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Coal Liquefaction Process Solvent Characterization and Evaluation

Technical Progress Report, January 1, 1986, Through March 31, 1986

R. A. Winschel
G. A. Robbins
F. P. Burke

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Conoco Inc.
Coal and Chemicals Research and Development
Coal Research Division
4000 Brownsville Road
Library, PA 15129

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

APPENDICES

Section 1

INTRODUCTION

This is the Technical Progress Report for the fifth quarter of activities under Contract No. DE-AC22-84PC70018. It covers the period January 1, 1985, through March 31, 1986.

OVERVIEW

Conoco Coal Research Division 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. In addition, 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.

CONTRACT ACTIVITIES

- A set of one hundred and two process oils from Wilsonville Run 249, made with Clovis Point mine (Wyoming subbituminous) coal in the Reconfigured Integrated Two-Stage Liquefaction (RITSL) mode, with and without ash recycle, was analyzed to provide information on process performance.

- A variety of coal liquefaction process oils were dewaxed by variants of commercial processes in order to improve their quality as donor solvents. This work demonstrated the technical feasibility of such a concept. An invention conception was disclosed to DOE. A paper summarizing this work, accepted for presentation at the 1986 Fall National Meeting of the American Chemical Society in Anaheim, CA, appears in Appendix 3.

- Twenty-five oils were analyzed from Hyrocarbon Research Incorporated's (HRI) Catalytic Two-Stage Liquefaction (CTSL) Run 227-27. This run was made as a demonstration of the process with Clovis Point mine subbituminous coal. Two start-up oils for CTSL Run 227-30 were also tested in the microautoclave for solvent quality.

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

- Nineteen samples of coal and reaction products of coal and potassium/crown ether, supplied by Purdue University, were analyzed by infrared spectroscopy to derive quantitative and qualitative structural information.

Section 2

SUMMARY

This report includes results and interpretations of Conoco's analyses of 102 process-oil samples from Wilsonville Run 249 operated from June through September 1985 in the RITSL mode with Wyodak subbituminous (Clovis Point mine) coal. Analytical results and interpretations are presented for a set of twenty-five process oils from HRI CTSL Run 227-27, a process demonstration run made with the same coal. Ten microautoclave tests were made to "calibrate" the reactivity of the standard coal used in this contract. Infrared spectroscopy was used to obtain structural information of nineteen samples of coal and coal reaction products made by Purdue University. Results of experiments demonstrating the use of dewaxing technology to improve coal liquefaction solvent quality are presented in Appendix 3.

Our results from this work are summarized below.

- Wilsonville Run 249 - RITSL Mode, Subbituminous Coal

  Increasing hydrotreater temperature results in decreasing distillate and resid aromaticity, decreasing resid preasphaltenes and asphaltenes content, decreasing distillate and resid phenolic content, and improved donor solvent quality in the (whole) hydrotreater product. Decreasing aromaticity with increasing temperature indicates that increasing hydrotreater temperatures increased hydrogenation during Run 249. Excluding the ash recycle test, the whole (unfractionated) oils produced at the higher temperatures were not overhydrogenated, but this may result only from the increased resid concentrations that coincide with higher hydrotreater temperatures. There are indications that the distillate oils were overhydrogenated with respect to donor solvent quality. At a hydrotreater temperature of 700°F near the end of Run 249, the hydrotreater product oil properties indicated less hydrogenation than was achieved at 660°F at the beginning of the run. This appears to be an indication of catalyst deactivation toward hydrogenation and deoxygenation.

During the ash recycle test, all the process oils contained 2-4 wt % more THF-soluble resid (IOM- and ash-free basis) and the resid contained more preasphaltenes and asphaltenes than during comparable periods with CSD operation. During ash recycle, the oils were lower in aromaticity and in cyclic/alkyl ratio and higher in paraffinicity. The hydrogenated oils (V-131B, V-1067) were lower in donor solvent quality. This suggests that the distillate oils during this test were overhydrogenated with respect to donor solvent quality. High hydrogenation during ash recycle may have resulted from the catalytic effect of mineral matter and/or the longer residence time of resid components. Resid phenolic contents increased during the ash recycle test, presumably because of the increased preasphaltenes and asphaltenes contents resulting from removal of the CSD.

Catalyst activity for resid conversion (as measured by the calculated first-order kinetic pre-exponential factor) decreased in Run 249 over the entire run from catalyst ages of 617 to 1870 lbs resid/lb catalyst, presumably from catalyst deactivation. The activity was somewhat higher during the ash recycle test than during normal CSD deashing, perhaps indicating mineral catalysis. Resid conversion activity in Run 249 was higher than in earlier bituminous coal runs, but was lower than in subbituminous coal Run 246 which used fresh catalyst.

In the RITSL mode, coal not converted in the dissolver could potentially be converted in the hydrotreater. However, our data show average coal conversions (to THF solubles) after the dissolver and after the hydrotreater were 87.1 ±4.2% and 89.0 ±4.2%, respectively. The average improvement in coal conversion across the hydrotreater, 1.9 ±2.2%, is not statistically significant.

The addition of iron oxide (disposable catalyst) appears to improve hydrogenation and resid quality in the first stage, in addition to increasing coal conversion. This is evident in lower distillate and resid aromaticity and lower resid preasphaltenes and asphaltenes in the first stage product oils when iron oxide is added.

The addition of water may have limited hydrogen transfer in the first stage. When water was added, the first stage product oils showed somewhat greater aromaticity, higher preasphaltenes and asphaltenes in the resid, and higher distillate and resid phenolic content. These results are consistent with Catalytic's findings that hydrogen utilization was low during this period, even though coal conversion was higher.

The Critical Solvent Deasher (CSD) selectively rejected preasphaltenes and (to a lesser extent) asphaltenes in addition to insoluble organic matter (IOM) and ash from the hydrotreated resid processed in the RITSL configuration.

Hydrotreated resid improved the solvent quality (as measured by microautoclave tests) of hydrotreated distillate from Run 249. When unhydrogenated resid is added to unhydrogenated distillate, the solvent quality is sometimes worse and sometimes better, but on the average it is unchanged.

Donor solvent quality of distillate oils was lower in Run 249 than in Run 246 and the bituminous coal runs. The higher catalyst age and hydrotreater space velocity in Run 249 may have been factors, but it appears likely that the distillate oils became over-hydrogenated from the high hydrotreater temperatures used in Run 249. Distillate and resid aromaticities and phenolic contents were very similar to those in bituminous coal runs and were different from the Run 246 values. This indicates that the aromaticity and phenolic contents of process oils are determined primarily by hydrotreater temperature, since in Run 249 the hydrotreater temperature was similar to that used with bituminous coals and higher than in Run 246. Distillate cyclic/alkyl ratios and the resid and preasphaltenes content of the process oils were generally equivalent to Run 246 values, but considerably different from the bituminous coal runs. These parameters clearly reflect the difference between subbituminous and bituminous coals.

With the sample set obtained from Catalytic, it is not possible to determine the effects of dimethyl disulfide (DMDS) addition or the effects of forced first-stage reactor backmixing on oil properties or process performance.

- <u>HRI CTSL Run 227-27</u>

Over the length of the twenty-one day process demonstration run, CTSL Run 227-27, the pressure-filter liquid (PFL) and first-stage inventory oils increased in 850°F$^+$ resid content. The resids became more aromatic and more phenolic and increased in preasphaltenes content. The 850°F$^-$ distillates became more aromatic and phenolic. The donor solvent quality (by microautoclave) of the PFL oils generally increased over the length of the run. These changes in process-oil characteristics all appear to be related, directly or indirectly, to catalyst age. Hydrogenation, cracking and deoxygenation activities are all reduced with time. The effects of the other variables tested on oil properties are much smaller. The resid content of the PFL oils decreased in response to two 5°F increases in second-stage temperature. There is no apparent effect of coal drying method on oil characteristics.

The PFL (second-stage) samples contain less resid and have lower concentrations of phenolics than the first-stage oils, reflecting the additional upgrading afforded by the second-stage reaction. The greater aromaticity of the PFL samples, as compared to the corresponding first-stage oils, is consistent with a lower hydrogen content resulting from the higher reactor temperature in the second stage.

Oils from Run 227-25 are higher quality (in terms of resid and preasphaltenes content, aromaticity and phenolic concentration) than those produced at ostensibly similar operating conditions in Runs 227-26 and 227-27. The cause of this difference is not apparent, but it may relate to the poorer than anticipated performance of the two demonstrations runs (227-26 and 227-27). The characteristics of the oils from the two demonstration runs are very similar, particularly at the ends of the runs at which point the second-stage temperatures were the same.

Microautoclave tests of two potential start-up oils for Run 227-30 show no difference between the two.

- The standard coal used in this contract for microautoclave work shows no statistically significant deterioration in extractability relative to the beginning of the contract.

- Fourier transform infrared (FTIR) spectroscopic analysis was performed on nineteen Purdue University samples from potassium-crown ether reactions with Wyodak and Illinois 6 coals. The concentrations of OH groups in the samples were determined by a literature method and are reported. Approximate relative concentrations of carbonyl groups and aliphatic hydrogen groups are also provided. Infrared spectra of all samples are included in this report. The OH concentrations in the samples were determined to be ca. 2 to 3 wt % O as phenolic OH, ca. 1 to 2 wt % O as alcoholic OH, and 3.5 to 5.7 wt % O as total OH.

  Wyodak coal had ca. 1 wt % more O as phenolic OH and ca. 1 wt % more O as alcoholic OH than Illinois 6 coal. Wyodak coal also apparently contains more carbonyl groups than Illinois 6 coal.

Illinois 6 reaction products contained more total hydroxyl than the parent coal, whereas Wyodak reaction products contained less hydroxyl than the parent coal.

The presence of a significant carbonyl peak in all of the reaction product spectra indicates either a valid chemical change which produces carbonyl during the course of the potassium-crown ether reaction or contamination or some other artifact resulting from the work-up procedure. In either case, a better understanding of the chemistry involved is desirable.

An apparent increase in carbonyl content in methylated samples also indicates carbonyl formation during methylation or contamination or carbonyl formation during the sample work-up procedure. FTIR evidence for carbonyl formation during methylation has been presented in the literature.

Two samples contained an unidentified contaminant as indicated by a strong sharp peak at 2094 cm^{-1}.

Section 3
DISCUSSION

WILSONVILLE RUN 249

Process Description

Wilsonville Run 249 was operated from 6/1/85 through 9/18/85 with Upper Wyodak seam subbituminous (Clovis Point mine) coal. An analysis of the feed coal is given in Table 1. A complete description of Run 249 is given elsewhere.(1,2,3) Run 249 was operated in the Reconfigured Integrated Two-Stage Liquefaction (RITSL, Figure 1) mode. The general objectives of Run 249 included: to improve yields with subbituminous coal (relative to Run 246), to compare operation with forced dissolver backmixing with normal dissolver operation, to determine the effect of alternate deashing (ash recycle), and to determine the effects of iron oxide, dimethyl disulfide, and water addition to the first stage.

In the RITSL mode, coal is slurried with a mixture of hydrotreater flashed bottoms and deashed hydrotreater resid. The pasting solvent stream is called V-131B. The slurry is mixed with hydrogen and passed through preheater and dissolver. This is the first stage, referred to as the Thermal Liquefaction Unit (TLU). 100% of the dissolver volume was used in Run 249. The dissolver was backmixed by an added pump, except during an outage on July 10-13 and during a planned test on September 16-18. After gases are flashed, the first-stage product is distilled to remove a light oil net product and to produce a heavy distillate (V-178) and a resid. The heavy distillate and resid are re-blended in V-1064 to make the feed to the ebullated-bed H-Oil hydrotreater (HTR) unit. The catalyst used in Run 249 was 1/32" extrudate Shell 324M (Ni/Mo on alumina). Gases and a net light oil product are flashed from the hydrotreater products. The remaining stream is the hydrotreater flashed bottoms product (V-1067). This material is then separated into a distillate and a resid. The distillate (V-1072) is recycled to V-131B as a portion of the pasting solvent and the resid is deashed in the Kerr-McGee Critical Solvent Deashing (CSD) unit which rejects an ash concentrate and produces a deashed resid product. The deashed resid is recycled to V-131B as the second component of the pasting solvent. During the alternate deashing test, the CSD unit was bypassed as described below.

During normal RITSL operations, ashy resid (vacuum tower bottoms) is fed to the CSD unit. To begin the alternate deashing test on August 26, the CSD unit was bypassed and a portion of the ashy resid was recycled to the first stage. The remainder was removed from the system. To increase the ash concentration to the desired level to start the test, ash concentrate was added to the first stage feed until the hydrotreater resid product (i.e., the recycled material) contained 50% cresol insolubles. At this point (September 3), addition of ash concentrate was discontinued and the process flows were adjusted so that the ash rejected was equal to the ash fed in the coal for the remainder of Run 249. The rejected ashy resid was fed to the CSD unit off-line to product deashed resid for future use.

Run 249 began on June 1, 1985, without the addition of disposable catalyst to determine if acceptable coal conversion could be achieved. Since coal conversion was low (about 82%), addition of about 1.5 wt % MF Kerr-McGee porous Fe_2O_3 and about 0.9 wt % MF dimethyl disulfide (DMDS) to the first stage began on June 4. Iron oxide addition was stopped on July 13 and resumed on July 18 for the remainder of the run. Catalytic, Inc., reported a drop in coal conversion during that period. On July 3, dimethyl disulfide addition to the first stage was stopped, and dimethyl disulfide addition to the hydrotreater began. The addition of DMDS to the first stage was stopped because the coal could potentially supply the necessary sulfur to form the catalytic iron sulfide species. However, DMDS was added to the hydrotreater to ensure that the hydrotreater catalyst sulfur level was not reduced.

Since no adverse effects were noted, the remainder of Run 249 was made with dimethyl disulfide addition only to the hydrotreater.

Water was added to the first stage during two periods. Water addition (10% MF) began June 20 and stopped on June 21, and resumed (15% MF) on July 5 and stopped on August 3.

The dissolver outlet temperature began at 790°F and was increased to 810°F on June 21 to increase coal conversion. On July 19, it was lowered to 800°F to reduce the gas made and on August 9 it was raised back to 810°F to increase coal conversion.

The hydrotreater temperature began at 670°F and was lowered in 10-30°F steps to 615°F through July 11 to reduce resid conversion. It was then increased in 20-30°F steps to 700°F by July 28 to increase resid conversion. From July 28 to the end of Run 249, the hydrotreater temperature remained at 700°F.

Operating conditions for those periods of Run 249 from which we received samples are given in Table 2. Operating conditions and yield structures for portions of Run 249 are given in Table 3.

The start-up solvent for Run 249 was made in Run 248, which used Illinois 6 bituminous coal (Burning Star mine) in the ITSL/DITSL modes. The initial catalyst charge was 432 lbs of aged Shell 324M from Run 246. This charge had an initial catalyst age of 617 lbs resid/lb catalyst and it aged to 1870 lb resid/lb catalyst by the end of Run 249. Hydrotreater space velocity (WHSV) ranged from 0.78 to 2.07 lb feed/hr/lb cat, but was typically 1.1-1.3 lb feed/hr/lb cat for the majority of the run and about 1.6 lb feed/hr/lb cat during the alternate deashing test.

Over the course of Run 249 the major operating variables were dissolver and hydrotreater temperature, catalyst age, deashing mode, and the presence or absence of Fe_2O_3, dimethyl disulfide, and water in the first stage.

Sample Description

The set of Wilsonville Run 249 samples we received, most contained in 1-quart or 1-pint metal cans or glass jars, included:

- 26 samples of V-131B (pasting solvent for first stage)
- 24 samples of V-1064 (second-stage (hydrotreater) feed)
- 24 samples of V-1067 (second-stage (hydrotreater) flashed bottoms product)
- 24 samples of V-178 (heavy distillate product from first stage; distillate portion of second-stage feed)
- 4 samples of V-1072 (distillate portion of second stage (hydrotreater) flash bottoms product)

Sample withdrawal dates ranged from 6/4/85 - 9/14/85. To conserve effort, we did not analyze all the V-178 samples. These were considered the least informative of the samples we received.

Effect of Hydrotreater Temperature and Catalyst Age on Oil Characteristics

Hydrotreater temperature began at 670°F on 6/4 and was lowered in steps every few days to 616°F on 7/9. It was increased to 700°F by 7/28 and remained at 700°F until the end of the run. The only major temperature variance from the above description occurred on 6/10 and 6/11 when an ebullating pump outage disrupted hydrotreater operation.(1)

Data from 6/4 will not be included in this discussion because those samples represent operation without iron oxide/DMDS addition to the first stage. Average values of various measured properties of the hydrotreater feed (V-1064) and flashed bottoms product (V-1067) are summarized in the table below as a function of temperature. Complete data are given in the tables of this report.

RUN 249 HYDROTREATER CONDITIONS AND AVERAGE OIL PROPERTIES

Date, 1985	6/6	6/14-6/20	6/24-6/25	7/9	7/11-7/18	7/22-7/26	7/28-8/22*
Hydrotreater Conditions							
Temp., °F	660	640	625	616	640	660	700
Cat. Age, lb Resid/lb Cat.	659	693-752	791-800	913	934-1006	1049-1094	1119-1407
V-1067 Distillate Properties							
% Aromaticity	9.5	10.7	13.9	16.9	16.9	15.6	11.3
Phenolic Concentration, meq/g	0.16	0.30	0.46	0.55	0.48	0.35	0.14
Microautoclave Conversion, wt % MAF	79.0	75.9	76.1	75.3	76.1	77.2	77.9
V-1067 Resid Properties							
% Aromaticity	17.7	18.3	23.8	28.8	29.6	25.4	21.4
Phenolic Concentration, meq/g	0.45	0.65	0.82	0.97	0.88	0.76	0.43
Preasphaltenes Content, wt %	1.7	3.3	5.1	10.2	10.1	7.6	4.3
V-1067 Whole Oil Properties							
% Soluble Resid	27.8	28.8	32.7	29.0	33.2	35.3	37.6
Microautoclave Conversion, wt % MAF	90.1	87.2	87.3	83.1	80.1	85.3	85.4
V-1064 Distillate Properties							
% Aromaticity	16.5	15.0	17.4	20.2	20.6	20.6	18.5
Phenolic Concentration, meq/g	0.67	0.66	0.82	0.88	0.87	0.92	0.89
Microautoclave Conversion, wt % MAF	61.6	61.6	61.2	59.2	58.0	60.9	59.2
V-1064 Resid Properties							
% Aromaticity	30.0	27.4	33.5	39.0	42.1	38.2	34.3
Phenolic Concentration, meq/g	0.99	1.08	1.15	1.24	1.20	1.21	1.02
Preasphaltenes Content, wt %	10.5	10.5	10.4	14.7	14.6	13.5	10.5
V-1064 Whole Oil Properties							
% Soluble Resid	38.8	33.7	35.7	31.8	34.6	38.5	41.0
Microautoclave Conversion,	71.4	69.1	62.2	59.6	54.3	59.1	63.2

*Excludes ash recycle test.

As the hydrotreater temperature decreased from 670°F to 616°F and then increased again to 700°F several changes occurred: aromaticities and phenolic concentrations of the V-1067 distillate and resid samples increased and then decreased, the preasphaltenes contents of the V-1067 resid increased and then decreased, and the microautoclave conversion (whole samples only) decreased and then increased. The V-1064 (hydrotreater feed) distillate and resid samples generally showed similar (though smaller) trends. Because the Wilsonville plant is an integrated recycle system, this is to be expected. Most of the observed characteristics (aromaticity, etc.) reached a turnaround point during the 616°F hydrotreater temperature period or the following 640°F period. Resid concentration generally increases with hydrotreater temperature. At first glance, this appears the reverse of the expected trend. However, it should be recognized that at the Wilsonville plant, hydrotreater temperature is increased to remove resid by conversion. Therefore, it is increased as resid concentration increases.

Though other operating condition changes may have played some role in this comparison, hydrotreater temperature is clearly the dominating factor. Aromaticity, phenolic concentration, and resid preasphaltenes content have been found in several previous Wilsonville TSL runs to decrease with increasing hydrotreater temperature. Hydrotreater temperature clearly played the major role in the trends observed here. In fact, the correlation between hydrotreater product phenolic content and hydrotreater temperature is much more evident in Run 249 than in any of the previous runs. It is clear that high hydrotreater temperatures (660°F) are required to effectively reduce phenolic contents to low levels (below 0.2 meq/g). The effect of decreasing distillate and resid aromaticity with increasing hydrotreater temperature indicates that hydrogenation of distillate and resid is not equilibrium-controlled. The correlation of donor solvent quality (whole samples only) with hydrotreater temperature (and thus with lower aromaticity) indicates that the increased hydrogenation at higher temperature increased the content of donor molecules in the whole solvent. This indicates that the whole solvents produced at the higher temperatures during Run 249 were not overhydrogenated. Note, however, that the oils produced at higher hydrotreater temperatures contained higher concentrations of resid. Since it is known that hydrotreated resid is an excellent donor, as discussed later, the improvement in solvent quality with hydrotreater temperature may only reflect the increased resid content and does not indicate that the fractions (distillate and resid) are not overhydrogenated. The solvent quality of the distillates changes little with hydrotreater temperature and thus overhydrogenation cannot be ruled out for them. The high microautoclave coal conversion observed for the V-131B and V-1067 distillates through about 6/10/85 appears to result from the continued presence of start-up oil (bituminous coal derived). This is suggested by the relatively low levels of paraffinic protons (alkyl β) in relation to aromaticity.

The effect of catalyst deactivation is also evident in the data in the above table. Note that at the hydrotreater temperature of 700°F (7/28-8/22) near the end of the run, not all of the oil properties had approached the values obtained with a hydrotreater temperature of 660°F (6/6) at the beginning. These results suggest that near the end of the run, hydrotreater temperatures of 700°F or greater would be necessary to obtain levels of oil properties that were obtained earlier at 660°F. This deactivation effect is apparent in the % resid, aromaticity, phenolic concentration, and microautoclave results. This suggests that hydrogenation and deoxygenation were affected by catalyst aging.

The conversion of benzene insolubles (Table 24, discussed in a later section) roughly follows hydrotreater temperature, with high benzene insolubles conversion at high temperature. It appears that benzene insolubles conversion may also show a deactivation effect with catalyst age.

Effect of Alternate Deashing (Ash Recycle)

Catalytic reported a very successful outcome from the ash recycle test, achieving the highest coal conversion (94%) obtained at Wilsonville with subbituminous coal.(3) Ash recycle was found to increase C_4 + distillate yields by 6% in the first stage and by 1% overall. The effect of ash recycle on oil properties will be examined by comparing data from 8/22 (CSD deashing) with data from 9/8 and 9/14 (ash recycle). Data from 8/28 will not be considered as part of the ash recycle test since it was a transient period to allow ash to build up to the desired test level. The table below summarizes the compositions of oils produced on 8/22 with those from the ash recycle period.

CHANGES IN OIL COMPOSITION DURING ASH RECYCLE

	Components of Whole Oil				Components of THF-Soluble Resid	
Date, 1985	wt % THF Sol. Resid	wt % IOM	wt % Ash	wt % THF Sol. Resid (IOM- and Ash-Free)	wt % Asph.	wt % Preasph.
V-131B						
8/22	34.2	0.2	0.1	34.7	15.4	1.4
9/8, 9/14*	28.0	8.8	15.5	37.6	25.0	8.0
V-1064						
8/22	37.3	4.5	4.7	41.2	23.5	8.9
9/8, 9/14*	32.4	9.2	15.7	43.4	26.1	12.4
V-1067						
8/22	34.3	6.2	4.5	38.9	17.7	6.2
9/8, 9/14*	32.4	9.5	17.2	43.0	27.4	6.8

*Ash recycle test.

During ash recycle, the IOM and ash levels in all the oils were around 9% and 16%, respectively. On 8/22 the IOM and ash levels were each about 5% in the V-1064 and V-1067 samples, and were 0.2% or less in the V-131B sample. On an IOM- and ash-free basis, however, the THF-soluble resid contents of these oils were only 2 to 4 wt % higher during ash recycle than during CSD operation on 8/22. THF-soluble resid contents (IOM- and ash-free) were 37.6 to 43.4 wt % during the ash recycle test. The THF-soluble resids produced during the ash recycle test also contained less oils and more asphaltenes and preasphaltenes than the corresponding 8/22 resids. This is consistent with the observation that the CSD selectively removes preasphaltenes and perhaps asphaltenes, as discussed later. Other oil properties from 8/22 and the ash recycle test are compared below.

CHANGES IN OIL PROPERTIES DURING ASH RECYCLE

	Aromaticity, %		Cyclic/ Alkyl Ratio	Phenolic Concentration, meq/g		Microautoclave Conversion, % MAF	
Date, 1985	Dist.	Resid	Dist.	Dist.	Resid	Dist.	Whole
V-131B							
8/22	11.0	21.6	0.64	0.13	0.52	77.7	87.0
9/8, 9/14*	9.9	20.1	0.60	0.14	0.62	72.7	80.9
V-1064							
8/22	17.3	33.9	0.57	0.82	0.97	58.3	66.6
9/8, 9/14*	14.2	29.4	0.53	0.76	1.09	62.1	64.5**
V-1067							
8/22	10.7	21.9	0.60	0.13	0.42	76.3	85.8
9/8, 9/14*	9.6	19.9	0.58	0.14	0.62	72.0	79.8

*Ash recycle test.
**Omitting the low value of 44.7% on 9/14.

The data show that the aromaticity of the distillates and resids were lower during ash recycle, indicating that those oils were more hydrogenated than oils produced on 8/22. This is in agreement with data of Catalytic, Inc., showing high hydrogen consumption during ash recycle.(3) Higher hydrogenation might result from the catalytic effect of mineral matter and/or from the longer residence time of resid components as a result of their recycle. The distillate cyclic/alkyl ratio was also lower during ash recycle, indicating that these oils contain fewer hydrogen donor species. This is evident in the microautoclave results for the hydrogenated oils (V-131B, V-1067) which are about 4 to 6 % lower during ash recycle than on 8/22. This would indicate that the distillate oils may have been overhydrogenated with respect to donor solvent quality. The lower microautoclave solvent quality measured for the whole samples from the ash recycle test probably contains contributions from the lower solvent quality of the distillate portions and the increased solids content of the solvents (which reduces the proportion of liquid present during the microautoclave test). The distillates of the hydrogenated oils (V-131B and V-1067) made during ash recycle were extremely paraffinic. This is apparent from the high proportion of alkyl β protons (Tables 15 and 17). These oils formed large quantities of precipitated paraffin wax upon standing. Gas chromatography showed that the V-1067 distillate of 9/14 contained 6.2% n-paraffins plus additional branched paraffins (see Appendix 3). The hydrotreater feed oils (V-1064) produced during ash recycle appear to be comparable in donor solvent quality to those produced on 8/22.

The phenolic OH contents of the distillate oils were the same (V-131B and V-1067) or perhaps somewhat lower (V-1064) during ash recycle compared to 8/22. However, the phenolic contents of the resids were all somewhat higher during ash recycle than on 8/22. This appears to be a result of bypassing the CSD, thus increasing the concentration of preasphaltenes and asphaltenes which contain relatively high concentrations of phenols.

Hydrotreater Resid Conversion

Conoco analyzed samples of both hydrotreater feed (V-1064) and flashed bottoms product (V-1067) samples from nineteen common periods of Run 249. Hydrotreater resid (850°F$^+$) conversions and first-order kinetic rate constants calculated from the analyses are presented in Table 24. The calculation method is given in Appendix 1. 850°F$^+$ resid conversions for those nineteen periods average 18.4 ±6.6%. Catalytic, Inc. reported(1) resid conversions for the same periods averaging 20.8 ±4.9%. The lower Conoco value arises primarily from the use of a different distillation end-point to define resid, as discussed earlier.(4)

Calculated first-order kinetic pre-exponential factors are plotted vs catalyst age in Figure 2 and are tabulated in Table 24. The calculation method is given in Appendix 1 and assumes an energy of activation of

23.5 kcal/mol. The plot shows a decreasing trend with catalyst age, presumably the result of catalyst deactivation with respect to resid conversion. It is also apparent that the resid conversion activity was higher during ash recycle as shown by the last three points on the plot, perhaps indicating catalysis by mineral matter.

Average values for hydrotreater conversions and kinetic constants are shown below for Wilsonville Runs 246 and 249, along with general run conditions.

Run No.	246(5)	249
Mode	ITSL/DITSL	RITSL
Cat. Age, lbs resid/lb cat	0-617	617-1870
WHSV, lbs resid/lb cat/hr	0.7-1.0	ca. 1.2
HTR Temp., °F	605-645	615-700
Resid Conversion, %	14.3 ± 6.7	18.4 ± 6.6
A, pre-exponential factor, 10 lbs resid/lb cat/hr	21.2 ± 9.5	16.0 ± 6.5

The resid conversions during Run 249 averaged 18.4%, slightly higher than the conversions of about 14% for Run 246. Catalytic, Inc., also reported that resid conversions were higher in Run 249 than in Run 246 (28% vs 17%).(3) This is surely the result of the higher hydrotreater temperature employed in the later run. The resid conversion activity (pre-exponential factor), however, is lower than in Run 246. The lower activity for Run 249 relative to Run 246 is caused by the greater catalyst age in Run 249. Note that (except for 6/4) the initial activities in Run 249 (through 7/9, Table 24) are as high as the average for Run 246.

Even though resid conversion activities were lower in Run 249 than in Run 246, they were still greater than activities observed in earlier bituminous coal runs (Runs 242(4), 247(6), and 248(7)).

Based on the data in Table 24 from days 7/9 through 7/29, during which the hydrotreater temperature increased from 616 to 700°F, an activation energy of 14.5 kcal/mol was calculated (Appendix 1). It was assumed in this calculation that no catalyst deactivation occurred during this period from 913 to 1131 lb resid/lb cat. This activation energy is quite low compared to Conoco's values of 28.8 kcal/mol for Runs 246 and to the value of 24.7 kcal/mol reported by Catalytic, Inc. for Run 249.(1)

Data for the conversion of benzene insolubles (BI) are shown in Table 24 using Conoco data and the calculation method given in Appendix 1. There was some indication of a decrease in BI conversion with catalyst age. The days which had the highest BI conversions (6/4, 7/29, 8/10, 8/18, Table 24) also had high resid content (as a process variable) and relatively high hydrotreater temperature (660°F or greater). The extremely low value of 5.6 on 8/22 may result from a system lag. The resid content of the process recycle solvent was reduced on that date.(1) Note also that Conoco's calculation shows a low (two stage) coal conversion (Table 23) on that date, based on the hydrotreater product composition. The hydrotreater product sample taken on that date may be more representative of the earlier, high resid period. This would result in a low calculated value.

