysts used in the other five runs discussed above. HRI also noted, based on low water yields (6), that deoxygenation was poor during Run I-22.

SUMMARY

The major conclusions of this work are summarized below. Detailed results are presented and discussed later.

- The pressure-filter liquids and first-stage inventory oils produced in CTSL Runs I-22 and I-23 with NiW and FeMo catalysts, respectively, show poorer qualities than oils produced in earlier tests using four different fresh NiMo catalysts at otherwise identical operating conditions. Poorer qualities are manifested in greater resid, preasphaltenes and phenolic contents and greater aromaticities. With the exception of phenolic contents, differences in oil properties from these two runs and from an earlier test using a "cascaded" NiMo catalyst approach analytical uncertainty. Phenolic contents are somewhat lower for the FeMo catalyst test, but significantly higher for the NiW catalyst test. The high phenolic contents of oils produced in the NiW catalyst test are consistent with the low water yields obtained during the test.

- Oil properties changed with catalyst age in these runs in the same manner as in the other CTSL runs analyzed previously. In general terms, these changes corresponded to declines in the quality of the product oil.

- Differences between first- and second-stage product oils are the same as in other CTSL runs analyzed previously.

- Oils produced at the "higher conversion" conditions of Run I-23 contain less resid and preasphaltenes and are more aromatic than those produced at the "baseline" conditions. The "higher conversion" conditions produced much smaller changes in oil properties during three earlier tests using NiMo catalysts.

- The addition of 0.5% ground spent NiMo catalyst to the feed slurry during part of Run I-22 had no discernible effect on the properties of the pressure-filter liquid.

SAMPLE DESCRIPTIONS

We obtained a total of 11 oils (ca. 50g each) from Mr. J. B. McLean of HRI. The set included six daily pressure-filter liquid (PFL) samples and five daily first-stage reactor inventory samples from Runs I-22 and I-23.

The pressure-filter liquid is the major second-stage product and, in most cases discussed in this report, it was the only component of the recycle oil. It is obtained by filtering the atmospheric-still bottoms (Figure 1). First-stage oils, which are samples of the first-stage reactor inventory, were filtered by HRI prior to shipment. The sampling procedure used by HRI (6) is to take the PFL sample first, then to take the first-stage sample while maintaining constant operating conditions. As a result, any first-stage sample corresponds most closely to the PFL sample taken one period earlier (7). Where possible, we have chosen to illustrate the discussion of the data using PFL samples instead of first-stage samples. The first-stage samples and the data collected on them are generally less reliable than the PFL samples and data because the first-stage samples are instantaneous reactor inventories.

OBJECTIVES

Consol R&D objectives for work with these samples were to 1) compare the properties of oils produced with the different catalysts tested, 2) define the effects of catalyst age on process-oil characteristics, 3) compare first- and second-stage oil properties, and 4) define the effects of the process variables on oil properties.

ANALYSES

Proton distributions were obtained by ^{1}H-NMR for each whole sample (Table 14). Each whole sample was tested in the microautoclave at the modified equilibrium conditions (Table 18). Each sample was distilled (Table 12) to 320°C pot/270°C column/5 torr (850°F/atm). Each 850°F$^+$ resid was analyzed by solubility fractionation (Table 13), ^{1}H-NMR (Table 16) and FTIR for phenolic content (Table 17). Each 850°F$^-$ distillate was analyzed by ^{1}H-NMR (Table 15) and FTIR (Table 17). Microautoclave coal conversions are calculated assuming that the oils are solids-free.

Similar analyses of other HRI CTSL runs have been reported by Consol R&D including bituminous coal Runs 227-18, 227-20 (I-11) (8), I-12 through I-15 (4), I-16 through I-18 (5), and I-19 (earlier section of this report), and subbituminous coal Runs 227-22 (9), 227-25 (10), 227-26 (11), and 227-27 (12).

CATALYST CHOICE AND OIL PROPERTIES

Equivalent samples were analyzed from two different run periods of each of Runs I-13, 15, 16, 17, 18, 22 and 23 at Condition 1. Oil properties at each of these two periods differed somewhat because of catalyst aging effects. However, comparisons of average oil properties at these run periods allow a general comparison of the performance of the catalysts. Selected PFL properties (averages of periods 5 and 9) are compared below for the seven runs. Generally similar comparisons are also observed using first-stage oil properties.

Run No.	I-15	I-13	I-16	I-17	I-18	I-22	I-23
Catalyst Type	NiMo Cascaded 1/16" Amocat 1C	NiMo Fresh 1/16" Amocat 1C	NiMo Fresh 1/32" Amocat 1C	NiMo UOP RCM-4 Spheres	NiMo Shell S-317 1/32"	NiW UOP RCM-1 Spheres	FeMo Ketjen Extrud. 1/20"
850°F$^+$ resid content, wt %	47.1	42.9	38.8	41.8	41.0	49.4	49.6
Preasphaltenes, wt % of resid	7.4	4.1	4.0	9.0	2.8	8.9	7.8
H-Aromaticity, %							
- whole sample	18.0	15.6	12.8	13.4	12.8	18.6	18.6
- distillate	13.7	12.2	10.0	10.6	9.8	14.9	14.9
- resid	24.2	21.5	18.4	19.3	18.6	24.8	24.6
Phenolic conc., meq/g							
- distillate	0.20	0.10	0.06	0.06	0.06	0.30	0.18
- resid	0.78	0.48	0.42	0.52	0.46	0.90	0.62
Microautoclave coal conv., wt % MAF	----	82.0	79.8	79.6	79.7	83.0	80.9

Complete data for Runs I-13 and 15 through 18 were presented earlier (4,5). Those for Runs I-22 and I-23 are given in Tables 12 through 18 of this report. The comparisons are illustrated in Figures 10 through 17. As noted earlier in a more detailed discussion of that subject (4), the cascaded catalyst (I-15) produced oils of poorer quality than the same fresh catalyst (I-13) at equivalent points of the run. Poorer quality is identified by the greater concentrations of resid, preasphaltenes and phenolics and greater aromaticity. In this regard, it is also apparent that the fresh 1/32" Amocat 1C (I-16) produced higher quality oils than the fresh 1/16" Amocat 1C (I-13). Oils produced in Runs I-16, 17 and 18 are of higher quality than those from the other runs. For those three runs, most of the average parameters are nearly the same to within experimental error. A notable exception is the high preasphaltenes content in Run I-17. For most parameters measured, oils produced in Runs I-22 and I-23 are poorer in quality than those from the other five runs. With the exception of phenolic contents, the difference in oil properties from these two runs and the catalyst cascading test (I-15) approach analytical uncertainty. Phenolic contents are somewhat lower for the FeMo catalyst test (I-23), but significantly higher for the NiW catalyst test (I-22). The high phenolic contents of oils produced in Run I-22 are consistent with the noted (6) low water yields during that run.

Except for the catalyst, Condition 2 of Runs I-16, 17, 18 and 23 were identical. Condition 2 of Run I-22 was different. As illustrated in Figures 2 through 8, PFL properties from Run I-23 were significantly poorer than the other three runs at this condition as well.

OIL PROPERTIES AND CATALYST AGE

During Runs I-22 and I-23, oil properties changed with catalyst age in much the same way as previously discussed (5). The observed changes in oil properties with catalyst age are consistent with catalyst deactivation effects. Hydrogenation, cracking and deoxygenation functions all appear to be directly or indirectly reduced with age. Similar catalyst aging effects have been observed for all other CTSL runs analyzed to date.

COMPARISON OF PFL AND FIRST-STAGE OILS

Differences between first-stage and PFL samples taken at any one set of operating conditions reflect the additional upgrading that occurs in the second-stage reactor. It should be recognized, however, that the direct comparison of the characteristics of the first-stage oils and PFL samples has two limitations. First, the samples we obtained from HRI are all filtered and thus contain no unconverted coal or ash. Coal not converted to solubles in the first stage has the opportunity to be converted in the second stage. Therefore, the filtered first- and second-stage soluble samples represent different proportions of each reactor's inventory. The second limitation is that the PFL samples are atmospheric still bottoms with an initial boiling point of ca. 500°F. The first-stage samples, which are collected at reaction temperature (750-775°F), contain some amount of 500°F$^-$ oil, but less 650°F$^-$ than the PFL samples (6). Therefore, the two types of samples represent different parts of the liquid inventory. The first-stage oils do not contain that material that is converted to solubles in the second stage. The PFL samples do not contain the light oil. Being aware of these differences, the oil properties can be compared.

Runs I-22 and I-23 are qualitatively similar to other catalytic/catalytic CTSL runs analyzed. Compared to the first-stage products, PFL samples contain less resid and less of the resid is preasphaltenes. Aromaticities are higher in the whole PFL samples and in their two fractions and phenolic concentrations are lower in both the PFL distillate and resid. The first-stage oils perform somewhat better in the microautoclave test than the corresponding PFL samples. The one exception to these generalizations is the resid contents of the oils from Run I-23. In that run, the resid contents of the PFL samples are higher than the corresponding first-stage resids in two of three cases.

"HIGHER CONVERSION" CONDITIONS - RUN I-23

Beginning on day 10 of Run I-23, operating conditions were changed to increase reaction severity and, thereby, conversions. First-stage temperatures were increased by 25°F, second-stage temperatures were increased by 10°F and the solvent/coal ratio was reduced from 1.6 to 1.1. Since coal space velocity remained unchanged, the reduced solvent-to-coal ratio decreased overall space velocity. For Condition 2, the continuous atmospheric still reboiler temperature was increased from 610 to 625°F. This increased the lower boiling point of the PFL and resulted in a higher boiling recycle solvent. This second set of operating conditions, called "higher conversion conditions" by HRI, was used until run termination (day 13). The effects of the increased reaction severity on oil properties can be best observed by comparing oils properties from days 9 and 12 (Conditions 1 and 2, respectively). Though this is the best comparison available, it is not ideal because the latter period reflects the combined effects of a catalyst age increase of 33%, the use of the higher boiling recycle oil, and the change in operating severity. PFL properties for days 9 and 12 are compared below:

Period No.	9	12
Condition No.	1	2
Resid content, wt %	55.4	51.4
Preasphaltenes, wt % of resid	10.0	6.4
H-Aromaticity, % - whole sample	20.4	24.0
- distillate	16.0	18.9
- resid	26.4	31.0
Phenolic conc., meq/g - distillate	0.21	0.28
- resid	0.67	0.69
Microautoclave coal conv., wt % MAF	80.1	75.8

The "higher conversion" conditions produced a lighter (less resid and less preasphaltenes), more aromatic PFL. In general, the first-stage oils show the same trends. Presumably, this reflects improved conversion of high molecular weight material at the more severe conditions. Similar tests performed during Runs I-16, 17 and 18 showed a much smaller effect on oil properties (5).

SLURRY-PHASE CATALYST ADDITION - RUN I-22

Conditions 1 and 2 of Run I-22 were identical except that ground spent catalyst (Shell S-317 NiMo from Run I-19) equivalent to 0.5 wt % of fresh catalyst on a coal basis was added to the feed slurry in Condition 2 to determine if any incentive existed for such a practice (13). In order to compare oil properties with and without the slurry-phase catalyst, the age of the ebullated-bed catalyst must be considered. Figures 10 through 17 provide a convenient way to do this. As the figures illustrate, oil properties from Run I-22 at Condition 2 (day 12) are very close to those expected based on a linear extrapolation of the data from Condition 1 (days 5 and 9). For almost all properties measured, the measured value is within experimental error of the value predicted from extrapolation. We, therefore, conclude that PFL properties were not significantly affected by the addition of slurry-phase catalyst in this test. No first-stage sample from this test was provided by HRI.

USE OF AROMATICITY AND PHENOLIC CONCENTRATION TO DETERMINE THE FEEDSTOCK SOURCE OF UOP COPROCESSING PRODUCTS

INTRODUCTION

Recent work (5) showed the utility of carbon isotope ratios for determining the contributions of the two feedstocks to the various products in coal/oil coprocessing. It is possible that other analytical methods can be used for the same purpose. For example, coals are generally much more aromatic and contain much more oxygen than petroleums. Products of similar boiling point distributions made from these two sources at identical conditions would be expected to reflect these differences. Also, since coal liquids, unlike petroleum products, often contain preasphaltenes, the preasphaltenes content of coprocessing products may indicate the presence of coal products. Coprocessing products made in the Signal Research/UOP continuous coprocessing bench unit were previously analyzed for carbon isotope ratios (5). Here, we report analyses of these same materials by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy for aromaticity and by Fourier Transform infrared (FTIR) spectroscopy for phenolic concentration. Phenolic concentrations were measured because the major oxygen containing functional group in these materials is expected to be phenols and because an accurate quantitative method exists for their determination. Preasphaltenes were not measured because all products supplied by UOP were either distillable or toluene soluble and should contain no preasphaltenes.

SUMMARY

This work showed that though both aromaticity and phenolic concentration appear to be sensitive to the feedstock source of the coprocessed products, neither analysis can provide a reliable quantitative measurement. Presumably, this is because of the aromatic ring saturation and deoxygenation reactions that proceed during processing.

RESULTS AND DISCUSSION

Aromaticity

Operating data for tests 1 through 16, supplied by UOP, (14,15) are given in Table 19. The % coal carbon/total carbon for each sample (determined previously from carbon isotope ratios (5)) is given in Table 20. Proton distributions by ^{1}H-NMR are given in Tables 21 and 22. H-aromaticities are plotted in Figure 18 as a function of the % coal carbon/total carbon for all samples except those produced in test No. 1 which used the 17-R7 resid feedstock. As expected, the bottoms samples are more aromatic than the corresponding overhead samples. For the bottoms materials, aromaticity decreases in the order Illinois 6, 1.5/1 S/C > Illinois 6, 2/1 S/C > Wyodak, 2/1 S/C > resid feedstock. In addition, for the bottoms, there appears to be a general trend of increasing aromaticity with increasing % coal carbon/total carbon. The aromaticity of the overhead products show no apparent sensitivity to % coal carbon/total carbon. Perhaps the variation in the aromaticity of the overhead products results primarily from operating condition changes. However, as expected, the products made with Illinois 6 coal are more aromatic than those made with Wyodak coal.

Based on these results, it appears that aromaticity is not a good indicator of the relative contributions of the two feedstocks to the product oils, though it may provide some indication of this for the vacuum bottoms products.

Phenolic Concentrations

Phenolic concentrations, determined by FTIR on each sample, are given in Table 23. These data, except those from test No. 1, are plotted as a function of % coal carbon/total carbon in Figure 19. As shown in the figure, all products including the overheads contain more phenolics than the feed petroleum resid, presumably reflecting the contribution of coal materials to the products. For the vacuum bottoms products, there appears to be a trend of increasing phenolic concentration with % coal carbon/total carbon. The overhead products show no trend in this regard. As with aromaticity, it may be that for the overhead products phenolic concentration responds more to operating conditions than to % coal carbon/total carbon.

Interestingly, in every case excluding test No. 1, the overhead products have greater concentrations of phenolics than the respective bottoms products. This is the opposite of our experience with coal liquefaction products made in a variety of processes at a wide variety of conditions and with many coals. The difference between the overhead and bottoms product is greater for the Wyodak coal products than the Illinois 6 coal products. This appears to relate to the greater difference in the coal contribution to the two products in the case of the Wyodak coal tests as shown below.

	Difference (Overhead Products - Bottoms Products), Mean ± Std Dev	
Coal Feedstock	Phenolic Concentration meq/g	% Coal Carbon/Total Carbon
Illinois 6	0.08 ±0.07	-1.5 ±4.1
Wyodak	0.14 ±0.07	14.9 ±4.0

These data show that, with Illinois 6 coal, the overheads and bottoms contain comparable amounts of both phenolics and of coal carbon as a percentage of total carbon. With Wyodak coal, the overheads contain substantially greater amounts of both phenolics and of coal carbon as a percentage of total carbon than do the bottoms products.

As with aromaticity, phenolic concentrations appear to reflect the contributions of coal materials to the products. However, it is doubtful that either analysis can provide a reliable quantitative measurement of the contributions of the feedstocks to the individual products.

SIGNAL RESEARCH/UOP LONG-TERM COPROCESSING TEST

INTRODUCTION AND SUMMARY

In early 1987, Signal Research/UOP conducted a long-term operability test of their coal/oil coprocessing process using a continuous bench-scale unit. Eight samples of product fractions, obtained after 1795 hours of continuous uninterrupted operation, were obtained from Mr. C. P. Luebke. We analyzed the samples for carbon isotope ratios by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy for proton distributions and by Fourier-Transform infrared (FTIR) spectroscopy for phenolic concentrations. The operating conditions and feedstocks used in the long-term test (16) were the same as those used in the earlier test No. 2-0502 (Table 19).

Analyses of the feedstocks and products from test No. 2-0502 were reported earlier (5). Additional analyses of products from test No. 2-0502 are presented in the immediately preceeding section of this report. The eight product samples supplied by UOP from the long-term operability test were the total vacuum overhead, the toluene soluble portion of the total vacuum bottoms and three distillation fractions of each. The products were composites from periods 106 to 108 (1317 to 1341 hours on stream) from Run 570. The total vacuum bottoms sample was found to contain about 0.5% toluene by ^{1}H-NMR. No evidence for toluene contamination was found in any of the three fractions from this sample. The effects of this minor contaminant on the results presented here are expected to be slight.

The results of this work indicate that the two feedstocks supply differing relative amounts of carbon to the various product fractions. However, the products analyzed (90.6% of MAF feed) account for 113% of the ^{13}C fed. Neither aromaticity nor phenolic concentration show a simple relationship with % coal carbon/total carbon.

RESULTS AND DISCUSSION

During the portion of the long-term test at which the samples were produced, the following product yields (17) were obtained.

Product	Yield, wt % of MAF Feed
H_2O, COx	4.9
H_2S	2.3
C_1 x C_4	2.7
C_5 x 371°C	28.1
371°C x 510°C	26.7
510°C$^+$ Solubles	34.0
IOM	3.6
H-consumption	-2.3

The yields and carbon contents of each sample are shown in Table 24 as supplied by UOP (17). Table 24 also presents the carbon isotope ratios and the % coal carbon/total carbon for each sample obtained by the carbon isotope method detailed earlier (5). The contribution of coal to the product carbon is small (13 ±3%) for the lowest boiling fraction; it reaches a maximum of 54 ±8% for the highest boiling overhead fraction, then decreases to 31 ±2% for the highest boiling bottoms fraction. The residue carbon was determined to be 40 ±2% coal derived. Therefore, the two feedstocks contribute carbon to the product fractions to differing extents.

