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Coal Liquefaction Process Solvent Characterization And Evaluation

Technical Progress Report, April 1 Through June 30, 1986

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

Conoco Inc.
Coal and Chemicals Research and Development
Coal Research Division

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Section 1
INTRODUCTION

This is the Technical Progress Report for the sixth quarter of activities under Contract No. DE-AC22-84PC70018. It covers the period April 1, 1986, through June 30, 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. All samples are treated using conventional methods of analysis and preparation so that unit performance parameters, such as conversions and yields, can be independently determined to assure sample validity and correlation of analytical results among various plant operations. In addition to this more routine analytical work, specific coal liquefaction research topics are being addressed and specialized analytical methods are being developed under this contract.

CONTRACT ACTIVITIES

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

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

- A set of thirty-two process oils from the Hydrocarbon Research, Inc. (HRI) Catalytic Two-Stage Liquefaction (CTSL) bench unit was analyzed to provide information on process performance. The oils were produced in Runs I-12, I-13, I-14 and I-15. Each run was a "process variable" test made with Burning Star #2 mine (Illinois 6 bituminous) coal.

- The Fourier-Transform infrared (FTIR) spectroscopic method for the determination of phenolics in coal liquids was further verified as follows. Several liquefaction products were fractionated by distillation and solubility fractionation. Phenolic determinations by FTIR gave very good phenolic material balances. The good material balances further confirm our confidence in the method.

- A set of four tetrahydrofuran-soluble products from Purdue Research Foundation's reactions of coal/potassium/crown ether, analyzed by GC/MS and FTIR, were found to consist primarily of paraffins (excluding contaminants).

- Characterization data (elemental analyses, ^{1}H-NMR and phenolic concentrations) were obtained on a set of twenty-seven two-stage liquefaction oils produced at Penn State University. Results were corrected for two contaminants.

- Two activities were begun but not completed. First, analyses were started on oils from Wilsonville Run 250 (close-coupled ITSL). Also, a carbon isotopic method is being examined for utility in determining the relative proportion of coal and petroleum products in coprocessing oils. Preliminary results with both laboratory mixtures and Lummus coprocessing oils are encouraging. Contact was made with UOP/Signal Research to initiate characterization of oils from their coprocessing operation. Results of these two activities will appear in a future report.

- The successful results of a project to demonstrate the technical feasibility of dewaxing coal liquefaction recycle oils to improve solvent quality were presented in the last quarterly progress report. This work will be presented at the Fall National ACS Meeting. Quantitation of n-paraffins was then further improved for this work by determining gas chromatographic response factors for all even carbon-numbered n-paraffins from C_{10} through C_{36}. The results using the improved quantitation will be presented at the 1986 DOE Direct Liquefaction Contractors' Review Meeting. The complete and final results of this program appear in a paper accepted for publication in *Fuel*. This paper, "Improvement in Coal Liquefaction Solvent Quality by Dewaxing", is presented in Appendix 1.

- Another paper, "Oil Agglomeration as a Pretreatment for Coal Liquefaction", was also accepted for publication in *Fuel*. The experimental work was performed and the results reported under a previous DOE contract. The analysis of the data to identify the relationship between the quality of the oils as liquefaction solvents and the quality of the oils as agglomeration agents was performed under this contract. This paper is presented in Appendix 2.

Section 2

DISCUSSION

HRI CTSL RUNS I-12 THROUGH I-15

Conoco analyzed a total of thirty-two oils from HRI's Catalytic Two-Stage Liquefaction (CTSL) development program. The samples analyzed were from bench unit Runs I-12 through I-15. Each run was a "process variable" run in which several operating conditions were changed to determine their effects on process performance. Burning Star #2 (Illinois 6) bituminous coal was used for each run. Process flows in the CTSL bench unit are shown schematically in Figure 1 (1). The nominal throughput of the bench unit is 50 lbs/day (2) and each reactor has a capacity of 2000 cc (1). The operating conditions (3-6) used for Runs I-12 through I-15 are given in Table 1. Each run is separately discussed in detail in this report. The major conclusions from this work are highlighted below.