Coal Conversion in HTR Not Statistically Significant

In the RITSL mode, the coal not converted in the first stage has the opportunity of being converted in the hydrotreater. In normal ITSL, this is not possible because the unconverted coal or insoluble organic matter (IOM) is removed between stages. This is one of several ways that the RITSL mode can be advantageous for overall process yields when compared to ITSL. To examine this topic, we calculated coal conversions both upstream and downstream of the hydrotreater.

Conversions of coal to THF solubles were calculated based on our analyses of hydrotreater feed (V-1064, Table 5) and hydrotreater flashed bottoms product (V-1067, Table 6) samples. The calculations are based on the following assumptions: 1) there is a perfect ash balance, and 2) the quantity of solids in the recycle oil is negligible. With these assumptions in mind, conversion is calculated as

$$\text{Coal Conversion} = 1 - \frac{\text{Ash In}}{\text{MAF Coal In}} \times \frac{\text{\% IOM In Sample}}{\text{\% Ash In Sample}}$$

where

$$\text{Ash in} = \text{MF Fe}_2\text{O}_3 \text{ Feed Rate} + \left(\frac{\text{wt \% MF Coal Ash}}{100}\right) \times \text{MF Coal Feed Rate}$$

and

$$\text{MAF Coal in} = \text{MF Coal Feed Rate} \times \left(1 - \frac{\text{wt \% MF Coal Ash}}{100}\right)$$

with data for Fe_2O_3 feed rate, coal feed rate, and wt % coal ash from Catalytic, Inc.(1)

Results shown in Table 23 agree well with the average conversions to cresol solubles reported by Catalytic, Inc.(1) Conversions were 87.1 ± 4.2% MAF for the hydrotreater feed samples and 89.0 ± 4.2% MAF for the flashed bottoms product samples. The average difference in conversion across the hydrotreater, i.e., the additional coal conversion afforded by the hydrotreater is 1.9 ± 2.2% MAF, which is not a statistically significant difference.

Note that the two lowest first-stage coal conversions (below 80%) occurred on 6/4 and 7/18. These were both days on which the addition of Fe_2O_3 to the first stage began and are more representative of those periods without Fe_2O_3 addition. These results are consistent with those of Catalytic, Inc., that iron oxide generally increased coal conversion by about 4%.(1)

We obtained samples from only one other day, 7/16, in which Fe_2O_3 was not used. Calculated coal conversion for that day was 90.5%; again this is consistent with the value reported by Catalytic, Inc.(1) The high conversion on that day is the apparent result of a system lag. Fe_2O_3

addition was stopped late on 7/15, but reduced coal conversion was not measured until 7/17.(1)

Dissolver Conditions Significantly Affect Coal Conversion

Coal conversion during Run 249 ranged from about 82 to 93% MAF (76 to 91% MAF in first stage) for the periods shown in Table 23. The table below and the following discussion indicate the effects of iron oxide addition, water addition and dissolver temperature on coal conversion.

EFFECT OF DISSOLVER CONDITIONS ON COAL CONVERSION

Dates	Fe_2O_3 Addition	H_2O Addition	Target Dissolver Temp., °F	% MAF Coal Conversion	
				First Stage	Two Stages
6/4, 7/18	No	No/Yes	790/810	78.2 ± 2.6	82.0 ± 0.4
6/6-6/18	Yes	No	790	85.2 ± 1.5	86.1 ± 0.7
6/25	Yes	No	810	89.2	91.2
7/9-7/29*	Yes	Yes	810/800	90.5 ± 0.9	93.0 ± 0.5
8/5	Yes	No	800	88.6	92.0
8/10 - 8/22	Yes	No	810	89.5 ± 0.5	91.5 ± 1.1**

*Excludes low values on 7/18 due to absence of Fe_2O_3.

**Excludes low value of 84.5% on 8/22.

The MAF coal conversion increased by 7 and 4%, respectively, in the first stage and both stages when iron oxide was added (compare 6/4 and 7/18 with 6/6-6/18). A comparison of values from 6/6-6/18 with those from 6/25 shows that a 20°F increase in dissolver temperature resulted in an increase in coal conversion of 4 to 5%. A smaller temperature increase of 10°F (8/5 compared with 8/10-8/22) resulted in about a 1% increase in coal conversion. By comparing the values from 7/9-7/29 with the values from 6/25 and with the values from 8/5, it can be seen that water addition resulted in a 1 to 2% increase in coal conversion. Thus, the highest coal conversions (not including the ash recycle period) were obtained with iron oxide and water addition and a dissolver temperature of 800 to 810°F. These results are in agreement with those reported by Catalytic, Inc.(1)

Effect of Fe_2O_3 Addition on Oil Characteristics

Samples received by Conoco did not permit an unambiguous evaluation of the effect of Fe_2O_3 addition during the test in July (7/16, 7/18). Data comparisons potentially useful for this purpose were complicated by other changes in operating conditions. Run 249 began without iron oxide addition. Iron oxide addition started on 6/4 at 17:00 to increase coal conversion. Therefore, the 6/4 samples should largely represent the process oils produced without iron oxide addition. These will be compared with samples from 6/6, after two days of operation with iron oxide addition. Because the hydrotreater conditions changed somewhat (from 670°F and WHSV = 1.22 on 6/4 to 659°F and WHSV = 0.89 on 6/6), this discussion will focus on V-1064 (first stage product) samples relative to V-131B (first stage feed) samples. Net (two-stage) product differences between the two days likely resulted from changes in conditions in both stages and may not be assignable to one particular change.

The following table illustrates several trends in oil properties which are discussed below.

Date	THF-Sol. Resid Content wt %	THF-Soluble Resid Fractions, wt % Oils	Asphaltenes	Preasphaltenes	Distillate Aromaticity	Resid Aromaticity
V-131B						
6/4	33.4	75.1	24.6	0.3	10.8	20.9
6/6	30.3	79.0	18.8	2.2	10.7	20.4
V-1064						
6/4	37.3	56.7	29.2	14.1	17.9	38.6
6/6	38.8	64.7	24.8	10.5	16.5	30.0

Although the THF-soluble resid content of the first stage feed (V-131B) was lower by 3 wt % on 6/6 (relative to 6/4), the resid content of the first stage product (V-1064) was higher by 1.5 wt %. This combined with a higher IOM + ash content in that sample (Table 5) to give a first stage product (V-1064) with 3.8 wt % less 850°F$^-$ distillate during Fe_2O_3 addition, even though the first stage feed (V-131B) contained 3.8 wt % more distillate (Tables 4 and 5). It is not clear if higher resid content and lower distillate content is truly representative of Fe_2O_3 addition. Catalytic reported an increase in MAF coal conversion from 81% on 6/4 to 85% on 6/6.(1) The higher coal conversion may have resulted in the increased resid content in the first stage products. The first stage feed (V-131B) resid on 6/6 was 4 wt % higher in oils, 6 wt % lower in asphaltenes and 2 wt % higher in preasphaltenes than the corresponding feed resid on 6/4. The 6/6 first-stage product (V-1064) resid was 8 wt % higher in oils, 4 wt % lower in asphaltenes and 4 wt % lower in preasphaltenes than the 6/4 first-stage product resid. Thus, iron oxide addition appears to result in higher oils and lower preasphaltenes in resid produced in the first stage. Proton distributions of first-stage feed (V-131B) whole, distillate, and residual oils are virtually identical for both days (Tables 10, 15 and 18). Proton distributions of first-stage product (V-1064) whole, distillate, and residual oils and V-178 oils show that oils produced on 6/6 were less aromatic (Tables 11, 16, 19 and 13). Thus, even though the first-stage feed oils were equivalent, the first-stage product oils were more hydrogenated when iron oxide was added. These results show that iron oxide addition resulted in greater hydrogenation in the first stage and consequently improved resid quality.

The effect of DMDS addition to the first stage could not be assessed because the initial omission of DMDS from the first stage occurred in conjunction with the beginning of water addition in the samples Conoco received. Also, we received no samples from the backmixing test to allow us to determine the effects of backmixing.

Effect of H_2O Addition on Oil Characteristics

The effect of H_2O addition can be illustrated by comparing data from 8/5, during which no water was injected into the first stage, with data from 7/29, during which water was added. Although the resid content of the process oils was about the same on both dates (Tables 4-6), the soluble resid samples from 8/5 (no water) contained somewhat more oils and somewhat less asphaltenes and preasphaltenes than the corresponding samples from 7/29 (water addition) (Tables 7-9). No other conditions differed between these two periods. On closer inspection, this trend is found to be more general, as the following discussion shows. Trends in the solubility fractionation data during Run 249 will be illustrated by V-1064 data. Inspection of the corresponding V-1067 and V-131B solubility fractionation data (Tables 7 and 9) will show that they follow the same trends. The V-1064 solubility fractionation data (Table 8) show three periods of low oils, and high asphaltenes and preasphaltenes: 6/4, 7/9-7/29, and 8/28-9/14. The 6/4 period represents operation without iron oxide and DMDS and was already discussed. The period 8/28-9/14 represents the ash recycle test, also discussed in another section. The period of 7/9 through 7/29 is the period of water addition to the first stage. During that period, the resids contained 58-63 wt % oils, 24-27 wt % asphaltenes and 13-17 wt % preasphaltenes. During all remaining periods analyzed the resids contained 64-69 wt % oils, 20-25 wt % asphaltenes and 9-11 wt % preasphaltenes. Thus the low oils and high asphaltenes and preasphaltenes content from 7/9-7/29 appear to be related to H_2O addition. These data are consistent with the observation of Catalytic, Inc., that the CSD feed was higher in preasphaltenes during water addition.(1) Note, however, that changes in other conditions during this period may also have contributed to the observed changes in the resid characteristics. The period without water addition coincides with the period without DMDS addition to the first stage. In addition, the dissolver back-mix pump was out of service on 7/10-13 and was later restored at a lower pumping rate to reduce erosion.(1) Fe_2O_3 addition was stopped during 7/15-18. The hydrotreater temperature varied from 616°F on 7/9 to 700°F on 7/29 during this period of water addition. The contribution of these factors to the apparent effect of H_2O addition is unknown. However, the comparison of data from 8/5 and 7/29 should not be confounded by these other factors.

Proton distributions of first-stage product (V-1064) resids (Table 19) and distillates (Tables 13 and 16) likewise show somewhat higher aromaticities for the 7/9-29 period relative to the periods before and after it. The microautoclave results also showed that the 8/5 whole first-stage product sample (V-1064) was substantially higher in donor solvent quality than the corresponding 7/20 sample, even though the first-stage feed was perhaps slightly poorer on 8/5 (Table 22).

The above observations suggest that water addition may have limited H_2 transfer in the thermal stage. Water addition resulted in first-stage products containing fewer oils and more asphaltenes and preasphaltenes and greater aromaticity. These results are consistent with the findings of Catalytic, Inc., that hydrogen utilization and C_4 + distillate yield were lower during water addition, even though coal conversion was higher.(1) Less hydrogenation during water addition might be explained solely by a reduction in H_2 partial pressure resulting from the presence of water vapor.

In addition to the other effects, all the oil samples (V-131B, V-1064, V-1067) from 7/29 (water addition) were higher in phenolic concentration than their 8/5 counterparts (Table 21). Limited hydrogen transfer (as discussed above) could account for this observation. Another factor could be involved, however. To the extent that hydrodeoxygenation is equilibrium-controlled, the presence of additional water may suppress deoxygenation, since water is the primary product.

No Effect of Dissolver Temperature on Oil Characteristics

Although dissolver temperature affected coal conversion (as previously discussed), there were no clearly observable effects of dissolver temperature over a 10-20°F range on oil properties. A comparison of the properties of first-stage feeds (V-131B) and first-stage products (V-1064) on 8/5 (dissolver temperature of 796°F, 800°F target) with those on 8/18 (temperature of 805°F, 810°F target) shows no difference in oil properties. Furthermore, a comparison of oil properties on 6/14 through 6/18 (dissolver temperature 788°F, 790°F target, hydrotreater temperature 642°F) with those on 6/24 and 6/25 (dissolver temperature 807°F, 810°F target, hydrotreater temperature 626°F) showed no differences which were attributable to dissolver temperature.

Effect of CSD on Resid Composition

In the RITSL mode, the Critical Solvent Deashing (CSD) unit removes solids from the hydrotreater product stream to prepare a substantially solids-free recycle oil for the first stage (Figure 1). In Run 249 (excluding the ash recycle test), the non-distillable portion of the hydrotreater product (V-1067) typically contained about 12% THF-insoluble material, of which about 7% was ash and about 5% was IOM (Table 6). After CSD processing, THF insolubles (IOM and ash) were generally reduced to well below 0.5% of the non-distillable recycle oil (V-131B, Table 4). Other than removing solids, the CSD unit tends to selectively reject the preasphaltenes (and perhaps, asphaltenes) fractions of the soluble resid. This is demonstrated by comparing the compositions of the hydrotreater product soluble resid (Table 8) and the recycle solvent soluble resid (Table 9) which are summarized below:

	Average wt %*		
Soluble Resid Sample Type	Oils	Asphaltenes	Preasphaltenes
HTR Product (V-1067)	74	20	6
Recycle Oil (V-131B)	81	18	2

*Data from 6/8-6/11 and 8/28-9/14 excluded.

The proton distribution of the soluble resid is largely unaffected by CSD processing as seen by comparing data in Tables 20 and 18. For example, average aromaticities are 23 ± 4% for the V-1067 resids and 23 ± 4% for the V-131B resids during the periods used in the above table. Rejection of preasphaltenes by the CSD was observed in previous runs,(5,6) but selective rejection of asphaltenes was not seen before.

Hydrotreated Resid Good Donor Solvent

Donor solvent qualities by microautoclave assay are presented in Table 22 for the various whole or "as-is" samples and for the corresponding 850°F$^-$ distillates of each sample. The 850°F$^+$ resid content of each whole sample is given in Tables 4 through 6. By comparing the microautoclave results for any whole sample and its distillate fraction, it can be seen whether the resid improves or decreases solvent quality relative to the distillate.

The recycle solvent (V-131B) distillates gave 73 to 80% conversion in the microautoclave whereas the whole samples (25 to 45 wt % resid) gave 81 to 88% conversion. The hydrotreater flashed bottoms (V-1067) distillates gave 71 to 81% conversion and the whole samples (16 to 39 wt % resid) gave 77 to 90% conversion. Therefore, for the hydrotreated oils, replacement of less than half of the distillate with resid improves donor solvent quality. Similar results have been seen in previous runs.(5,6,7)

The pasting solvent (V-131B) donor solvent quality correlates with the resid content. A linear regression of whole V-131B microautoclave results (Table 22) with wt % THF-soluble resid content (Table 4) gives

$$\text{\% conversion in microautoclave} = 0.374 \times \text{wt \% THF-Soluble Resid} + 72.3$$

with a correlation coefficient (R) of 0.75. Resid contents ranged from 25 to 45 wt % and microautoclave conversions ranged from 81 to 89%. These results indicate that resid content is probably a major factor in pasting solvent donor quality. As discussed earlier, this is one reason for the improved solvent quality of the oils produced at high hydrotreater temperatures.

The hydrotreater feed (V-1064) distillates averaged 60.4% conversion, and the whole samples (31 to 42 wt % resid) averaged 61.9% conversion.

It is interesting to note that the distillate results varied only slightly, from 57.2 to 63.5%, but the whole sample results varied considerably, from 52.9 to 74.6% (omitting the low value of 44.7%). Thus for thermal oils, addition of ca. 35 wt % resid sometimes improved donor solvent quality and sometimes reduced it. On the average, the resid did not change the donor solvent quality of the first-stage product.

Comparison of Oil Properties from Run 249 with Previous Runs

A previous comparison of oil properties from Runs 242, 243, 246 and 247(6) showed that subbituminous oils differed from bituminous oils in their characteristic properties. Though many of these differences probably result from the differences in the parent coal structures, aromaticities, which relate to hydrogen contents, were found to depend primarily on hydrotreater temperature. Thus, aromaticity differences between subbituminous and bituminous oils resulted primarily from differences in the hydrotreater temperatures typically used for the two coals (≤640°F for subbituminous and >640°F for bituminous). Since most of Run 249 was made using the higher hydrotreater temperatures typically employed in past runs with bituminous coal, it provides the first opportunity to examine this effect on subbituminous oil properties.

Properties of oils from Run 249 (excluding the ash recycle period) will be compared with properties of oils from the ITSL portion of Run 246 with Wyodak coal, from the ITSL portions of three earlier bituminous coal runs (242, 243, and 248) and from RITSL Run 247 with bituminous coal. Data for Run 249 are tabulated in this report. The data from Runs 242,(4) 243,(4) 246,(5) 247,(6) and 248(7) were presented earlier.

Differences in run conditions may have affected oil properties being compared. Relevant conditions of Run 246 and 249 were summarized in the section of this report entitled "Hydrotreater Resid Conversion". An earlier comparison showed that the properties of oils produced from bituminous coal were essentially the same, regardless of whether they were produced in the RITSL (Run 247) or ITSL (Runs 242 and 243) configuration.(6) However, the properties of oils from Run 248 have not been compared with those from other bituminous runs. The conditions during the ITSL portion of Run 248 which varied significantly from the earlier bituminous coal runs were: 1) use of the low contact time (LCT) dissolver, and 2) operation at a low hydrotreater space velocity (WHSV) of 0.7 lbs feed/hr/lb cat. Space velocities in the other runs were typically ca. 1.0 lb feed/hr/lb cat. or higher. All the Run 248 oil properties given in this report are from the ITSL period with 100% LCT dissolver volume.

The paths of the distillate (850°F$^-$) process oils are essentially the same for both ITSL and RITSL operations. Selected average properties of the distillates from the various runs are compared below.

	Run No.	Aromaticity, % (Range)	Cyclic/ Alkyl Ratio	Microautoclave Conversion, wt % MAF Coal ± Std Dev	Phenolic -OH Concentration, meq/g (Range)
HTR Feed	242	17.4 (17-20)	0.64	70 ± 1	0.64
(V-1064)	243	17.1	0.69	74	-
	247	17.1 (15-19)	0.61	69 ± 2	0.59
	248	18.1 (17-19)	0.53	66 ± 1	0.71
	246	22.1 (20-23)	0.51	66 ± 2	-
	249	17.7 (14-21)	0.55	60 ± 2	0.80
Flashed Product	242	11.3 (10-12)	0.68	83 ± 1	(0.41-0.11)
(V-1067)	243(a)	11.0	0.65	83	-
	247	10.5 (8-14)	0.71	81 ± 2	0.16 (0.25-0.11)(c)
	248	11.7 (11-12)	0.68	82 ± 1	0.27 (0.32-0.23)
	246	16.1 (15-18)	0.58	85 ± 2	0.75 (0.66-0.84)(a)
	249(b)	12.4 (9-17)	0.61	77 ± 2	0.26 (0.51-0.12)

(a) V-131B Sample.
(b) Excludes data from 6/8/85.
(c) Excludes 9/27/84.

The Run 249 aromaticities are very close to the bituminous values, whereas their cyclic to alkyl aliphatic ratios are close to the Run 246 values. Thus, the lower distillate aromaticity appears to be related to the higher hydrotreater temperatures of Run 249 relative to Run 246.

In contrast, the cyclic to alkyl aliphatic ratio seems to be dominated by the feed coal properties, though other factors probably also play a role. Note that the cyclic to alkyl aliphatic ratio of the Run 248 hydrotreater feed (V-1064) is similar to the subbituminous values, whereas the corresponding hydrotreater product (V-1067) cyclic to alkyl ratio is similar to those for the other bituminous coal runs. Perhaps the low value for the hydrotreater feed resulted from unique characteristics and operating conditions of the LCT dissolver used in Run 248.

It is clear that the microautoclave conversions produced by Run 249 samples are lower than those produced by samples from all the other runs. It is not clear that the higher catalyst age during Run 249 was the only factor in this, since donor solvent quality near the end of Run 246 was better than the solvent quality near the beginning of Run 249. (Note that Run 249 was made with used catalyst from Run 246.) The slightly higher hydrotreater space velocity (about 1.2 lb feed/hr/lb cat) in Run 249 may have been a minor factor in the solvent quality differences. It appears likely that the major cause of poor solvent quality in the Run 249 distillate oils relative to Run 246 was overhydrogenation resulting from high hydrotreater temperatures.

The phenol content of the hydrotreater product (V-1067) was fairly low in Run 249, in spite of the higher phenolic content in the hydrotreater feed (V-1064) and the higher hydrotreater space velocity and catalyst age during Run 249 relative to the other runs. As discussed earlier, the hydrotreater temperature is a major factor in achieving low phenol concentration in the hydrotreater product.

The amount of THF-soluble resid (850°F$^+$) in the whole process oils is given below.

	Soluble Resid, wt % of Sample, Range		
Run No.	HTR Feed (V-1064)	Flashed Product (V-1067)	Recycle Oil (V-131B)
242	57-67	52-60	-
243	66	-	63
247	63-65 (a)	55-63 (a)	55-61
248	63-69	52-61	50-61
246	37-44	33-41	35-41
249	31-42	28-39 (b)	25-45

(a) These data are on a wt % of solids-free sample basis.
(b) Excludes data from 6/8/85.

The soluble resid content of Run 249 oils is similar to that of Run 246 and is much lower than that of the bituminous oils. This indicates that the resid content depended primarily on the feed coal and was not greatly affected by RITSL vs ITSL processing. Because the residual oil streams follow different paths in the two plant configurations (RITSL vs ITSL), the resid composition may vary with run configuration. The data below show that the preasphaltenes content of the resid in Run 249 was intermediate between Run 246 and most of the bituminous run values.

	Preasphaltenes, wt % of Soluble Resid, ± Std Dev		
Run No.	HTR Feed (V-1064)	Flashed Product (V-1067)	Recycle Oil (V-131B)
242	19 ± 2	13 ± 3	-
243	19	-	12
247	19 ± 2	13 ± 3	8 ± 3
248	8 ± 1	1 ± 1	1 ± 1
246	7 ± 1	3 ± 1	3 ± 1
249	12 ± 2	6 ± 3(a)	1 ± 1

(a) Excludes data from 6/8/85.

The higher preasphaltenes content in the hydrotreater feed and product of Run 249 relative to Run 246 results from differences in RITSL and ITSL processing. Since the CSD removes preasphaltenes (discussed above) and the V-1064 and V-1067 streams are not deashed in the RITSL configuration, higher preasphaltenes are expected in the RITSL (vs ITSL) V-1064 and V-1067 resids. The preasphaltenes contents of the Run 248 resids were quite low relative to the other bituminous coal runs (242, 243 and 247). This is largely a result of the low hydrotreater space velocity in that run, since the conversion of benzene insolubles in the hydrotreater was quite high (70-95%) during that portion of Run 248.(7)

The table below shows that the Run 249 resid aromaticities were identical to those in the bituminous coal runs.

	Resid Aromaticity, % Std Dev		
Run No.	HTR Feed (V-1064)	Flashed Product (V-1067)	Recycle Oil (V-131B)
242	34 ± 2	22 ± 3	-
243	33	-	22
247	36 ± 1	23 ± 1	23 ± 2
248	35 ± 1	22 ± 1	22 ± 1
246 (ITSL)	40 ± 1	28 ± 1	27 ± 1
249	34 ± 5	22 ± 4	23 ± 4

The phenolic content of the resids are similar for Runs 247, 248 and 249. They are not available for Runs 242, 243 and 246. These data substantiate the previous observation(6) that the distillate and resid aromaticities and phenolic contents are determined primarily by hydrotreater temperature, since the Run 249 values were the same as those of the bituminous runs and unlike those of the low-temperature subbituminous run.

HRI CTSL RUN 227-27

Run Description

Continuous bench unit Run 227-27 was made by Hydrocarbon Research, Inc. (HRI) during July, 1985 as part of the Catalytic Two-Stage Liquefaction (CTSL) process development program. Run 227-27 was twenty-one days in duration and was designed to demonstrate the performance of the process with Clovis Point mine, Upper Wyodak seam subbituminous coal. An earlier demonstration run (227-26) produced poorer than expected yields;(8) Run 227-27 was a second attempt to meet yield expectations which were based on an even earlier process-variable run (227-25). Though excellent yields were obtained in Run 227-27 (see below), the anticipated yields were never realized.

Process flows(8) are shown schematically in Figure 3. Each reactor has a capacity of 2000 cc.(8) The nominal throughput of the bench unit is 50 lbs/day.(9) Operating conditions(10) are given in Table 25. Variables included second-stage temperature (815-825°F) and coal drying method (oven or slurry). With operating conditions being nearly constant, the primary variable with time was catalyst age which reached 641 lbs MF coal/lb catalyst(11) based on the second-stage catalyst charge.

Analyses of the two start-up oils for this run, termed "light" and "heavy", were reported earlier.(7) The light start-up oil was used to bring the unit to temperature. The heavy start-up oil was then introduced prior to and during the initial introduction of coal. Target operating conditions had been attained before the first introduction of coal.(11) The last balance period was twenty-one days into the run though a first-stage sample was withdrawn on the twenty-second day. Reported yields and conversions(8) from the twenty-first day of the run are shown below.

Yields, wt % MAF	
C_1-C_3 gas	8.3
C_4-390°F	18.9
390-650°F	33.1
650-975°F	11.7
975°F$^+$ residuum	4.8
Hydrogen consumption	6.9

Conversions, wt % MAF	
Coal conversion	90.1
975°F$^+$ conversion	85.4

Sample Descriptions

We obtained a set of twenty-seven oils (ca. 20 to 40g each) from J. B. McLean and T. O. Smith of HRI. The set included twenty-one daily pressure-filter liquid (PFL) samples and four first-stage oils from Run 227-27 and two oils to be used as start-up oils for Run 227-30. The pressure-filter liquid is the major second-stage product and, in Run 227-27, it was the only component of the first-stage pasting oil. First-stage oils, which are samples of the first-stage reactor inventory, were pressure filtered by HRI prior to shipment. Since these samples were all filtered by HRI, they were assumed to be solids-free. The two start-up oils for Run 227-30 are distillate oils that originated from Illinois 6 coal at the Wilsonville pilot plant. The first-stage sample from day 16 appears somewhat unusual. Perhaps it is not a representative sample.

Objectives

The objectives of Conoco's work with these samples were to 1) define the effects of catalyst age on process-oil characteristics, 2) compare first- and second-stage oil properties, 3) compare properties of oils from Run 227-27 with those of oils from earlier subbituminous runs, and 4) determine the solvent quality of the two start-up oils for Run 227-30 by microautoclave tests.

Analyses

Except for the two start-up oils, proton distributions were obtained by ^{1}H-NMR for each whole sample (Table 28). Selected whole samples were tested in the microautoclave at the modified equilibrium conditions (Table 32). Certain whole samples were distilled (Table 26) to 320°C pot/270°C column/5 torr (850°F/atm). Each 850°F$^+$ resid was analyzed by solubility fractionation (Table 27), ^{1}H-NMR (Table 30) and FTIR for phenolic content (Table 31). Each 850°F$^-$ distillate was analyzed by ^{1}H-NMR (Table 29) and FTIR (Table 31). The two start-up oils were tested in the microautoclave (Table 33).

Effects of Catalyst Age on Oil Characteristics

The measured characteristics of the PFL evolved in a regular manner with time. As Run 227-27 progressed and the catalyst aged, the 850°F$^+$ resid content of the PFL increased from 11 to 25% on days 1 and 21, respectively (Table 24, Figure 4). During the same time, the PFL resid increased in preasphaltenes from 0.3 to 6% and in asphaltenes from 13 to 21% (Table 27 and Figure 5), and increased in hydrogen aromaticity from 17 to 38% (Table 30 and Figure 6). Phenolic concentration increased from 0.16 to 0.58 meq/g in the PFL resid from day 1 to day 21 of the run (Table 31 and Figure 8).

As the resid content of the PFL increased, the distillate content decreased from 89 to 75% on days 1 and 21, respectively (Table 24). The aromaticity of the PFL distillate increased from 9 to 14% (Table 29 and Figure 6) and the phenolic concentration increased from 0.02 to 0.12 meq/g over the same time (Table 31 and Figure 8).

The aromaticities of the whole PFL samples increased from 10% on day 1 to 17% on day 21 (Table 28 and Figure 6) reflecting the increasing aromaticities of the component fractions (distillate and resid) and the increasing proportion of the more aromatic resid. Excluding the data point from the first day of the run which may be in error, the donor solvent quality of the whole PFL samples, as measured by the modified equilibrium microautoclave test, increased from about 60% on days 3 through 9 to 66% at the end of the run (days 19 and 21, Table 32 and Figure 9). Therefore, for days 9 through 19, donor solvent quality actually improved with decreasing hydrogen content (increasing aromaticity).

The first-stage samples show trends with run time or catalyst age generally similar to those of the PFL samples. Preasphaltenes increase (Table 27 and Figure 5), aromaticities of the whole sample (Table 28 and Figure 7) and of both of its fractions (distillate and resid) increase (Tables 29 and 30 and Figure 7), and phenolic content increases with time (Table 31 and Figure 8). An exception to this is the first-stage sample from period 16 which contains far less resid and preasphaltenes than expected, apparently resulting from an error in sampling.

These changes in process-oil characteristics can all be related to catalyst age and thus, all appear to be related to catalyst activity. Hydrogenation, cracking and deoxygenation activities are all directly or indirectly reduced with run time. Nearly identical trends were observed in Run 227-26.(7)

Effects of Other Variables on Oil Characteristics

Though two other processing conditions were changed during the run, catalyst age clearly had the largest effect on oil characteristics in Run 227-27. The two other variables were second-stage temperature and coal drying method.

Second-stage temperature was increased in 5°F steps from 815 to 825°F. Each temperature increase decreased the $850°F^+$ resid content and increased the distillate content of the PFL samples by perhaps 3% absolute when compared to the trend of the data at the lower temperature. This is illustrated in Figure 4 by comparing the data before and after the temperature increases made on days 8 and 16. The unexpectedly high resid content of the PFL sample of day 7 may be the result of an analytical or sampling error. The decreased resid content is consistent with the expected increase in second-stage resid conversion resulting from the higher temperatures.

The feed coal was oven dried during days 1 through 4 and days 10 through 21 and slurry dried during days 5 through 9. There is no apparent relationship between process-oil characteristics and the coal drying method used (slurry drying or oven drying).

Comparison of First-Stage and PFL Samples

The direct comparison of the characteristics of the first-stage oils and PFL samples has two limitations. First, the samples we obtain 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°F), contain some amount of $500°F^-$ oil, but less $650°F^-$ oil than the PFL samples.(11) 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.