The measured % coal carbon/total carbon values for the total overhead and total soluble bottoms products are in fairly good agreement with the same values calculated by weighting the three distillation fractions of each as shown below.

	% Coal Carbon/Total Carbon	
	Measured	Calculated from Three Subfractions
Total Vacuum Overhead	43 ±2	40
Total Soluble Vacuum Bottoms	35 ±2	39

The fairly good agreement demonstrates the integrity of the data.

Based on the analyses of the total vacuum overhead and the total soluble vacuum bottoms, the % coal carbon/total carbon in the total (vacuum overhead plus soluble vacuum bottoms) product is 38.71%. This is substantially greater than the value at perfect non-selectivity which is 32.49%. In fact, the overhead and soluble bottoms product, which account for only 90.6% of the MAF feed and for only 94.6% of the total feed carbon, account for 113.2% of the coal carbon, i.e., ^{13}C, fed.

It is impossible for selective isotopic fractionation to cause this result. However, this result can arise from a variety of sources, including:

1. The feedstocks used for this test (not analyzed by Consol) are not identical to those used in test No. 02-0502 (analyzed by Consol).
2. The feedstocks were fed at some ratio other than 2/1 petroleum/ MAF coal.
3. Yield or total carbon data are incorrect.
4. Isotope data are incorrect.

In fact, as shown below, significant differences exist between results from the long-term test and test No. 02-0502 though both were operated at ostensibly the same conditions.

	Test	
	No. 02-0502	Long-Term
Yield, % MAF Feedstock		
Vacuum Overhead	43.4	41.3
Soluble Vacuum Bottoms	36.6	49.3
Phenolic Concentration, meq/g		
Vacuum Overhead	0.51	0.40
Soluble Vacuum Bottoms	0.27	0.38
% Coal Carbon/Total Carbon		
Vacuum Overhead	31.4	43.0
Soluble Vacuum Bottoms	37.3	35.2

The above data are taken from Tables 19, 20, 23, 24 and 26. Our use of triplicate analyses and both primary and secondary references for determining isotope ratios supports the accuracy of those data.

At this point, the cause of the high recovery of ^{13}C remains unknown.

^1H-NMR analyses of the samples from the long-term test are shown in Table 25. As expected, aromaticity increases with boiling point. Phenolic concentration data are shown in Table 26. Phenolics decrease with boiling point for the overhead fractions and increase with boiling point for the bottoms fractions. Neither aromaticity nor phenolic concentration show an obvious relationship with % coal carbon/total carbon for these samples.

shown to have a standard deviation 1.2% absolute (8). Therefore, the standard coal shows a small but experimentally significant loss in reactivity from aging over the course of this contract.

CALIBRATION OF STANDARD COAL

For most of our routine microautoclave solvent quality assays we use a single standard coal: Old Ben mine #1, Indiana 5. The original sample was obtained in February, 1981, from the batch used by Lummus in Integrated Two-Stage Liquefaction (ITSL) Run 3LCF7. The coal has been stored as 5-gallon aliquots in sealed plastic bags. Since January 1985, one single 5-gallon aliquot has been used. It is periodically opened and resealed as needed to withdraw 16 oz aliquots for use. Since its receipt, the coal has undergone mild oxidation. This is apparent in the analyses shown in Table 27. The recent analyses (1/87) show increased sulfate and oxygen levels and a slightly decreased calorific value compared to the analysis of the coal at the beginning of this contract (1985) and at near the time of receipt (4/81).

In order to determine the effect of this oxidation on the performance of the coal in the microautoclave assay and to formulate solvent calibration curves, sets of microautoclave tests are made periodically using this coal and solvents containing varying ratios of tetralin and 1-methylnaphthalene at our commonly used test conditions. Microautoclave tests were made at the same times as the analyses appearing in Table 27 were obtained. The coal conversions from these tests, presented in Table 28, can be used as reference points for liquefaction solvents tested in this contract. The earlier data are taken from Reference 12. Similar data for an earlier (1979) batch of the same coal appear in Reference 18.

The entire microautoclave data set shows a continuous but relatively slow decrease in reactivity with time since April 1981.

Using all twelve tests common to the data sets of 1/85 and 1/87, coal conversion is seen to have decreased by an average of 2.9% over the duration of this contract. The repeatability of this assay has been

Section 3
EXPERIMENTAL

Experimental details are described, where appropriate, in the Discussion section of this report. Details of the other analytical techniques used in this work were reported previously (8,11).

Section 4

ACKNOWLEDGEMENT

The carbon isotope analyses were performed by the Research Services Division of Conoco Inc., under the direction of Lois Jones and Arnold Taylor, Jr.

Section 5

REFERENCES

1. McLean, J. B., letter to R. A. Winschel, January 9, 1987.

2. McLean, J. B., Comolli, A. G., Duddy, J. E. and Smith, T. O., "The Catalytic Two-Stage Liquefaction Process", proceedings of the 1985 DOE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, PA, November 1985.

3. Comolli, A. G. and McLean, J. B., "The Low Severity Catalytic Liquefaction of Illinois 6 and Wyodak Coals", proceedings of the Second Annual Pittsburgh Coal Conference, Pittsburgh, PA, September 1985.

4. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report for April 1 through June 30, 1986", DOE Contract No. DE-AC22-84PC70018, November 1986.

5. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation, Second Annual Report, January 1 through December 31, 1986", DOE Contract No. DE-AC22-84PC70018, June 1987.

6. McLean, J. B., personal communication to authors.

7. McLean, J. B., letter to R. A. Winschel, December 6, 1985.

8. Burke, F. P., Winschel, R. A. and Robbins, G. A., "Recycle Slurry Oil Characterization - Final Report", DOE Contract DE-AC22-80PC30027, March 1985.

9. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation - Technical Progress Report for January 1 through March 31, 1985", DOE Contract No. DE-AC22-84PC70018, May 1985.

10. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation, Annual Report, January 1 through December 31, 1985", DOE Contract No. DE-AC22-84PC70018, March 1986.

11. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation - Technical Progress Report for July 1 through September 30, 1985", DOE Contract No. DE-AC22-84PC70018, December 1985.

REFERENCES (Continued)

12. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report for January 1 through March 31, 1986", DOE Contract No. DE-AC22-84PC70018, July 1986.

13. McLean, J. B., letter to R. A. Winschel, March 26, 1987.

14. Luebke, C. P., letter to R. A. Winschel, August 7, 1986.

15. Luebke, C. P., letter to R. A. Winschel, December 10, 1986.

16. Luebke, C. P., letter to R. A. Winschel, March 25, 1987.

17. Gatsis, J., personal communication with author, July 2, 1987.

18. Kleinpeter, J. A., Burke, F. P., Dudt, P. J. and Jones, D. C., "Process Development for Improved SRC Options: Interim Short Residence Time STudies", EPRI Project 1134-1, Interim Report No. EPRI AF-1158, August 1979.

19. Luebke, C. P., letter to R. A. Winschel, March 16, 1987.

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TABLE 1

OPERATING CONDITIONS (1)
HRI CTSL Run I-19 (227-39)

Feed Coal:	Burning Star No. 2 mine (Illinois 6) cleaned by various methods
Temperature, °F:	First Stage - 750 Second Stage - 800
Catalyst:	Shell S-317 (Ni/Mo on alumina, bimodal, 1/32" extrudates)
Coal Space Velocity:	0.67 (a,b)
Recycle Oil:	Pressure Filter Liquid, solids free
Solvent/Coal Ratio (b):	1.6 in slurry feed, additional solvent added through buffer pumps increases ratio by about an additional 0.3
Pressure:	2500 psig
Start-up Oil:	Wilsonville distillate, recycled during various start-ups

Condition No.	Days	Feed Coal
1	1-6	Burning Star No. 2, conventionally cleaned at preparation plant
2	7-11A	Same as No. 1, additionally cleaned by BCR
3	11B-16A	Same as No. 1, additionally cleaned by AED
4	16B-17A	Same as No. 1, additionally cleaned by REI

(a) Coal space velocity on a reactor volume basis, relative to Run I-11 (227-20). On a settled catalyst volume basis, coal space velocity was about 45 lbs MF/h ft^3 (each stage).

(b) Feed rate of whole coal adjusted in conditions 2, 3 and 4 to give constant MAF coal feed rate, coal space velocity and solvent/coal ratio on an MAF basis.

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TABLE 2

FEED COAL ANALYSES
HRI CTSL Run I-19

	Burning Star No. 2 (Illinois 6) Coal			
HRI No.	Conventionally Cleaned 4758	BCR Cleaned 4759	AED Cleaned 4760	REI Cleaned 4761
Moisture, wt % as determined	3.08	2.44	3.23	1.95
Proximate, wt % dry basis				
Volatile Matter	38.20	40.41	39.79	40.29
Fixed Carbon	51.55	54.08	55.22	56.08
Ash	10.25	5.51	4.99	3.63
Ultimate, wt % MAF basis				
Carbon	77.49	78.19	78.17	76.07
Hydrogen	5.33	5.42	5.20	5.48
Nitrogen	1.49	1.40	1.36	1.76
Oxygen (diff)	11.60	11.80	11.94	11.44
Sulfur, Total	4.03	3.15	3.29	3.41
Pyritic	0.95	0.50	0.47	1.04
Sulfatic	0.65	0.30	0.37	0.05
Organic (diff)	2.43	2.35	2.45	2.32
Chlorine	0.06	0.04	0.04	1.84
HHV, Btu/lb MAF basis	13,731	13,988	14,027	13,621
Elemental, wt % of ash				
Na_2O	0.26	0.28	0.30	0.28
K_2O	1.79	1.93	1.74	2.06
CaO	4.14	1.98	4.33	9.40
MgO	0.85	0.96	1.01	2.16
Fe_2O_3	22.33	21.26	25.70	38.83
TiO_2	0.94	1.17	1.42	1.30
P_2O5	0.06	0.06	0.07	0.22
SiO_2	45.91	47.68	42.58	5.51
Al_2O_3	18.71	21.42	17.74	21.64
SO_3	4.34	2.08	3.38	15.68
Unaccounted	0.66	1.19	1.75	2.91

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TABLE 3

PETROGRAPHIC ANALYSES OF FEED COALS
HRI CTSL Run I-19

	Conventionally Cleaned	BCR Cleaned	AED Cleaned	REI Cleaned
Mean Maximum Reflectance (R_o), %	0.55	0.53	0.52	0.54
Maceral Analysis, vol. %				
Reactives	88.2	91.5	92.6	90.1
Vitrinite	82.8	88.2	88.1	85.7
Type 4	20.7	23.8	38.6	19.7
Type 5	45.5	57.5	37.1	58.3
Type 6	16.6	7.1	12.4	7.7
Exinite	4.1	2.7	3.2	3.0
Resinite	0.2	0.1	0.2	0.0
1/3 Semifusinite	1.1	0.5	1.1	1.4
Inerts	11.8	8.5	7.4	9.9
2/3 Semifusinite	2.3	1.1	2.2	2.8
Micrinite	0.8	3.3	1.1	3.5
Fusinite	1.9	0.3	0.5	0.8
Mineral Matter	6.8	3.8	3.6	2.8

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TABLE 4

DISTILLATION RESULTS
HRI CTSL Run I-19

Condition No.	Run Period	Sample No.	wt % of Sample 850°F Distillate	Resid
Pressure-Filter Liquids				
1	6	4752	58.0	40.8
2	10	4753	54.8	45.6
3	15	4755	51.3	48.5
Filtered Charge-Pot Oil				
4	17A	4757	75.0	24.7
First-Stage Samples				
2	11A	4754	51.5	48.0
3	16A	4756	68.9	30.8

/ls

TABLE 5

SOLUBILITY FRACTIONATION ANALYSES OF RESIDS
HRI CTSL Run I-19

Condition No.	Run Period	wt % of Pyridine-Soluble Resid Oils	 Asphaltenes	 Preasphaltenes
Pressure Filter Liquids				
1	6	78.7	16.6	4.8
2	10	76.7	17.1	6.2
3	15	74.6	17.8	7.5
Filtered Change-Pot Oil				
4	17A	78.0	18.8	3.2
First-Stage Samples				
2	11A	76.7	18.7	4.6
3	16A	78.6	17.2	4.2

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TABLE 6

PROTON DISTRIBUTIONS OF WHOLE SAMPLES
HRI CTSL Run I-19

		Proton Distribution, %						
Condition No.	Run Period	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquids								
1	6	10.7	4.0	14.0	8.3	21.3	25.8	15.9
2	10	11.5	4.2	14.7	8.5	21.4	24.4	15.3
3	15	12.9	4.5	15.4	8.7	20.4	23.3	14.7
Filtered Charge-Pot Oil								
4	17A	8.0	4.3	12.0	8.3	21.6	28.1	17.7
First-Stage Samples								
2	11A	12.3	4.0	14.1	8.6	19.1	26.9	15.0
3	16A	7.3	4.5	13.0	8.7	22.6	26.7	17.1

Samples dissolved in pyridine-d_5 (99.96% D), integrated electronically.

/ls

TABLE 7

PROTON DISTRIBUTIONS OF 850°F$^-$ DISTILLATES
HRI CTSL Run I-19

		Proton Distribution, %						
Condition No.	Run Period	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquids								
1	6	7.1	4.6	13.3	8.0	23.2	27.2	16.6
2	10	7.2	4.7	13.6	8.3	23.2	26.7	16.3
3	15	7.9	5.1	14.4	8.7	22.4	25.9	15.6
Filtered Charge-Pot Oil								
4	17A	5.1	4.8	12.0	8.2	22.7	29.1	18.0
First-Stage Samples								
2	11A	7.6	4.9	12.8	8.4	19.2	30.1	17.0
3	16A	3.8	5.2	12.1	8.5	23.6	28.6	18.1

/ls

TABLE 8

PROTON DISTRIBUTIONS OF 850°F$^+$ RESIDS
HRI CTSL Run I-19

		Proton Distribution, %						
Condition No.	Run Period	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquids								
1	6	17.8	3.1	18.4	8.8	19.7	20.3	11.9
2	10	18.6	3.0	19.2	8.8	19.5	19.4	11.5
3	15	20.6	3.2	20.2	9.0	18.8	17.8	10.3
Filtered Charge-Pot Oil								
4	17A	20.4	3.0	19.1	9.0	18.5	19.1	10.9
First-Stage Samples								
2	11A	19.9	3.1	17.8	8.8	17.6	21.8	11.0
3	16A	16.6	3.2	19.5	9.4	19.8	19.9	11.6

Samples dissolved in pyridine-d_5 (99.96% D), integrated electronically.

/ls

TABLE 9

PHENOLIC CONTENTS OF DISTILLATES AND THF-SOLUBLE RESIDS
HRI CTSL Run I-19

Condition No.	Run Period	Phenolic Concentrations, meq/g 850°F Distillate	 850°F$^+$ Resid
Pressure-Filter Liquids			
1	6	0.07	0.46
2	10	0.09	0.50
3	15	0.11	0.59
Filtered Charge-Pot Oil			
4	17A	0.13	0.52
First-Stage Samples			
2	11A	0.02	0.60
3	16A	0.12	0.59

Peak maxima between 3314 and 3320 cm^{-1} for all distillates and between 3299 and 3302 cm^{-1} for all resids.

/ls

TABLE 10

MICROAUTOCLAVE TESTS WITH WHOLE SAMPLES
HRI CTSL Run I-19

Condition No.	Run Period	THF Coal Conversion wt % MAF
Pressure-Filter Liquids		
1	6	81.3
2	10	82.7
3	15	82.6
Filtered Charge-Pot Oil		
4	17A	76.5
First-Stage Samples		
2	11A	76.0
3	16A	80.9

Condition: MOD-EQ Test, 6g Old Ben No. 1 (Indiana 5) coal, 9g solvent, 750°F, 30 min.

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TABLE 11

OPERATING CONDITIONS (13)
HRI CTSL Runs I-22 and I-23

Condition No.	Days	Temperature, °F 1st Stage	Temperature, °F 2nd Stage	S.V. (a)	S/C (b)	Ebullated-Bed Catalyst (c)	Additional Slurry Catalyst Used (d)
Run I-22 (227-42)							
1	1-10A	750	800	0.67	1.6	NiW	No
2	10B-12	750	800	0.67	1.6	NiW	Yes
Run I-23 (227-43)							
1	1-10A	750	800	0.67	1.6	FeMo	No
2	10B-13A	775	810	0.67	1.1	FeMo	No

Feed Coal:	Illinois 6 bituminous (Burning Star No. 2 mine)
Start-up Oil:	Wilsonville distillate, recycled during various start-ups
Pressure:	2500 psig

a) Coal space velocity on a reactor volume basis, relative to Run I-11 (227-20). On a settled catalyst volume basis, coal space velocity was about 45 lbs MF/h/ft^3 (each stage) for the run that used extrudate catalysts (I-23). About 10 vol % more catalyst was used in Run I-23 because of improved ebullation with the spherical catalyst giving a space velocity of about 40 lbs MF/hr/ft^3 of settled catalyst (each stage).

b) Solvent-to-coal ratio. Solvent consisted of pressure-filter liquid. Additional solvent added through buffer pumps increases ratio by 0.2 to 0.3.

c) Ebullated-bed catalyst used in both stages:
Run I-22 - UOP RCM-1-2202/2203 NiW spheres (1/20-inch)
Run I-23 - Ketjen FeMo extrudates (1/20-inch)

d) Approximately 0.5 wt % (equivalent to fresh catalyst, on a coal basis) of ground, spent Shell S-317 NiMo catalyst from Run I-19 was added to slurry charge in Condition 2 of Run I-22.