Highlights

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

- Catalyst aging manifests itself in parallel reduction in the quality of both the first-stage and second-stage oils. Both oils increase in 850°F^{+} resid content. The resids become more aromatic and more phenolic and increase in preasphaltenes content. The 850°F^{-} distillates become more aromatic and phenolic. 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.

- For all cases examined here, increases in reaction temperature (either stage) or decreases in coal space velocity tended to offset the changes in oil properties caused by catalyst aging, except for aromaticity. Aromaticity increases with catalyst age and with coal space velocity and second-stage temperature. Aromaticity increases with first-stage temperature at low overall space velocity. At high overall space velocity, the effect of first-stage temperature on oil aromaticity is not clear. Surprisingly, a change in solvent/coal ratio from 1.6 to 1.1 appears to affect oil properties very little.

- In general, second-stage processing has qualitatively, i.e., directionally similar effects on the process-oil properties whether the catalyst is fresh, cascaded or absent. In almost all cases examined, second-stage products contain less 850°F$^+$ resid and fewer preasphaltenes and they are more aromatic and have lower concentrations of phenolics than the corresponding first-stage oils. Clearly, the second stage plays a major role in the conversion of resid and preasphaltenes and in the removal of phenols whether it is operated with fresh, cascaded or no catalyst. However, in the absence of second-stage catalyst, there is no reduction in the concentration of phenolics in the 850°F$^-$ distillate in that reactor. Also, with a catalytic first stage and a thermal second stage operated at only 25°F higher temperature, second-stage resid conversion appears to be very small or absent.

- Oils produced in the normal catalytic/catalytic mode are compared here to oils produced in both the catalytic/thermal and simulated catalyst cascading tests. For both tests, oil properties deteriorate to any point in about half the time that they do in the normal mode. Unfortunately, no direct comparison is available between the catalytic/thermal and simulated catalyst cascading tests.

- Oils produced in the catalytic/thermal mode (Run I-14), i.e., those produced in the absence of second-stage catalyst, have much poorer quality than those produced at essentially identical operating conditions and catalyst age in the catalytic/catalytic mode (Runs I-11 and I-13). One period of both Run I-14 and Run I-13 used identical operating conditions except that the former was made in the catalytic/thermal mode. Similar amounts of coal had been processed at both periods. For both the first- and second-stage oils, those from Run I-14 contain more resid, are more aromatic and much more phenolic and are poorer donor solvents.

Another similar point of comparison is between period 7 of Run I-14 (catalytic/thermal) and all of Run I-11 (catalytic/catalytic). The second-stage oil from Run I-14 contains much more resid, is much more aromatic and phenolic and is a poorer donor solvent than the corresponding oil produced at similar catalyst age in Run I-11. In fact, by period 7 of Run I-14, most oil properties had deteriorated to the point reached in Run I-11 by period 11 to 19. Phenolic concentrations in the oils from Run I-14 increased even faster. For example, the concentration of phenolics in the second-stage oil from period 7 of Run I-14 was greater than the concentration in the corresponding oil from period 25, the last period, of Run I-11. Therefore, for this one comparison we see that in the catalytic/thermal mode, most oil properties deteriorated to a particular point in about half the time they do in the catalytic/catalytic mode.

- The oils produced during the catalyst cascading experiment (Run I-15) are less highly upgraded than those produced during the same run period at essentially identical conditions with fresh catalyst in both stages (Run I-13). Differences in oil properties from the two runs are apparent in both first- and second-stage samples, and are consistent with the greater overall catalyst age in the cascading run. Therefore, for this simulation of catalyst cascading, oil properties were inferior to those produced without cascading at equivalent run periods.

With catalyst cascading, most oil properties deteriorated by day 5 to day 7 to the same point as they did by day 9 with fresh catalyst in both reactors. Phenolic concentrations in the oils increased even faster. This agrees well with the reduction of 975°F$^+$ conversion. HRI data show that, with catalyst cascading, 975°F$^+$ conversion declined by day 3 to the same point it was at on day 9 with fresh catalyst in both reactors.