The PFL samples contain less resid (Table 26), and fewer phenols (Table 31) than the first-stage samples reflecting the additional upgrading afforded by the second stage. The preasphaltenes contents are comparable for the two sample types (Table 27). The distillate oils from the PFL samples are generally somewhat more aromatic (Table 29) and the PFL resids are substantially more aromatic (Table 30) than the corresponding first-stage fractions. Differences in boiling point distributions of the two sample types may contribute to differences in aromaticities. However, the 850°F$^-$ distillates of the PFL samples are more aromatic than the corresponding first-stage distillates even though they were distilled to the same final point and even though the PFL samples have a greater concentration of 650°F$^-$ material. An increase in aromaticity (decreased H/C) would be expected at equilibrium upon second-stage processing because of the 65 to 75°F increase in reactor temperature relative to the first stage. The first-stage and PFL whole samples perform comparably in the microautoclave tests (Table 32).

Generally similar comparisons of the two sample types were reported for Run 227-26.(7)

Comparison with Samples from Earlier Subbituminous CTSL Runs

Conoco analyzed oils from three other CTSL runs made with the same coal. Runs 227-22 and 227-25 were "process variable" runs in which several operating conditions were varied to determine optimum operating conditions. Very favorable yields were obtained in Run 227-25 at conditions 3, 4 and 5 (periods 12 through 20). HRI chose these same conditions for the planned 45 day "demonstration run" (Run 227-26). However, Run 227-26 was terminated after 23 1/2 days because distillate yields were somewhat lower than expected and because of problems with the second-stage ebullating-pump.(8) A second "demonstration" run (Run 227-27) was made at similar operating conditions except that the solvent/coal ratio was slightly higher and the second-stage temperature was increased slowly to its final value in hopes of increasing distillate yields to the high levels obtained in Run 227-25. Operating conditions and complete analytical data were reported for samples from Runs 227-22,(12) 227-25,(13) and 227-26.(7)

Characterization data for PFL samples from selected periods of Run 227-25, 26 and 27 are compared below. The periods chosen for comparison were operated at similar processing conditions, i.e., T = 750 and 825°F, SV = 45 to 46 lbs MF coal/hr/ft^3 of settled catalyst in each stage, P = 2500 psig and Catalyst = Amocat 1C and Amocat 1A. The periods from Run 227-27 were operated at higher solvent/coal ratios (1.5 vs 1.2), however. The period numbers (days into the run) of the run portions shown below are the same, indicating similar catalyst ages.

Run	Cond. No.	Period No.	Average Values, PFL Samples							
			Resid, wt %	Preasph., wt % of Resid	Aromaticity, %			Phenolics, meq/g		Microautoclave Coal Conv., % MAF
					Whole Sample	Dist.	Resid	Dist	Resid	
227-25	4&5	16-19	16.2	1.1	12.5	10.4	25.6	0.07	0.32	63.6
227-26	---	16-19	21.6	3.0	16.0	13.0	35.1	0.12	0.58	65.2
227-27	---	16-19	22.8	4.4	15.2	12.8	32.7	0.08	0.46	64.0

The samples from Run 227-25 are clearly of higher quality than those from the two other runs in terms of resid and preasphaltenes content, aromaticity (H-content) and phenolic concentration. The same statement is true for the first-stage samples. The cause of the production of poorer quality oils in Runs 227-26 and 227-27, when compared with Run 227-25 at ostensibly the same operating conditions, is not apparent. However, the difference in oil properties may relate to the poorer than anticipated(8) yields produced in Runs 227-26 and 227-27.

The primary differences between the two "demonstration runs" (227-26 and 227-27) were the use of a slightly higher solvent/coal ratio (1.5 vs 1.2) and the gradual increase in second-stage temperature in Run 227-27, as opposed to constant temperature in Run 227-26. The characteristics of the oils from the two "demonstration runs" are very similar, particularly at the ends of the runs at which point the second-stage temperatures were the same. This is apparent in the data shown above and is also demonstrated in Figure 10 where the 850°F$^+$ resid contents of the PFL samples are plotted vs run time for both runs.

Start-up Oils for Run 227-30

As requested by HRI, we tested two potential start-up oils for Run 227-30 in our standard microautoclave test. Results of these tests plus analytical data on the oils which were supplied by HRI(14) are given in Table 33.

The microautoclave tests showed no difference between the two samples as might be expected based on HRI's analyses. The microautoclave results were calculated assuming the oils were solids-free.

If both of these oils were taken from vessel V-123 of the Wilsonville pilot plant, they are the heaviest portion of the flashed oils from the hydrotreater and are somewhat lower boiling than the distillate (850°F$^-$) portion of the recycle oil which is primarily 650°F$^+$ material. As a comparison, most Wilsonville hydrotreated distillate (850°F$^-$) recycle solvents from Illinois 6 coal give about 80-85% conversion in this microautoclave test, whereas most hydrotreater feed distillates (850°F$^-$) give about 67-74% conversion.(7,15)

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 its receipt, the coal has undergone mild oxidation. This is apparent in the analyses shown in Table 34. The recent analyses (2/86) 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 tetraline and 1-methylnaphthalene at our commonly used test conditions. Microautoclave tests were made at the same times as the analyses appearing in Table 34 were obtained. The coal conversions from these tests, presented in Table 35, can be used as reference points for liquefaction solvents tested in this contract. The earlier data are taken from references 12 and 16. Similar data for an earlier (1979) batch of the same coal appear in reference 17.

The data in Table 35 show that coal conversions decreased by an overall average of 1.1% absolute over the duration of this contract, i.e., between 1/85 and 2/86. The repeatability of this assay has been shown to have a standard deviation 1.2% absolute.(5) Therefore, the standard coal shows a small but perhaps experimentally insignificant loss in reactivity from aging over the course of this contract.

FTIR OF POTASSIUM/CROWN-ETHER TREATED COALS

Description of Samples

Nineteen samples of various types from experiments on the potassium-crown ether (K-CE) reaction with Illinois 6 and Wyodak coals were generated and provided by Dr. Ramani Narayan of Purdue University. The purpose of these experiments was to use solvated electrons to cause chemical cleavage of alkyl and ether linkages in the coal, producing soluble moieties for structural characterization.(18) By conducting these selective reactions at low temperature, it was hoped that this structural data would bear a direct relationship to the original parent coal structure. The work reported here consisted of infrared spectroscopic analyses of coals and products of the K-CE treatment to derive quantitative and qualitative structural information.

The samples analyzed included untreated feed coals, alkali-soluble aqueous extracts, and residual coal material from successive potassium-crown ether treatments and work-ups. In addition, our samples included derivatized (acetylated and/or methylated) forms of all of the coal and reaction product samples. These provide information on the hydroxyl content of the underivatized samples. For convenience, the samples will be identified by abbreviated codes as follows: I for Illinois 6 coal, W for Wyodak coal, C for feed coal, E for alkali soluble extract, R for residual (unextractable) product; a number 1, 2, or 4 indicating which step in successive potassium-crown ether treatments a product is from; A for acetylated sample, M for methylated, MA for sample acetylated and then methylated. For example, IE2-A is an acetylated alkali extract sample from a second successive potassium-crown ether reaction with Illinois 6 coal. Using this format, the 19 samples analyzed are listed below:

IC	IC-A	IC-M	WC	WC-A	WC-M
IE1	IE1-A		WE1	WE1-A	WE1-MA
IE2	IE2-A		WR1	WR1-A	
IR4	IR4-A		WR2	WR2-A	

These codes correspond to the identification provided on the sample vials as follows:

Code	Purdue Sample ID			Code	Purdue Sample ID		
IE1	Ill. 6	H3-6A	Alk.	WE1	Wyodak	H2-41A	Alk.
IE2	Ill. 6	H3-6B	Alk.	WR1	Wyodak	H2-41A	Residue
IR4	Ill. 6	H3-6D	Residue	WR2	Wyodak	H2-42	Residue

The feed coals IC and WC and the products IE1, IE2, IR4, WE1, WR1, and WR2 were the samples to be characterized. The other 11 acetylated/methylated samples merely provided supplemental data on these 8 samples.

In addition to qualitative observations about the samples, the infrared spectra were used to determine a relative quantitation of OH, aliphatic CH and C=O groups for the samples of interest. Absolute quantitation requires a calibration (extinction) coefficient, which was not available in every case. The results of each of the comparisons are discussed below in a separate section.

General Observations

The OH concentrations in the samples were determined by Painter's method (Reference 19) and reported in Table 36. However, the accuracy of the results is limited by several factors (discussed in the Experimental section). Table 37 gives integrated peak intensities for the primary samples in the aliphatic CH stretch region and in the carbonyl C=O stretch region. Within the limitations of the methods involved, these data provide an approximate relative concentration of these functional groups.

Other observations about the samples are more interesting and informative. The apparent increase in carbonyl content in methylated samples and the presence of an unusual peak at 2094 cm^{-1} in two other sample spectra suggest the possibility that some samples may be contaminated by unidentified materials or reagents. This possibility may warrant further attention. The presence of a significant carbonyl peak in all of the reaction product spectra likewise indicates either a valid chemical change which produces carbonyl during the course of the potassium-crown ether reaction or contamination or some other artifact resulting from the work-up procedure. In either case, a better understanding of the chemistry involved is desirable.

The spectra of two samples, IE1 and IE1-A, showed a strong sharp peak at 2094 cm^{-1} (Appendix 2, spectra 4 and 5). Since this peak occurs only in these two spectra, it evidently represents contamination of the IE1 sample prior to acetylation. The peak is atypical of coal materials and is found in a region where very few functional groups have peaks. The identity of the contaminant is unknown, but the Merck, Sharp and Dohme spectral interpretation program(20) identifies the functional groups azide, carbodiimide, and isothiocyanate as possibilities (listed in order of decreasing likelihood). There was no obvious inorganic candidate species to which the peak could be assigned.

The infrared spectrum of the Illinois 6 feed (Appendix 2, spectrum 1) showed evidence of mild to moderate organic oxidation of that coal (shoulders at ca. 1685 and ca. 1635 cm^{-1} on the peak at 1600 cm^{-1}).

OH Group Concentration and Effects of Derivatization

There are potentially both direct and indirect methods for obtaining the OH group concentration. The direct measurement involves the measurement of peak height or integrated area in the O-H bond stretch region of the spectrum (ca. 3600-3100 cm^{-1}). However, several factors contribute to uncertainty in measurements in this region. These are 1) a rather broad indistinct OH peak resulting from H-bonding, 2) contribution from N-H bond stretches, 3) contribution from variable sample moisture contents, and 4) contribution from a sample preparation artifact which introduces a somewhat variable OH feature in each spectrum. Realizing these limitations, we included data for a direct OH measurement to determine if this approach had any practical value.

Acetylated and methylated samples were used in an indirect approach to obtain the hydroxyl content by measuring the loss or gain in certain regions relative to the corresponding underivatized samples. The data clearly showed that the OH peak area was consistently reduced by acetylation or methylation. Using the method of Painter, et al.,(19) quantitation of phenolic and alcoholic OH groups is obtained from the heights or areas of C=O peaks resulting from formation of acetyl esters derived from those groups. In addition to using this method based on ester peak height (Table 36), we obtained peak areas in other regions to determine if other indirect measures were of practical value. From a comparison of acetylated samples with the corresponding underivatized samples, we used integrated peak intensity to attempt to determine loss of OH, gain of total aliphatic C-H, gain of CH_3 groups, gain of esters (C=O peak area), and gain of total C=O (Table 38).

The hydroxyl contents (determined by Painter's method(19)) of the eight primary samples are given in Table 36. Phenolic OH contents range from ca. 2 to 3 wt % as OH, alcoholic OH contents range from ca. 1 to 2 wt % as OH, and total OH contents range from 3.5 to 5.7 wt % O as OH. The Wyodak feed coal was slightly higher in phenolic and alcoholic OH than the Illinois 6 feed coal. However, the products from the chemical treatment of the two coals are nearly equivalent. Thus, the Illinois 6 coal appears to have gained OH by the chemical treatment, whereas the Wyodak coal appears to have lost OH by the chemical treatment. The accuracy and reproducibility of these data are unknown, so it is unclear what constitutes a real difference in OH content between two samples. In general, we may conclude that the samples are similar in hydroxyl content. We note that values of 4.1 to 7.5 and 5.7 to 8.1 wt % O as OH (dmmf basis) were reported, respectively, by various techniques for a set of three high volatile C bituminous coals and a set of three subbituminous B coals.(19) Our values are on an as-determined basis (but with the samples apparently containing 5 wt % or less moisture). Thus, our values appear to be reasonable ones.

Reported in Table 38 are the results of relative OH quantitation by other direct and indirect means. Sample differences and integration regions for carbonyl and aliphatic CH groups are illustrated in Figures 11 and 12. We attempted to correlate the results from each method (i.e., each row in the table) with each of the other methods. The two meaningful correlations obtained (ignoring the high correlations of gain in methyl CH stretch peak area with total aliphatic C-H stretch peak and of gain in ester C=O peak area with gain in total C=O peak area) were wt % O as OH with gain in ester C=O stretch peak area (r=0.943) and wt % O as OH with gain in total C=O stretch peak area (r=0.646). The high correlation of the determination based on ester peak height (wt % O as OH) with the gain in ester C=O stretch peak area is not surprising, since Painter, et al.,(19) report that their method will work with either area or height. However, Painter used curve resolving methods, while we did not. The direct OH measurement shows only one meaningful relation: within each parent coal subgroup there appears to be a linear relation between (direct) OH stretch peak area with the corresponding loss of OH stretch peak area on acetylation. This seems to indicate that the two methods are measuring the same quantity within a group of samples from the same coal. That the two coals respond differently may reflect differences in coal structure.

In general, we see that there is essentially no agreement of the use of OH or aliphatic CH peaks for OH determination with the use of the ester C=O peaks in these samples. Direct measure of OH by the OH stretch peak in these samples does not appear to be practical, since there is no agreement with the established method of Painter, et al.

Methylation was observed to increase the aliphatic C-H stretch peak area and decrease the OH stretch peak area. Methylated samples showed a larger increase in CH peak area and an equivalent or larger decrease in OH peak area relative to the underivatized samples than did the corresponding acetylated samples. The other effect of methylation was to significantly increase carbonyl content, a surprising result. In the carbonyl region, the only anticipated changes should result from conversion of carboxylic acid groups into methyl esters. This would tend to shift intensity from the 1650-1700 cm^{-1} region to the 1730-1770 cm^{-1} region. It was not expected to have a large effect on the overall intensity in the carbonyl region. Of the three methylated samples provided, two were methylated feed coals and one was a methylated Wyodak alkali-soluble extract which had already been acetylated. Methylation of an acetylated material was expected to have little further effect except that the methylating agent may be capable of better penetration into the coal than the acetylating agent. Thus, the changes at most would represent derivatization of some additional OH groups (phenols would become methyl ethers and carboxylic acids would perhaps become methyl esters). However, it is apparent especially in the Wyodak samples that methylation significantly increases the intensity of the carbonyl peak at ca. 1710 cm^{-1}. FTIR evidence for surface carbonyl formation resulting from methylation by the method used recently appeared in the literature.(21) Furthermore, it was found that the carbonyl groups were produced after generation of coal anions in the methylation procedure and prior to actual methylation of the desired groups. The FTIR results presented here are in agreement with those observations; however, this work indicates that these changes are probably not limited to the surface as suggested in Reference 21. The formation of carbonyl species with a peak at 1686 cm^{-1} was attributed to base-promoted decomposition of peroxide species.(21) This hypothesis, if accurate, would explain the increased carbonyl observed in our methylated samples. Furthermore, since coal anions are generated in the K-CE reaction, this explanation might account for the increased carbonyl content of all the product samples.

C=O and Aliphatic C-H Group Determination

A visual comparison of the spectra clearly shows that all product samples contain a significant carbonyl peak at ca. 1710 cm^{-1}, much more intense than in the parent coals. It is thus evident that carbonyl groups of some type are introduced during the chemical treatment and/or work-up procedure. The peak location of ca. 1710 cm^{-1} is assigned to saturated ketones, certain types of diketones, and/or carboxylic acid groups. The complexity of coal does not allow an unequivocal assignment. The spectra show that this peak appears in a very consistent location, suggesting that the species observed in each case are of the same type. The nature of the samples and infrared data do not permit one to establish whether the production of carbonyl groups results from the potassium-crown ether treatment or subsequent sample work-up. Thus, the production of the carbonyl species could result from either one.

Although not obvious on casual inspection of the spectra, the product samples also have more intense aliphatic C-H stretch peaks. Table 37 gives the integrated peak intensities for selected regions of the aliphatic C-H stretch band and the C=O stretch band. It is apparent that there is no direct correlation between C=O band intensity and aliphatic C-H band intensity. Two factors affect the C-H band intensity: 1) the number of C-H bonds, and 2) the extinction coefficients of the C-H bonds which are influenced by the type of C-H bonds present. Bellamy(22) has noted that the extinction coefficients of CH bonds in oxygenated materials are appreciably greater than in hydrocarbons. Thus, although the chemical treatment and work-up appear to increase the number of C-H bonds, a contributing factor to the apparent increase may be an increase in the extinction coefficients of aliphatic groups near new oxygen-containing groups.

One trend evident in the C=O intensity data is that the alkali extract samples are consistently higher in carbonyl content than the residual materials. The intensity increases (Region 1 C=O) relative to the parent coal were 15.0, 13.7 and 10.4 units for the extracts, but only 6.5, 5.1 and 6.9 units for the residual materials. Because the alkali extracts are acidic, this trend suggests that the 1710 cm^{-1} peak may result from carboxylic acids. An alternative explanation is that the

1710 cm^{-1} peak represents ketone groups which are extractable because they are attached to molecules which also contain acidic groups. For samples IR4 and WR2 the increased intensity in the 1780-1630 cm^{-1} region relative to the feed coals appears to be accompanied by a slightly decreased intensity in the 1630-1524 cm^{-1} region. If the effect is real, it may result from a loss of aromatic C-C bonds or a loss of carboxylate ions, since both groups contribute in that region.

In an attempt to better identify the nature of the species responsible for the peak at ca. 1710 cm^{-1}, the spectrum of WR1 was subtracted from the spectrum of WR2. It was apparent beforehand that the carbonyl peak was slightly higher in WR2. Otherwise, the spectra of these residue samples were similar. The resulting difference spectrum shown in Figure 13 represents species present in higher concentration in WR2 than in WR1. We note that the carbonyl peak in the difference spectrum occurs at the slightly higher frequency of ca. 1724 cm^{-1} (relative to ca. 1710 cm^{-1} observed in the sample spectra). This may represent a slightly different carbonyl species than is represented by the 1710 cm^{-1} peak, or it may be a subtraction artifact. The concomitant occurrence of one species with another (for example, aliphatic CH with carbonyl) does not necessarily imply that they occur in the same molecule or result from the same reaction. Analysis of the difference spectrum by the Merck, Sharp and Dohme spectral interpretation program(20) gave the following possible functional groups in order of decreasing likelihood: primary amine, methyl group, lactam (4 member ring), ketone (5 member ring), carboxylic acid, aldehyde, mercaptan, and others of lesser likelihood. Further chemical and perhaps spectroscopic characterization is required to identify the carbonyl species. Since the carbonyl peak is a dominant one in the spectra of the coal products, it is evident that a thorough description of the chemistry of the crown ether treatment and work-up procedure requires that it be better characterized and accounted for.

Method

All samples were run by transmittance (Appendix 2, spectra 1-19) in KBr pellets (sample concentration ca. 0.3 wt % in KBr). Preliminary qualitative spectra of selected samples (diluted to ca. 0.5% by weight in KBr) were obtained by diffuse reflectance (Appendix 2, spectra 20-28) with a Harrick accessory. During sample preparation, each weighed sample was diluted and then ground for 30 seconds in an agate vial in a Wig-L-Bug mixer/grinder. Based on the sample and pellet weights, the infrared pellet spectra were scaled to represent 0.889 mg of sample. Infrared spectra obtained by this pellet technique are generally quantitatively reproducible to about ±5% relative absorbance. All samples were run at a nominal resolution of 4 cm^{-1} or 2 cm^{-1} on a Nicolet 7199 FTIR system. Standard routines for spectral integration, subtraction and interpretation as supplied by Nicolet were used in data analysis. Regions used for integration are reported in the tables with the sample data. Baseline correction was used in all cases.

We note several limitations in the use of these data for quantitative purposes. First, since only single samples of each type were analyzed, there is no experimental determination of the effect on spectral reproducibility of the procedures such as acetylation and methylation. Quantitation from such procedures is limited by the completeness of derivatization and elimination of reagents from the products. One limitation inherent in the infrared spectroscopic data is a broad sloping baseline feature in the 2000-3600 cm^{-1} region of most of the spectra (commonly observed in coal and coal-derived materials). This may limit the usefulness of the OH and CH stretch peaks for quantitative applications. Accurate peak height and area information is also difficult to obtain when peaks overlap. In such a case, the most accurate peak areas and heights are obtained by judicious use of curve resolving techniques. No such techniques were used to interpret the data reported here.

Section 4

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TABLE 1

ANALYSIS OF FEED COAL
Wilsonville Run 249

Coal	Upper Wyodak Seam Clovis Point Mine
Proximate, wt % as determined	
Moisture	24.37
Volatile Matter	37.36
Fixed Carbon (diff)	30.20
Ash	8.07
Ultimate, wt % MF	
Carbon	65.07
Hydrogen	4.58
Nitrogen	0.76
Oxygen (diff)	17.77
Sulfur, Total	1.14
Pyritic	0.15
Sulfate	0.07
Organic (diff)	0.92
Chlorine	0.01
Ash	10.67
Dry Heating Value, Btu/lb	11,125
Ash Analysis, wt %	
Na_2O	1.29
K_2O	0.65
CaO	18.20
MgO	3.71
Fe_2O_3	6.19
TiO_2	0.92
P_2O_5	0.70
SiO_2	36.64
Al_2O_3	17.30
SO_3	14.06
Undetermined	0.34

Note: Average of nine batches.
Source: Reference 2.

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TABLE 2

OPERATING CONDITIONS(1)
Wilsonville Run 249

	First Stage				Second Stage			
Date, 1985	H_2O Addn	1.5 wt % Fe_2O_3 Addn	0.9 wt % DMDS Addn	Target Dissolver Temp., °F	Catalyst Age, lbs Resid/ lb Cat	Avg. Temp., °F	WHSV, lbs feed/hr/ lb Cat	Letter Designation of Operating Conditions
6/4	N	N/Y	Y	790	645	670	1.22	-
6/6	N	Y	Y	790	659	659	0.89	-
6/8	N	Y	Y	790	-	-	-	-
6/9	N	Y	Y	790	667	658	0.93	-
6/10	N	Y	Y	790	672	558	0.78	-
6/11	N	Y	Y	790	680	612	1.02	-
6/14	N	Y	Y	790	693	642	1.11	-
6/17	N	Y	Y	790	721	642	1.22	-
6/18	N	Y	Y	790	732	641	1.37	-
6/20	Y	Y	Y	790	752	640	1.27	-
6/24	N	Y	Y	810	791	626	1.14	B-I
6/25	N	Y	Y	810	800	626	1.20	B-II
7/9	Y	Y	N	810	913	616	1.27	C
7/11	Y	Y	N	810	934	639	1.14	-
7/16	Y	N	N	810	980	641	1.35	-
7/18	Y	N/Y	N	810	1006	639	1.46	-
7/22	Y	Y	N	800	1049	660	1.30	-
7/25	Y	Y	N	800	1081	660	1.29	-
7/26	Y	Y	N	800	1094	659	1.22	-
7/28	Y	Y	N	800	1119	699	1.25	D
7/29	Y	Y	N	800	1131	699	1.25	D
7/31	Y	Y	N	800	1157	699	1.28	D
8/5	N	Y	N	800	1221	701	1.24	E
8/8	N	Y	N	800	1259	699	1.31	-
8/10	N	Y	N	810	1283	702	1.13	-
8/13	N	Y	N	810	1305	700	1.21	-
8/18	N	Y	N	810	1362	699	1.20	F
8/22	N	Y	N	810	1407	700	1.30	G
8/28	N	Y	N	810	1490	699	1.58	-
9/8	N	Y	N	810	1703	701	1.63	H
9/14	N	Y	N	810	1807	701	1.58	H

COMMON CONDITIONS

Coal - Subbituminous, Clovis Point Mine
Operating Mode - RITSL

First Stage Conditions
Dissolver Volume - 100% (a)
Slurry Concentration - ca. 40 wt % MF Coal (b)
Gas Feed Rate - ca. 28,000 SCF/ton MF Coal
Outlet Pressure - ca. 2400 psig
Coal Feed Rate - ca. 250 lbs/hr MF
Coal Space Rate - ca. 13.9 lbs/hr/ft^3
Gas Purity - ca. 85% H_2

Second Stage Catalyst
Shell 324 M (Ni/Mo), 1/32" extrudate

(a) Forced backmix in effect except for July 10-13 and after September 16.
(b) After August 26, MF coal concentration was 33%.

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TABLE 3

OPERATING CONDITIONS AND YIELD STRUCTURES(1)

Wilsonville Run 249

Operating Period	249A	249B-I	249B-II	249C	249D	249E	249F	249G	249H (a)
Thermal Stage									
Avg Reaction Temp., °F	788	807	807	807	796	796	805	805	803
Coal Space Vel. [lb/hr-ft^3(>700°F)]	14.3	14.9	14.5	14.2	13.6	14.0	13.9	13.8	14.4
Solvent to Coal (MF) Ratio	1.45	1.43	1.44	1.41	1.51	1.45	1.44	1.48	2.02 (1.52) (b)
Iron Oxide (1.5 wt % MF)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Dimethyl Disulfide (0.9 wt % MF)	Yes	Yes	Yes	No	No	No	No	No	No
Water	No	No	No	Yes	Yes	No	No	No	No
Solvent Resid Content, wt %	12	15	13	15	30	29	28	21	21 (28) (b)
Catalytic Stage									
Avg Reaction Temp., °F	641	626	626	617	699	701	700	700	701
Space Vel.(lb feed/hr-lb cat)	1.20	1.13	1.25	1.25	1.25	1.24	1.19	1.28	1.63
Catalyst Age [lb (res+ash+UC)/ lb/cat]	703-742	772-791	800-819	913-924	1119-1183	1208-1246	1317-1362	1407-1431	1683-1825
Dimethyl Disulfide	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes
Deashing - Type	CSD	CSD	CSD	CSD	CSD	CSD	CSD	CSD	Ash Recycle
Yield, % MAF Coal									
Water	15.1	12.8	14.0	12.4	13.8	14.0	14.6	14.4	13.8
Heterogases	9.3	9.9	10.7	11.2	10.3	8.3	9.1	9.8	9.5
C_1-C_3 Gas	5.8	8.8	8.6	9.3	7.2	6.1	7.6	8.0	6.8
C_4+ Distillate	44.9	46.2	43.9	39.7	52.6	57.0	54.7	50.6	55.9
Resid	4.1	-0.3	6.0	3.8	0.5	-3.9	-4.4	1.2	-6.5
Ash Concentrate	25.9	27.9	22.1	28.3	20.6	23.6	23.7	21.2	26.1
Hydrogen Consumption	-5.0	-5.4	-5.3	-4.7	-5.7	-5.8	-6.1	-5.8	-6.3
Hydrogen Efficiency (lb C_4+ Dist/lb H_2 Consumed)	9.0	8.5	8.4	8.4	9.3	9.9	9.0	8.8	8.9
Distillate Selectivity (lb C_1-C_3/lb C_4+ Dist)	0.13	0.19	0.20	0.23	0.14	0.10	0.14	0.16	0.12
Energy Content of Feed Coal Rejected to Ash Conc., %	35.0	34.3	27.9	35.3	24.9	29.5	26.8	25.5	30.8 (c)
Coal Conversion, % MAF (d)									
Thermal Stage	85.6	89.7	89.6	91.5	91.9	89.3	90.6	90.2	92.8
Thermal + Catalytic Stage	86.0	89.0	90.1	92.7	91.7	90.2	90.3	90.0	93.5
HTR Conversion, % Feed									
Resid	30.8	23.9	29.5	22.4	24.4	27.5	26.5	31.5	21.3
Resid + UC	25.4	22.1	25.8	22.1	22.1	25.0	23.4	28.9	17.4

(a) Alternate deashing tests without CSD unit operation.
(b) Data in parentheses based on Cl-free.
(c) On solvent-free basis.
(d) Cresol solubles.