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TABLE 12

DISTILLATION RESULTS
HRI CTSL Runs I-22 and I-23

Run	Condition	Run Day	Sample No.	wt % of Sample 850°F Distillate	 850°F$^+$ Resid
Pressure-Filter Liquids					
I-22	1A	5	4772	55.0	44.8
	1B	9	4774	45.7	54.1
	2	12	4776	42.6	57.3
First-Stage Samples					
I-22	1A	6A	4773	43.7	56.1
	1B	10A	4775	42.5	57.0
Pressure-Filter Liquids					
I-23	1A	5	4777	56.2	43.7
	1B	9	4779	43.8	55.4
	2	12	4781	48.5	51.4
First-Stage Samples					
I-23	1A	6A	4778	50.7	49.1
	1B	10A	4780	46.6	53.1
	2	13A	4782	54.0	45.7

/ls

TABLE 13

SOLUBILITY FRACTIONATION ANALYSES OF RESIDS
HRI CTSL Runs I-22 and I-23

Run	Condition	Run Day	wt % of Pyridine-Soluble Resid		
			Oils	Asphaltenes	Preasphaltenes
Pressure-Filter Liquids					
I-22	1A	5	70.6	21.1	8.2
	1B	9	68.8	21.6	9.6
	2	12	69.8	21.8	8.3
First-Stage Samples					
I-22	1A	6A	59.7	24.0	16.3
	1B	10A	59.5	25.3	15.2
Pressure-Filter Liquids					
I-23	1A	5	78.6	15.7	5.7
	1B	9	69.7	20.2	10.0
	2	12	74.6	19.1	6.4
First-Stage Samples					
I-23	1A	6A	71.4	18.2	10.4
	1B	10A	65.1	21.1	13.8
	2	13A	70.0	19.2	11.0

/ls

TABLE 14

PROTON DISTRIBUTIONS OF WHOLE SAMPLES
HRI CTSL Runs I-22 and I-23

			Proton Distributions, %						
Run	Condition	Run Day	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquids									
I-22	1A	5	12.4	4.6	15.8	8.9	19.6	23.2	15.4
	1B	9	14.0	6.2	15.9	9.7	17.9	21.2	15.1
	2	12	15.4	6.0	17.5	10.0	18.0	19.8	13.3
First-Stage Samples									
I-22	1A	6A	12.2	5.8	15.7	9.7	18.2	23.0	15.4
	1B	10A	12.4	6.0	16.1	10.0	17.6	22.6	15.3
Pressure-Filter Liquids									
I-23	1A	5	12.2	4.6	15.6	8.6	19.4	24.9	14.6
	1B	9	15.2	5.2	16.6	9.3	18.2	21.4	14.1
	2	12	17.3	6.7	15.7	9.6	16.6	20.0	14.1
First-Stage Samples									
I-23	1A	6A	11.5	5.2	15.9	9.5	19.5	23.5	15.0
	1B	10A	12.6	6.3	15.9	10.5	18.2	22.0	14.5
	2	13A	14.4	5.9	15.6	10.4	18.2	21.8	13.8

/ls

TABLE 15

PROTON DISTRIBUTIONS OF DISTILLATES
HRI CTSL Runs I-22 and I-23

			Proton Distributions, %						
Run	Condition	Run Day	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquids									
I-22	1A	5	7.8	6.0	13.4	8.5	20.2	27.0	17.1
	1B	9	9.6	6.4	14.4	9.3	19.9	24.5	15.9
	2	12	10.1	6.8	16.4	9.6	19.8	23.2	14.0
First-Stage Samples									
I-22	1A	6A	7.7	6.0	12.8	8.7	19.9	27.3	17.6
	1B	10A	7.5	6.3	13.1	9.2	18.9	27.7	17.4
Pressure-Filter Liquids									
I-23	1A	5	8.3	5.5	13.5	9.2	20.9	26.6	15.9
	1B	9	9.7	6.3	14.3	9.1	20.1	26.8	13.7
	2	12	13.1	5.8	15.5	9.1	19.3	23.3	13.8
First-Stage Samples									
I-23	1A	6A	7.6	5.7	14.1	9.1	21.2	26.7	15.6
	1B	10A	8.9	7.0	14.9	9.6	19.4	24.9	15.2
	2	13A	9.8	7.5	14.1	10.0	18.7	26.3	13.5

/ls

TABLE 16

PROTON DISTRIBUTIONS OF RESIDS
HRI CTSL Runs I-22 and I-23

			Proton Distributions, %						
Run	Condition	Run Day	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquids									
I-22	1A	5	19.1	4.6	20.4	9.4	17.9	17.8	10.7
	1B	9	21.2	4.7	21.0	9.8	17.0	16.1	10.3
	2	12	21.5	5.1	21.3	9.9	16.8	16.0	9.4
First-Stage Samples									
I-22	1A	6A	18.4	5.0	21.9	10.3	17.4	16.9	10.0
	1B	10A	19.2	5.6	21.9	10.5	16.5	16.2	10.2
Pressure-Filter Liquids									
I-23	1A	5	19.8	3.1	20.2	9.5	18.5	18.5	10.4
	1B	9	22.3	4.1	19.6	9.3	17.5	17.2	10.1
	2	12	26.7	4.3	20.4	9.3	16.2	14.8	8.2
First-Stage Samples									
I-23	1A	6A	17.4	4.5	20.0	9.9	18.5	18.7	11.1
	1B	10A	20.0	4.7	21.1	9.8	17.5	17.0	9.9
	2	13A	22.5	4.5	21.4	9.7	16.5	16.1	9.2

Samples dissolved in pyridine-d_5 (99.96% D), integrated electronically.

/ls

TABLE 17

PHENOLIC CONTENTS OF DISTILLATES AND THF-SOLUBLE RESIDS
HRI CTSL Runs I-22 and I-23

			Phenolic Concentration, meq/g	
Run	Condition	Run Day	850°F$^-$ Distillate	850°F$^+$ Resid
Pressure-Filter Liquids				
I-22	1A	5	0.25	0.87
	1B	9	0.36	0.93
	2	12	0.45	1.00
First-Stage Samples				
I-22	1A	6A	0.39	1.24
	1B	10A	0.45	1.23
Pressure-Filter Liquids				
I-23	1A	5	0.15	0.56
	1B	9	0.21	0.67
	2	12	0.28	0.69
First-Stage Samples				
I-23	1A	6A	0.34	0.84
	1B	10A	0.38	0.90
	2	13A	0.41	0.89

Peak maximum between 3307 and 3314 cm^{-1} for all distillates, and between 3297 and 3299 cm^{-1} for all resids.

/ls

TABLE 18

MICROAUTOCLAVE TESTS WITH SELECTED SAMPLES
HRI CTSL Runs I-22 and I-23

Run	Condition	Run Day	THF Coal Conversion, wt % MAF
Pressure-Filter Liquids			
I-22	1A	5	83.6
	1B	9	82.3
	2	12	82.6
First-Stage Samples			
I-22	1A	6A	83.0
	1B	10A	79.5
Pressure-Filter Liquids			
I-23	1A	5	81.7
	1B	9	80.1
	2	12	75.8
First-Stage Samples			
I-23	1A	6A	83.6
	1B	10A	79.0
	2	13A	81.6

Conditions: Mod-EQ Test, 6g Old Ben mine No. 1 (Indiana 5) coal, 9 g solvent, 750°F, 30 min

/ls

TABLE 19

OPERATING CONDITIONS, CONVERSIONS, YIELDS AND ANALYSES (14,15)
UOP Coprocessing Tests 1 Through 16

	Operating Conditions			Conversions, wt %		Product Yields, wt % of MAF Feed			Carbon Contents, wt %	
Test No.	Resid/MAF Coal wt Ratio	Space Velocity (a)	T, °C	Coal Conv. (b)	510°C$^+$ Conv. (c)	Vacuum Overhead	Soluble Vacuum Bottoms	Other Products (d)	Vacuum Overhead	Soluble Vacuum Bottoms
Proprietary Catalyst and Illinois 6 Coal										
16-0915	1.5	B	414	84.8	43.2	29.8	51.6	20.6	84.40	85.30
14-0905	1.5	B	425	90.2	56.5	42.6	39.3	20.5	84.80	86.25
15-0907	1.5	B	434	91.2	63.8	45.1	35.1	22.5	85.25	86.55
4-0513	2	1.25B	425	85.9	53.3	38.5	42.7	21.1	85.75	86.80
3-0508	2	B	413	81.7	44.9	30.1	50.7	21.4	--	85.75
2-0502	2	B	426	91.0	60.4	43.4	36.6	22.6	85.70	87.20
6-0522	2	B	431	90.2	63.8	47.3	34.9	20.2	85.45	86.70
1-0311(e)	2	0.75B	423	88.0	59.9	28.1	46.8	27.3	85.45	86.80
5-0521	2	0.75B	424	89.8	58.8	42.7	37.5	22.0	85.60	87.05
Proprietary Catalyst and Wyodak Coal										
10-1111	2	1.25B	427	82.2	62.1	44.7	32.2	26.0	85.40	86.80
7-1102	2	B	414	80.6	55.2	39.8	38.8	24.2	86.45	85.75
9-1108(f)	2	B	425	83.0	58.7	42.5	32.8	27.9	85.60	86.60
8-1107	2	B	426	88.6	63.2	46.7	34.2	22.4	85.40	86.65
13-1122	2	B	426	85.0	59.0	50.0	34.4	18.4	85.20	86.70
12-1118	2	B	431	87.2	67.0	49.9	28.8	24.5	85.50	87.10
11-1116	2	0.75B	425	86.3	59.1	45.0	31.0	27.1	85.75	86.90

(a) Overall space velocity, based on both coal and petroleum. "B" refers to proprietary base conditions.
(b) Coal conversion to toluene solubles, wt % MAF.
(c) MAF coal counted as 510°C$^+$ for this calculation.
(d) Difference from 100% represents hydrogen consumption. These data provided in Reference 19.
(e) All tests used Lloydminster vacuum resid. This test used sample #17-R7. All others used #18-R8.
(f) This test used recycle gas rate of 1.13 times the base value. All others used the base value.

/ls

TABLE 20

CARBON SOURCE BY CARBON ISOTOPE ANALYSIS (5)
UOP Coprocessing Tests 1 through 16

Test No.	Coal Carbon as % of Total Carbon Vacuum Overhead	Soluble Vacuum Bottoms
Illinois 6 Coal Products		
16-0915	36.8	36.9
14-0905	41.6	38.6
15-0907	41.8	43.9
4-0513	32.1	32.3
3-0508	32.7	28.4
2-0502	31.4	37.3
6-0522	30.9	36.8
1-0311	31.1	30.3
5-0521	31.2	37.0
Wyodak Coal Products		
10-1111	36.1	22.3
7-1102	36.4	19.0
9-1108	36.3	20.4
8-1107	36.1	22.5
13-1122	42.6	20.8
12-1118	37.1	23.9
11-1116	35.0	26.1

/ls

TABLE 21

PROTON DISTRIBUTIONS OF VACUUM OVERHEADS
UOP Coprocessing Tests 1 through 16

	Proton Distribution, %						
Sample	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
1B-0311	4.2	4.6	8.8	8.0	16.4	36.1	21.8
2B-0502	3.7	5.2	8.1	8.7	14.5	36.5	23.3
3B-0508	3.5	4.8	9.1	8.4	16.2	35.6	22.4
4B-0513	3.9	5.2	7.9	9.4	14.8	35.9	22.8
5B-0521	4.1	4.8	8.5	8.5	15.6	35.7	22.8
6B-0522	4.4	4.8	8.5	8.6	14.9	35.6	23.2
7B-1102	3.2	4.4	8.0	7.9	16.8	36.5	23.0
8B-1107	3.1	4.3	7.5	7.7	15.9	37.5	24.0
9B-1108	3.0	4.4	7.1	7.5	14.6	38.6	24.8
10B-1111	2.7	4.3	6.7	7.4	14.8	38.8	25.2
11B-1116	3.2	4.1	6.9	7.5	15.8	38.2	24.3
12B-1118	2.9	4.5	6.0	10.1	14.1	37.0	25.4
13B-1122	3.5	4.1	6.9	7.3	15.8	37.3	25.1
14B-0905	3.2	5.7	6.3	8.2	14.5	35.7	26.4
15B-0907	4.3	5.6	9.1	9.0	15.4	34.5	22.2
16B-0915	3.9	5.7	8.7	8.9	16.1	33.7	22.9

/ls

TABLE 22

PROTON DISTRIBUTIONS OF SOLUBLE VACUUM BOTTOMS
UOP Coprocessing Tests 1 through 16

	Proton Distribution, %						
Sample	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
1A-0311	10.1	5.6	11.3	8.0	14.7	33.3	16.9
2A-0502	8.0	5.5	9.1	7.6	14.0	36.6	19.1
3A-0508	6.0	4.6	8.0	7.3	14.8	37.7	21.5
4A-0513	7.7	4.8	11.2	7.9	15.9	35.4	17.1
5A-0521	10.5	4.6	12.8	8.2	16.1	33.3	14.4
6A-0522	9.9	5.4	11.7	8.4	15.4	33.3	16.0
7A-1102	6.4	3.5	11.3	7.6	17.1	36.9	17.2
8A-1107	6.5	3.7	10.6	8.1	15.7	38.0	17.4
9A-1108	6.2	3.8	9.8	7.6	15.5	39.1	18.1
10A-1111	6.2	4.0	9.9	7.6	16.2	38.0	18.1
11A-1116	7.7	3.8	9.7	7.6	15.2	38.3	17.7
12A-1118	7.6	4.3	9.4	7.8	15.5	36.9	18.5
13A-1122	7.0	3.9	9.5	7.7	15.4	37.6	18.8
14A-0905	9.0	5.7	11.5	8.0	15.3	33.4	17.1
15A-0907	10.6	5.6	11.2	7.8	14.3	33.2	17.8
16A-0915	7.8	6.3	11.1	8.8	15.3	33.0	17.7
17-R7(a)	4.0	3.0	11.0	7.7	16.6	37.0	20.6
18-R8(b)	4.1	3.2	10.3	7.7	17.7	35.9	21.0

(a) Petroleum feedstock for Test No. 1

(b) Petroleum feedstock for Test Nos. 2 through 16

All samples dissolved in $CDCl_3$

/ls

TABLE 23

PHENOLIC CONCENTRATIONS BY FTIR
UOP Coprocessing Tests 1 through 16

	Phenolic -OH Concentration, meq/g	
Test	Vacuum Overhead	Soluble Vacuum Bottoms
1-0311	0.28	0.41
2-0502	0.51	0.27
3-0508	0.30	0.23
4-0513	0.31	0.25
5-0521	0.39	0.37
6-0522	0.40	0.40
7-1102	0.37	0.19
8-1107	0.41	0.19
9-1108	0.31	0.19
10-1111	0.30	0.19
11-1116	0.32	0.21
12-1118	0.37	0.24
13-1122	0.43	0.24
14-0905	0.51	0.45
15-0907	0.48	0.44
16-0915	0.58	0.48
17-R7(a)	----	0.16
18-R8(b)	----	0.16

(a) Petroleum feedstock for Test No. 1
(b) Petroleum feedstock for Test Nos. 2 through 16

Peak maxima between 3312 and 3315 cm^{-1} for all vacuum overheads and between 3302 and 3311 cm^{-1} for all vacuum bottoms.

/ls

TABLE 24

YIELDS AND CARBON ISOTOPE ANALYSES
UOP Long-Term Coprocessing Test

Sample Designation	Description	Yield, wt % of MAF Feed (16)	Carbon Content, wt % (16)	$\delta\ ^{13}C$, ± Std Dev, per mil (a)	% Coal Carbon/ Total Carbon, ± Std Dev (b)
23-19141	Total Vacuum Overhead	41.3	85.6	-27.53 ±0.08	43.04 ±2.34
24-19141	Overhead Fraction, IBP x 177°C	5.5	82.3	-29.22 ±0.14	12.86 ±3.11
25-19141	Overhead Fraction, 177 x 343°C	21.2	86.1	-27.92 ±0.16	36.07 ±3.41
26-19141	Overhead Fraction, 343°C$^+$	14.6	86.3	-26.89 ±0.45	54.46 ±8.25
27-19141	Total Soluble Vacuum Bottoms	49.3	87.6	-27.97 ±0.05	35.18 ±2.06
28-19141	Bottoms Fraction, IBP x 510°C	13.2	86.0	-27.56 ±0.38	42.50 ±7.03
29-19141	Bottoms Fraction, 510°C x EP	8.4	86.0	-28.18 ±0.09	31.43 ±2.46
30-19141	Bottoms Fraction, Residue	27.7	83.65	-27.72 ±0.01	39.64 ±1.86

(a) Values shown are based on three replicate analyses. NBS #22 was analyzed five times during this series; determined values ranged from -29.63 to -29.66 per mil, accepted value is -29.71 per mil.

(b) Standard deviations were calculated assuming that the δ value of each feedstock has a standard deviation of 0.06 per mil. At perfect non-selectivity, % coal carbon/total carbon = 32.49.

/ls

TABLE 25

PROTON DISTRIBUTIONS
UOP Long-Term Coprocessing Test

	Proton Distribution, %						
Sample Description	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Total Vacuum Overhead	3.6	4.8	7.8	8.2	15.7	36.2	23.8
Overhead Fraction, IBP x 177°C	1.5	4.0	1.8	6.0	16.5	35.6	34.6
Overhead Fraction, 177 x 343°C	3.2	5.7	7.9	9.2	14.6	35.4	24.1
Overhead Fraction, 343°C$^+$	5.1	3.8	9.0	7.6	14.8	37.2	22.5
Total Soluble Vacuum Bottoms	7.4	5.6	8.8	7.6	14.1	36.0	20.5
Bottoms Fraction, IBP x 510°C	6.2	4.1	8.2	7.1	14.1	37.8	22.6
Bottoms Fraction, 510°C x EP	6.5	4.2	7.0	6.4	12.4	40.8	22.7
Bottoms Fraction, Residue	10.2	7.1	10.4	8.2	14.0	32.8	17.2

/ls

TABLE 26

PHENOLIC CONCENTRATIONS
UOP Long-Term Coprocessing Test

Sample Description	Phenolic Concentration, meq/g
Total Vacuum Overhead	0.40 (a)
Overhead Fraction, IBP x 177°C	0.50
Overhead Fraction, 177 x 343°C	0.48
Overhead Fraction, 343°C$^+$	0.30
Total Soluble Vacuum Bottoms	0.38 (b)
Bottoms Fraction, IBP x 510°C	0.32
Bottoms Fraction, 510°C x EP	0.37
Bottoms Fraction, Residue	0.49

(a) Value shown was measured. Based on yields and concentrations of fractions, it is calculated to be 0.41.

(b) Value shown was measured. Based on yields and concentrations of fractions, it is calculated to be 0.42.