Another point of comparison shows that the second-stage oil produced on day 13 with catalyst cascading has properties similar to the corresponding oil taken on day 27 with fresh catalyst in both reactors. Taken as a whole, these data suggest that, in the catalyst cascading experiment, oil properties deteriorated to any one point in about half the time as when using fresh catalyst in both reactors. It should not be surprising that oil properties deteriorated more quickly with cascading. However, it is not obvious that using second-stage catalyst aged to 34 days is the best simulation of cascading. Assuming that Run I-15 was a good model for catalyst cascading, overall catalyst addition rates with catalyst cascading will clearly be greater than 50% of the replacement rate required without cascading.

- The importance of the catalyst and its activity for removing phenolics from the oils has been apparent throughout this work. However, the catalytic/thermal test (Run I-14) underscores this observation.

- The oils produced from the high temperature second stage are consistently more aromatic than those produced from the lower temperature first stage. At first this may appear to be a thermodynamic equilibrium effect such that the degree of hydrogenation decreases with increasing temperature. However, the comparisons between the "normal" catalytic/catalytic and the simulated cascading modes and between the "normal" catalytic/catalytic and the catalytic/thermal modes show that the increase in oil aromaticity is greatest in the absence of catalyst and lowest with a fresh catalyst. Therefore, the hypothesis that the degree of hydrogenation of the second-stage oils is controlled by thermodynamic equilibrium appears to be unjustified for the majority of operating conditions tested.

- Operating the second stage at "thermal cracking" conditions, i.e., at low space velocity and very high temperature, improves resid conversion in that reactor but produces a very highly aromatic second-stage product oil. This product is a very poor donor solvent. The magnitude of the aromaticity increase across the second stage is such that the oils may have been dehydrogenated at these atypical operating conditions.

- At otherwise identical operation conditions, both catalyst age and feed solvent composition should affect second-stage product composition. However, when a recycle oil similar to those from periods 1 through 7 of Run I-11 was fed during period 20 of Run I-12, the second-stage product was very similar to those produced between periods 14 and 20 of Run I-11. Therefore, for this case, catalyst age is clearly the more important factor for second-stage product properties.

Sample Descriptions

We obtained a total of 51 oils (20 to 40g each) from Mr. J. B. McLean of HRI. The set included 28 daily pressure-filter liquid (PFL) samples and 20 daily first-stage reactor inventory samples from Runs I-12 through I-15, one "solvent hydrogenation" sample, one sample of start-up oil (used for Runs I-13 through I-15), and one sample of filter-cake extract.

The pressure-filter liquid is the major second-stage product and, in most cases discussed in this report, it was the only component of the recycle oil. It is obtained by filtering the atmospheric-still bottoms

(Figure 1). In several cases discussed here, the light ends of the PFL were removed by using N_2 stripping during distillation. First-stage oils, which are samples of the first-stage reactor inventory, were filtered by HRI prior to shipment. The sampling procedure used by HRI (7) is to take the PFL sample first, then to take the first-stage sample while maintaining constant operating conditions. As a result, any first-stage sample corresponds most closely to the PFL sample taken one period earlier (3).

In this report, the characteristics of corresponding PFL and first-stage oils are frequently compared to show changes that occur in the second-stage reactor. It should be recognized, however, that the direct comparison of the characteristics of the first-stage oils and PFL samples has two limitations. First, the samples we obtained from HRI are all filtered and thus contain no unconverted coal or ash. Coal not converted to solubles in the first stage has the opportunity to be converted in the second stage. Therefore, the filtered first- and second-stage soluble samples represent different proportions of each reactor's inventory. The second limitation is that the PFL samples are atmospheric still bottoms with an initial boiling point of ca. 500°F. The first-stage samples, which are collected at reaction temperature (725-775°F), contain some amount of 500°F$^-$ oil, but less 650°F$^-$ oil than the PFL samples (7). 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 start-up oil analyzed was used in Runs I-13 through I-15 and is a distillate produced in the Wilsonville pilot plant (7). Run I-12 used a different distillate from the H-Coal pilot plant (7). The one filter-cake extract sample analyzed was produced in Run I-13 and was used to supplement the PFL recycle oil during conditions 6 and 7 of that run. This oil was obtained by extracting the pressure-filter cake (Figure 1) with toluene. Toluene was then removed by distillation. A ^{1}H-NMR spectrum of this sample showed that some toluene still remained. It was removed in our laboratory by rotary evaporation prior to further analysis. Weight loss was 4.8%. The data presented for this sample were obtained from the toluene-free portion.