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TABLE 4

COMPONENT DISTRIBUTION OF V-131B SAMPLES
Wilsonville Run 249

Sample			wt % of Sample			
Date, 1985	Time*	Number	850°F Dist	THF-Sol. Resid	IOM	Ash
6-4	DC	48876	65.1	33.4	0.4	0.2
6-6	DC	48950	68.9	30.3	0.1	0.0
6-10	1:45	49056	67.4	29.8	1.3	0.8
6-10	DC	49145	69.9	29.3	0.1	0.1
6-11	DC	49199	74.0	25.2	0.0	0.0
6-17	DC	49514	69.8	29.4	0.2	0.0
6-18	DC	49593	71.2	28.0	0.2	0.0
6-20	DC	49727	69.4	29.6	0.2	0.0
6-24	DC	49991	67.3	31.8	0.0	0.0
7-9	DC	50894	72.5	26.7	0.0	0.0
7-11	DC	51026	72.8	26.3	0.0	0.0
7-16	DC	51335	71.2	28.0	0.1	0.0
7-18	DC	51464	66.3	32.9	0.0	0.0
7-22	DC	51702	.	.	.	.
7-25	DC	51886	61.0	38.1	0.0	0.0
7-29	DC	52146	59.5	39.6	0.1	0.0
7-31	DC	52282	.	.	.	.
8-5	DC	52560	60.1	39.0	0.2	0.2
8-8	DC	52786	.	.	.	.
8-10	DC	52883	54.3	44.5	0.2	0.2
8-13	DC	53079	56.7	41.9	0.5	0.4
8-18	DC	53383	58.2	40.7	0.2	0.0
8-22	DC	53621	64.5	34.2	0.2	0.1
8-28	DC	53943	46.1	37.0	6.6	9.7
9-8	DC	54586	45.4	29.4	8.5	15.5
9-14	DC	54903	47.3	26.6	9.0	15.4

*DC = Daily Composite

/ls

TABLE 5

COMPONENT DISTRIBUTION OF V-1064 SAMPLES
Wilsonville Run 249

Sample			wt % of Sample			
Date, 1985	Time*	Number	850°F Dist	THF-Sol. Resid	IOM	Ash
6-4	DC	48826	49.9	37.3	8.2	4.4
6-6	DC	48997	46.2	38.8	7.0	6.7
6-9	7:00	49063	.	.	6.6	6.3
6-14	DC	49301	52.0	34.6	7.2	5.7
6-17	DC	49506	53.5	33.5	7.0	5.3
6-18	DC	49580	55.0	33.0	6.5	4.9
6-25	DC	50043	53.1	35.7	5.0	5.7
7-9	DC	50881	59.2	31.8	3.5	5.0
7-11	DC	51013	53.1	35.7	4.7	5.9
7-16	DC	51384	54.1	35.5	4.2	5.3
7-18	DC	51451	53.2	32.5	6.8	4.3
7-22	DC	51689	.	.	.	.
7-25	DC	51819	50.9	38.5	3.6	6.2
7-29	DC	52139	47.0	42.3	3.8	6.0
7-31	DC	52270	.	.	.	.
8-5	DC	52553	47.7	40.4	4.9	6.5
8-8	DC	52768	.	.	.	.
8-10	DC	52885	46.3	42.0	5.2	5.8
8-13	DC	53058	47.8	42.1	4.9	4.6
8-18	DC	53370	48.3	41.6	4.8	4.7
8-22	DC	53605	53.2	37.3	4.5	4.7
8-28	DC	53936	43.2	40.3	6.2	9.5
9-8	DC	54578	40.7	33.7	9.1	16.0
9-14	DC	54894	43.7	31.0	9.3	15.4

*DC = Daily Composite

/ls

TABLE 6

COMPONENT DISTRIBUTION OF V-1067 SAMPLES
Wilsonville Run 249

Sample			wt % of Sample			
Date, 1985	Time*	Number	850°F Dist	THF-Sol. Resid	IOM	Ash
6-4	DC	48865	48.8	36.3	8.3	5.0
6-6	DC	48998	59.5	27.8	6.3	5.8
6-8	7:00	49064	73.7	15.5	6.2	4.1
6-14	DC	47302	58.0	28.1	7.2	6.1
6-17	DC	49548	57.3	29.6	6.4	6.0
6-18	DC	49581	58.6	28.3	6.4	5.5
6-25	DC	50094	52.7	32.7	5.7	8.0
7-9	DC	50882	59.9	29.0	3.4	6.2
7-11	DC	51014	52.9	33.5	4.3	8.2
7-16	DC	51320	53.9	32.8	4.1	7.7
7-18	DC	51452	53.2	33.2	6.7	5.5
7-22	DC	51690	•	•	•	•
7-25	DC	51880	52.4	35.3	3.5	7.8
7-29	DC	52140	49.7	37.8	3.9	7.7
7-31	DC	52271	•	•	•	•
8-5	DC	52554	48.7	35.5	5.1	9.7
8-8	DC	52769	•	•	•	•
8-10	DC	52886	47.0	38.9	5.7	8.0
8-13	DC	53059	46.7	39.9	5.5	6.9
8-18	DC	53371	48.2	38.9	5.5	6.3
8-22	DC	53606	53.9	34.3	6.2	4.5
8-28	DC	53937	45.0	36.9	6.4	10.6
9-8	DC	54579	40.4	30.9	9.5	18.2
9-14	DC	54893	45.1	27.9	9.4	16.2

*DC = Daily Composite

/ls

TABLE 7

SOLUBILITY FRACTIONATION OF V-131B SAMPLES
Wilsonville Run 249

Date, 1985	wt % of THF-Soluble Resid Oils	Asphaltenes	Preasphaltenes
6-4	75.1	24.6	0.3
6-6	79.0	18.8	2.2
6-10(a)	84.7	14.8	0.5
6-10(b)	86.4	13.4	0.2
6-11	87.8	11.8	0.4
6-17	83.7	15.5	0.8
6-18	82.4	15.9	1.6
6-20	90.0	9.9	0.1
6-24	80.1	17.8	2.0
7-9	77.5	21.1	1.4
7-11	77.9	20.2	2.0
7-16	75.5	21.6	2.9
7-18	74.3	22.4	3.3
7-25	75.3	22.2	2.5
7-29	79.0	18.5	2.5
8-5	81.0	16.4	1.9
8-10	85.8	14.0	0.2
8-13	83.9	15.1	0.9
8-18	86.9	11.4	1.7
8-22	83.3	15.4	1.4
8-28	74.4	20.1	5.4
9-8	67.0	25.7	7.4
9-14	67.2	24.3	8.5

(a) Sample Time 1:45
(b) Daily Composite

/ls

TABLE 8

SOLUBILITY FRACTIONATION OF V-1064 SAMPLES
Wilsonville Run 249

Date, 1985	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
6-4	56.7	29.2	14.1
6-6	64.7	24.8	10.5
6-14	64.9	24.7	10.4
6-17	65.3	25.2	9.4
6-18	64.1	24.3	11.6
6-25	65.4	24.1	10.4
7-9	59.0	26.3	14.7
7-11	60.1	26.5	13.3
7-16	59.8	26.7	13.6
7-18	57.7	25.5	16.8
7-25	61.1	25.4	13.5
7-29	62.6	24.2	13.1
8-5	66.8	23.8	9.4
8-10	63.6	25.1	11.3
8-13	66.3	23.9	9.8
8-18	69.0	20.8	10.2
8-22	67.6	23.5	8.9
8-28	62.8	25.1	12.1
9-8	61.7	26.4	11.9
9-14	61.4	25.7	12.9

/ls

TABLE 9

SOLUBILITY FRACTIONATION OF V-1067 SAMPLES
Wilsonville Run 249

Date, 1985	wt % of THF-Soluble Resid Oils	 Asphaltenes	 Preasphaltenes
6-4	68.0	23.1	8.9
6-6	83.6	14.6	1.7
6-8	83.6	16.3	0.1
6-14	79.1	17.3	3.6
6-17	78.4	18.6	3.1
6-18	78.3	18.6	3.1
6-25	75.9	19.0	5.1
7-9	66.6	23.2	10.2
7-11	65.7	22.7	11.6
7-16	68.8	21.9	9.4
7-18	65.3	25.0	9.4
7-25	70.2	22.2	7.6
7-29	74.0	19.9	6.2
8-5	80.2	16.9	3.0
8-10	79.3	18.4	2.3
8-13	79.1	17.8	3.1
8-18	76.0	19.0	5.0
8-22	76.0	17.7	6.2
8-28	72.3	22.4	5.3
9-8	66.4	27.6	6.0
9-14	65.3	27.1	7.6

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TABLE 10

PROTON DISTRIBUTION OF V-131B WHOLE SAMPLES
Wilsonville Run 249

Date, 1985	Proton Distribution, % Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	7.9	5.9	15.9	9.8	20.5	25.8	14.3
6-6	7.7	6.0	15.5	9.8	20.6	25.9	14.5
6-10(a)	5.8	5.9	12.9	8.7	20.5	28.9	17.3
6-10(b)	5.3	5.5	13.4	9.4	20.8	28.9	16.7
6-11	5.1	5.5	13.3	9.4	21.0	28.9	16.8
6-17	7.3	6.1	13.0	9.6	20.1	28.4	15.5
6-18	6.7	5.8	13.1	9.3	19.6	29.2	16.2
6-20	6.5	5.7	13.6	9.7	19.5	29.5	15.4
6-24	9.4	6.7	14.7	9.7	17.6	27.8	14.1
7-9	11.2	7.9	14.4	9.8	15.3	27.3	14.2
7-11	12.6	7.7	15.2	10.4	14.7	27.1	12.3
7-16	11.1	7.2	14.0	9.8	16.3	26.8	14.7
7-18	12.8	7.2	15.8	10.2	16.0	25.8	12.2
7-22	11.9	6.7	17.2	10.0	17.0	25.6	11.6
7-25	11.5	7.0	16.6	9.9	16.3	27.0	11.8
7-29	11.1	5.9	17.7	10.0	18.3	25.9	11.1
7-31	10.3	5.5	17.2	9.9	18.8	26.8	11.5
8-5	9.4	5.6	16.3	9.5	19.2	27.1	12.9
8-8	9.2	5.4	15.6	9.3	19.3	27.7	13.5
8-10	9.2	5.0	16.7	9.4	19.3	27.8	12.5
8-13	9.0	5.4	15.7	9.1	19.6	27.7	13.6
8-18	9.1	5.3	16.9	9.4	19.8	26.9	12.7
8-22	8.7	5.3	15.8	9.2	19.6	27.6	13.7
8-28	9.3	5.5	15.9	9.0	18.6	28.4	13.3
9-8	8.2	5.1	15.5	9.0	19.3	29.6	13.4
9-14	7.3	4.9	14.2	8.7	19.3	31.0	14.6

All samples dissolved in $CDCl_3$, integrated electronically.

(a) Sample time 1:45
(b) Daily composite

/ls

TABLE 11

PROTON DISTRIBUTION OF V-1064 WHOLE SAMPLES
Wilsonville Run 249

Date, 1985	Proton Distribution, % Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	14.8	9.3	12.7	9.8	15.1	23.5	14.7
6-6	13.2	8.4	12.7	9.8	15.3	24.8	15.8
6-9	12.4	8.7	12.4	9.7	15.3	24.9	16.4
6-14	11.3	7.0	12.6	9.3	16.3	27.3	16.2
6-17	12.0	6.9	13.7	9.5	16.6	26.3	15.0
6-18	11.8	6.6	14.0	9.7	16.7	26.4	14.7
6-25	14.9	7.8	14.0	10.0	14.3	25.5	13.3
7-9	16.2	8.5	13.3	10.6	12.6	25.7	13.0
7-11	17.0	9.7	12.8	10.7	11.9	25.3	12.6
7-16	17.1	9.2	13.3	10.7	12.6	24.9	12.3
7-18	18.8	7.0	14.5	11.0	12.7	25.2	10.8
7-22	19.1	8.6	14.8	11.1	12.0	24.0	10.3
7-25	19.3	6.7	16.0	10.5	12.9	24.3	10.3
7-29	19.4	7.1	15.5	10.6	13.0	24.4	10.1
7-31	18.7	7.7	15.1	10.6	12.9	24.4	10.6
8-5	18.4	5.7	17.2	9.9	14.6	24.6	9.7
8-8	16.6	7.4	16.6	10.3	12.7	25.1	11.2
8-10	16.9	7.1	15.7	10.4	14.4	24.8	10.6
8-13	16.3	7.2	15.5	10.2	15.1	23.7	12.1
8-18	16.6	6.9	15.1	9.7	14.2	25.7	11.8
8-22	16.1	6.5	15.2	9.8	14.9	26.0	11.5
8-28	15.1	7.2	15.2	10.0	14.7	25.4	12.4
9-8	11.8	7.5	13.7	9.6	15.6	27.7	14.1
9-14	11.8	5.8	14.5	9.7	16.4	28.7	13.0

All samples dissolved in $CDCl_3$, integrated electronically.

/ls

TABLE 12

PROTON DISTRIBUTION OF V-1067 WHOLE SAMPLES
Wilsonville Run 249

	Proton Distribution, %						
Date, 1985	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	8.5	6.3	16.3	10.0	20.0	24.2	14.6
6-6	6.0	5.2	14.2	9.3	21.2	27.9	16.1
6-8	4.6	5.0	13.0	8.9	22.5	29.1	16.8
6-14	6.7	5.8	14.5	9.3	19.8	28.2	15.7
6-17	7.2	5.5	15.3	9.4	19.7	28.3	14.6
6-18	7.4	5.5	14.0	9.3	19.5	28.8	15.5
6-25	10.1	6.7	15.6	9.9	17.1	26.8	13.8
7-9	12.5	6.9	17.1	9.9	15.6	26.3	11.5
7-11	13.7	7.5	16.2	10.1	15.2	25.3	12.1
7-16	12.7	7.2	17.2	10.2	15.8	25.0	11.8
7-18	13.9	6.6	17.8	10.1	15.5	25.0	11.2
7-22	12.2	6.5	18.1	10.1	16.5	25.5	11.0
7-25	12.4	6.4	17.5	9.9	17.1	25.4	11.3
7-29	9.8	5.8	17.3	9.8	18.6	26.4	12.2
7-31	10.6	5.5	18.0	9.8	18.8	26.2	11.1
8-5	9.1	5.1	16.0	9.5	19.2	27.7	13.3
8-8	9.4	5.2	17.4	9.8	19.5	25.9	12.9
8-10	8.9	5.3	16.8	9.6	19.9	25.8	13.6
8-13	9.0	5.4	16.3	9.4	19.5	27.3	13.1
8-18	10.1	5.0	17.7	9.5	19.9	26.8	11.0
8-22	9.2	5.1	16.8	9.4	19.4	27.9	12.2
8-28	9.9	5.2	17.1	9.4	18.7	27.1	12.5
9-8	8.6	4.8	16.4	9.5	19.0	28.2	13.5
9-14	7.2	5.3	13.6	8.8	19.2	30.9	15.1

All samples dissolved in $CDCl_3$, integrated electronically.

/ls

TABLE 13

PROTON DISTRIBUTION OF V-178 WHOLE SAMPLES
Wilsonville Run 249

		Proton Distribution, %						
Date, 1985	Number	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	48870	9.9	6.6	11.8	9.7	17.6	27.5	16.8
6-6	49007	9.5	6.6	11.1	10.0	17.6	28.1	17.1
6-10	49141	9.6	6.0	11.9	9.4	18.1	28.3	16.8
6-14	49310	8.2	6.3	11.3	9.4	17.5	29.7	17.6
6-17	49515	8.3	6.5	11.6	9.5	18.1	28.8	17.2
6-18	49589	8.5	6.5	11.6	9.4	17.4	29.2	17.5
6-24	49987	10.1	6.9	11.4	9.6	15.5	29.8	16.7
7-9	50893	12.5	7.5	11.7	10.4	13.1	30.2	14.5
7-11	51024	14.0	7.9	12.0	10.4	13.0	29.1	13.7
7-16	51334	13.5	8.3	11.5	10.6	12.5	29.3	14.3
7-18	51462	13.5	6.5	12.8	10.6	13.7	30.0	13.0
7-22	51700	14.7	6.6	13.1	10.8	12.6	30.5	11.7
7-25	51893	14.1	6.7	13.1	11.0	12.9	30.6	11.5
7-29	52153	13.2	6.7	12.6	10.6	12.9	31.4	12.6
7-31	52264	13.1	6.3	12.6	10.2	13.3	32.2	12.3
8-5	52546	11.4	6.7	12.3	9.9	14.4	32.1	13.2
8-8	52778	10.9	6.6	12.6	10.1	15.1	31.3	13.4
8-10	52876	10.3	6.9	11.4	10.0	14.4	32.7	14.3
8-13	53065	10.5	7.2	12.0	10.4	15.1	30.6	14.3
8-18	53376	10.7	6.6	12.3	9.8	15.2	31.1	14.3
8-22	53611	11.0	6.2	12.1	9.7	14.9	31.8	14.3
8-28	53943	10.1	6.1	12.2	9.6	16.1	31.1	14.6
9-8	54586	7.8	6.1	11.9	9.2	16.8	33.7	14.5
9-14	54903	6.7	6.1	11.1	9.2	16.6	35.0	15.3

Samples dissolved in $CDCl_3$, integrated electronically.
All samples are daily composites.

/ls

TABLE 14

PROTON DISTRIBUTION OF V-1072 WHOLE SAMPLES
Wilsonville Run 249

	Proton Distribution, %						
Date, 1985	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-10	3.9	5.3	12.2	8.9	21.9	30.3	17.5
6-20	6.2	5.6	13.2	9.2	20.1	30.5	15.3
7-26	8.4	6.9	12.7	9.9	17.7	30.4	14.1
7-28	6.9	6.7	12.7	9.5	19.4	30.4	14.5

Samples dissolved in $CDCl_3$, integrated electronically.

All samples are daily composites.

/ls

TABLE 15

PROTON DISTRIBUTION OF V-131B DISTILLATES
Wilsonville Run 249

Date, 1985	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	5.2	5.6	13.7	9.3	22.0	28.0	16.1
6-6	5.3	5.4	13.3	9.0	21.7	28.4	16.8
6-10(a)	3.9	5.3	13.0	9.2	22.6	29.7	16.3
6-10(b)	3.7	5.0	12.7	8.8	23.2	29.9	16.6
6-11	4.1	5.1	12.7	8.8	22.6	30.0	16.7
6-17	5.2	5.3	13.7	9.0	20.7	30.3	15.8
6-18	5.5	5.5	13.2	9.2	20.9	29.9	15.8
6-20	4.8	5.9	12.2	9.2	20.4	31.0	16.6
6-24	7.7	5.7	14.5	9.5	19.3	29.7	13.5
7-9	10.2	6.3	14.9	9.8	17.0	29.1	12.8
7-11	11.0	6.5	14.2	9.8	15.7	29.4	13.4
7-16	8.9	6.6	13.6	9.8	17.0	30.4	13.6
7-18	10.3	6.3	15.0	9.8	17.1	28.4	13.0
7-25	9.9	5.6	14.3	10.2	18.5	28.4	13.2
7-29	7.5	5.9	15.0	9.6	19.4	29.1	13.4
8-5	7.0	5.1	15.3	9.6	20.5	29.3	13.1
8-10	5.7	5.1	14.5	9.1	21.1	30.9	13.6
8-18	5.8	5.2	13.8	9.3	20.6	30.1	15.3
8-22	6.1	4.9	14.2	9.2	20.4	30.9	14.3
8-28	6.1	5.2	14.0	8.7	20.3	31.4	14.3
9-8	5.1	5.0	13.3	8.5	20.9	32.2	15.0
9-14	4.9	4.8	12.8	8.6	20.3	32.6	15.9

(a) Sample Time 1:45
(b) Daily Composite

/ls

TABLE 16

PROTON DISTRIBUTION OF V-1064 DISTILLATES
Wilsonville Run 249

Date, 1985	Proton Distribution, % Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	12.8	5.1	13.5	9.4	17.4	27.2	14.6
6-6	10.9	5.6	13.2	9.8	17.8	27.6	15.1
6-14	9.3	5.6	12.2	9.3	17.8	29.7	16.2
6-17	9.6	5.3	13.2	9.9	17.8	29.0	15.1
6-18	9.4	5.7	13.1	9.4	17.9	29.6	14.9
6-25	11.9	5.5	13.7	9.7	15.6	29.7	14.0
7-9	14.1	6.1	13.8	10.1	14.5	28.6	12.8
7-11	14.9	6.1	13.4	10.3	13.6	29.2	12.4
7-16	15.3	5.4	14.7	10.1	14.5	28.9	11.1
7-18	14.6	5.5	13.6	10.3	14.1	30.3	11.6
7-25	14.6	6.0	13.6	10.0	13.9	29.3	12.4
7-29	15.0	6.2	13.6	10.6	13.0	30.1	11.6
8-5	12.7	6.1	13.4	10.1	14.9	30.3	12.5
8-10	11.0	6.6	12.6	10.2	15.7	30.4	13.6
8-18	11.8	5.6	13.9	9.9	16.0	30.3	12.5
8-22	12.0	5.3	14.0	9.7	16.0	30.7	12.3
8-28	11.4	5.5	13.7	9.2	16.3	30.7	13.2
9-8	8.4	6.1	12.4	9.6	17.1	31.7	14.8
9-14	8.0	5.8	12.6	9.4	17.2	32.1	14.9

/ls

TABLE 17

PROTON DISTRIBUTION OF V-1067 DISTILLATES
Wilsonville Run 249

	Proton Distribution, %						
Date, 1985	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	5.2	6.0	14.3	10.1	22.2	26.5	15.7
6-6	4.1	5.4	13.6	9.8	22.7	27.9	16.6
6-8	3.8	5.3	13.2	9.6	23.3	27.4	17.4
6-14	4.6	5.6	13.0	9.6	21.7	27.8	17.6
6-17	4.8	6.0	12.4	10.0	20.9	28.5	17.4
6-18	5.3	5.9	12.2	9.8	20.7	28.1	18.0
6-25	7.3	6.6	13.6	10.1	18.2	29.4	14.9
7-9	9.4	7.5	13.9	10.5	16.5	27.6	14.6
7-11	10.5	6.9	14.6	10.0	16.9	28.4	12.7
7-16	9.8	6.7	13.8	10.2	17.0	29.5	13.0
7-18	10.6	6.2	14.5	10.1	16.8	28.7	12.9
7-25	9.0	6.6	14.6	10.3	17.6	28.6	13.2
7-29	6.7	6.1	14.5	9.6	19.7	28.9	14.5
8-5	5.7	5.7	13.9	9.5	20.4	29.9	14.9
8-10	5.0	5.5	12.9	8.9	20.2	32.0	15.6
8-18	5.3	5.6	13.4	9.3	20.4	30.3	15.8
8-22	5.4	5.3	13.3	8.9	20.0	31.5	15.6
8-28	5.8	5.0	13.2	8.7	20.2	32.3	14.7
9-8	5.0	4.9	12.7	8.4	20.7	33.0	15.3
9-14	4.5	4.8	12.5	8.5	20.3	33.2	16.2

/ls

TABLE 18

PROTON DISTRIBUTION OF V-131B RESIDS
Wilsonville Run 249

	Proton Distribution, %						
Date, 1985	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	15.1	5.8	20.7	10.1	17.9	21.0	9.4
6-6	15.0	5.4	20.8	10.1	18.1	21.1	9.5
6-10(a)	12.6	5.3	19.0	9.6	18.3	24.2	10.9
6-10(b)	12.5	4.5	18.4	9.5	18.8	25.0	11.3
6-11	11.5	4.6	18.2	9.4	18.8	25.5	12.0
6-17	13.2	4.6	19.3	9.5	18.0	25.3	10.2
6-18	13.2	4.8	19.2	9.5	17.8	25.3	10.2
6-20	12.7	5.5	18.8	9.3	17.2	25.8	10.7
6-24	16.8	6.2	19.1	9.9	15.8	22.6	9.6
7-9	21.9	7.4	20.6	10.3	13.8	18.4	7.5
7-11	22.9	7.1	21.2	10.5	13.4	17.6	7.1
7-16	21.1	5.5	20.7	10.8	14.8	18.6	8.6
7-18	22.8	6.6	22.5	10.8	12.3	16.5	8.5
7-25	19.3	6.3	20.7	10.4	16.1	18.7	8.6
7-29	17.7	6.1	21.0	10.4	17.3	19.1	8.5
8-5	16.9	4.6	21.5	10.0	18.1	19.9	8.9
8-10	15.1	4.5	20.3	9.6	18.8	22.6	9.1
8-18	15.4	5.2	19.4	9.6	17.9	22.2	10.4
8-22	16.4	5.2	19.5	9.5	17.4	21.3	10.7
8-28	16.6	4.9	21.3	9.7	17.8	21.3	8.3
9-8	15.2	4.9	19.7	9.3	17.9	23.4	9.6
9-14	14.9	5.1	18.1	9.2	17.7	22.6	12.4

All samples dissolved in $CDCl_3$, electronically integrated.

(a) Sample time 1:45
(b) Daily Composite

/ls

TABLE 19

PROTON DISTRIBUTION OF V-1064 PYRIDINE-SOLUBLE RESIDS
Wilsonville Run 249

	Proton Distribution, %						
Date, 1985	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	33.8	4.8	20.1	9.5	12.0	13.4	6.4
6-6	26.8	3.2	20.8	9.0	14.4	17.8	8.0
6-14	23.8	3.8	19.7	9.0	14.9	19.9	8.9
6-17	23.0	4.2	19.4	9.0	15.2	20.0	9.2
6-18	22.4	5.1	18.0	9.1	14.1	21.5	9.9
6-25	29.4	4.1	20.7	9.4	12.7	16.6	7.0
7-9	34.1	4.9	19.9	9.7	10.8	14.5	6.1
7-11	36.4	5.0	20.4	9.5	10.2	13.1	5.5
7-16	35.6	4.7	20.0	9.6	10.9	13.0	6.2
7-18	38.5	6.2	19.4	9.8	9.4	11.5	5.2
7-25	34.2	4.0	20.4	9.7	11.6	14.7	5.5
7-29	33.5	4.3	20.2	9.7	11.5	14.9	5.8
8-5	30.8	3.1	21.4	9.2	13.5	15.7	6.4
8-10	27.6	4.2	19.5	8.7	14.0	17.9	8.1
8-18	30.9	3.2	20.7	9.0	13.3	16.2	6.6
8-22	30.0	3.9	19.8	8.9	13.3	16.6	7.4
8-28	30.2	4.8	19.3	8.8	12.9	16.4	7.6
9-8	24.0	4.8	19.3	8.8	15.0	19.3	8.7
9-14	25.4	4.6	19.8	8.8	14.9	18.7	7.8

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

/ls

TABLE 20

PROTON DISTRIBUTION OF V-1067 RESIDS
Wilsonville Run 249

Date, 1985	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
6-4	15.7	6.6	20.7	10.3	17.8	18.7	10.3
6-6	12.1	5.6	17.9	10.0	18.7	23.1	12.6
6-8	9.9	4.1	18.2	9.5	20.0	26.5	11.9
6-14	12.5	5.2	20.0	9.8	17.8	23.0	11.8
6-17	13.6	4.7	21.4	10.0	17.9	22.9	9.6
6-18	14.1	4.8	21.2	9.9	17.8	23.1	9.1
6-25	17.8	6.0	23.0	10.3	15.9	19.0	8.0
7-9	23.2	5.6	23.8	10.6	14.2	16.3	6.3
7-11	23.1	6.5	23.6	10.3	13.5	15.4	7.5
7-16	23.0	5.7	24.3	10.5	14.4	15.5	6.6
7-18	22.5	7.9	23.4	10.6	13.5	14.5	7.6
7-25	17.6	7.8	21.0	10.7	15.7	17.2	10.0
7-29	16.6	6.3	20.9	10.2	17.2	18.2	10.6
8-5	15.3	5.1	22.5	10.2	18.6	19.8	8.4
8-10	14.9	5.1	20.6	9.7	18.4	21.5	9.8
8-18	16.6	5.1	22.1	9.8	18.0	19.6	8.8
8-22	17.3	4.6	20.5	9.3	18.2	20.2	9.9
8-28	17.0	5.1	20.6	9.6	17.6	21.0	9.1
9-8	15.5	5.0	19.8	9.4	17.6	22.3	10.4
9-14	13.9	5.4	18.0	9.1	17.7	24.3	11.7

All samples dissolved in $CDCl_3$, integrated electronically.

/ls

TABLE 21

PHENOL CONCENTRATION BY FTIR
Wilsonville Run 249

Date, 1985	Phenolic -OH Concentrations, meq/g							
	V-131B		V-1064		V-1067		V-178	V-1072
	Dist	Resid	Dist	Resid	Dist	Resid	Whole	Whole
6-4	0.20	0.46	0.49	1.03	0.20	0.53	0.62	.
6-6	0.20	0.46	0.67	0.99	0.16	0.45	0.72	.
6-8	.	.	.	.	0.11	0.29	.	.
6-10(a)	0.17	0.41	.	.	.	.	.	
6-10(b)	0.11	0.34	.	.	.	.	0.63	0.17
6-11	0.14	0.35	.	.	.	.	.	.
6-14	.	.	0.51	1.05	0.25	0.60	0.61	.
6-17	0.28	0.52	0.71	1.11	0.31	0.64	0.71	.
6-18	0.30	0.53	0.75	1.09	0.34	0.71	0.75	.
6-20	0.32	0.59	.	.	.	.	.	0.37
6-24	0.41	0.69	.	.	.	.	0.84	.
6-25	.	.	0.82	1.15	0.46	0.82	.	.
7-9	0.52	0.87	0.88	1.24	0.55	0.97	0.96	.
7-11	0.58	0.89	0.93	1.24	0.57	0.92	0.98	.
7-16	0.42	0.75	0.88	1.23	0.46	0.88	0.92	.
7-18	0.43	0.81	0.80	1.14	0.42	0.83	.	.
7-25	0.35	0.68	0.92	1.21	0.35	0.76	.	.
7-26	.	.	.	.	.	.	0.37	.
7-28	.	.	.	.	.	.	0.24	.
7-29	0.23	0.56	1.00	1.18	0.18	0.54	.	.
8-5	0.16	0.42	0.85	1.02	0.14	0.42	.	.
8-10	0.13	0.33	0.97	0.99	0.12	0.33	.	.
8-13	0.13	0.36	0.87	1.03	0.14	0.40	.	.
8-18	0.13	0.36	0.83	0.95	0.14	0.45	.	.
8-22	0.13	0.38	0.82	0.97	0.13	0.42	.	.
8-28	0.13	0.52	0.86	0.97	0.13	0.52	.	.
9-8	0.14	0.58	0.76	1.05	0.14	0.58	.	.
9-14	0.14	0.66	0.76	1.13	0.13	0.65	.	.

(a) Sample Time 1:45
(b) Daily Composite

/ls

TABLE 22

MICROAUTOCLAVE TEST RESULTS
Wilsonville Run 249

Date, 1985	Coal Conversion, wt % MAF							
	V-131B		V-1064		V-1067		V-178	V-1072
	Dist	Whole	Dist	Whole	Dist	Whole	Whole	Whole
6-4	80.0	87.0	63.5	63.6	81.2	.	60.7	.
6-6	80.3	85.9	61.6	70.6	79.0	90.1	.	.
6-8	.	.	.	.	79.7	85.9	.	.
6-9	.	.	.	72.1	.	.	.	.
6-10(a)	78.2	84.9	.	.	.	.	.	.
6-10(b)	79.1	85.4	.	.	.	.	.	80.3
6-11	77.0	83.7	.	.	.	.	.	.
6-14	.	.	62.8	73.6	76.6	89.2	.	.
6-17	76.2	82.3	61.0	74.6	75.2	87.7	.	.
6-18	75.7	80.9	61.1	59.1	75.8	84.8	.	.
6-20	73.7	82.6	.	.	.	.	.	79.0
6-24	74.6	82.5	.	.	.	.	.	.
6-25	.	.	61.2	62.2	76.1	87.3	.	.
7-9	74.5	81.3	59.2	59.6	75.3	83.1	.	.
7-11	73.5	81.7	58.2	52.9	74.8	79.6	.	.
7-16	76.1	83.1	58.6	56.6	78.0	83.5	.	.
7-18	75.2	85.7	57.2	53.5	75.6	77.1	.	.
7-25	77.5	86.8	60.9	59.1	77.2	85.3	.	.
7-26	.	.	.	.	.	.	.	81.5
7-28	.	.	.	.	.	.	.	82.9
7-29	78.7	89.0	57.9	53.3	79.0	86.7	.	.
8-5	78.6	86.6	60.1	65.9	79.8	87.1	.	.
8-10	78.4	88.2	60.3	64.0	78.2	88.3	.	.
8-18	76.9	87.8	59.5	66.3	76.3	78.9	.	.
8-22	77.7	87.0	58.3	66.6	76.3	85.8	.	.
8-28	76.3	81.8	61.6	65.1	77.7	84.5	.	.
9-8	72.8	81.0	62.7	64.5	73.2	81.0	.	.
9-14	72.6	80.8	61.4	44.7	70.8	79.5	.	.