Peak positions between 3308 and 3316 cm^{-1} for all overheads and between 3302 and 3309 cm^{-1} for all bottoms.

/ls

TABLE 27

ANALYSIS OF OLD BEN #1 MINE, INDIANA 5 COAL AS A FUNCTION OF STORAGE TIME

	Date			
	4/81	1/85	2/86	1/87
Proximate, wt % as determined				
Moisture	2.34	3.38	2.79	3.45
Volatile Matter	40.59	38.96	38.72	39.80
Fixed Carbon	46.78	47.62	48.35	46.91
Oxidized Ash	10.29	10.04	10.14	9.84
Ultimate, wt % dry basis				
Carbon	70.80	70.34	69.16	70.20
Hydrogen	4.94	4.82	4.90	5.00
Nitrogen	1.49	1.51	1.47	1.38
Oxygen (diff.)	8.59	9.37	10.60	9.75
Sulfur, Total	3.64	3.53	3.40	3.45
Pyritic	1.45	1.23	1.05	0.99
Sulfatic	0.02	0.37	0.48	0.56
Organic (diff.)	2.17	1.93	1.87	1.90
Chlorine	0.01	0.04	0.04	0.03
Oxidized Ash	10.54	10.40	10.43	10.19
Elemental, wt % Oxidized Ash				
Na_2O	0.36	0.30	0.34	0.28
K_2O	2.44	2.21	2.48	2.06
CaO	3.39	3.29	3.22	3.20
MgO	0.86	0.86	0.88	0.85
Fe_2O_3	22.60	24.95	24.00	24.10
TiO_2	0.66	0.86	0.87	0.90
P_2O_5	0.15	0.16	0.31	0.19
SiO_2	43.34	45.80	46.23	45.49
Al_2O_3	18.82	20.01	20.11	20.90
SO_3	2.05	1.63	1.51	0.89
Unaccounted	5.33	-0.07	0.05	1.14
Calorific Value, dry (HHV), Btu/lb	12,846	12,640	12,512	12,509

Wet Screen Tyler Mesh	wt %
+100	0.0
100 x 200	10.8
200 x 325	20.0
-325	69.2

/ls

TABLE 28

MICROAUTOCLAVE CALIBRATION TESTS

Solvent Composition, Tetralin/ 1-Methylnaphthalene	Kinetic (KIN) Test	Equilibrium (EQ) Test	Modified EQ (Mod-EQ) Test	Short Contact Time (SCT) Test
Sampled 4/81				
0/100	59.3	54.2	-	-
5/95	-	-	-	-
10/90	72.0	72.5	-	-
25/75	74.6	81.3	-	-
50/50	73.8	84.5	-	-
100/0	-	-	-	-
Sampled 1/85				
0/100	53.0	48.8	48.2	44.8
5/95	64.4	58.9	55.3	53.1
10/90	68.7	71.1	62.3	59.3
25/75	73.0	75.5	72.0	68.4
50/50	74.8/73.8(a)	80.7/80.9(a)	80.9	81.4
100/0	68.2/68.1	82.7	85.4	87.2
Sampled 2/86				
0/100	-	-	-	-
5/95	61.8/61.9	57.1	53.5	-
10/90	-	-	-	-
25/75	72.0	74.0	70.1	-
50/50	-	-	-	-
100/0	68.6	83.6	84.2/84.3(b)	-
Sampled 1/87				
0/100	-	-	-	-
5/95	58.9	55.4	51.9	-
10/90	-	-	-	-
25/75	69.6	72.7	68.3	-
50/50	71.4	78.1	77.2	-
100/0	66.1	82.9	84.4	-

(a) Second test shown made with coal sampled 11/84
(b) Second result shown from non-standard test made with 9 g solvent and 5 g coal

Conditions: KIN - 750°F, 10 min, 12 g solvent, 1.5 g coal
EQ - 750°F, 30 min, 10 g solvent, 5 g coal
Mod-EQ - 750°F, 30 min, 9 g solvent, 6 g coal
SCT - 860°F, 5 min, 9 g solvent, 5 g coal

Coal: Old Ben No. 1, Indiana 5

/ls

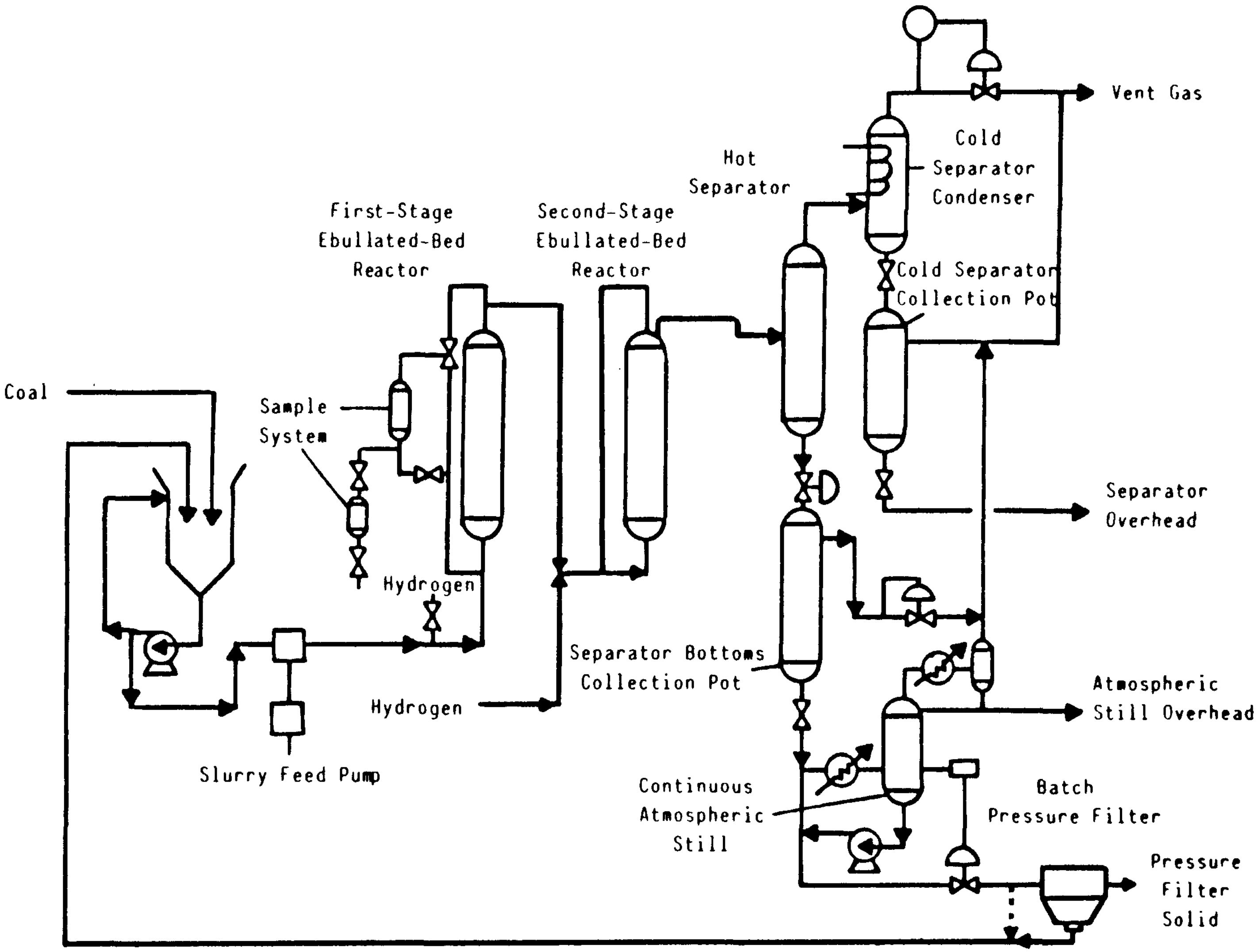

Figure 1. Ebullated-Bed Bench Unit 227. Source: Reference 2.

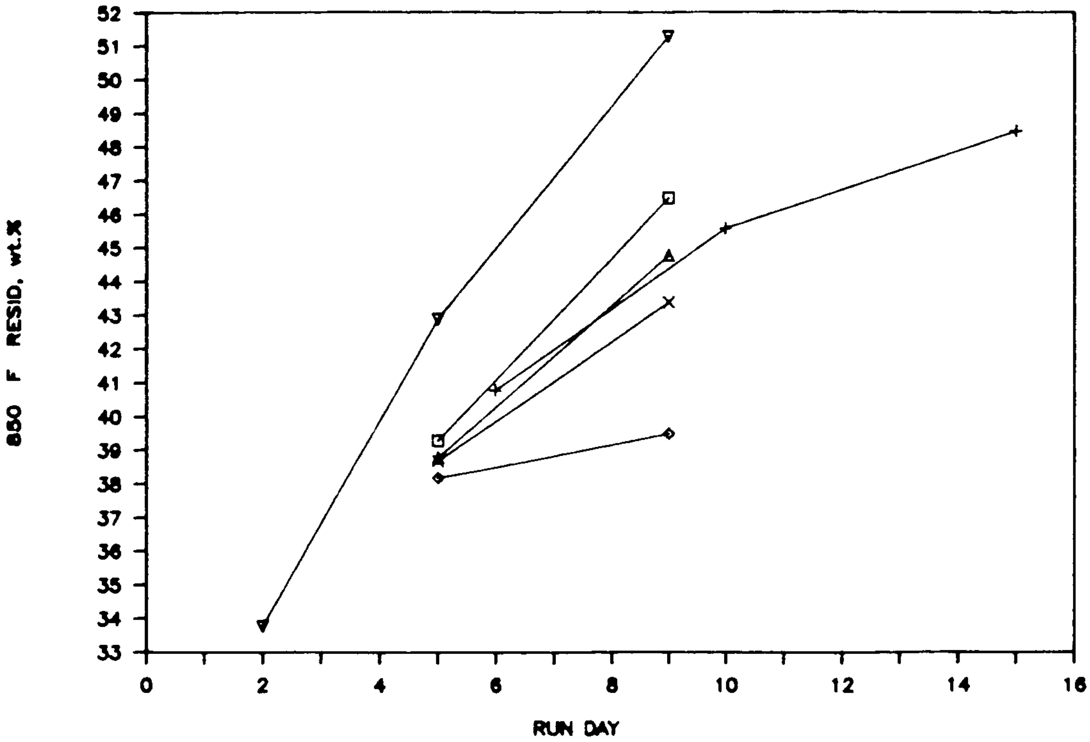

Figure 2. PFL $850^{\circ}F^{+}$ Resid Content. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

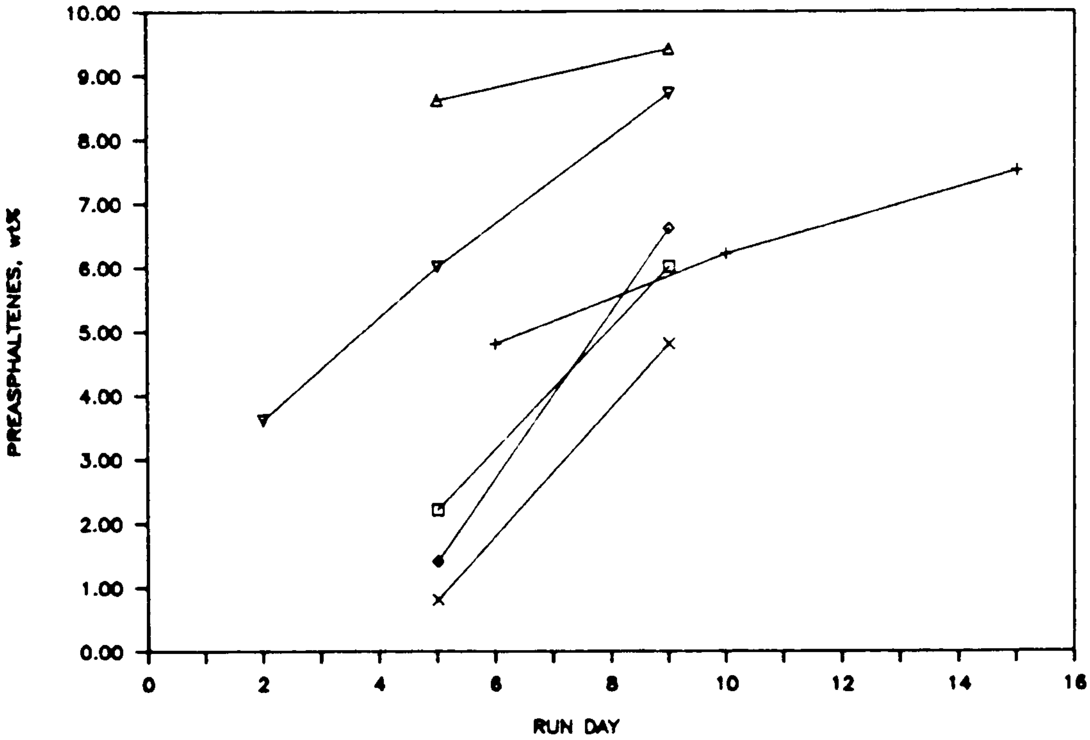

Figure 3. PFL Preasphaltenes, wt % of Soluble Resid. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

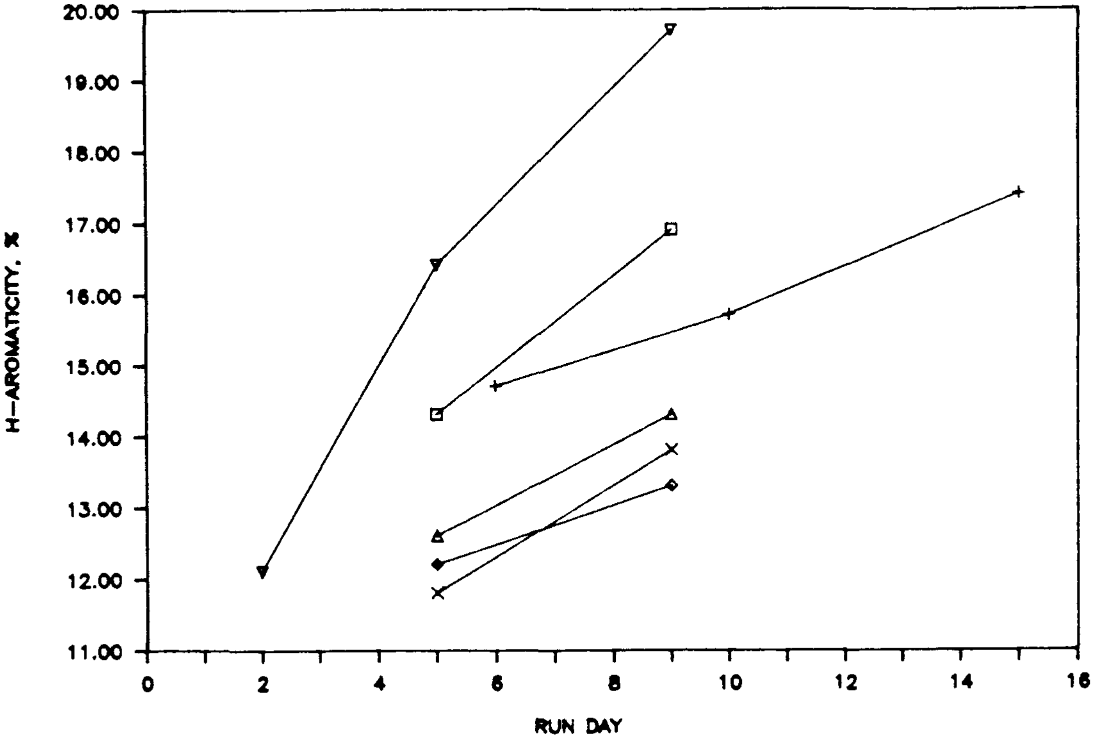

Figure 4. H-Aromaticity, PFL Whole Sample. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

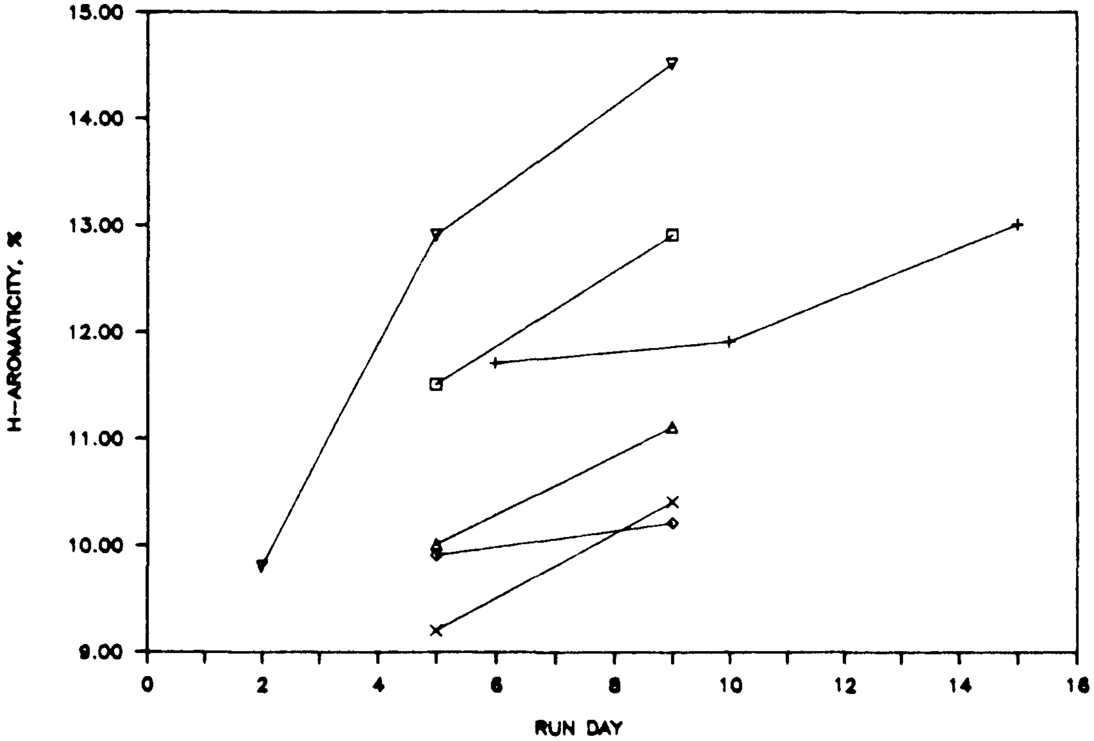

Figure 5. H-Aromaticity, PFL Distillate. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