One sample of hydrogenated solvent from Run I-12 was analyzed. This material is the second-stage product that was produced between conditions 4 and 5 of that run by omitting coal feed to the bench unit.

All samples supplied by HRI from Runs I-13 through I-15 were analyzed. Only the two samples considered most important by HRI of the 21 samples from Run I-12 were analyzed.

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) define the effects of the process variables on oil properties and 4) examine the properties of the start-up oil, the filter-cake extract and the hydrogenated solvent.

Analyses

Proton distributions were obtained by ^{1}H-NMR for each whole sample (Table 4). Each whole sample was tested in the microautoclave at the modified equilibrium conditions (Table 8). Each sample, except for the start-up oil, was distilled (Table 2) to 320°C pot/270°C column/5 torr (850°F/atm). Each 850°F$^+$ resid was analyzed by solubility fractionation (Table 3), ^{1}H-NMR (Table 6) and FTIR for phenolic content (Table 7). Each 850°F$^-$ distillate was analyzed by ^{1}H-NMR (Table 5) and FTIR (Table 7). Each resid sample from Runs I-14 and I-15 were ashed. Except for one unusual sample, all contained less than 0.1% ash on a whole sample basis. The one unusual sample (#4666) contained 0.6% IOM and 0.3% ash. Except for this sample, microautoclave coal conversions are calculated assuming that the oil is solids-free.

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

CTSL Run I-12

CTSL Run I-12 (HRI 227-32) was made during October and November, 1985. The run lasted 31 days and used eight sets of operating conditions (Table 1) to test recycle configuration, space velocity and solvent/coal ratio. The reactivities of two shipments of coal were also tested. The first portion of Run I-12 was a repeat of Run I-11 with two exceptions. A new shipment of coal was used for most of Run I-12. Also, in Run I-12, target operating temperatures were established very rapidly (7). This contrasts to the more gradual reactor heat-up (ca. 3 days) used in Run I-11.

A total of 21 oils were obtained from this run. Only the two considered most important by HRI were analyzed. These two samples are the hydrogenated solvent and the PFL from condition 5. The portions of Run I-12 in which these two samples were produced are described below.

Process results from the first 13 days of Run I-12 were poorer than expected based on Run I-11. For example, residuum conversion was about 2% lower (3). One theory for this was that the gradual reactor heat-up used in Run I-11 had produced an extensively hydrogenated, and superior, recycle solvent (3). To test this, coal feed was stopped during period 16 (condition 4) and the solvent inventory was hydrogenated at 700°F (called condition SH). Condition 5 was a repeat of condition 2 (periods 6 to 9) except that the freshly hydrogenated solvent was used. Since process results were poorer, HRI concluded that catalyst activity, not solvent quality, was the dominant factor (3).

Hydrogenated Solvent. The properties of the hydrogenated solvent measured by Conoco are given in the data Tables 2 through 8. This oil has a relatively low level of resid and preasphaltenes as might be expected from hydrogenation. Also, this oil gives the highest microautoclave coal conversion of all samples reported here, 87%, indicating that it is indeed a good donor solvent. However, the aromaticity of this oil is high when compared to other oils with similarly low resid contents such as the period 5 PFL of Run I-13 and the period 5 PFL of Run I-15 (Table 4). The aromaticities of the distillate and resid fraction of the hydrogenated solvent are also surprisingly high relative to the other oils reported here.