(a) Sample Time 1:45
(b) Daily Composite

/ls

TABLE 23

CALCULATED COAL CONVERSION IN THE THERMAL AND CATALYTIC STAGES
Wilsonville Run 249

Date, 1985	% MAF Coal Conversion*		
	Thermal Stage	Both Stages	Catalytic Stage**
6/4	80.0	82.2	2.2
6/6	86.6	86.1	-0.5
6/9	87.0	-	-
6/14	84.3	85.3	1.0
6/17	83.8	86.9	3.1
6/18	84.3	86.2	1.9
6/25	89.2	91.2	2.0
7/9	90.8	92.8	2.0
7/11	89.0	92.8	3.8
7/16	90.8	93.8	3.0
7/18	76.3	81.7	5.4
7/25	91.3	93.3	2.0
7/29	90.5	92.4	1.9
8/5	88.6	92.0	3.4
8/10	90.1	92.2	2.1
8/18	89.2	90.7	1.5
8/22	89.2	84.5	-4.7
Average	87.1 ± 4.2	89.0 ± 4.2	1.9 ± 2.2

* See text for calculation method.

**By difference, as % conversion in both stages - % conversion in thermal stage.

/ls

TABLE 24

HYDROTREATER CONVERSIONS AND KINETIC CONSTANTS
Wilsonville Run 249

Date, 1985	Feed Inputs, lbs/hr (a)	Withdrawal Tube Flush, lbs/hr (a)	Flashed Bottoms, lbs/hr (a)	850°F$^+$ Resid Inputs, lbs/hr (b)	850°F$^+$ Resid Outputs, lbs/hr (b)	850°F$^+$ Resid Conversion, % (b)	850°F$^+$ Resid SV, lbs/hr/lb cat (b)	First Order Rate Constant for Resid Conversion, k(T), lbs resid/lb cat/hr (b)	Pre-Exponential Factor for Resid Conversion, A, 10^6 lbs resid/lb cat/hr (b)	Conversion of Benzene Insolubles, % (b)
6/4	529.9	15.2	494.1	234.2	220.4	6.3	0.54	0.0338	5.19	17.8
6/6	384.4	15.2	365.8	169.1	124.7	35.6	0.39	0.1392	25.72	39.4
6/14	479.9	16.6	447.0	193.7	157.8	22.7	0.45	0.1018	25.24	26.6
6/17	527.5	15.9	493.7	207.2	177.7	16.6	0.48	0.0794	19.69	30.4
6/18	594.9	15.9	547.4	228.7	189.9	20.4	0.53	0.1075	27.11	33.4
6/25	519.4	17.1	481.2	204.4	184.8	10.6	0.47	0.0502	16.56	19.0
7/9	549.2	17.0	505.2	187.9	163.7	14.8	0.43	0.0642	25.39	26.2
7/11	493.0	17.0	443.3	192.3	167.6	14.8	0.44	0.0656	17.15	19.3
7/16	585.2	17.6	530.5	225.3	195.7	15.1	0.52	0.0787	19.85	25.6
7/18	632.7	17.6	549.2	241.7	219.1	10.3	0.56	0.0575	15.04	28.5
7/25	559.9	18.1	500.5	228.1	194.2	17.5	0.53	0.0918	16.67	35.1
7/29	543.3	17.0	465.5	242.6	194.1	25.0	0.56	0.1395	13.36	40.9
8/5	537.2	17.7	452.3	235.3	183.6	28.2	0.54	0.1529	14.19	38.3
8/10	491.4	17.7	414.8	223.6	185.0	20.9	0.51	0.1072	9.79	41.9
8/18	520.7	17.1	448.8	233.7	199.3	17.3	0.54	0.0930	8.90	26.6
8/22	565.5	17.7	485.5	229.0	196.6	16.5	0.53	0.0866	8.16	5.6
8/28	686.9	16.3	598.6	311.8	259.2	20.3	0.72	0.1457	13.95	32.7
9/8	705.5	18.8	623.0	293.9	251.7	16.8	0.68	0.1139	10.57	21.4
9/14	683.8	18.9	600.9	268.0	224.1	19.6	0.62	0.1210	11.23	21.7

(a) Source: Reference 1.

(b) Conoco Calculation, See Appendix 1.

/ls

TABLE 25

OPERATING CONDITIONS
HRI CTSL RUN 227-27

Coal:	Clovis Point Mine, Upper Wyodak seam, subbituminous
Temperature, °F:	First Stage - 750 Second Stage days 1 through 7 - 815 days 8 through 15 - 820 days 16 through 21 - 825
Catalysts:	First Stage - Amocat 1C (Ni/Mo) Second Stage - Amocat 1A (Co/Mo)
Coal Space Velocity, each stage:	46 lbs/hr/ft^3 settled catalyst
Pressure:	2500 psig
Solvent/MF Coal Ratio:(a)	1.5
Coal Drying:	Days 1 through 4 - oven dried (9-10% H_2O to reactor) Days 5 through 9 - slurry dried (5-7% H_2O to reactor) Days 10 through 21 - oven dried (7-9% H_2O to reactor)

(a) Solvent composed totally of pressure-filter liquid (IBP ca. 500°F) and contains no solids. Solvent/coal ratio in slurry fleed was 1.2 but additional solvent was continuously added through the buffer pumps to increase the overall ratio to 1.5.

Source: Reference 10.

/ls

TABLE 26

DISTILLATION RESULTS
HRI CTSL Run 227-27

Run Day	Sample	wt % of Sample 850°F$^-$ Distillate	 850°F$^+$ Resid
Pressure Filter Liquids			
1	4514	89.2	10.7
3	4516	85.6	13.9
5	4519	83.7	16.1
6	4520	83.7	16.2
7	4521	76.5	23.3
9	4523	82.6	17.3
11	4526	80.5	19.1
13	4528	78.2	21.5
15	4530	76.4	23.5
17	4533	77.6	22.2
19	4535	72.3	23.5
21	4537	75.0	24.7
First-Stage Samples			
4	4517	75.5	24.0
11	4525	73.5	25.8
16	4531	77.2	22.5
22	4538	66.4	33.2

/ls

TABLE 27

SOLUBILITY FRACTIONATION ANALYSES OF RESIDS
HRI CTSL Run 227-27

Run Day	Sample	wt % of Pyridine-Soluble Resid Oils	 Asphaltenes	 Preasphaltenes
Pressure-Filter Liquids				
1	4514	87.1	12.6	0.3
3	4516	89.9	9.5	0.6
5	4519	91.0	8.7	0.3
7	4521	87.4	11.2	1.3
9	4523	80.9	17.9	1.2
11	4526	84.1	15.2	0.7
13	4528	82.2	16.4	1.5
15	4530	75.4	21.0	3.6
17	4533	78.4	17.7	4.0
19	4535	74.6	20.5	4.9
21	4537	73.1	21.0	6.0
First-Stage Samples				
4	4517	89.1	10.2	0.7
11	4525	77.8	17.3	4.9
16	4531	79.5	18.9	1.6
22	4538	68.4	25.2	6.4

/ls

TABLE 28

PROTON DISTRIBUTIONS OF WHOLE SAMPLES
HRI CTSL Run 227-27

		Proton Distributions, %						
Run Day	Sample	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure Filter Liquids								
1	4514	4.2	5.3	10.6	7.8	21.7	32.6	17.9
2	4515	6.4	4.8	11.1	7.6	20.3	32.0	17.9
3	4516	6.7	4.9	10.9	7.5	20.1	31.9	17.9
4	4518	6.5	4.9	10.9	7.5	19.7	33.1	17.4
5	4519	6.8	4.6	11.0	7.4	19.9	33.1	17.2
6	4520	6.5	4.5	10.8	7.6	19.6	33.5	17.5
7	4521	6.2	4.4	11.5	7.4	20.1	33.5	16.9
8	4522	6.9	4.7	10.7	7.5	19.3	33.5	17.3
9	4523	7.4	4.8	11.0	7.6	18.8	33.7	16.7
10	4524	7.8	4.4	12.0	7.6	19.3	33.1	15.9
11	4526	8.0	4.8	11.8	7.6	18.7	32.7	16.4
12	4527	8.4	5.0	12.3	7.8	18.7	32.3	15.6
13	4528	8.3	5.2	12.0	7.9	18.7	31.9	15.9
14	4529	9.1	4.9	12.8	8.3	18.9	31.1	15.0
15	4530	9.6	5.0	12.3	8.0	18.4	31.3	15.4
16	4532	9.4	5.2	12.2	8.0	18.4	31.2	15.7
17	4533	9.7	5.3	12.6	8.2	18.2	30.7	15.3
18	4534	10.3	5.4	12.5	8.1	17.8	30.4	15.5
19	4535	10.4	5.2	12.5	8.2	17.9	30.3	15.5
20	4536	10.9	5.4	12.4	8.1	17.3	30.4	15.5
21	4537	11.8	5.6	12.8	8.1	17.1	29.7	15.0
First Stage Samples								
4	4517	4.7	4.4	11.2	7.7	21.0	33.6	17.5
11	4525	6.3	4.5	11.5	7.6	19.7	33.8	16.6
16	4531	7.5	4.8	11.6	7.7	19.3	32.1	16.9
22	4538	10.4	5.7	12.1	8.3	17.0	30.5	16.0

Samples dissolved in $CDCl_3$, integrated electronically.

/ls

TABLE 29

PROTON DISTRIBUTIONS OF DISTILLATES
HRI CTSL Run 227-27

		Proton Distributions, %						
Run Day	Sample	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure Filter Liquids								
1	4514	3.9	5.1	11.6	8.4	20.1	32.6	18.4
3	4516	5.8	4.2	10.3	7.5	20.4	33.6	18.0
5	4519	6.0	4.5	10.7	7.5	20.1	34.1	17.1
7	4521	5.6	4.3	10.3	7.5	20.3	34.2	17.8
9	4523	6.1	4.3	10.4	7.3	20.2	34.2	17.4
11	4526	6.2	4.4	11.1	7.4	20.1	33.8	16.9
13	4528	6.4	4.3	10.5	7.5	19.6	34.4	17.3
15	4530	6.6	4.6	10.8	7.7	19.1	34.1	17.0
17	4533	7.4	4.9	12.0	7.9	19.7	32.5	15.6
19	4535	8.4	4.8	12.7	8.1	19.4	31.9	14.8
21	4537	8.9	4.8	11.9	7.8	18.4	32.6	15.7
First-Stage Samples								
4	4517	4.2	4.1	11.1	7.7	22.2	33.3	17.4
11	4525	4.5	4.4	10.1	7.4	20.8	34.7	18.1
16	4531	5.7	4.5	11.2	7.6	20.4	33.5	17.0
22	4538	7.5	4.6	11.6	8.0	19.5	33.3	15.6

/ls

TABLE 30

PROTON DISTRIBUTIONS OF RESIDS
HRI CTSL Run 227-27

		Proton Distributions, %						
Run Day	Sample	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure Filter Liquids								
1	4514	13.2	3.7	16.9	8.7	18.5	26.7	12.1
3	4516	17.2	4.5	16.0	7.9	16.3	26.4	11.6
5	4519	17.4	4.3	16.8	8.2	16.8	26.2	10.3
7	4521	17.0	4.5	16.6	8.2	17.2	25.6	10.8
9	4523	17.8	5.1	16.5	8.2	16.2	24.4	11.8
11	4526	19.6	5.0	17.9	8.6	16.4	23.2	9.3
13	4528	20.6	6.0	17.8	8.8	15.5	21.9	9.5
15	4530	21.9	7.5	17.1	8.9	15.1	20.2	9.3
17(a)	4533	28.6	3.4	19.3	8.2	15.2	17.1	8.2
19(a)	4535	30.2	3.2	19.2	8.4	14.5	17.2	7.2
21(a)	4537	34.2	2.7	20.5	8.4	13.7	14.6	5.8
First Stage Samples								
4	4517	10.6	3.5	16.3	8.7	19.3	29.5	12.2
11	4525	14.0	4.9	16.3	8.6	17.2	27.6	11.5
16	4531	17.3	5.0	17.5	8.8	16.0	25.1	10.4
22	4538	20.7	7.6	17.4	9.4	14.3	21.9	8.7

(a) Samples dissolved in pyridine-d_5 (99.96%), integrated electronically. All other samples dissolved in $CDCl_3$, integrated electronically.

/ls

TABLE 31

PHENOLIC CONTENTS OF DISTILLATES AND THF-SOLUBLE RESIDS
HRI CTSL Run 227-27

Run Day	Sample	Phenolic Concentration, meq/g 850°F$^-$ Distillate	 850°F$^+$ Resid
Pressure Filter Liquids			
1	4514	0.02	0.16
3	4516	0.03	0.17
5	4519	0.04	0.19
7	4521	0.04	0.20
9	4523	0.06	0.27
11	4526	0.06	0.25
13	4528	0.07	0.30
15	4530	0.08	0.41
17	4533	0.08	0.44
19	4535	0.09	0.49
21	4537	0.12	0.58
First-Stage Samples			
4	4517	0.06	0.27
11	4525	0.09	0.44
16	4531	0.09	0.46
22	4538	0.20	0.87

Peak maxima between 3313 and 3338 cm^{-1} for all distillates and between 3296 and 3313 cm^{-1} for all resids.

/ls

TABLE 32

MICROAUTOCLAVE TESTS WITH WHOLE SAMPLES
HRI CTSL Run 227-27

Run Day	Sample	THF Coal Conversion, wt % MAF Whole Sample
Pressure-Filter Liquid		
1	4514	64.5
3	4516	60.0
5	4519	58.9
7	4521	60.4
9	4523	59.4
11	4526	61.4
13	4528	62.5
15	4530	64.3
17	4533	62.0
19	4535	66.1
21	4537	66.2
First-Stage Samples		
4	4517	64.0
11	4525	63.6
16	4531	61.5
22	4538	65.1

Conditions: Mod-EQ Test - 6g Old Ben #1 (Indiana 5) coal, 9g solvent, 750°F, 30 min.

/ls

TABLE 33

ANALYSES OF POTENTIAL START-UP OILS
HRI CTSL Run 227-30

Identification Sample No.	Hydrotreated Heavy Distillate From Ill. 6 Coal HRI 5192 (LO-4617)	V-123 Hydrotreated Solvent From Ill. 6 Coal HRI 5198 (LO-4618)
°API	16.8	17.0
Elemental, wt %		
C	88.8	88.2
H	11.2	11.1
N	0.08	0.14
S	0.04	0.04
D-1160 Distillation		
IBP, °F	431	441
IBP - 500°F, wt %	6.4	7.9
500-650°F, wt %	52.9	50.4
650°F - EP, wt %	34.3	38.9
EP$^+$, wt %	5.9	1.5
Loss, wt %	0.5	1.3
EP, °F	850	905
Microautoclave Coal Conversion, Mod-EQ, wt % MAF	70.7	70.6

Source of Analytical Data: Reference 14

/ls

TABLE 34

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

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

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

/ls

TABLE 35

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)	-

(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

TABLE 36

HYDROXYL CONTENT OF SAMPLES BASED ON PEAK HEIGHT (a)

	Ester C=O Peak Net Absorbance (b) (Acetylated-Unacetylated)		wt % O as OH As Determined		
Sample	Phenolic (1765 cm^{-1})	Alcoholic (1740 cm^{-1})	Phenol	Alcohol	Total
Illinois 6					
IC	0.2588	0.1829	2.21	1.24	3.45
IE1	0.2925	0.2292	2.52	1.56	4.08
IE2	0.3150	0.2765	2.73	1.90	4.63
IR4	0.2935	0.2673	2.53	1.84	4.37
Wyodak					
WC	0.3989	0.3096	3.53	2.14	5.67
WE1	0.2608	0.2750	2.23	1.89	4.12
WR1	0.3515	0.2764	3.07	1.90	4.97
WR2	0.2517	0.2354	2.15	1.61	3.76

(a) Method of Painter, et al. (Reference 19).

(b) Calculated as absorbance (height) of peak above corrected baseline in acetylated sample minus baseline-corrected absorbance in unacetylated sample. Absorbances scaled to 1 mg sample.

/ls

TABLE 37

INTEGRATED PEAK INTENSITIES IN THE ALIPHATIC CH STRETCH AND C=O STRETCH REGIONS

		Integrated Intensity, Abs-cm^{-1}							
		Illinois 6				Wyodak			
Peak Description	Integration Region, cm^{-1}	IC	IE1	IE2	IR4	WC	WE1	WR1	WR2
Samples As Determined									
Total Aliphatic CH	2994-2790	5.3	9.1	10.4	9.0	5.3	6.5	7.5	9.3
Methyl CH	2994-2940	1.0	2.0	2.3	1.5	0.8	1.1	1.2	2.1
Total C=O (a)	1780-1524	9.2	29.5	25.7	15.2	16.4	29.0	22.0	22.9
Region 1 C=O	1780-1630	3.1	18.1	16.8	9.6	7.8	18.2	12.9	14.7
Region 2 C=O (a)	1630-1524	6.1	11.4	8.9	5.6	8.6	10.8	9.1	8.2
Change (Product-Feed)									
Total Aliphatic CH	2994-2790	---	3.8	5.1	3.7	---	0.8	2.2	4.0
Methyl CH	2994-2940	---	1.0	1.3	0.5	---	0.3	0.4	1.3
Total C=O (a)	1780-1524	---	20.3	16.5	6.0	---	12.6	5.6	6.5
Region 1 C=O	1780-1630	---	15.0	13.7	6.5	---	10.4	5.1	6.9
Region 2 C=O (a)	1630-1524	---	5.3	2.8	-0.5	---	2.2	0.5	-0.4

(a) Includes contributions from the aromatic C-C stretch peak at 1600 cm^{-1}.

/ls

TABLE 38

PEAK AREAS POTENTIALLY USEFUL FOR DETERMINATION OF HYDROXYL CONTENT

		Integrated Intensity, Abs-cm $^{-1}$							
		Illinois 6				Wyodak			
Peak Description	Integration Region, cm $^{-1}$	IC	IE1	IE2	IR4	WC	WE1	WR1	WR2
Direct OH									
OH Stretch	3585-3100	11.1	21.5	17.0	9.6	15.0	17.6	19.6	19.7
Indirect OH (a)									
Loss OH Stretch	3585-3100	3.0	14.8	10.6	5.2	3.7	4.2	2.9	4.8
Gain Total Aliphatic CH Stretch	2994-2790	4.5	4.2	4.5	8.0	3.1	2.1	2.1	1.9
Gain Methyl CH Stretch	2994-2940	0.8	1.5	1.7	2.5	0.9	1.2	0.8	0.8
Gain Ester C=O Stretch	1824-1725	11.7	13.9	16.8	15.6	21.0	15.8	17.9	15.5
Gain Total C=O Stretch (b)	1824-1524	19.5	11.9	18.8	21.6	30.7	22.4	23.2	21.5
wt % O as OH (c)	---	3.45	4.08	4.63	4.37	5.67	4.12	4.97	3.76

(a) Calculated as baseline-corrected intensity for acetylated sample minus baseline-corrected intensity for corresponding unacetylated sample.

(b) Includes the aromatic C-C stretch peak at 1600 cm $^{-1}$.

(c) From Table 36 (based on peak height).

/ls

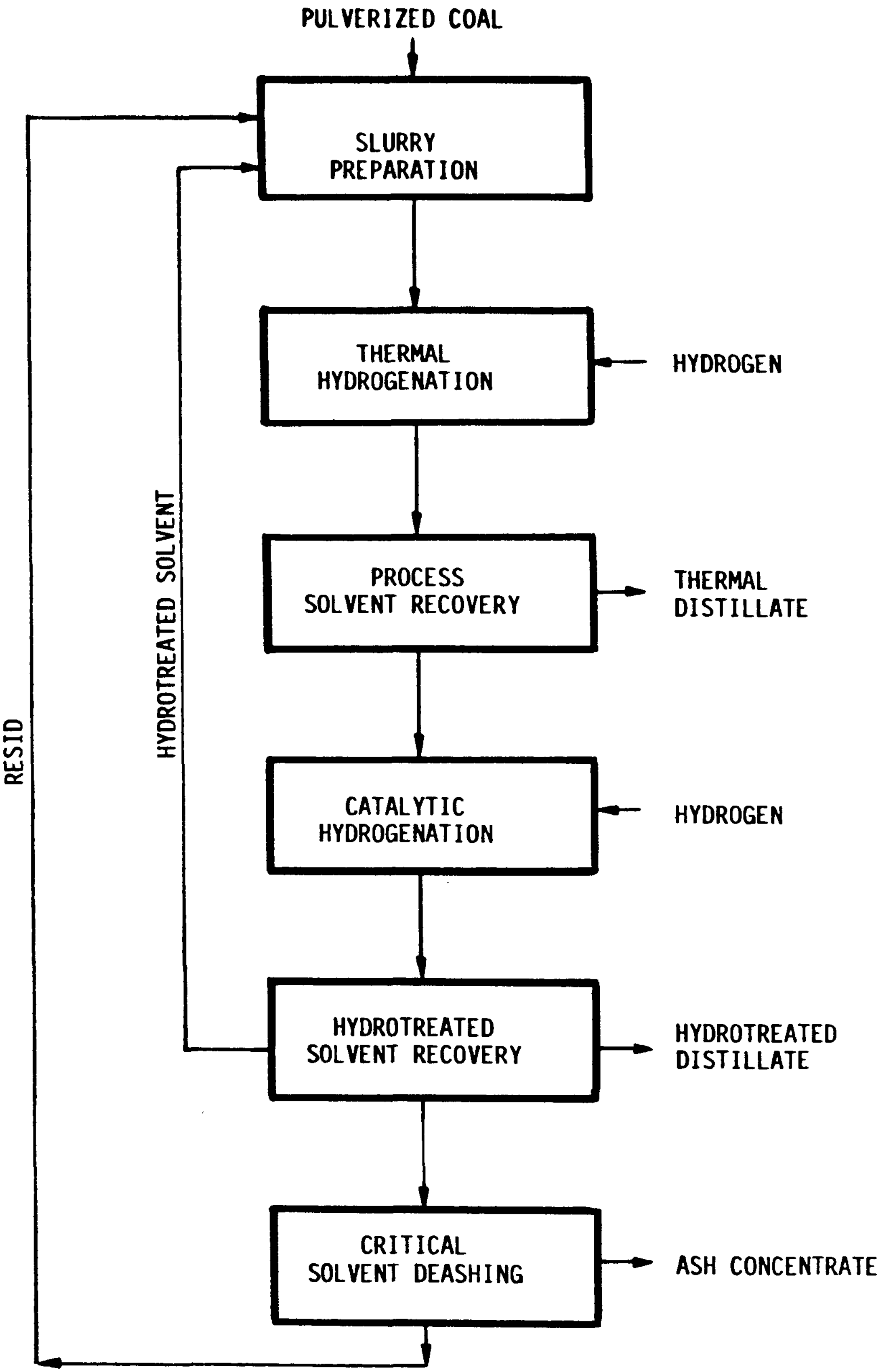


Figure 1. Block Flow Diagram - Reconfigured Integrated Two-Stage Mode.
Source: Reference 2.

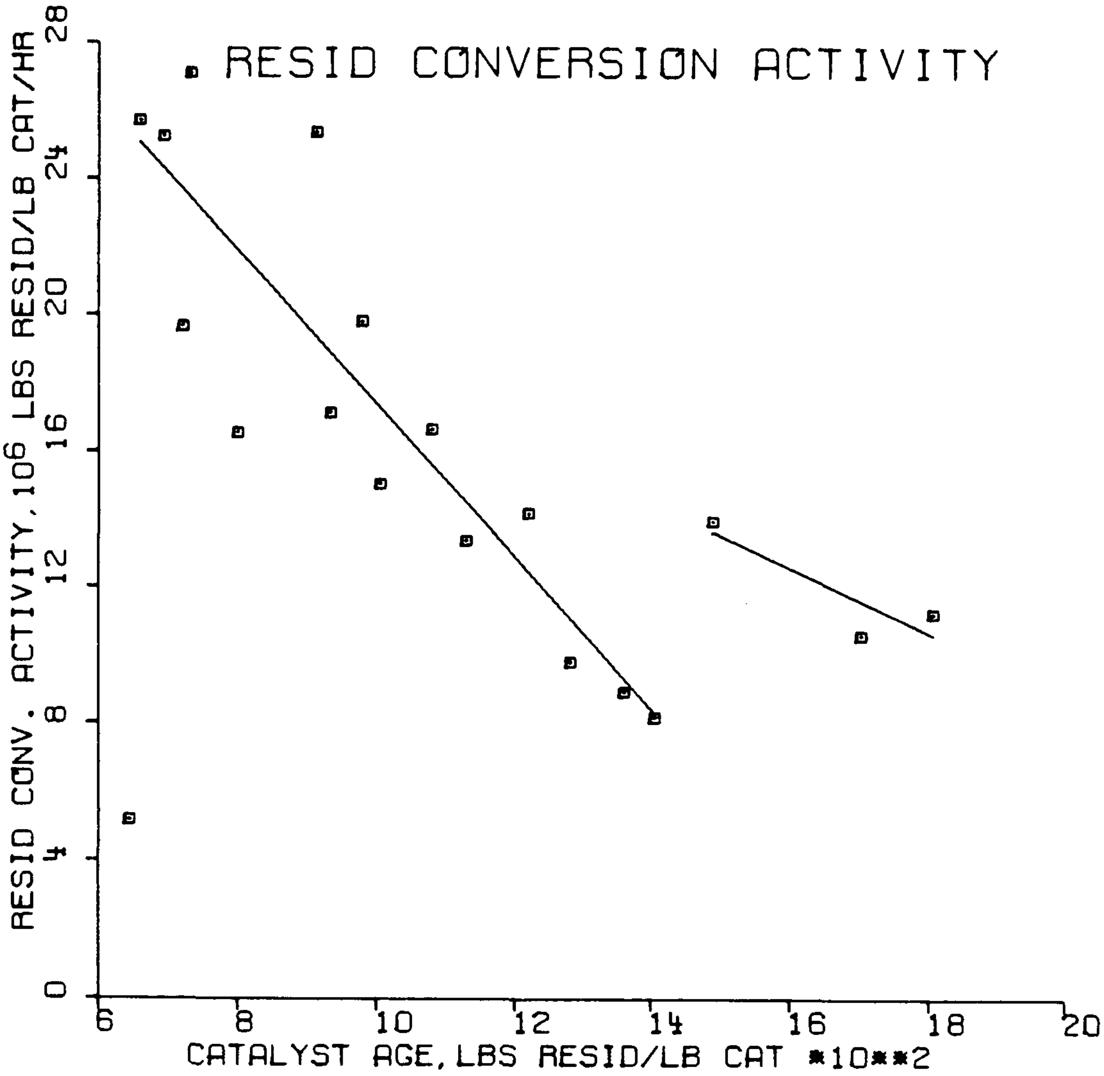


Figure 2. Resid Conversion Activity Plot for Run 249.

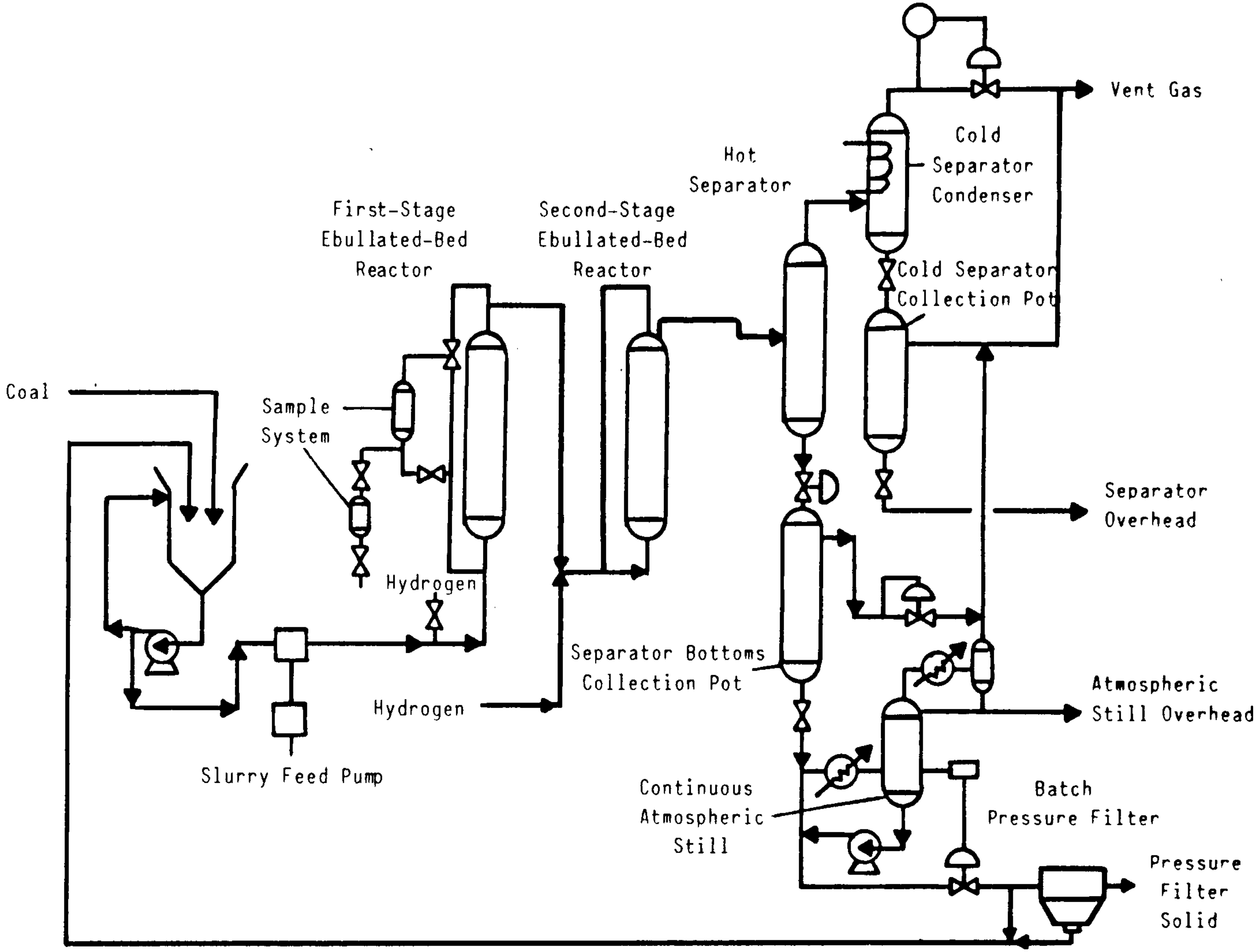


Figure 3. HRI Ebullated-Bed Bench Unit 227. Source: Reference 8.