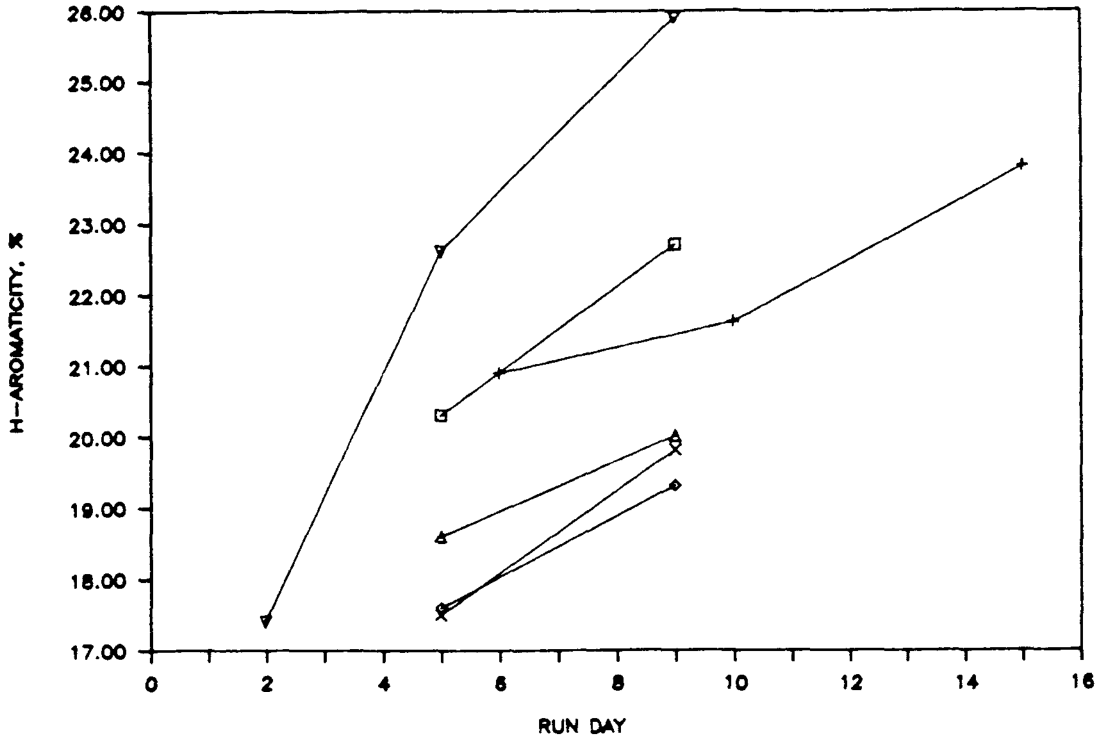

Figure 6. H-Aromaticity, PFL Resid. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

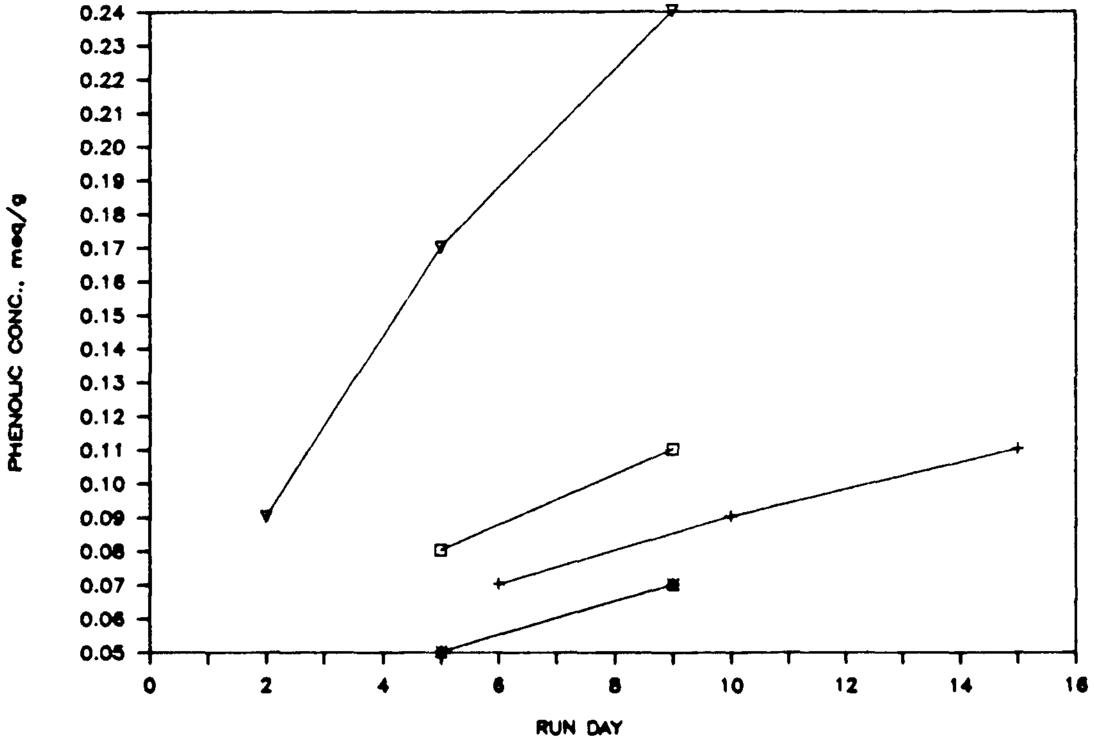

Figure 7. Phenolic Content of PFL Distillate. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

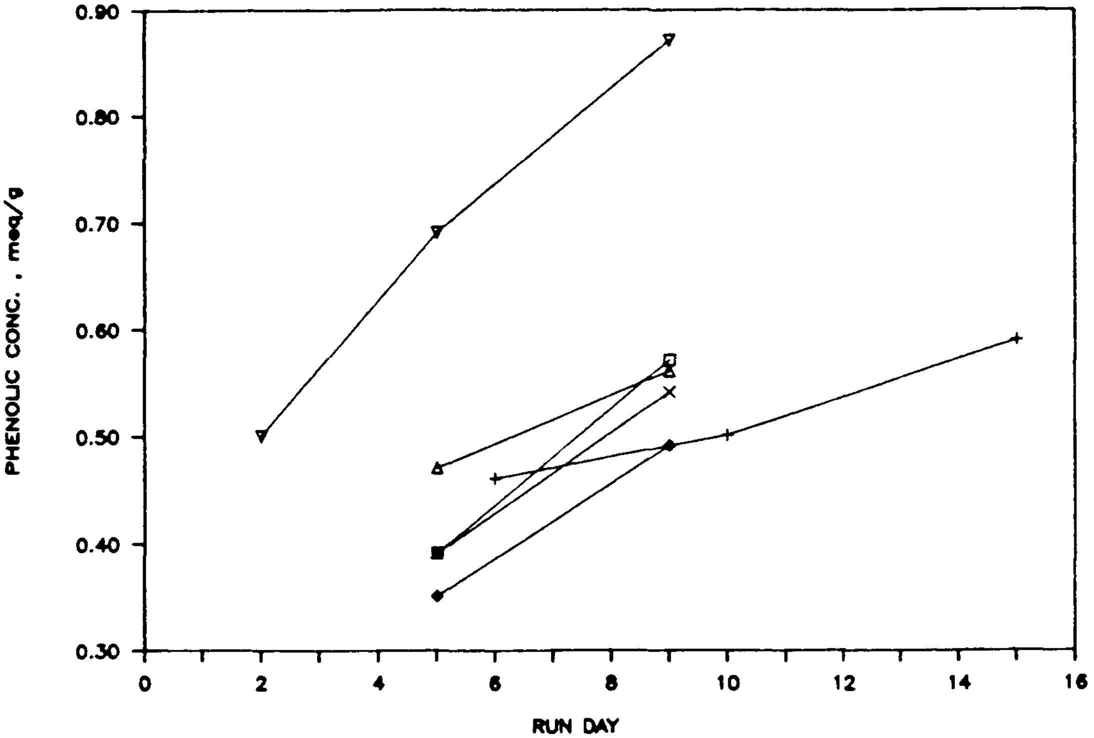

Figure 8. Phenolic Content of PFL Resid. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

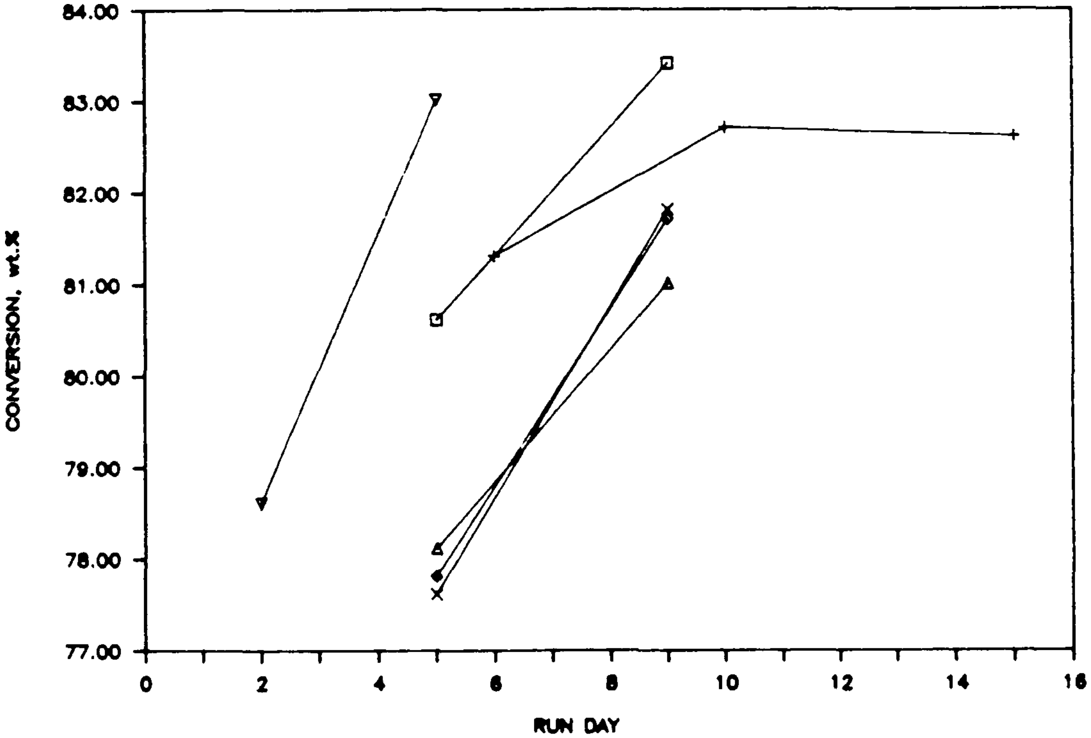

Figure 9. Microautoclave Tests, PFL Whole Sample. HRI CTSL Runs I-13 (□), I-15 (▽), I-16 (◇), I-17 (△), I-18 (X), and I-19 (+).

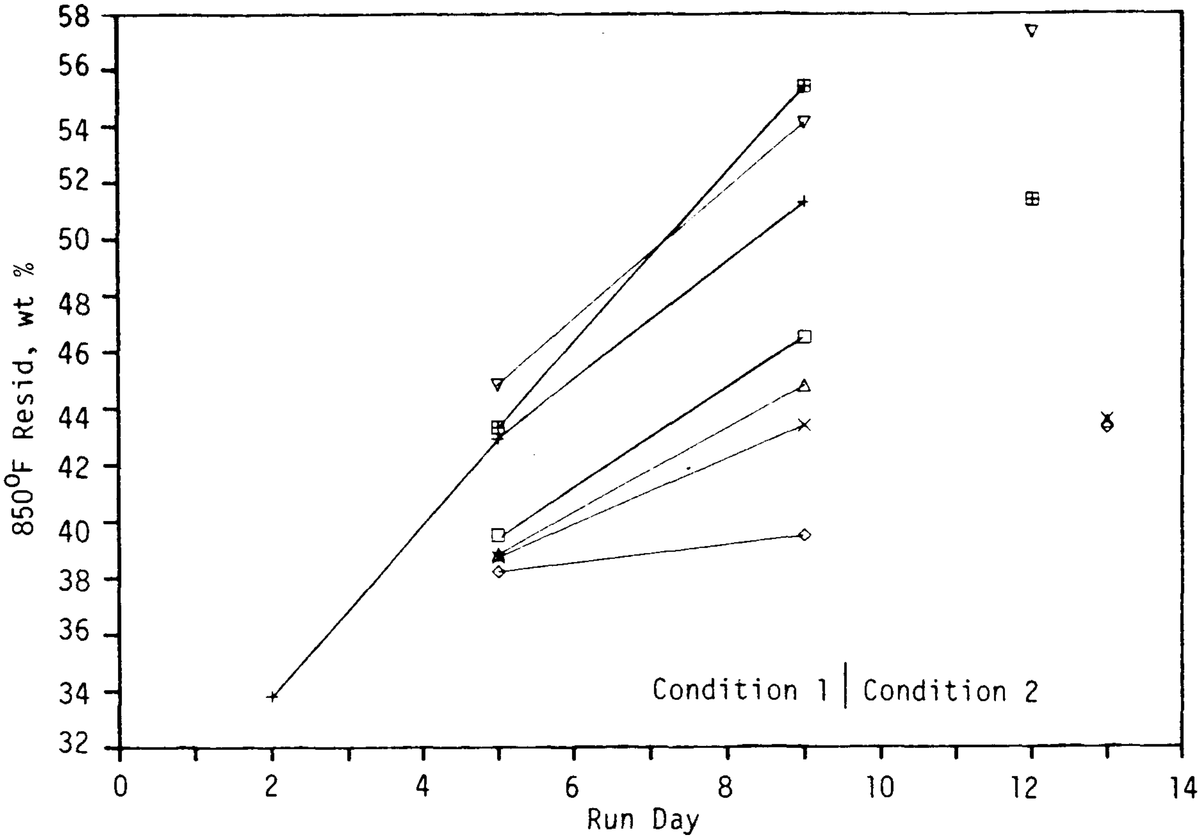

Figure 10. PFL 850°F Resid Content, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (△), I-18 (X), I-22 (▽), and I-23 (⊞).

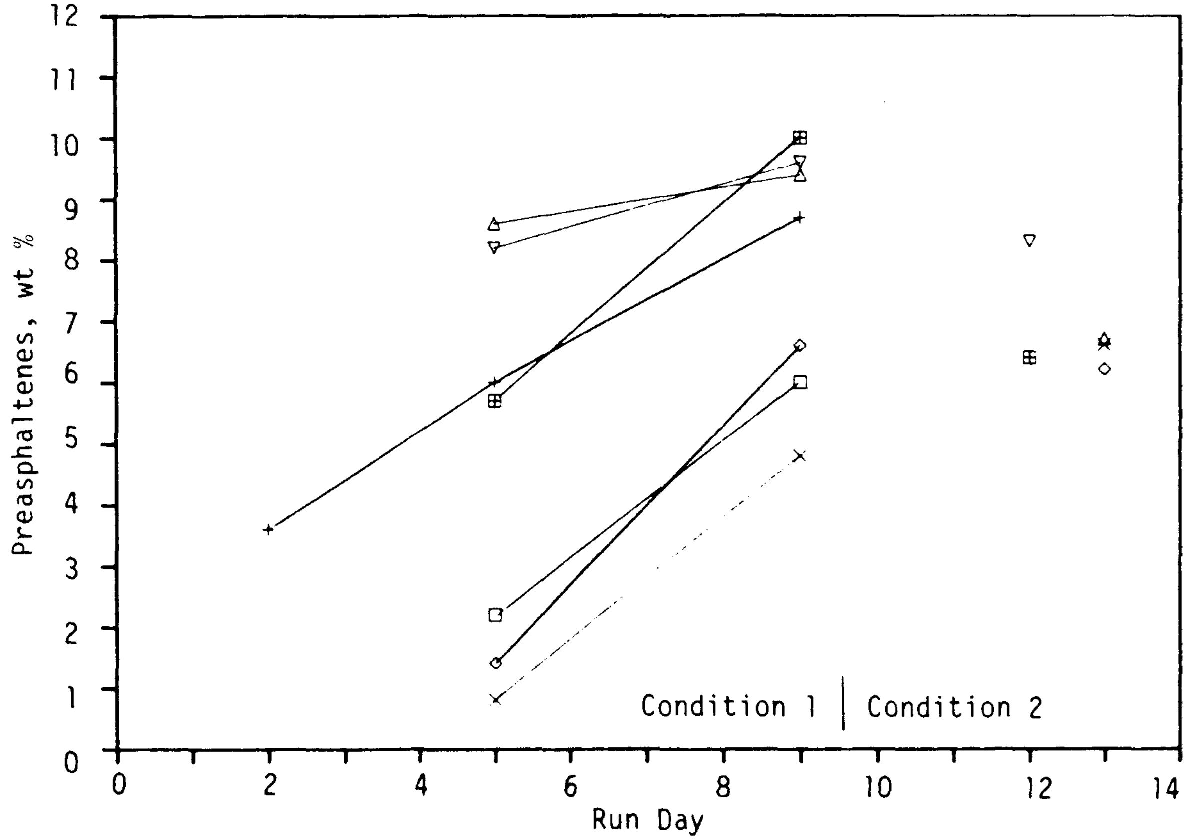

Figure 11. PFL Preasphaltenes, wt % of Soluble Resid, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (△), I-18 (X), I-22 (▽), and I-23 (⊞).