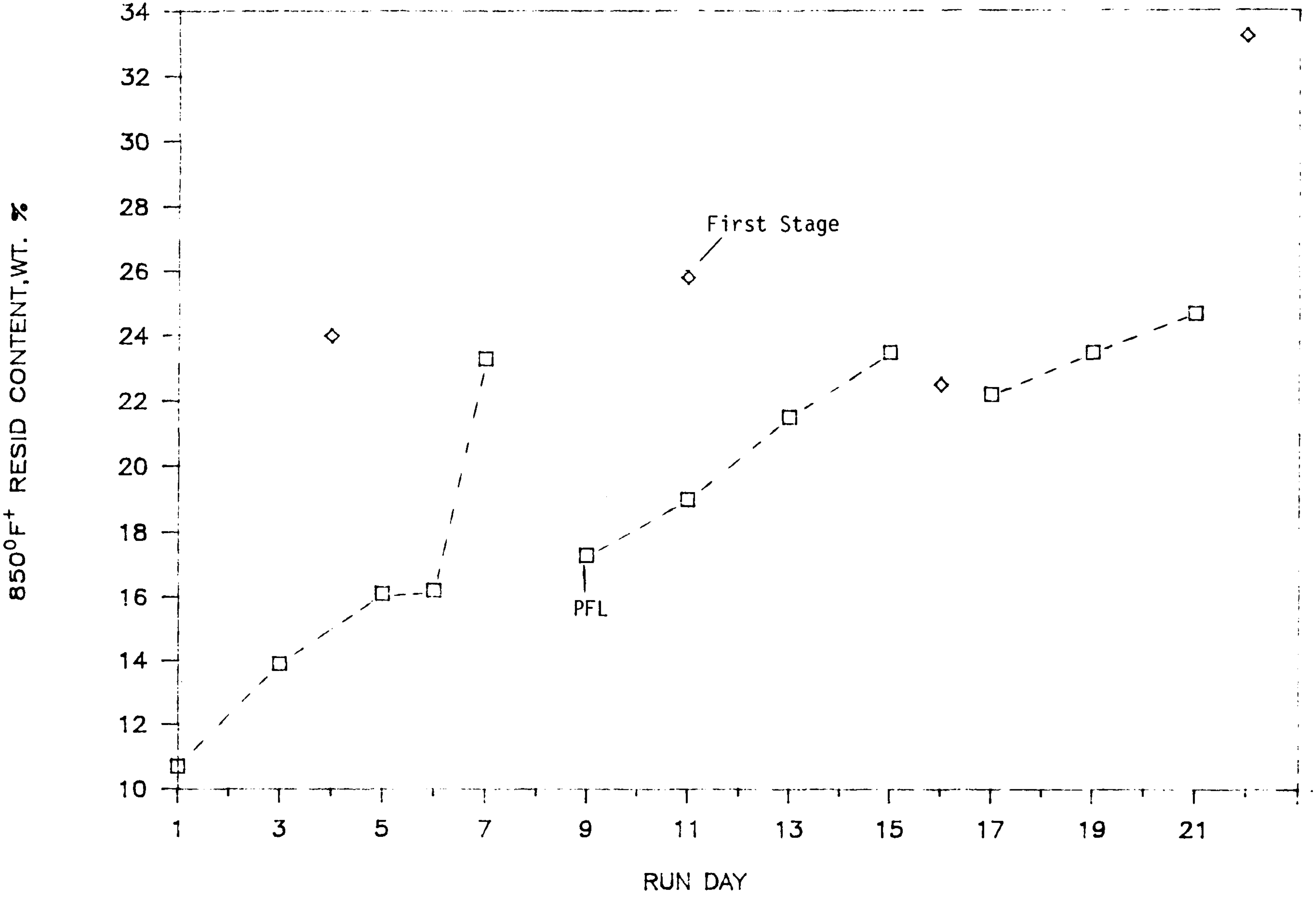


Figure 4. 850^oF^+ Resid Content vs Run Day - HRI CTSL Run 227-27.

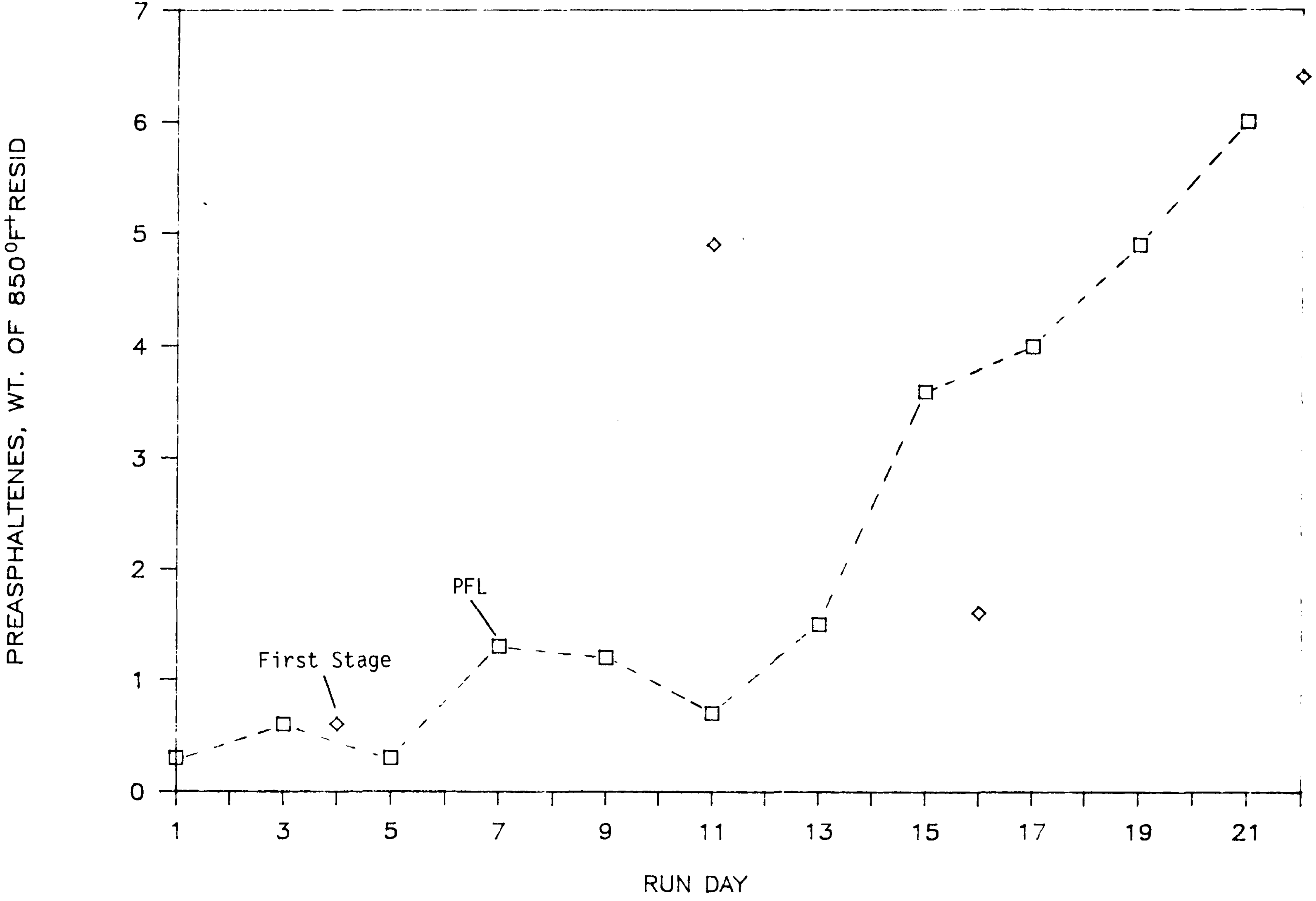


Figure 5. Resid Preasphaltenes Content vs Run Day - HRI CTSL Run 227-27.

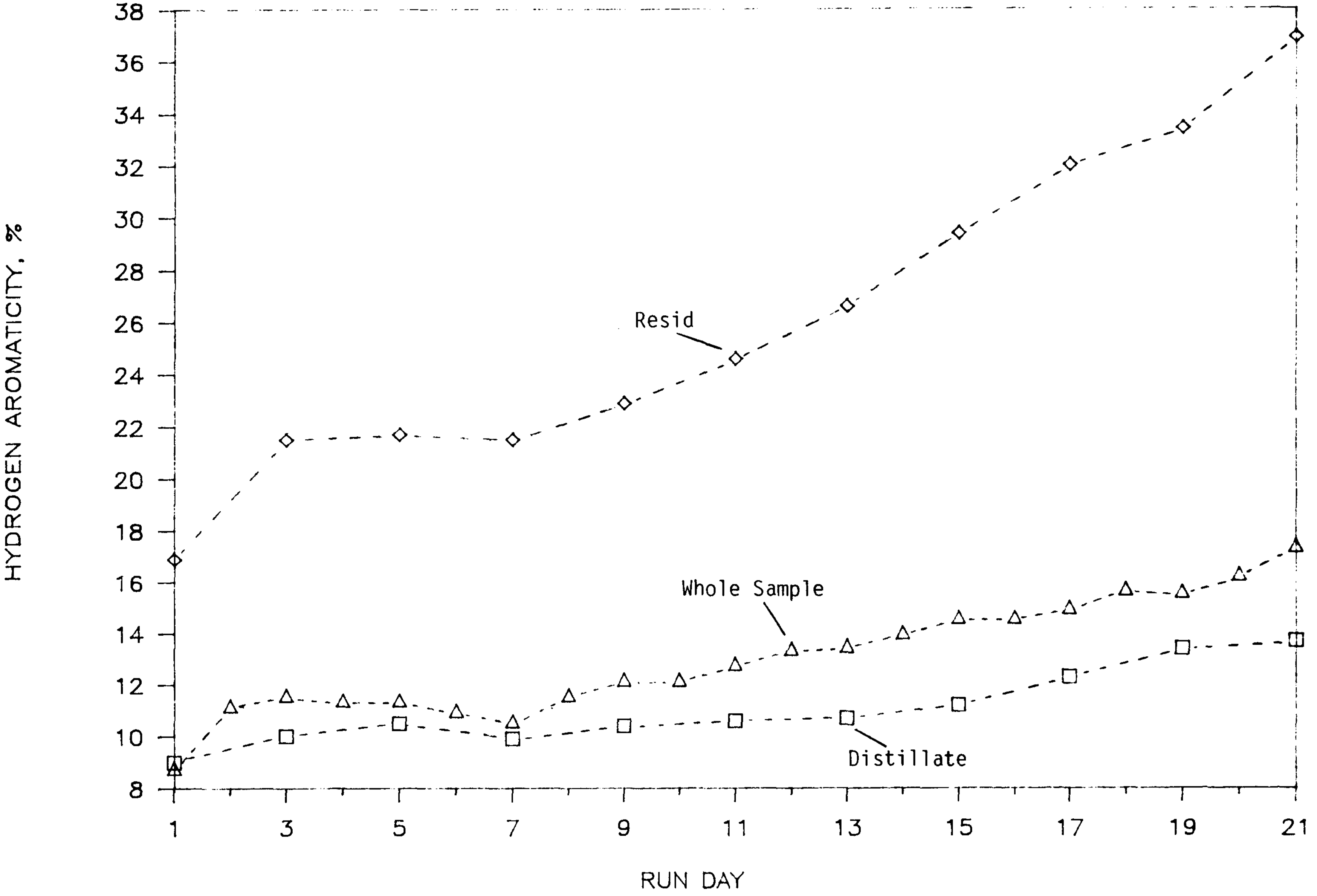


Figure 6. Aromaticity of PFL Samples vs Run Day - HRI CTSL Run 227-27.

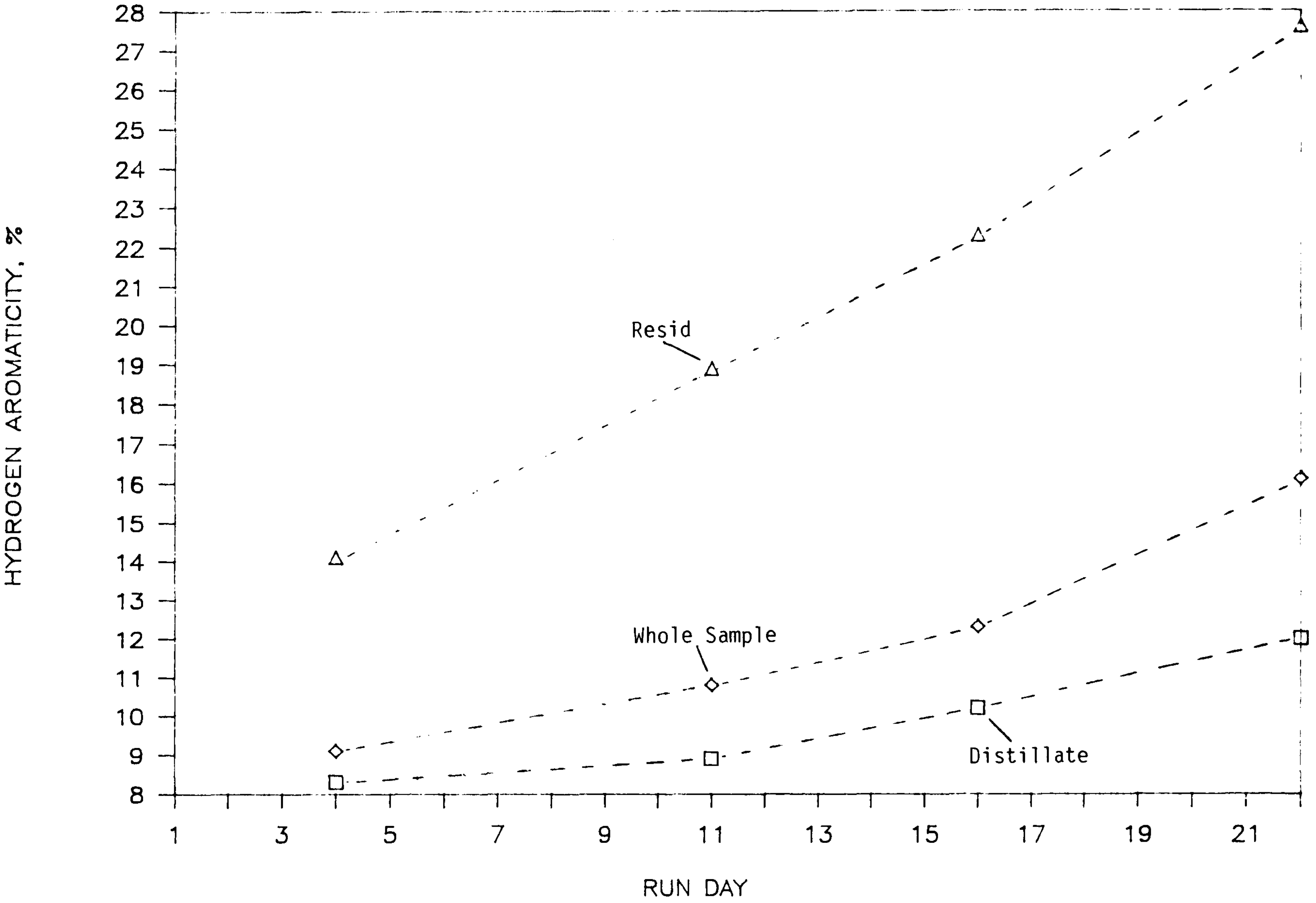


Figure 7. Aromaticity of First-Stage Oils vs Run Day - HRI CTSL Run 227-27.

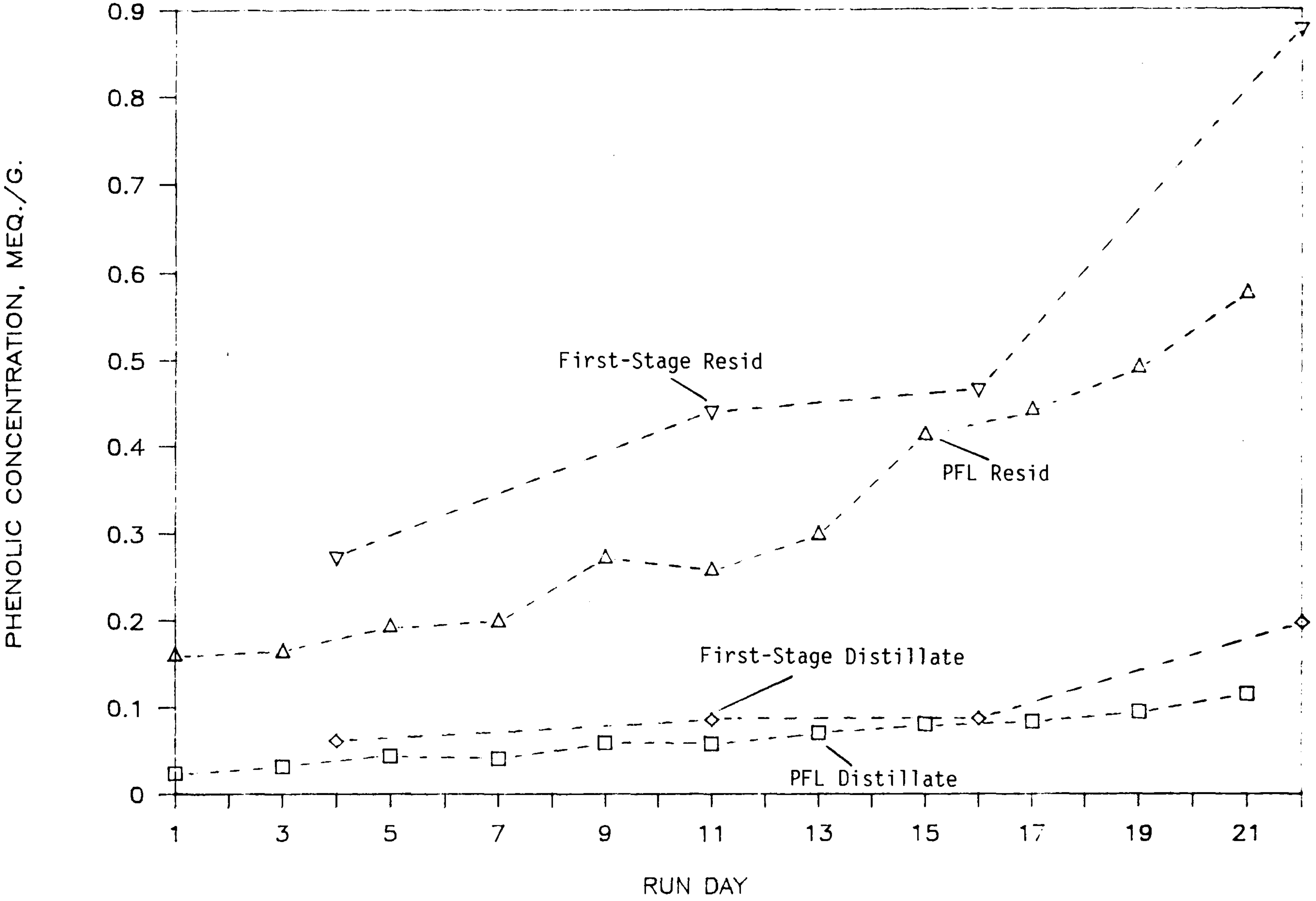


Figure 8. Phenolic Concentrations vs Run Day - HRI CTSL Run 227-27.

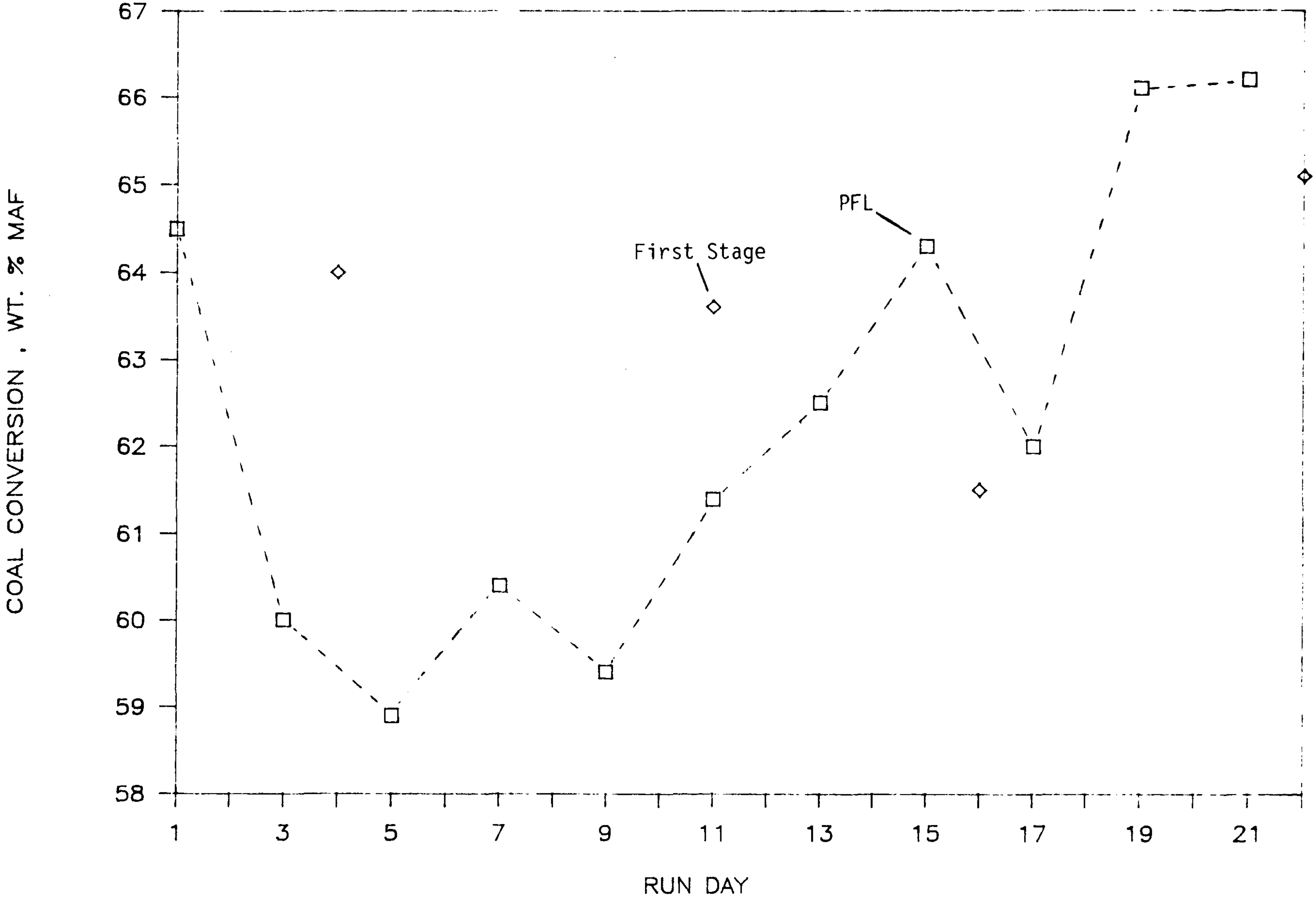


Figure 9. Microautoclave (Mod-EQ) Coal Conversion vs Run Day - HRI CTSL Run 227-27.

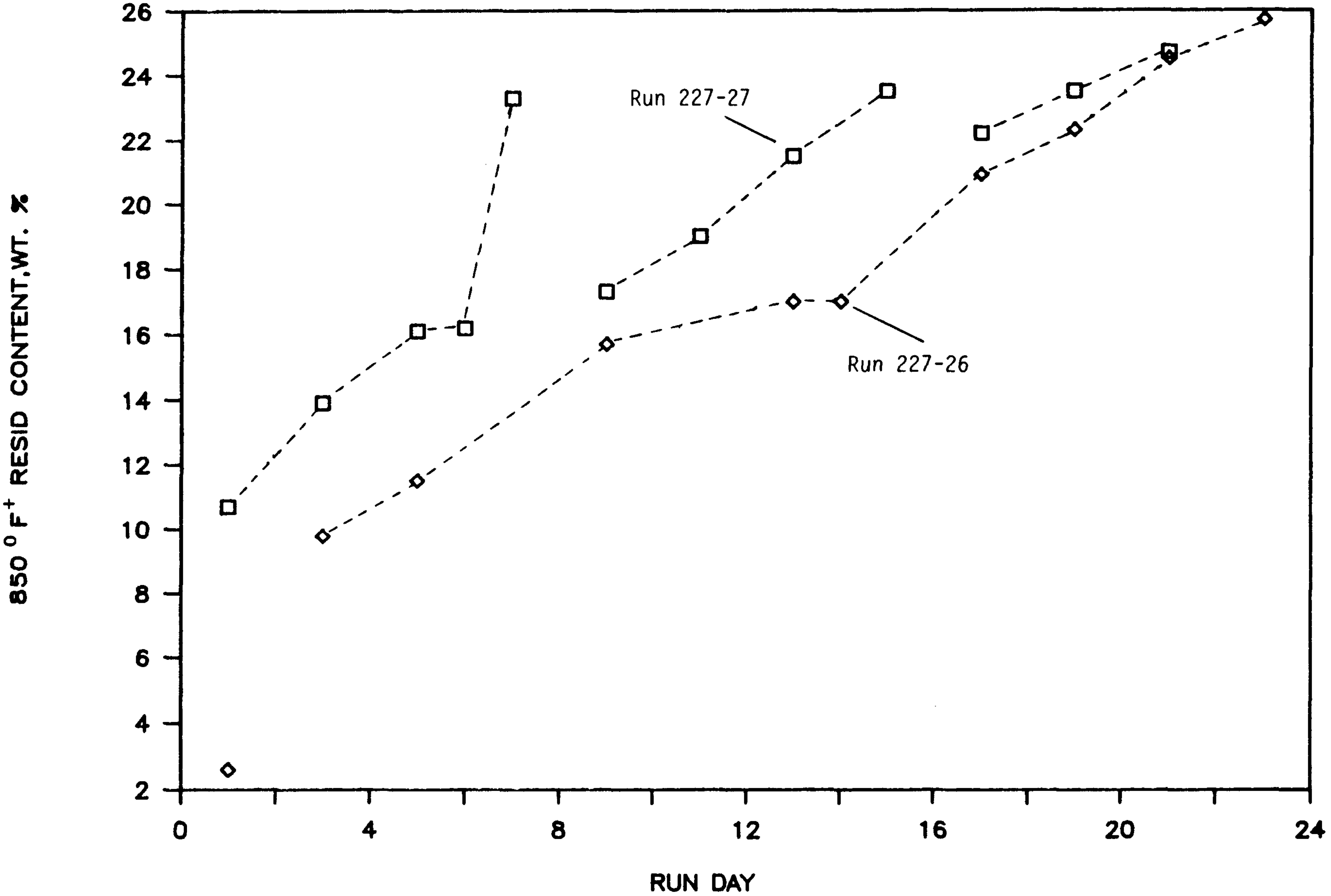


Figure 10. PFL Resid Contents vs Run Day - HRI CTSL Runs 227-26 and 227-27.

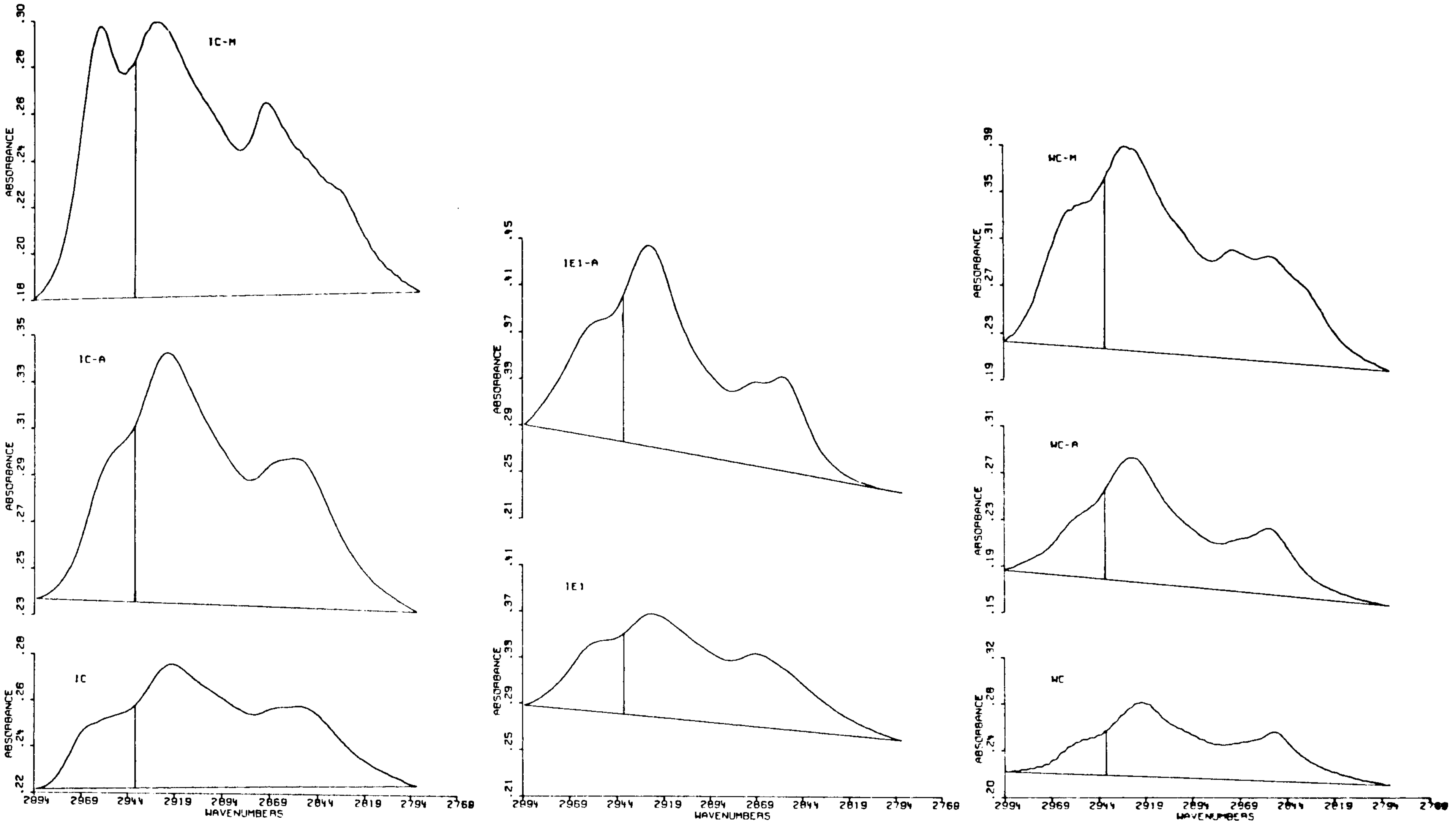


Figure 11. Aliphatic C-H Stretch Regions of Selected Sample Spectra Showing Integrated Regions and Effects of Derivatization.

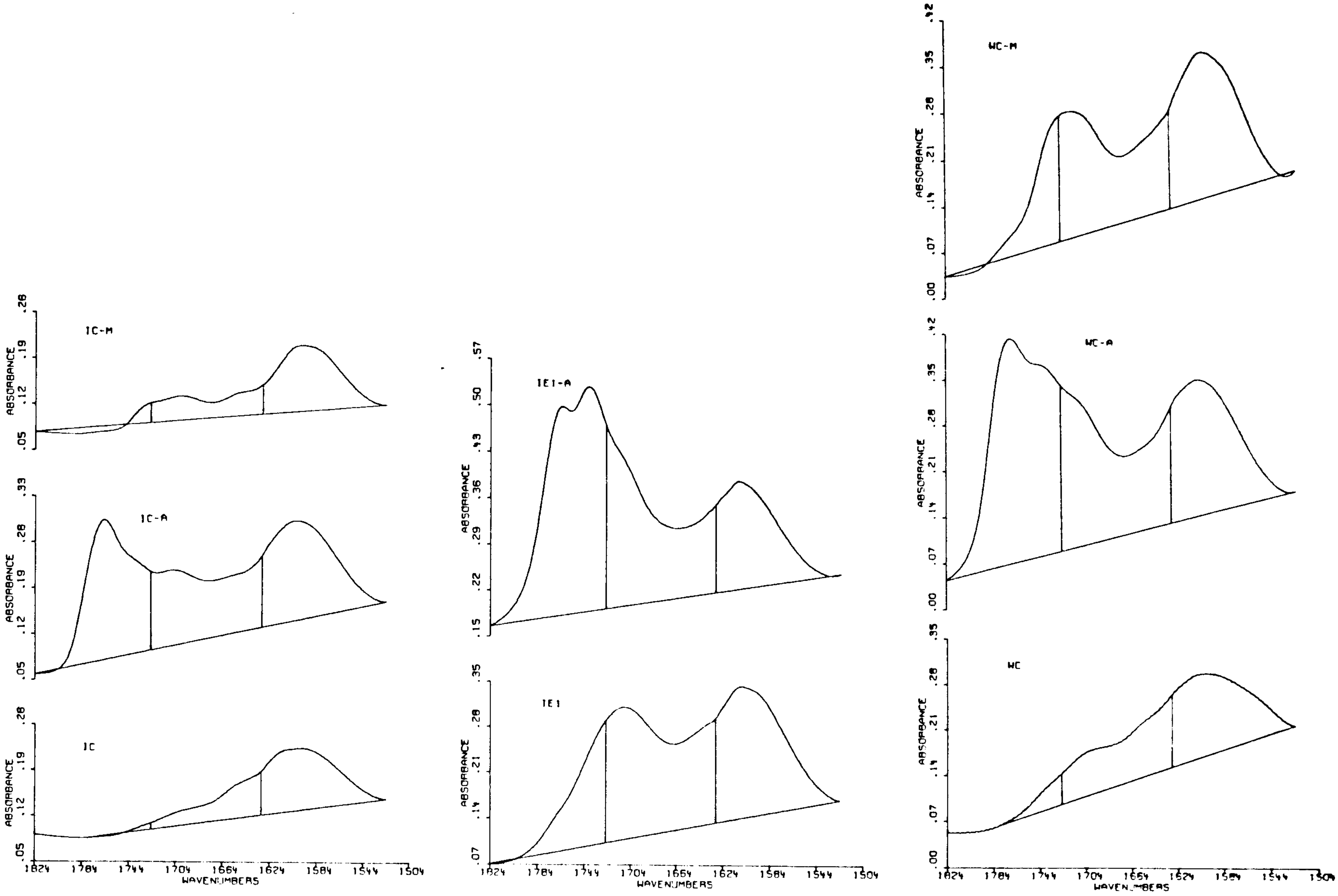


Figure 12. Carbonyl C=O Stretch Region of Selected Samples Spectra Showing Integrated Regions and Effects of Derivatization.

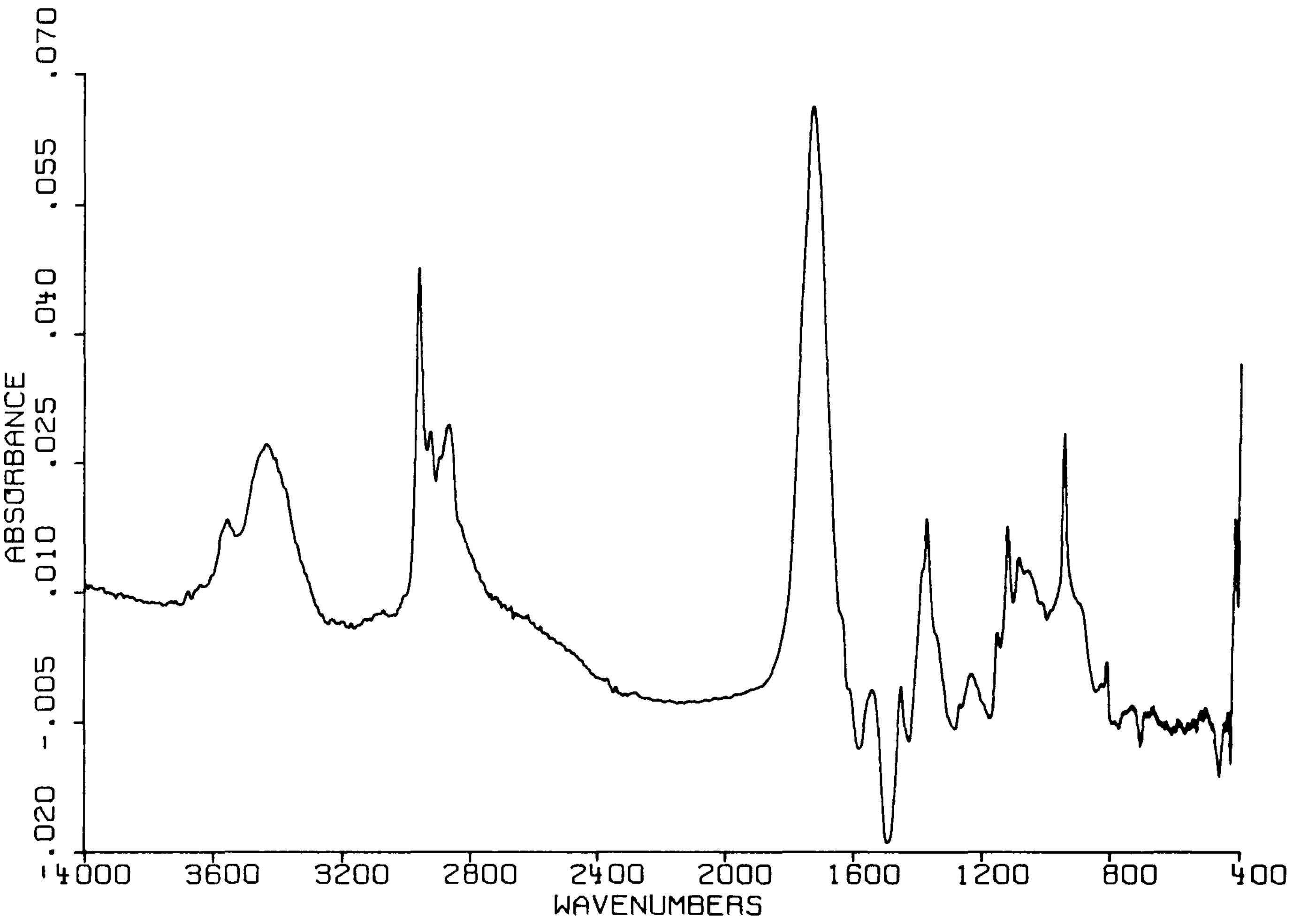


Figure 13. Difference Spectrum (WR2-0.94 x WR1) Showing Carbonyl Peak.

APPENDIX 1

CALCULATION METHOD FOR HYDROTREATER CONVERSIONS AND FIRST-ORDER KINETIC CONSTANTS FOR WILSONVILLE RUN 249

Hydrotreater resid (850°F$^+$) conversions for Run 249 were calculated from our analyses of V-1064 (HTR feed) and V-1067 (HTR flashed bottoms product) samples adjusted to their respective flow rates in lbs/h based on the reports by Stearns Catalytic.$^{(1)}$ The flow rate of resid fed to the hydrotreater was determined as:

wt fraction of ash-free 850°F$^+$ in V-1064 sample x (flowrates of total "feed inputs" - "withdrawal tube flush")

The flow rate of resid out of the hydrotreater was determined as:

wt fraction of ash-free 850°F$^+$ in V-1067 sample x flow rate of "flashed bottoms"

The flow rate of "flashed bottoms" was calculated as:

flow rate of "product outputs" + "water inject rate" - "sour H_2O rate" - flow rate of "flashed overheads"

Flow rate data are given in Table 24. Ash-free resid contents, which consist of soluble resid plus IOM, are given in Tables 5 and 6. 850°F$^+$ resid conversion was calculated as:

$$\frac{\text{flow rate of ash-free } 850^\circ\text{F}^+ \text{ fed} - \text{flow rate of ash-free } 850^\circ\text{F}^+ \text{ out}}{\text{flow rate of ash-free } 850^\circ\text{F}^+ \text{ fed}}$$

850°F$^+$ resid conversions are presented in Table 24.

Kinetic rate constants for the resid conversion reactions can be calculated if several assumptions are made including assumptions of the validity of a first-order model. These assumptions were discussed earlier.(4) For a single CSTR, the first-order rate constant for 850°F$^+$ resid conversion, k(T), is given as:

$$k(T) = SV \; \frac{850°F^+ \text{ IN} - 850°F^+ \text{ OUT}}{850°F^+ \text{ OUT}}$$

For these calculations, the flow rates of 850°F$^+$ resid into and out of the HTR, as given above, were used. SV was the 850°F$^+$ space velocity, calculated as:

$$\frac{\text{flow rate of } 850°F^+ \text{ ash-free resid IN}}{\text{flow rate of total input}} \times \text{overall SV}$$

The flow rate of resid IN is derived above, the flowrate of total input and the overall SV are given in Tables 24 and 2, respectively.

The pre-exponential factor, A, is calculated as:

$$A = ke^{Eact/RT}$$

Eact was assumed to be 23.5 kcal/mol. The calculated kinetic constants are given in Table 24.

Conversion of benzene insolubles (preasphaltenes plus IOM, BI) were calculated as follows. Flowrates of BI inputs were determined as:

[(preasphaltenes in V-1064 sol. resid x sol. resid in V-1064) + IOM in V-1064] x flow rates of ("feed inputs" - "withdrawal tube flush")

Flowrates of BI outputs were determined as:

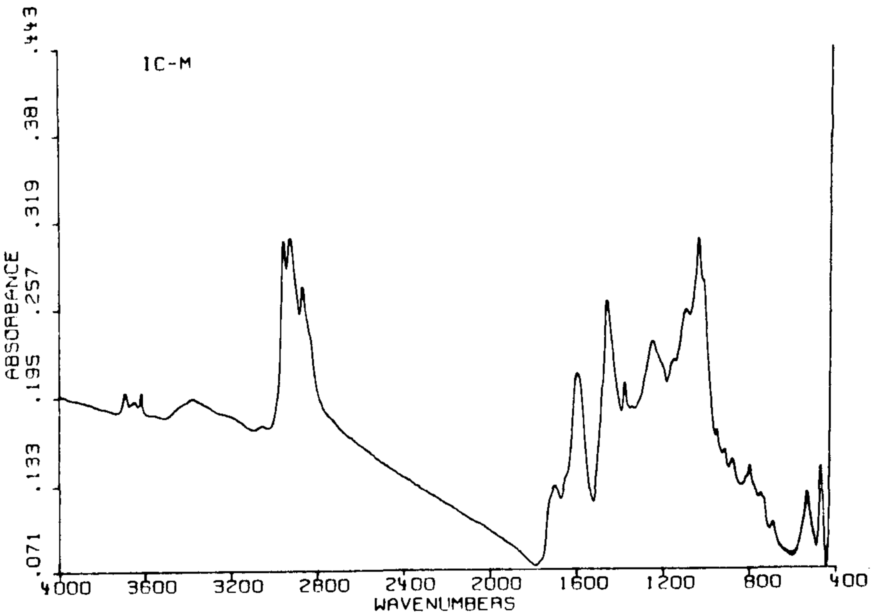
[(preasphaltenes in V-1067 sol. resid x sol. resid in V-1067) + IOM in V-1067] x flow rate of "flashed bottoms"

Preasphaltenes contents are given in Tables 8 and 9. Soluble resid and IOM contents are given in Tables 5 and 6. Benzene insolubles conversion is given as:

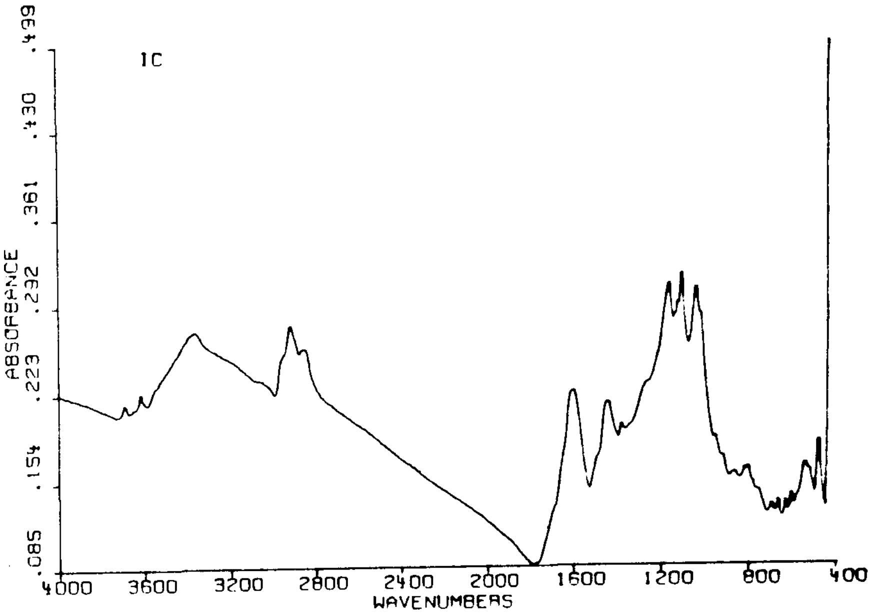
$$\text{BI Conversion} = \frac{\text{BI inputs} - \text{BI outputs}}{\text{BI inputs}}$$