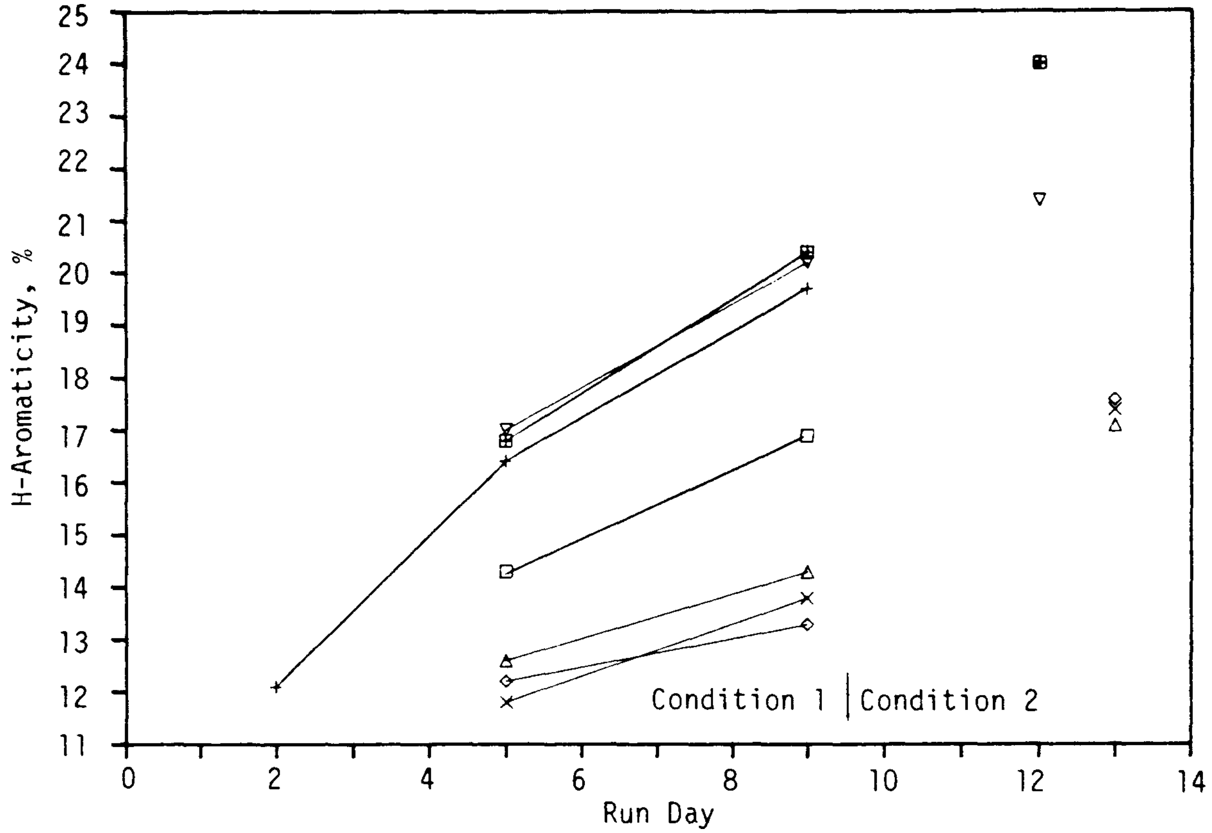

Figure 12. H-Aromaticity, PFL Whole Sample, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (△), I-18 (X), I-22 (▽), and I-23 (⊞).

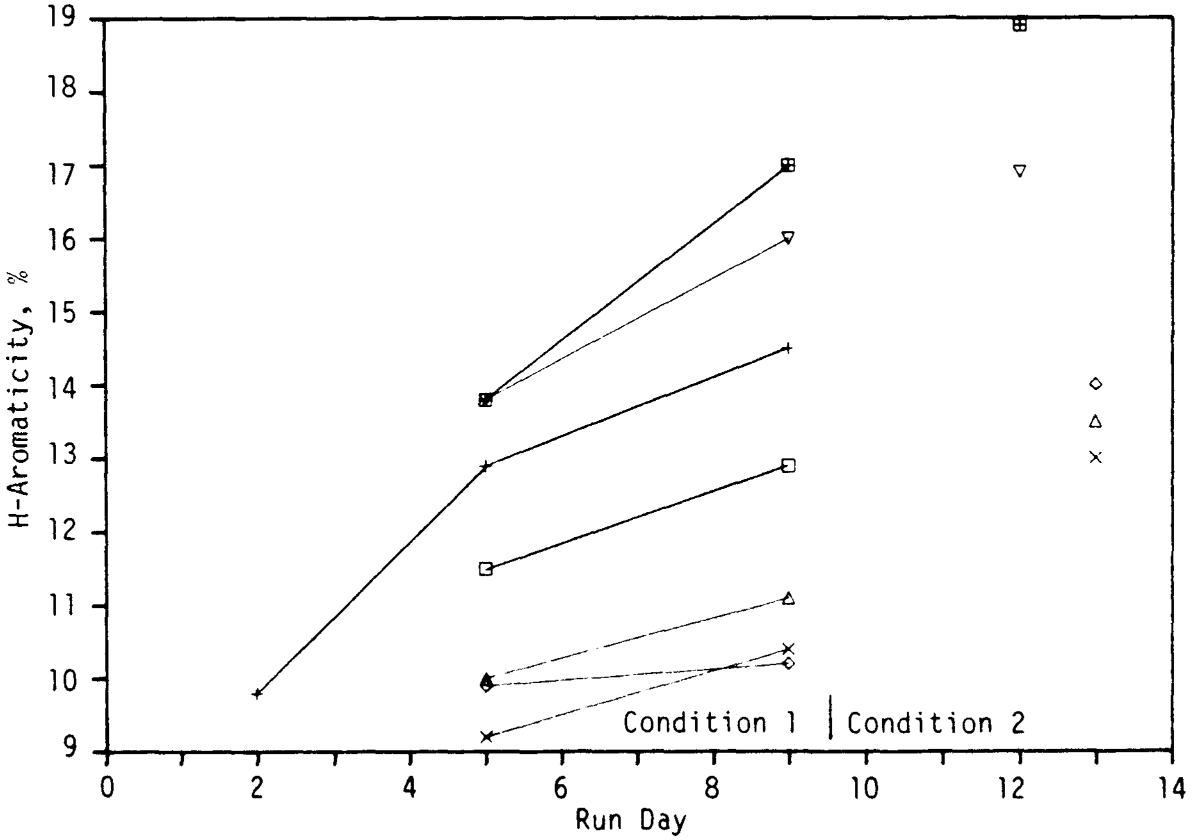

Figure 13. H-Aromaticity, PFL Distillate, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (△), I-18 (X), I-22 (▽), and I-23 (⊞).

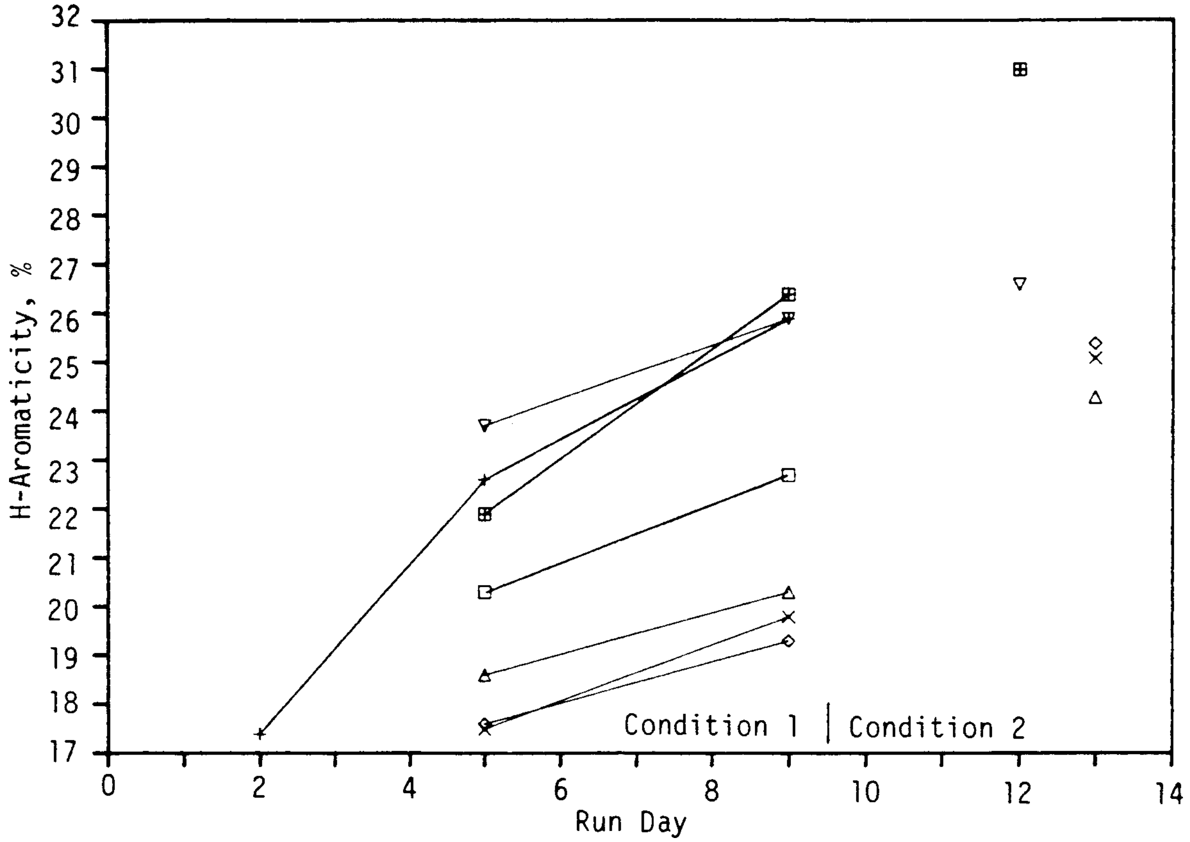

Figure 14. H-Aromaticity, PFL Resid, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (△), I-18 (X), I-22 (▽), and I-23 (⊞).

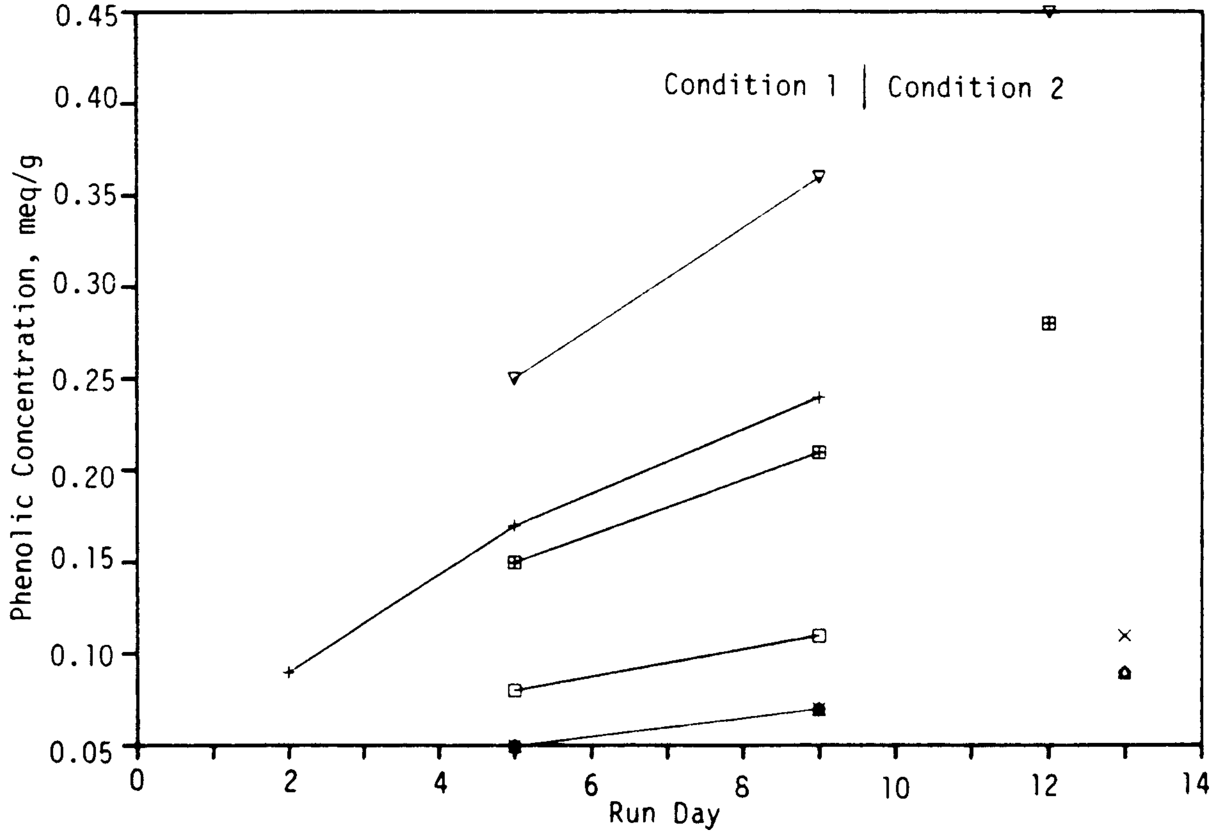

Figure 15. Phenolic Content, PFL Distillate, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (△), I-18 (X), I-22 (▽), and I-23 (⊞).

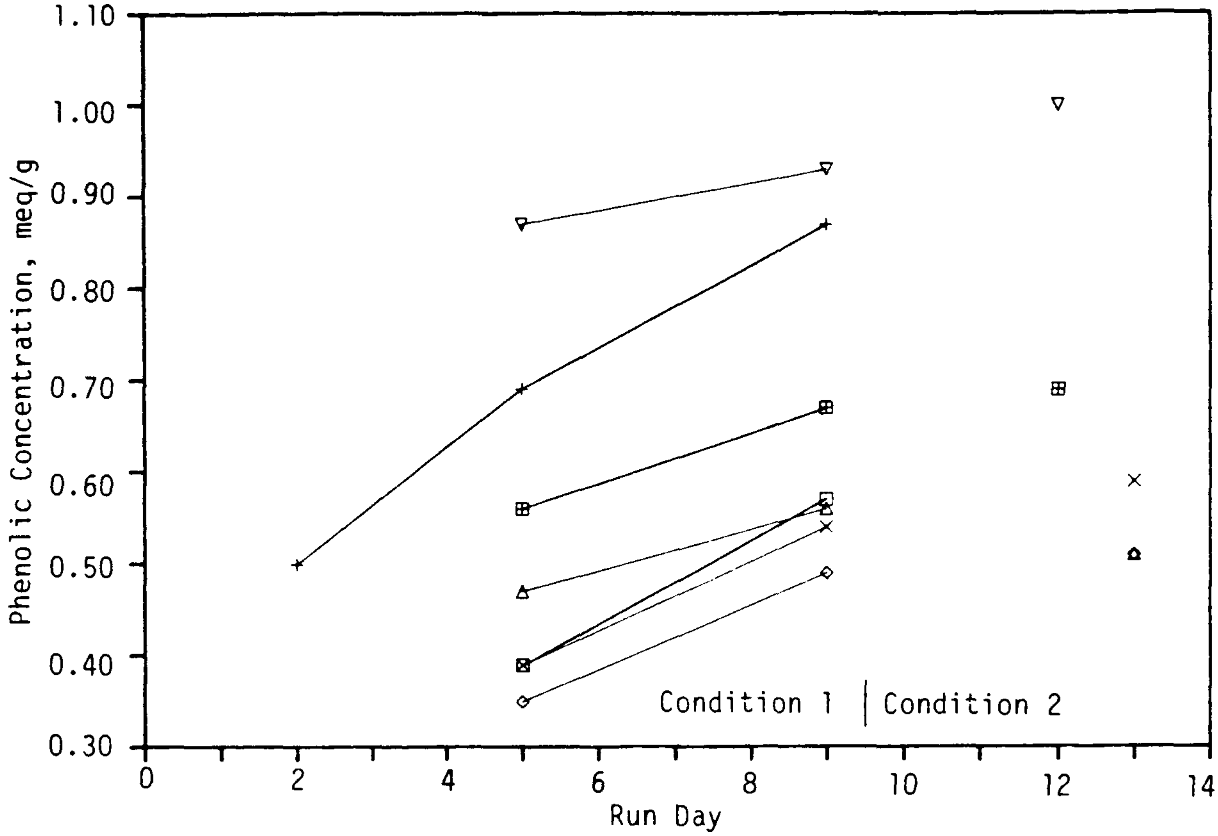

Figure 16. Phenolic Content, PFL Resid, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (Δ), I-18 (X), I-22 (▽), and I-23 (⊞).

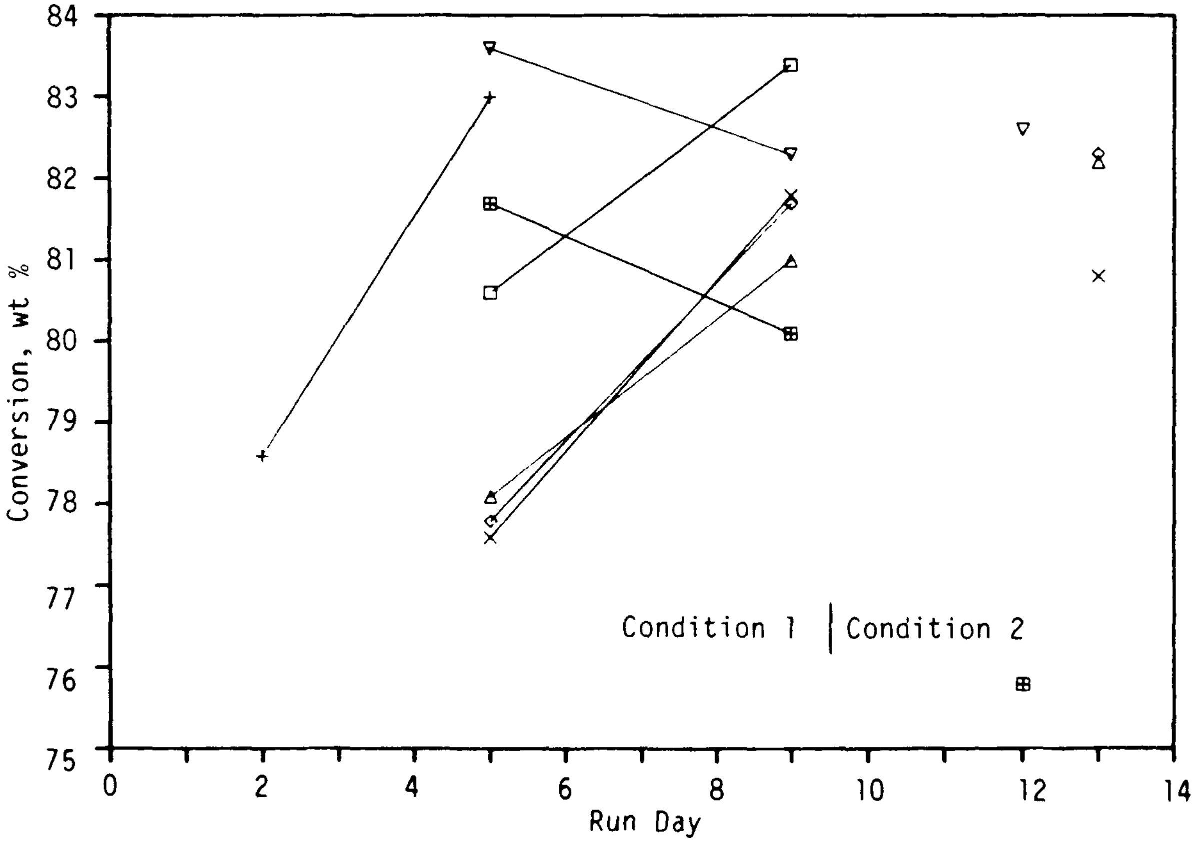

Figure 17. Microautoclave Tests, PFL Whole Sample, HRI CTSL Runs I-13 (□), I-15 (+), I-16 (◇), I-17 (Δ), I-18 (X), I-22 (▽), and I-23 (⊞).