APPENDIX 2

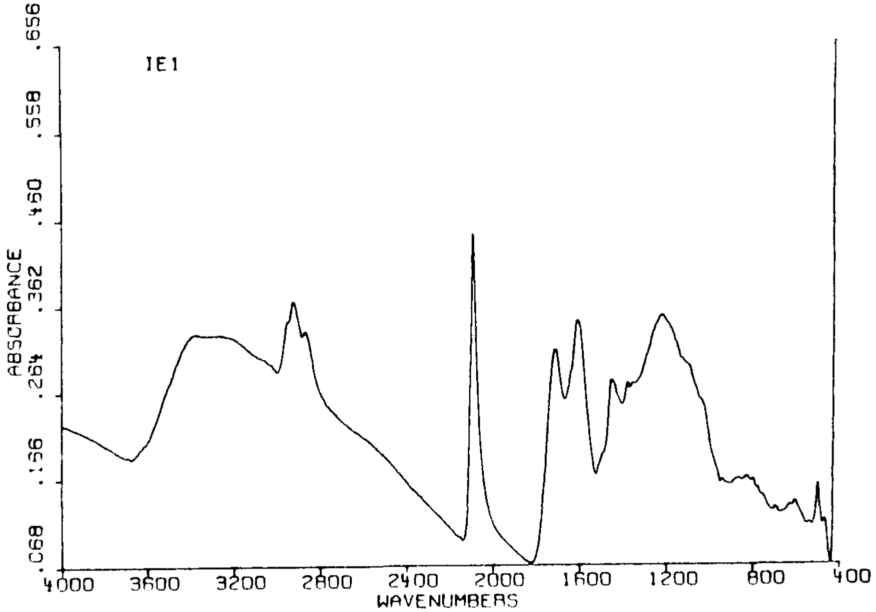
INFRARED SPECTRA OF POTASSIUM-CROWN ETHER TREATED COALS



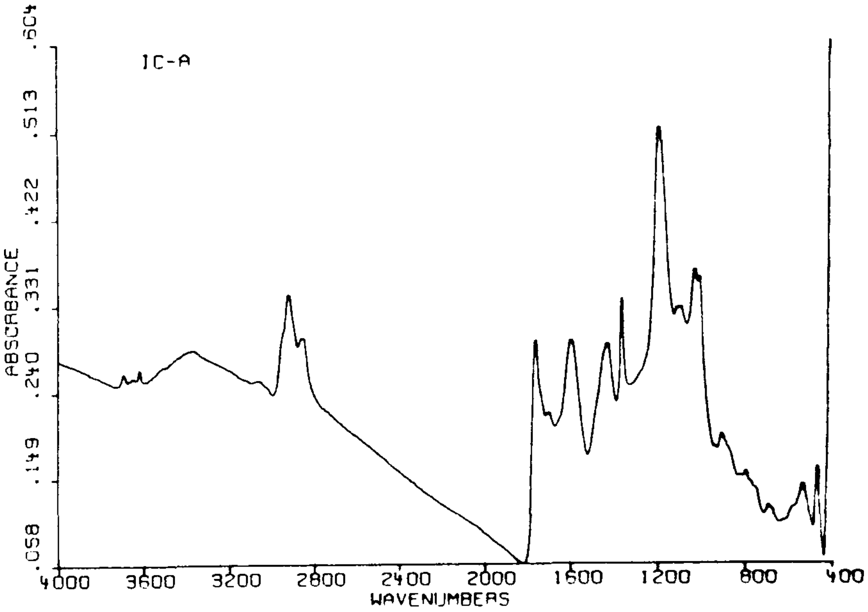
Spectrum 3



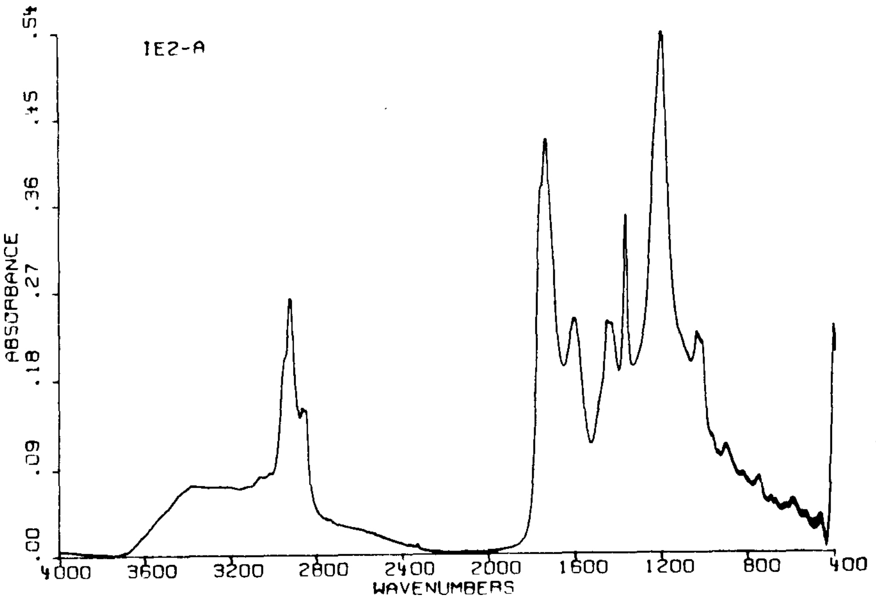
Spectrum 1



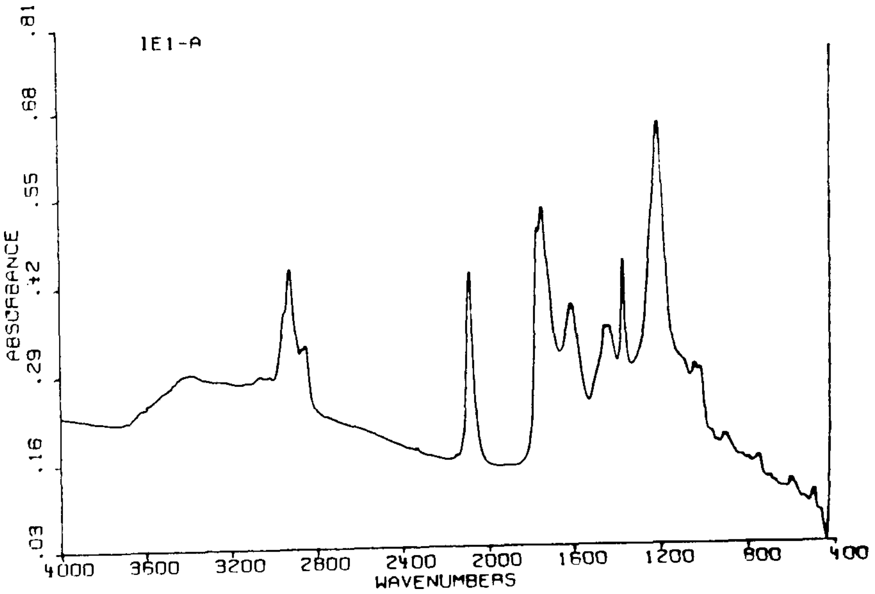
Spectrum 4



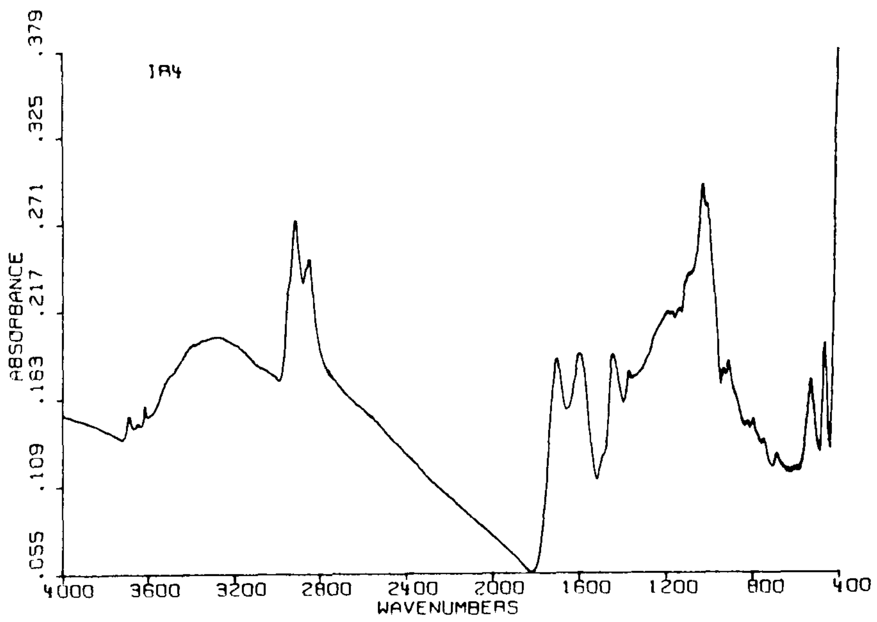
Spectrum 2



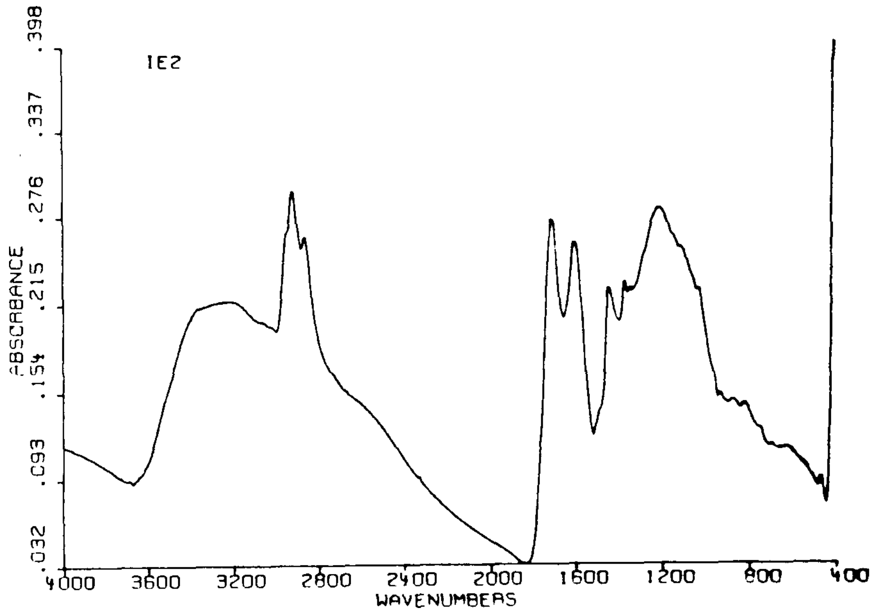
Spectrum 7



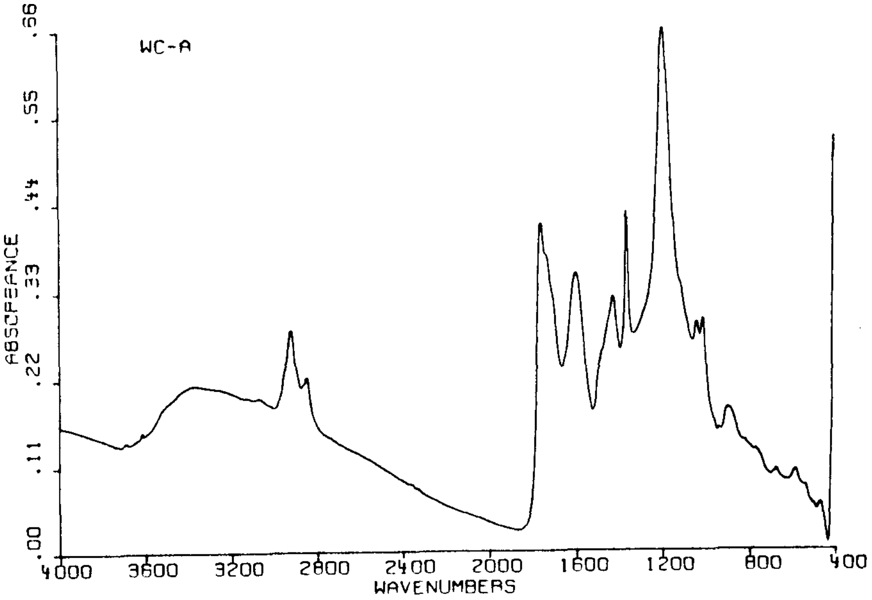
Spectrum 5



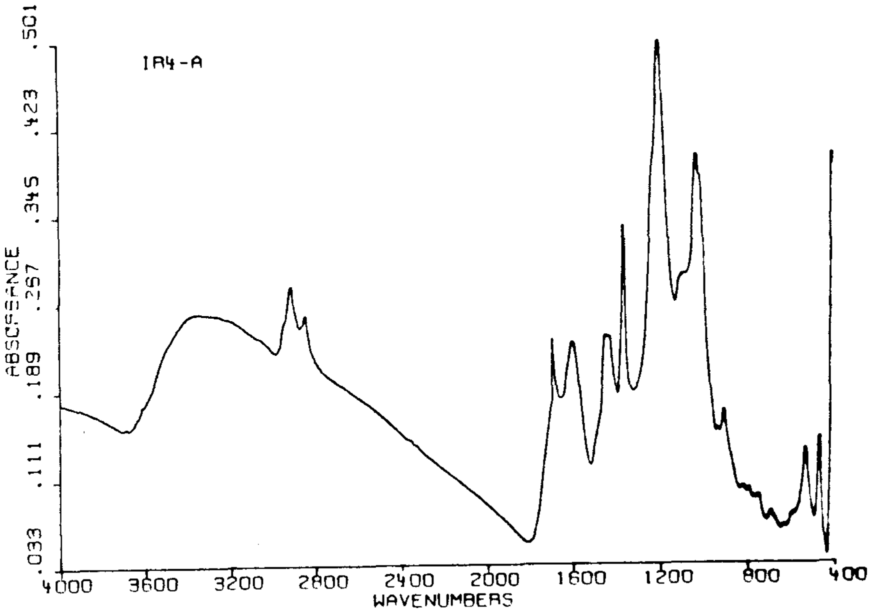
Spectrum 8



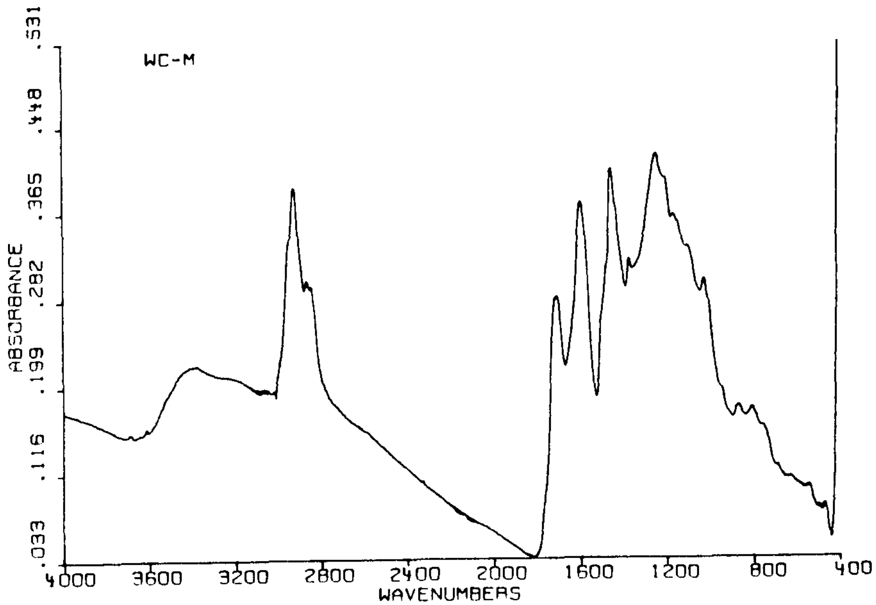
Spectrum 6



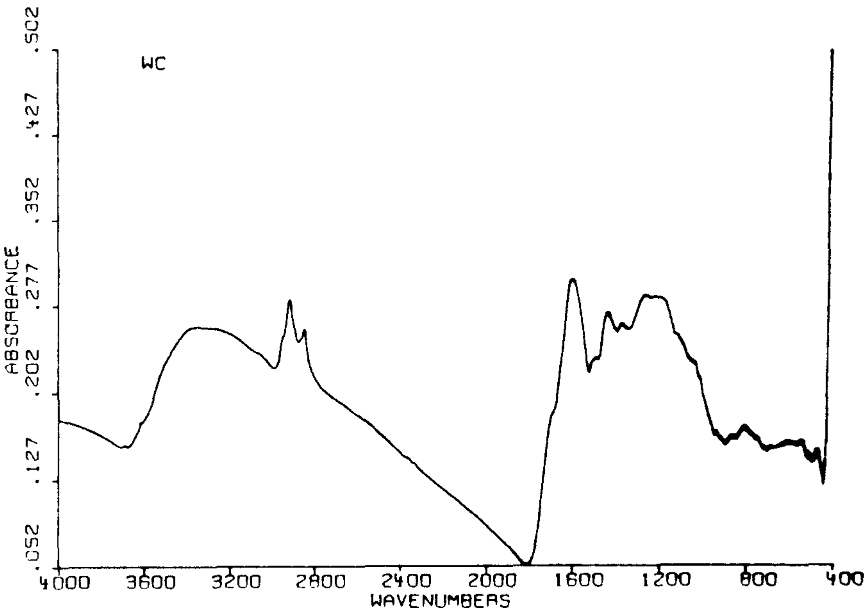
Spectrum 11



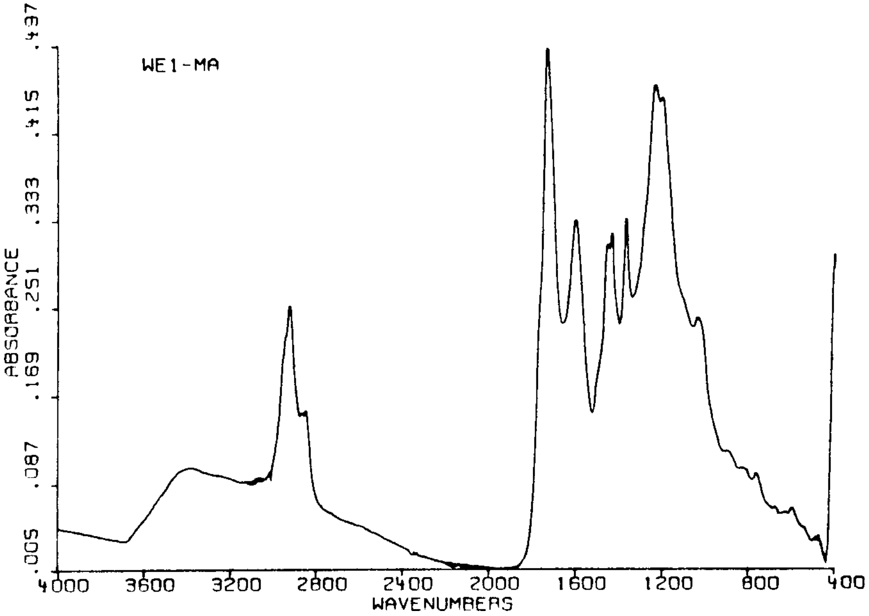
Spectrum 9



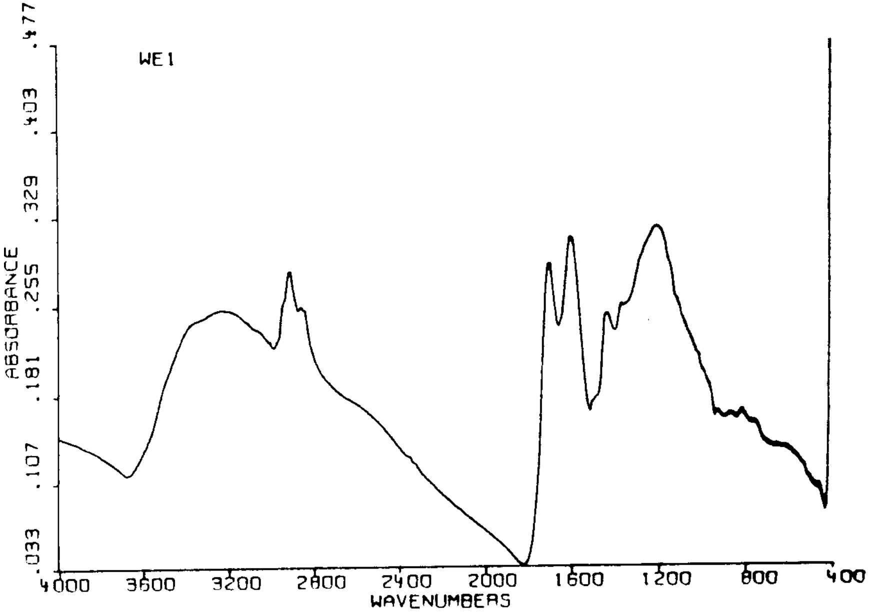
Spectrum 12



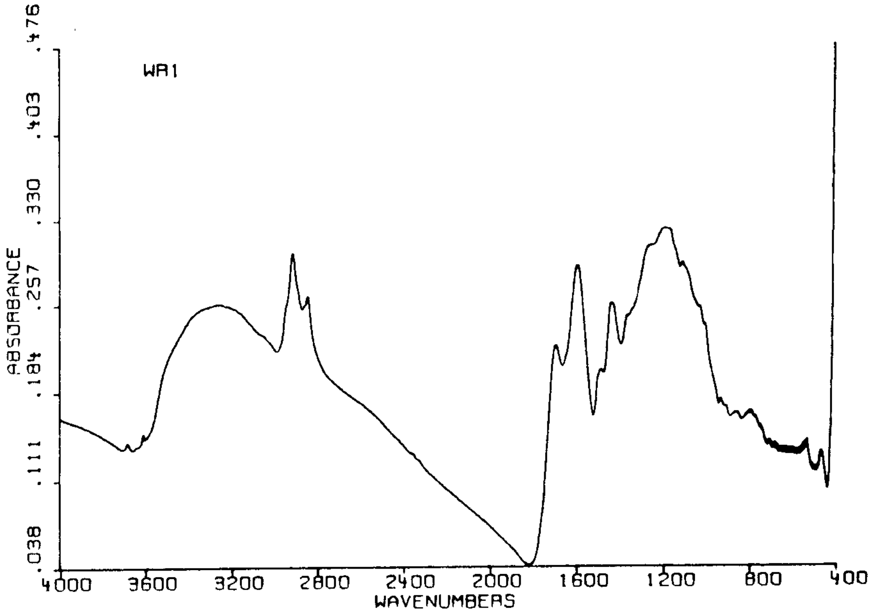
Spectrum 10



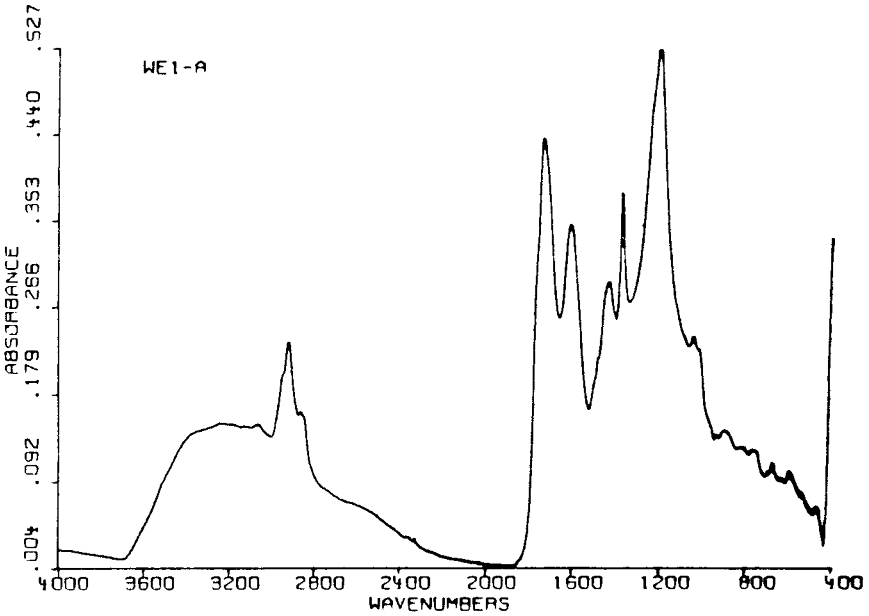
Spectrum 15



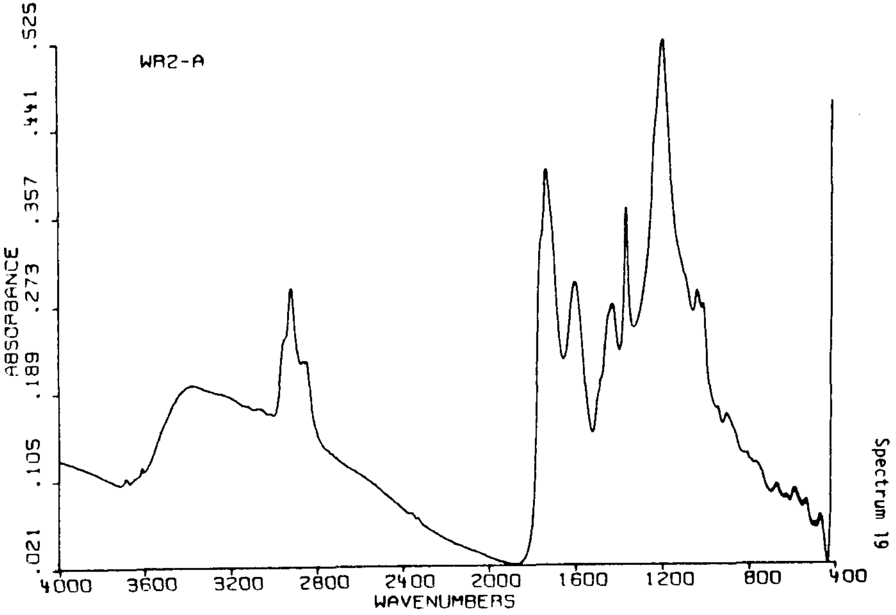
Spectrum 13



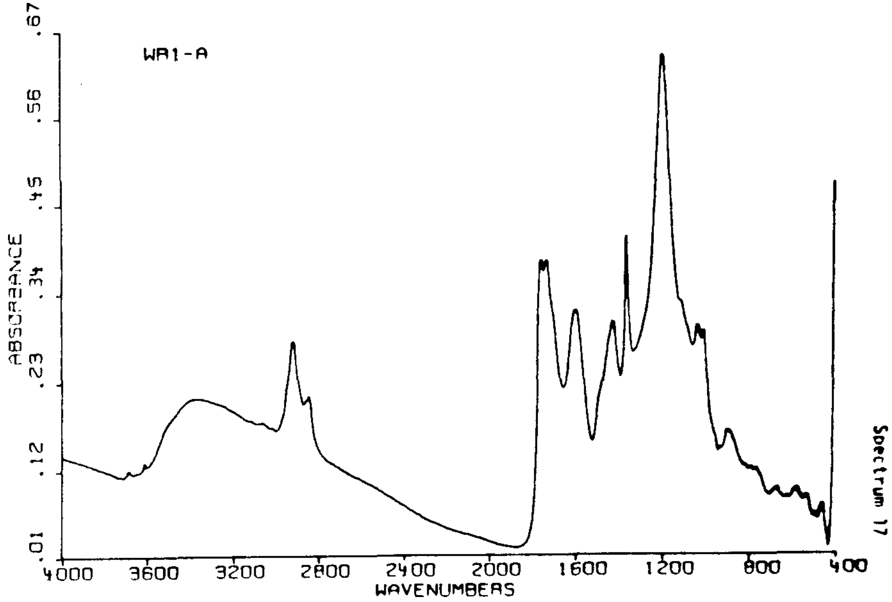
Spectrum 16



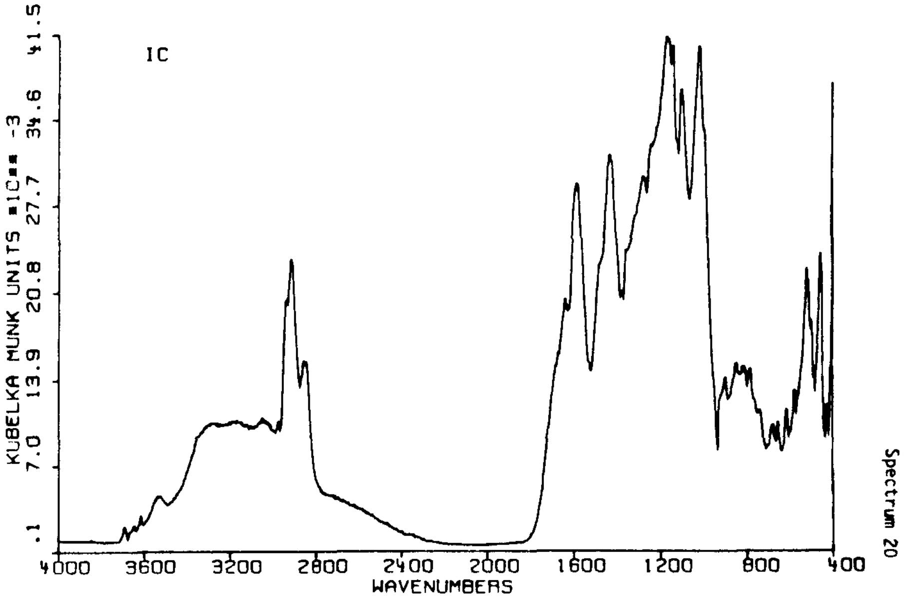
Spectrum 14



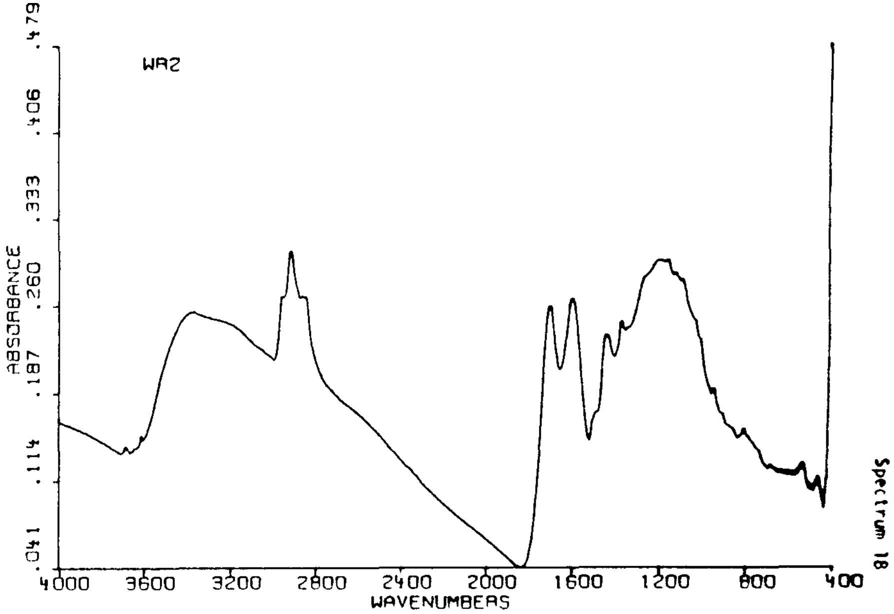
Spectrum 19



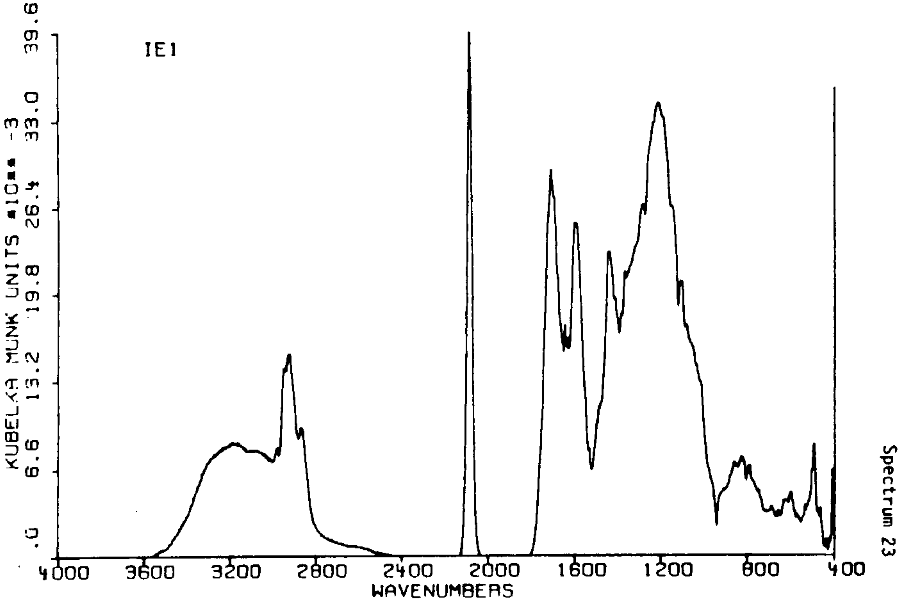
Spectrum 17

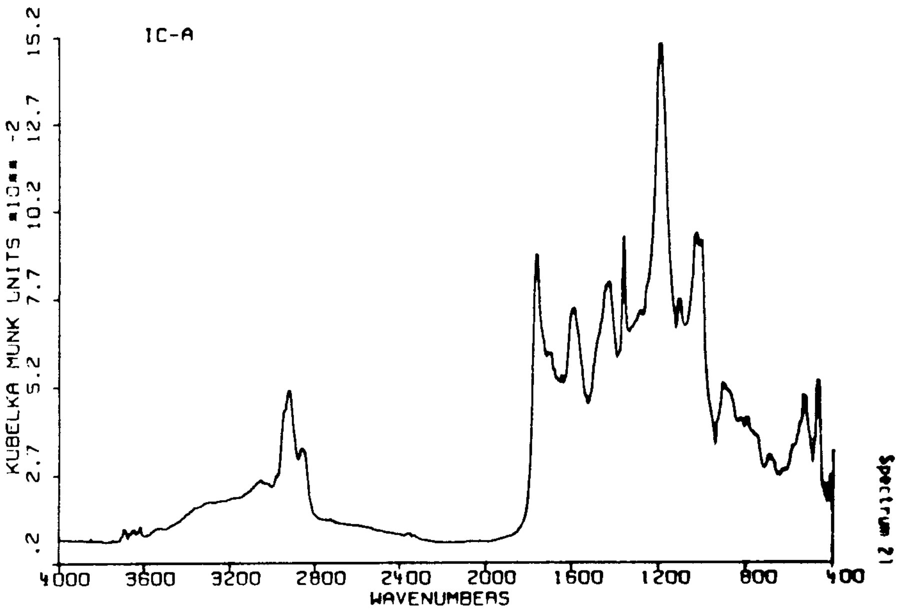


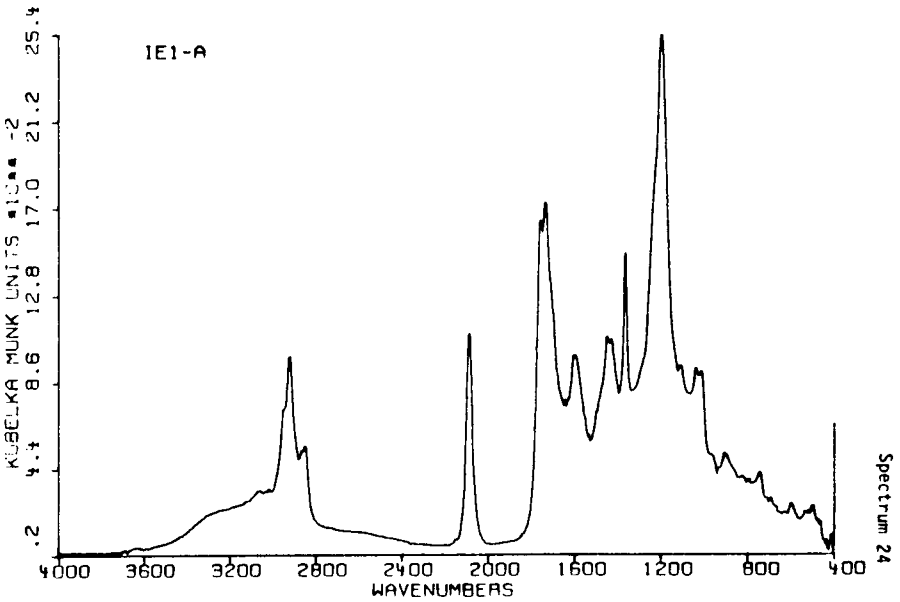
Spectrum 20

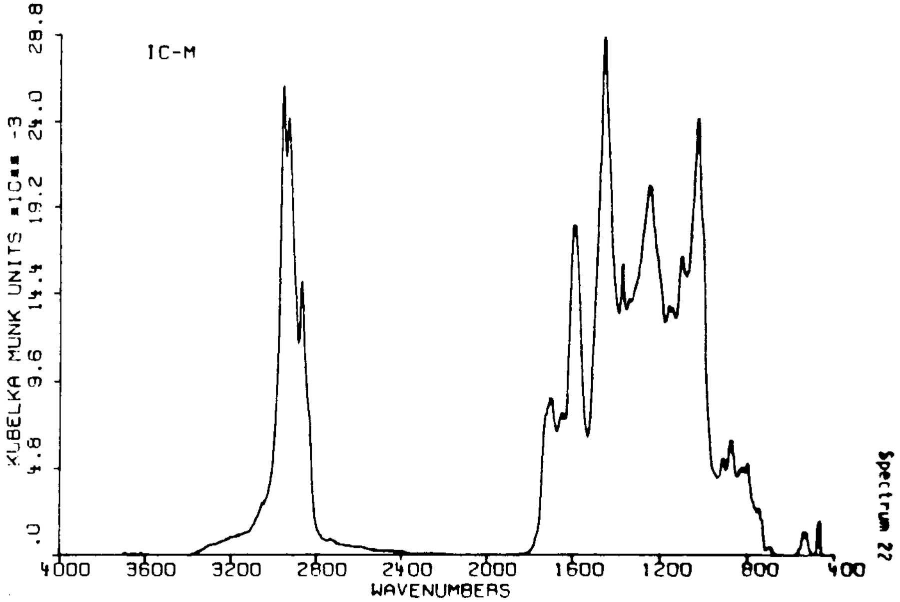


Spectrum 18


IE1
KUBELKA MUNK UNITS *10** -3
39.6
33.0
26.4
19.8
13.2
6.6
.0
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS
Spectrum 23


IC-A
KUBELKA MUNK UNITS *10** -2
15.2
12.7
10.2
7.7
5.2
2.7
.2
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS
Spectrum 21


IE1-A
KUBELKA MUNK UNITS *10** -2
25.4
21.2
17.0
12.8
8.6
4.4
.2
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS
Spectrum 24


IC-M
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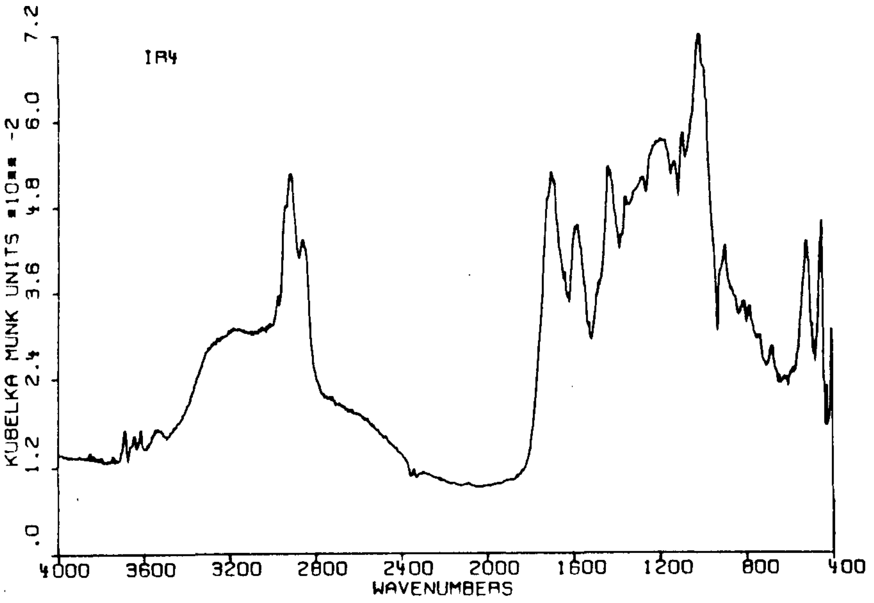
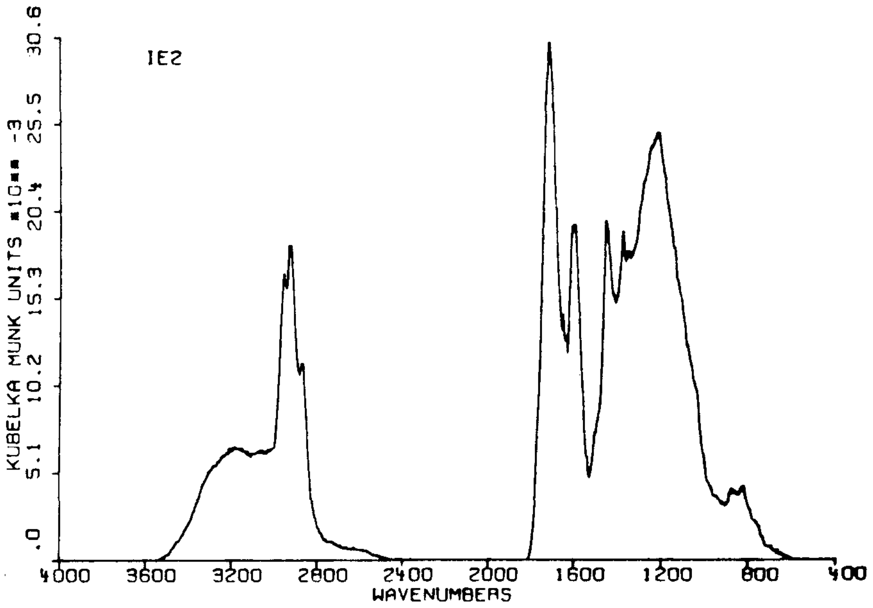
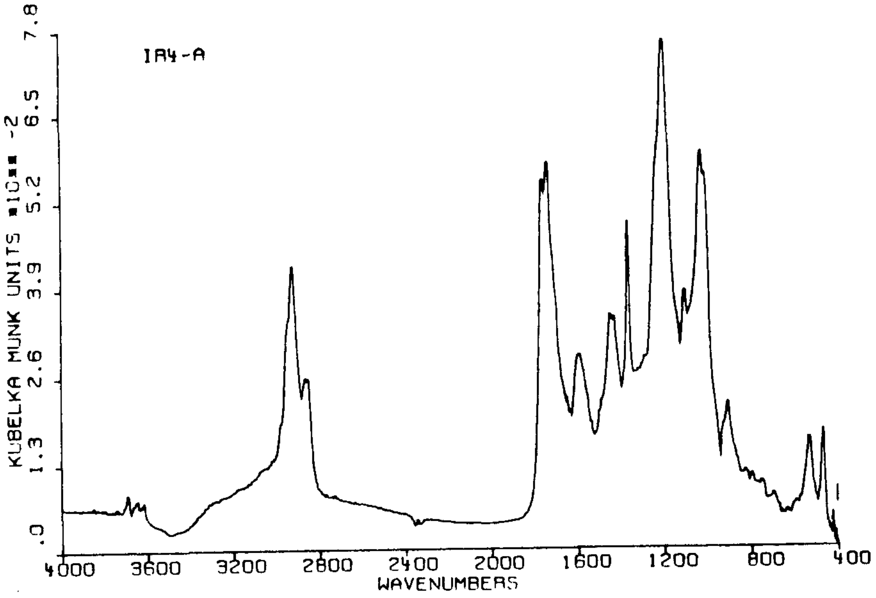
24.0
19.2
14.4
9.6
4.8
.0
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS
Spectrum 22



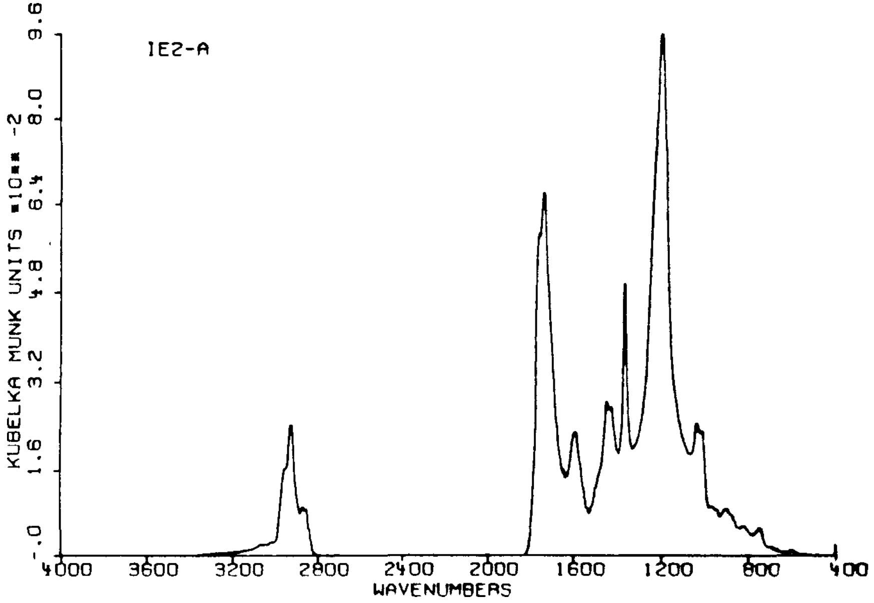
Spectrum 27



Spectrum 25



Spectrum 28



Spectrum 26