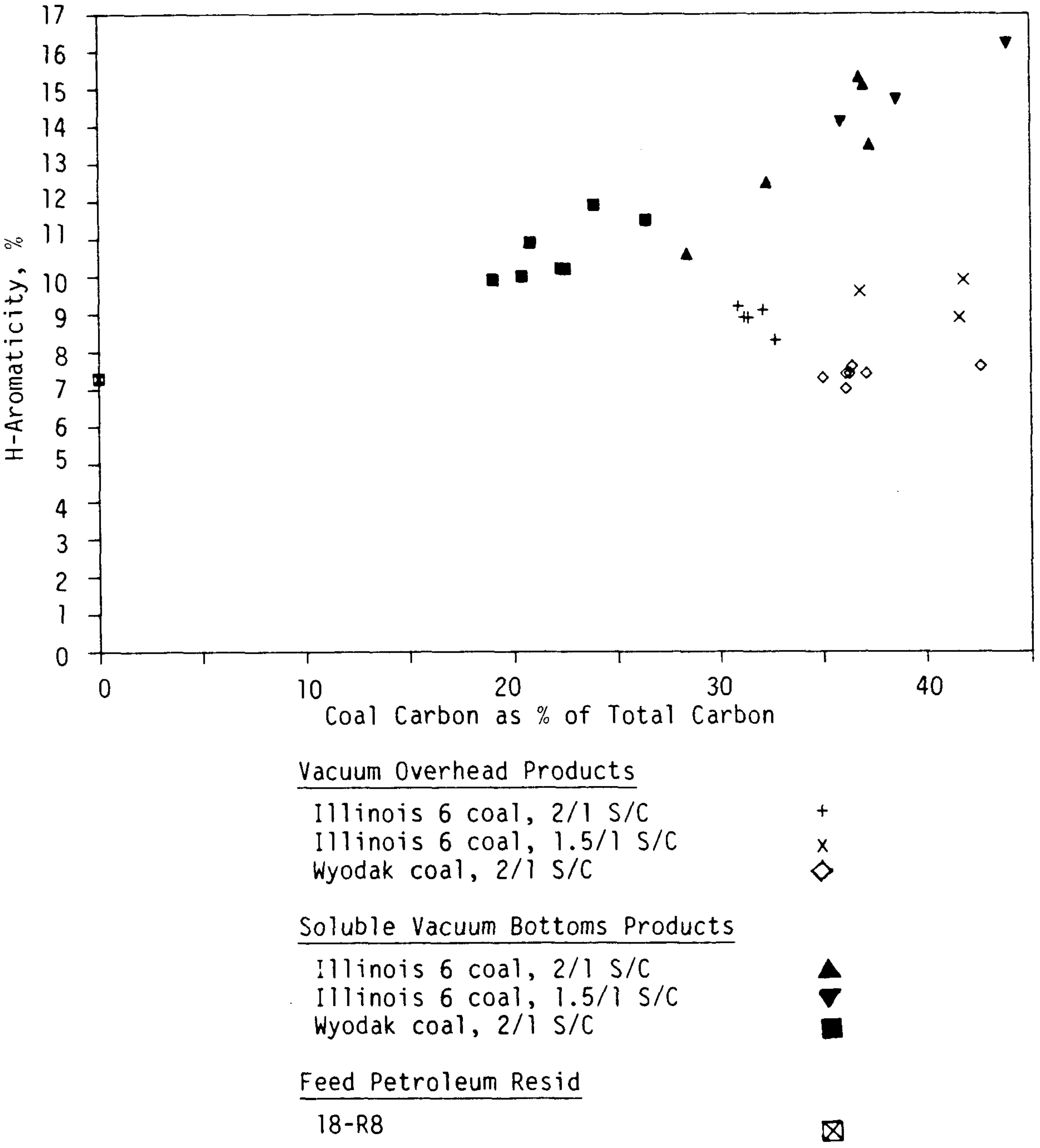

Figure 18. Aromaticity vs Carbon Source. UOP Coprocessing Tests 2 Through 16.

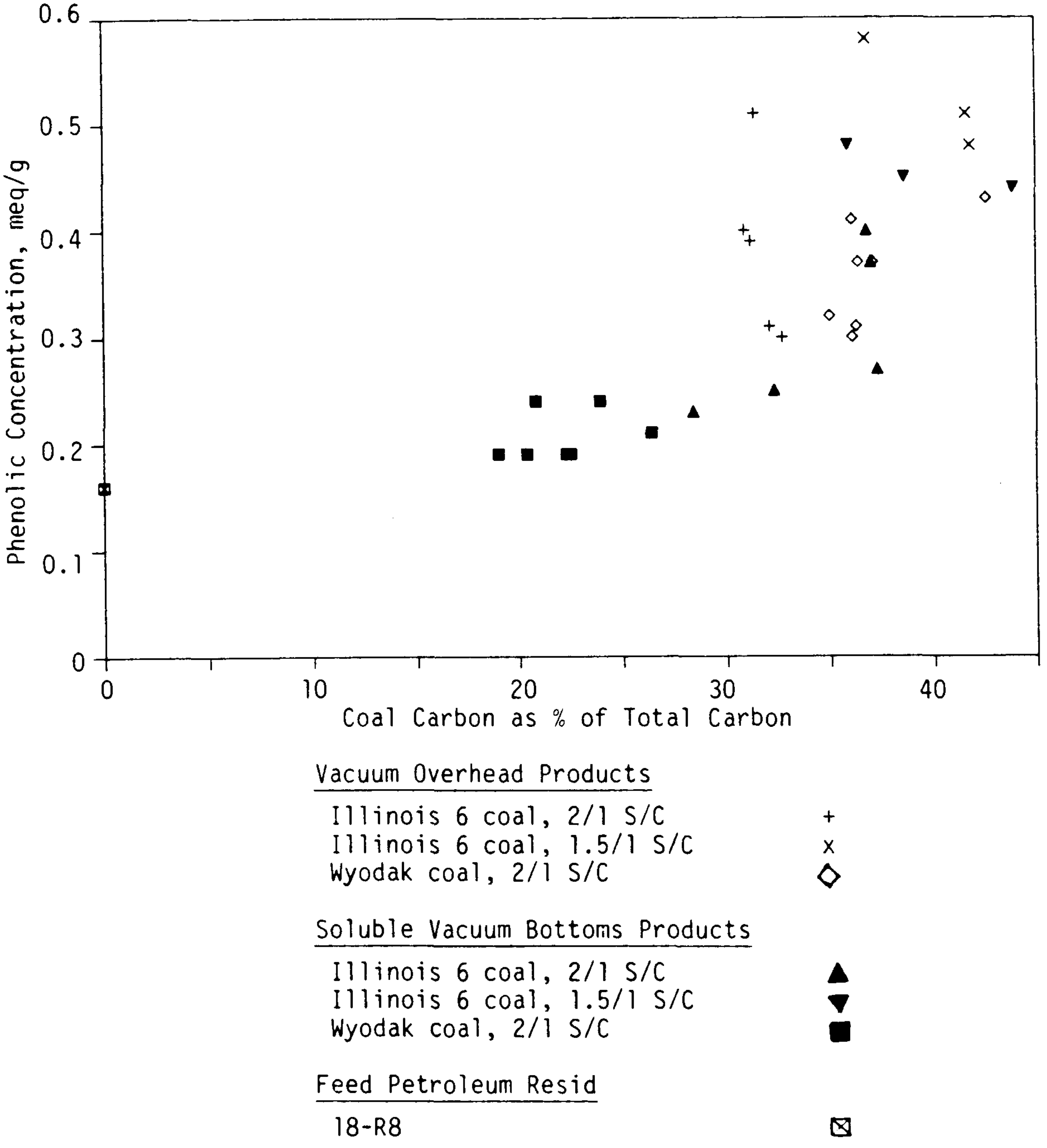

Figure 19. Phenolic Content vs Carbon Source. UOP Coprocessing Tests 2 Through 16.

APPENDIX 1

COAL AND PETROLEUM REACTIONS IN COAL/OIL COPROCESSING

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ABSTRACT

Coprocessing involves the simultaneous upgrading of coal and petroleum resid by catalytic hydroconversion. To obtain a kinetic/mechanistic description of the process, it is useful if not necessary to be able to distinguish the relative contributions of coal and petroleum to the product mixtures. In this paper, the method of stable carbon isotope ratio analysis is shown to be sufficiently sensitive to determine the relative concentrations of coal and petroleum carbon in coprocessing products. Selective isotopic fractionation does not appear to occur to a significant extent, although additional work is needed to confirm this preliminary conclusion. Application of the method to the coprocessing of Wyodak and Illinois 6 coals with a Lloydminster resid by the Signal Research/ UOP process is shown to yield valid results of use in process interpretation and optimization.

INTRODUCTION

In coprocessing, a petroleum resid is processed with coal to produce distillate mixtures which are either finished products or feeds for more conventional refining. Coprocessing can replace a portion of the petroleum feedstock with a lower cost hydrocarbon at lower capital cost than a grassroots coal liquefaction plant. If integrated with existing refinery capacity, coprocessing may find some near term application if conventional feedstocks are unavailable. An excellent overview of industrial and academic research in the area can be found in Reference 1.

In process development, it is important to be able to describe the hydrogenation, cracking and heteroatom (O,N,S) removal reactions in sufficient detail to develop a kinetic/mechanistic model for use in data interpretation and process optimization. For coprocessing, this is complicated by the presence of two greatly different feedstocks.

This paper describes the validation and application of the measurement of stable carbon isotope ratios to quantitatively determine the relative concentrations of coal- and petroleum-derived components in coprocessing products. Since the carbon contents of these materials are typically 85% to 90%, this provides an excellent estimate of the overall mass compositions. The measurement of carbon isotope ratios is standard practice in the petroleum industry and its application is conceptually straightforward. However, several significant questions must be resolved. First, is the method sufficiently precise and are the differences between the carbon isotope ratios of the relevant materials large enough to obtain experimentally meaningful results? Second, does selective isotopic fractionation occur? Third, do actual applications provide meaningful process results? The work described in this paper addresses these three questions.

CARBON ISOTOPE RATIOS OF COAL AND PETROLEUM RESIDS

Carbon isotope ratios are determined by quantitatively converting the carbon in a sample to CO_2 and measuring the relative amounts of the isotopically different CO_2 species. The resulting ratio, corrected for oxygen isotopes, is compared to that of a standard material and the result is reported as the relative difference. The standard used in this work is a Peedee belemnite (PDB)(2). Experimental details have been reported elsewhere (3).

If the carbon isotope ratios of the feedstocks are known and are not identical, the percentage of coal or petroleum carbon in a coprocessing product can be calculated using a standard mixing equation. This requires a sufficient difference between the carbon isotope ratios of the coal and petroleum to be of practical use. Table 1 presents the δ values for the coals and petroleum resids used in the work reported here. Despite the variation in the coal rank from subbituminous (Wyodak) to hvAb (Pittsburgh), the carbon isotope ratios of the coals are essentially the same. The resids show a greater range, but all have absolute values greater than those of the coals. The standard deviations based on at least triplicate analyses are comfortably small relative to the differences between the coal and petroleum resids.

VALIDATION OF METHOD

A critical assumption in this method is that significant isotopic fractionation does not occur. That is, the coal- or petroleum-derived portion of the product mixture must retain the same carbon isotope ratio as the parent feed. Although significant isotope fractionation is not expected (3), some work was done to verify this assumption. In the first test, a light oil, heavy oil and vacuum resid from the LC-Fining of an Arab Heavy crude, supplied by Lummus, were analyzed. These three product samples had an average δ of -26.87 ±0.09, indicating little selective fractionation. In a second test, a set of petroleum samples consisting of a Maya atmospheric tower bottoms (ATB) and its heptane soluble and insoluble fractions were analyzed. The average carbon isotope ratio was -27.53 ±0.22, indicating an insensitivity to this type of compound separation.

Next, products from Wilsonville coal liquefaction pilot plant operations with Illinois 6 (Burning Star coal) were compared. Results were obtained for a distillate (V-178) and resids ($850°F^+$) from two different runs. The average carbon isotope ratio was -23.91 ±0.20. As the standard deviation indicates, the product isotope ratios are in good agreement, and are also in reasonable agreement with the values for Illinois 6 coal given in Table 1, although neither of these Illinois 6 samples was obtained from Wilsonville.

Finally, carbon isotope ratios were determined for two distillate fractions of Lloydminster resid provided by Signal Research/UOP. Despite their considerably different boiling ranges, these resid fractions have equivalent carbon isotope ratios.

Resid	Vol % Overhead (D-1160)	mol wt (amu)	δ
17-R7	5.0	1117	-29.81
18-R8	26.5	755	-29.94

These results are not definitive, but indicate that extensive selective isotope fractionation is not occurring as a result of hydroprocessing, distillation, or solubility fractionation. Selective isotope enrichment of the gas may be significant, particularly at low gas yields (4). However, this would not significantly alter the carbon isotope ratios of the primary distillate and residual liquid products. Therefore, the possible effects of selective isotopic fractionation are ignored, with some reason for confidence, in this report.

APPLICATION TO SIGNAL RESEARCH/UOP COPROCESSING RUNS

The Signal Research/UOP (UOP) coprocessing technology employs a proprietary slurry-phase catalyst in a single-stage reactor. To evaluate the practical application of the carbon isotope method, feed coals, resid, and vacuum overhead and toluene-soluble vacuum bottoms products from sixteen continuous coprocessing runs were obtained from UOP. The toluene-insoluble portions of the vacuum bottoms were removed by UOP to provide samples free of their proprietary catalyst. Reaction conditions and yield data (Table 2) were provided by UOP; additional data are given elsewhere (3).

UOP made runs with Illinois 6 coal and with Wyodak coal. All the run periods reported here used a Lloydminster resid designated 17-R7. The carbon isotope data were used to calculate the ratios of coal carbon to total carbon in the two analyzed products (Table 3). By comparing these values to the percentage of coal carbon in the total feed, it is possible to calculate a "selectivity" as the ratio of the percentage of coal carbon in the product mixture to that of the feed mixture. A value greater than (less than) one indicates that the given fraction is selectively enriched (depleted) in coal carbon relative to petroleum carbon; a value close to unity indicates that the coal and petroleum respond similarly. In Figures 1 and 2, the selectivities for the runs with Wyodak and Illinois 6 coals are plotted versus vacuum bottoms yields, with increasing vacuum bottoms yields generally representing decreasing processing severity. The results show a clear distinction between the two coals. For the Wyodak coal, the vacuum overheads are consistently enriched in coal carbon, while the bottoms are depleted. This indicates that, per carbon atom, the Wyodak coal is more readily converted to distillate at these conditions than the petroleum resid. The Illinois 6 coal, by contrast, shows little average selectivity for the vacuum overheads, indicating that its carbon conversion to distillate is similar to that of the resid. There is some suggestion in the Illinois 6 data that the vacuum bottoms are depleted in coal carbon at low conversion (high vacuum bottoms yields) and enriched at high conversion. Since coal conversion from toluene insolubles to soluble resid increased with increasing severity, this may simply reflect higher coal conversion.

Table 4 gives the conversions of coal carbon and petroleum carbon to overhead products. These numbers are based on the carbon contents and yields of the products and their relative proportions of coal and petroleum carbon. Comparing the conversions with reaction temperature by linear regression analysis yields the following results.

Coal Carbon Conversion to Vacuum Overheads

Illinois 6 Coal: % Conv = -370 + 0.97 T (°F), $r^2 = 0.90$
Wyodak Coal: % Conv = -232 + 0.68 T (°F), $r^2 = 0.71$

Resid Carbon Conversion to Vacuum Overheads

Both Coals: % Conv = -267 + 0.73 T (°F), $r^2 = 0.91$

This analysis of the data underscores the significant difference in the coprocessing behaviors of the Wyodak and Illinois 6 coals. By contrast, a single linear equation appears to adequately describe the temperature response of the resid conversion regardless of the coal with which it was coprocessed. These experiments were not specifically designed to demonstrate the effect of temperature in coprocessing, and other reaction conditions were simultaneously varied. However, the results indicate that carbon isotope ratios can be used to independently assess the relative reactions of coal and petroleum in coprocessing. Additional work is required to fully exploit the value of this technique to process development.

The authors are grateful for the assistance provided by Charles Luebke (UOP) and John Gatsis (Signal Research), Marvin Greene (Lummus), Richard Lett (PETC) and Lois Jones and Arnold Taylor (Conoco). This work was performed under U.S. DOE Contract DE-AC22-84PC70018.

REFERENCES

1. "Symposium on Coprocessing and Integrated Two-Stage Liquefaction", preprints ACS Fuel Chem. Div., Anaheim, CA, September 1986.
2. Craig, H., Geochim. et Cosmochim. Acta, 3, 53-92 (1953).
3. Winschel, R. A., Robbins, G. A. and Burke, F. P., "Coal Liquefaction Process Solvent Characterization and Evaluation - Second Annual Report", DOE/PC-30027, May 1987.
4. Sackett, W. M., Geochim. et Cosmochim. Acta, 42, 571 (1978).

TABLE 1. CARBON ISOTOPE RATIOS OF COPROCESSING FEEDS

Coals	δ ‰
Illinois 6 (Burning Star)	-24.32 ±0.07
Illinois 6 (UOP)	-24.34 ±0.04
Wyodak (Sarpy Creek)	-24.66 ±0.06
Wyodak (UOP)	-24.36
Pittsburgh (McElroy)	-23.80 ±0.1
Pittsburgh (Ireland)	-23.68 ±0.01
Petroleums	
Lloydminster Resid (17-R7)	-29.81
Arab Heavy Vacuum Resid	-26.21 ±0.28
Athabasca Vacuum Resid	-29.50 ±0.2
Maya Atmospheric Tower Bottoms	-27.66 ±0.08

TABLE 2. OPERATING CONDITIONS, CONVERSIONS, YIELDS AND ANALYSES - UOP COPROCESSING TESTS

	Operating Conditions			Product Yields, wt % of MAF Feed	
Test No.	Resid/MAF Coal wt Ratio	Space Velocity (a)	T, °C	Vacuum Overhead	Soluble Bottoms
Illinois 6 Coal					
16-0915	1.5	B	414	29.8	51.6
14-0905	1.5	B	425	42.6	39.3
15-0907	1.5	B	434	45.1	35.1
4-0513	2	1.25B	425	38.5	42.7
3-0508	2	B	413	30.1	50.7
2-0502	2	B	426	43.4	36.6
6-0522	2	B	431	47.3	34.9
5-0521	2	0.75B	424	42.7	37.5
Wyodak Coal					
10-1111	2	1.25B	427	44.7	32.2
7-1102	2	B	414	39.8	38.8
9-1108	2	B	425	42.5	32.8
8-1107	2	B	426	46.7	34.2
12-1118	2	B	431	49.9	28.8
11-1116	2	0.75B	425	45.0	31.0

(a) Overall space velocity, based on both coal and petroleum. "B" refers to proprietary base conditions.

TABLE 3. CARBON ISOTOPE ANALYSIS - UOP COPROCESSING SAMPLES

	Carbon Isotope Analyses $\delta^{13}C$, ‰		Coal Carbon as % of Total Carbon	
Test No.	Vacuum Overhead	Soluble Vacuum Bottoms	Vacuum Overhead	Soluble Vacuum Bottoms
Illinois 6 Coal Products				
16-0915	-27.88	-27.93	36.8	35.9
14-0905	-27.61	-27.78	41.6	38.6
15-0907	-27.60	-27.48	41.8	43.9
4-0513	-28.14	-28.13	32.1	32.3
3-0508	-28.11	-28.35	32.7	28.4
2-0502	-28.18	-27.85	31.4	37.3
6-0522	-28.21	-27.88	30.9	36.8
5-0521	-28.19	-27.87	31.2	37.0
Wyodak Coal Products				
10-1111	-27.89	-28.67	36.1	22.3
7-1102	-27.87	-28.86	36.4	19.0
9-1108	-27.88	-28.78	36.3	20.4
8-1107	-27.89	-28.66	36.1	22.5
12-1118	-27.83	-28.58	37.1	23.9
11-1116	-27.95	-28.46	35.0	26.1

TABLE 4. CONVERSION OF COAL AND PETROLEUM CARBON TO VACUUM OVERHEADS - SIGNAL/UOP COPROCESSING

	% Conversion to Vacuum Overhead	
Test No.	Coal Carbon	Resid Carbon
Illinois 6 Coal		
16-0915	28.7	34.0
14-0905	46.6	43.2
15-0907	49.9	50.6
4-0513	39.6	43.2
3-0508	31.4	33.2
2-0502	43.5	44.0
6-0522	46.5	48.1
5-0521	42.7	42.3
Wyodak Coal		
10-1111	55.9	43.7
7-1102	50.8	39.2
9-1108	54.3	41.5
8-1107	58.7	45.7
12-1118	64.2	48.2
11-1116	54.8	44.9

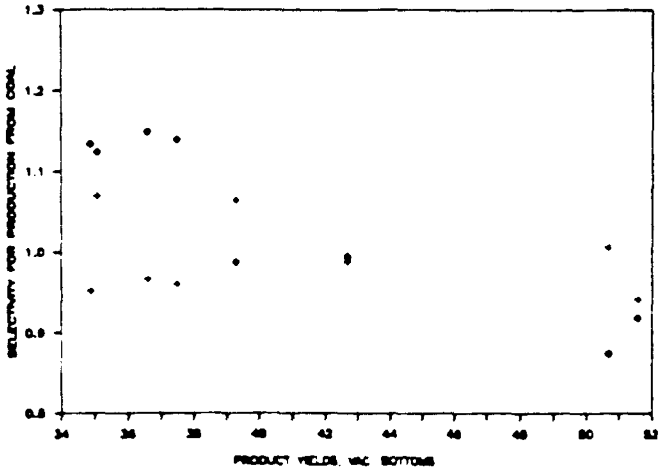

Figure 1. Selectivity vs Vacuum Bottoms Yields, UOP/Signal Research Coprocessing of Illinois 6 Coal, + - Vacuum Overhead, ◇ - Vacuum Bottoms.

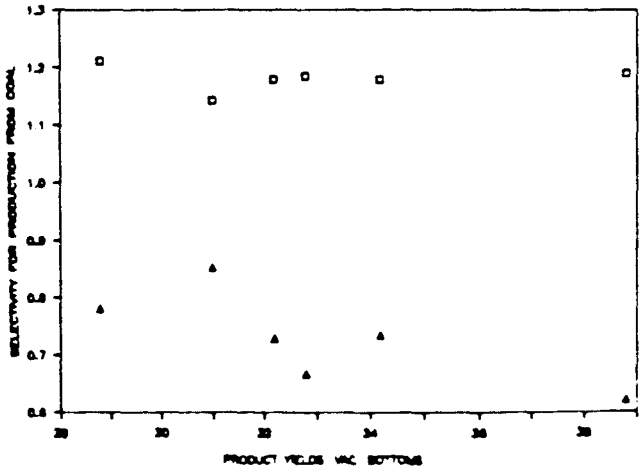

Figure 2. Selectivity vs Vacuum Bottoms Yields, UOP/Signal Research Coprocessing of Wyodak Coal, □ - Vacuum Overhead, △ - Vacuum Bottoms.

APPENDIX 2

SIMILARITIES IN THE STRUCTURAL UNITS OF DIFFERENT COALS

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INTRODUCTION

There is a growing acceptance that the two- or multi-component concept of coal structure offers a more realistic approach than other structural models to reconciling the available information on the composition of coal organic matter with coal behaviour. This proposition has appeared in a number of different forms since the earlier part of this century and has more recently been revised and investigated. Basically, the concept takes into account the presence and influence of the smaller and more mobile molecules in coals (molecular phase). The molecular phase is accommodated within the rigidly cross-linked, three-dimensional macromolecular network, which constitutes the greater proportion of the coal, by weak binding or physical entrapment.

Research has been directed to understanding the composition of the molecular phase, its interaction with the network and the proportion of the coal structure which it occupies (1,2). Similarly, efforts have been made to elucidate the structure of the network in terms of the nature of the basic structural units of which it is composed and the type and distribution of the connecting bonds (3,5).

It is in this context that we present some findings which concern the composition of the species which compose the molecular phase, how they relate to the network components and how both of these are influenced by coal rank. The results indicate that there are underlying structural similarities between the molecular phase and the network, both of individual coals and of different coals.

EXPERIMENTAL

The data presented were obtained by independent research efforts at The Pennsylvania State University (PSU) and at Consol.

PSU Research

The liquefaction of coals has been studied by catalytic hydrogenation of coal impregnated with a sulphided Mo catalyst. As no solvent was employed, the products were necessarily coal-derived. Mild conditions were chosen to minimize the extent of regressive reactions and promote hydrogenation (≤400°C, 7 MPa H_2 (cold) pressure). The experimental details have been fully described elsewhere (6). The oil fractions (hexane-soluble) of chloroform extracts from parent and hydrogenated coals were separated by preparative-scale high performance liquid chromatography (HPLC) into six fractions of different chemical class. The separation procedure is summarized in Table 1. The effectiveness of separation has been confirmed for model compounds. The sample size injected into the column was about 0.03 g oil in 0.5 mL CH_2Cl_2. Fractions were collected and the yields were determined by weighing after solvent removal. The reproducibility of fraction yields was ±5%.

Samples of each fraction were analyzed by gas chromatography to provide information on the distribution of components. Dibenzofuran was used as an internal marker to facilitate comparison. Compound identification was not attempted.

Two bituminous coals and one subbituminous coal from the PSU Coal Sample Bank have been investigated using the procedure described above: PSOC-1266, hvAb; PSOC-1510 hvAb; PSOC-1403, sub)

Consol Research

Since 1978, Consol has been characterizing samples of coal liquids produced in various U.S. process development efforts. By obtaining frequent (often daily) samples from large process-development and pilot units, it has been possible to examine the evolution of the process oil compositions and to assure that they represent authentic coal derived liquids. Techniques used for analytical characterization included distillation, GC/MS, ^{1}H-NMR, phenolic OH, and various liquid chromatographic applications. The results described here are based on characterization of daily samples of the distillate products (b.pt. ca. 200 x 500°C) of three 3TPD PDU runs (Syncrude mode) of the H-Coal process (7,8) made with Illinois 6 (Run 5), Kentucky 11 (Run 9) and Wyodak coals (Run 10), and two ITSL runs of the 3TPD Wilsonville pilot plant (9) made with Illinois 6 (Run 249) and Wyodak coals (Run 247).

RESULTS AND DISCUSSION

PSU Data

For each of the three coals studied, the weight distribution of HPLC fractions of the oil fractions from the parent coals and from the hydrogenated coals were quite similar despite significant differences in yield; for example, the oil yields for the subbituminous coal were 0.6% and 13.0%. This observation is consistent with that reported by Ross, et al. (10), who showed that there was a close similarity in the distribution of SESC fractions in the toluene-soluble products from the liquefaction of a bituminous coal (Illinois 6) over a wide range of conversion (29-60% toluene solubles). Their results suggest that network fragments are liberated by random bond cleavage (11) which, under conditions where regressive reactions are limited, would ensure that the product distribution was independent of conversion.

The HPLC data obtained in this research further indicate that there are similarities between the composition of the molecular phase (represented by the parent coal extract) and the network. This view is further reinforced by a comparison of the chromatograms for each HPLC fraction of the parent and hydrogenated coal pairs (figures not shown because of space restraints). For every HPLC fraction, there was a direct correspondence between the major peaks in the two oil products.

Between coals, and in particular between the bituminous and subbituminous coals, there were differences in the HPLC fraction distributions. As would be anticipated, the oil products from the low-rank coal contained higher proportions of saturates and less condensed aromatic structures. However, a comparison of the chromatograms for the individual HPLC fractions again showed a direct and striking correspondence.

Consol Data

Oils produced by the liquefaction of subbituminous coals contain a larger percentage of saturates than those produced from bituminous coals. However, the other major components are remarkably similar for oils produced from the two coals at similar liquefaction conditions. This can be seen in a comparison of ITSL oils from which the waxes, i.e., saturates (straight chain and branched paraffins and naphthenes) were separated by a conventional ketone dewaxing method. As reported elsewhere (9), the wax contents were 47.4% and 32.7%, respectively, for oils produced from Wyodak and Illinois 6 coals; n-paraffin contents were 12.0% and 3.4%. GC analyses of the dewaxed oils (Figure 1) allowed separation of about 170 major components which were qualitatively identical for the two oils and in very similar relative quantitative abundance. GC/MS showed that these components consist primarily of two- to four-ring aromatics and hydroaromatics and their alkylated homologs. Gas chromatography of the wax fractions (not shown) separated about 160 peaks, which were also essentially identical regardless of the feed coal. To demonstrate that this similarity was not a result of the specific liquefaction conditions used to produce the oils, a comparison was also made of product oils from the three H-Coal runs described above (7,8). GC/MS analyses of these oils allowed characterization of over 200 major components. Except for the enhanced saturates content of the oils produced from subbituminous coals, these again showed essentially identical composition. Since the heteroatoms (N,S,O) are largely removed in the liquefaction process, these data are most germane to a comparison of hydrocarbon structures and may not reflect significant differences in the means by which the structures are held together in the coal matrix.

SUMMARY

The data independently derived in the two laboratories were obtained only for the lower molecular weight products of coal liquefaction. This limitation notwithstanding, it appears that certain molecular structures or building blocks are common to different coals over a range of rank, both in the make-up of the network and the molecular phase. The relative proportions of those components differ, as presumably does the manner in which they are bonded. There must also be changes in component type and distribution between coals of different rank caused by the processes occurring during coalification. Despite these uncertainties, any attempt to model coal structure must take into account these demonstrated similarities in the major structural components, or explain how such similar products can be produced from dissimilar starting materials. In addition, any structural model must account for the significant concentrations of paraffinic moities in coal.

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REFERENCES

1. Given, P. H., et al., Fuel, 65, 155, 1986.
2. Derbyshire, F. J., et al., ACS Fuel Division Preprints, 32, No. 1, 98, 1987.
3. Larsen, J. W., Green, T. K, and Kovac, J., J. Org. Chem., 50, 4729, 1985.
4. Brenner, D., Fuel, 64, 167, 1985.
5. Shinn, J. H., Fuel, 63, 1187, 1984.
6. Stansberry, P. G., et al., J. Energy & Fuels, 1, 89, 1987.

REFERENCES (Continued)

7. Burke, F. P., Winschel, R. A. and Pochapsky, T. C., U.S. DOE Report No. DOE/ET/14503-3, January, 1981.
8. Burke, F. P. and Winschel, R. A., U.S. DOE Report No. DOE/PC/30027-24, July, 1982
9. Winschel, R. A., Robbins, G. A. and Burke, F. P., Fuel, 66, 654, 1987, and references therein.
10. Ross, D. S., et al., Fuel, 64, 1323, 1985.
11. Larsen, J. W., Lehigh University, Bethlehem, PA, USA, Private Communication.

TABLE 1

HPLC FRACTIONATION SCHEME
(Basic Alumina Column)

Fraction No.	Elution Solvent (vol %)	Compound Type
1	Hexane (100)	Saturates and mono-aromatics
2	Hexane/dichloromethane (98/2)	Di-aromatics
3	Hexane/dichloromethane (98/10)	Tri-aromatics
4	Hexane/dichloromethane (74/25)	Polycondensed aromatics
5	Tetrahydrofuran/methanol/dichloromethane (10/2/88)	Polycondensed aromatics, polars
6	Tetrahydrofuran/methanol/dichloromethane (10/2/88) Backflush	Highly polar compounds

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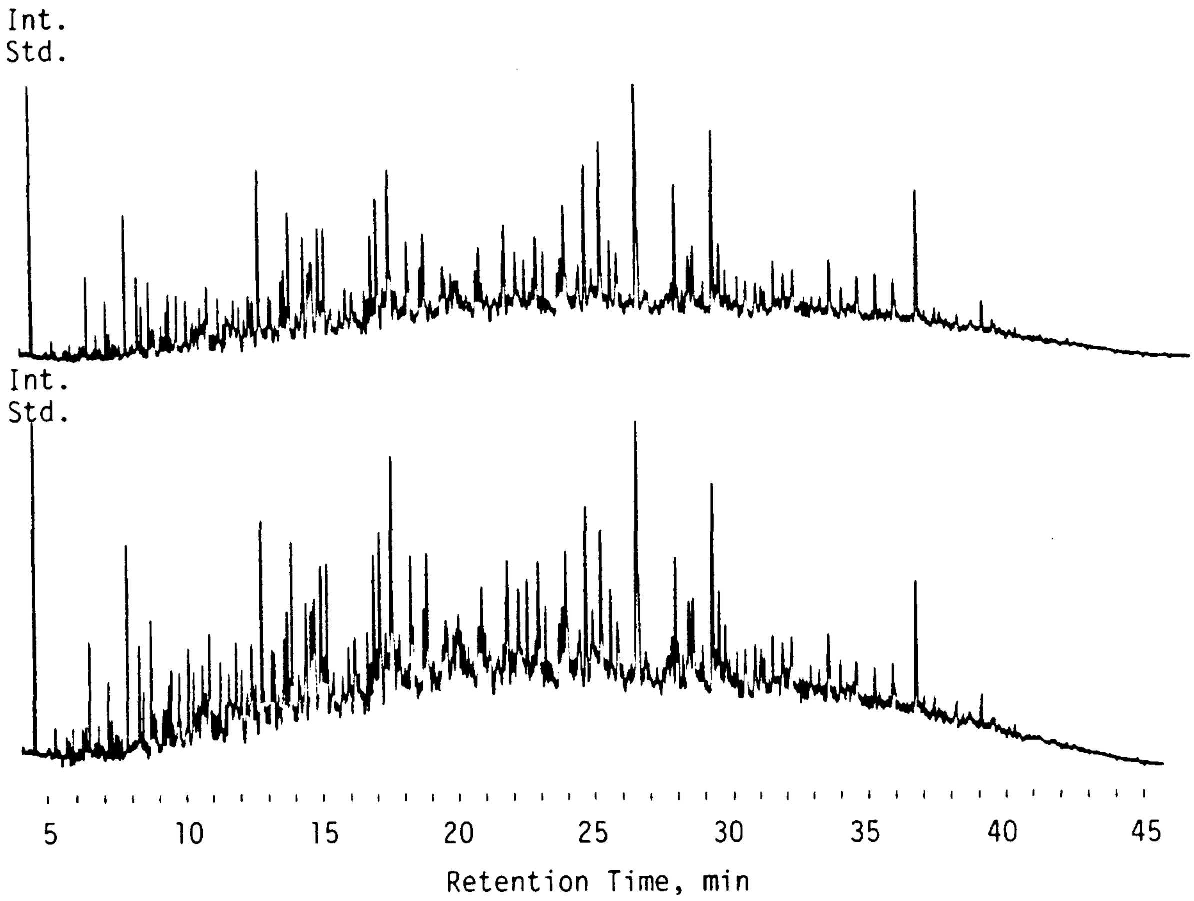

Figure 1. Gas Chromatograms (FID) of Dewaxed Wilsonville ITSL Distillates (<454°C) from Run 249 Using Wyodak Subbituminous Coal (Top) and Run 247 Using Illinois 6 Bituminous Coal (Bottom).