	H Aromaticity, %	
	Distillate	Resid
Hydrogenated solvent	17.1	27.5
PFL, Run I-13, period 21	15.4	28.9
1st-stage oil, Run I-14, period 8A	16.9	27.5
Start-up oil	7.5	---

For example, the distillation fractions have aromaticities close to those of the PFL from period 21 of Run I-13 and to the first-stage oil from period 8A of Run I-14. The latter oil was produced in the catalytic/thermal mode. In addition, the start-up oil used for Run I-13 through I-15 is much less aromatic than even the distillate fraction of this hydrogenated solvent.

Based on its aromaticity, the hydrogenated solvent would hardly be considered highly hydrogenated, yet the microautoclave test showed it to be a good donor solvent. This is because much of the hydrogen in this oil is hydroaromatic, as measured by the ratio of cyclic to alkyl aliphatic protons. For the distillate of the hydrogenated solvent, this ratio is 0.87 whereas for most of the other distillates reported here, this ratio is between 0.6 and 0.8.

Comparison With Run I-11. One theory (3) to explain the poorer than expected results of Run I-12 (relative to Run I-11) was that the rapid establishment of operating conditions in Run I-12 had produced a poorly hydrogenated recycle solvent. To test this idea, HRI repeated condition 2 (repeat called condition 5) except that the repeat test used a hydrogenated recycle solvent. The highly hydrogenated solvent was produced in period 16 by processing the oil inventory in the absence of coal. It is therefore desirable to compare the properties of the hydrogenated solvent to those of the recycle solvents from Run I-11. The earlier report (8) that addressed Run I-11 included a set of equations relating various oil properties and run period. By substituting the data of the hydrogenated solvent into these equations, it can be determined at which period of Run I-11 the PFLs had the same properties as the hydrogenated solvent. The hydrogenated solvent has properties similar to PFLs produced with relatively fresh catalyst; however, it is not identical to any of the PFLs from Run I-11. For example, based on resid/distillate content and on distillate aromaticity and distillate and resid phenolic content, the hydrogenated solvent is very similar to the PFL from period 7 of Run I-11. However, based on resid aromaticity, preasphaltenes content and microautoclave solvent quality, the hydrogenated solvent is most similar to the PFLs from periods 1 or 2 of Run I-11. In addition, the hydrogenated solvent shows a higher ratio of cyclic/alkyl aliphatic protons than the PFLs from Run I-11. This indicates that it has more donatable hydrogen than the Run I-11 PFLs of similar aromaticity.

Condition 5 of Run I-12 used the same operating conditions as the entirety of Run I-11 except that Run I-11 used a solids-containing recycle stream. The earlier report (8) that addressed Run I-11 (HRI 227-20) included a set of equations relating various oil properties and run period. Substituting the values for the PFL sample from condition 5 (period 20) of Run I-12 into these equations shows that similar oil properties were attained between periods 14 and 22 of Run I-11. Therefore, PFL properties at period 20 of these two runs were generally similar.

The feed solvent used in condition 5 was most similar to the recycle oils used in periods 1 through 7 of Run I-11 and the PFL product was most similar to the PFLs from periods 14 through 22. Therefore, it appears that catalyst age plays a greater role in PFL properties than feed solvent composition does.

CTSL Run I-13

CTSL Run I-13 (HRI #227-32) was made in January, 1985. The run lasted 27 days and used 7 sets of operating conditions (Table 1) to test the effects of first- and second-stage temperature, space velocity, solvent/coal ratio and recycle cut point. Conoco analyzed 8 PFLs, 8 first-stage oils, one filter-cake extract and one start-up oil from this run.

Comparison of PFL and First-Stage Oils. The difference in oil properties between a PFL and the corresponding first-stage oil reflects the additional upgrading that occurs in the second-stage reactor. As in other CTSL runs examined, the PFL samples contain less resid, fewer preasphaltenes and lower concentrations of phenolics from the additional processing. The PFL samples and their distillate and resid fractions are more aromatic than the first-stage oils. 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 (7). An increase in aromaticity would be expected at equilibrium upon second-stage processing because of the 40 to 50°F increase in reactor temperature relative to the first stage. However, the additional conversion of coal and resid that occurs in the second stage could also affect aromaticity. The first-stage oils perform somewhat better in the microautoclave test than the corresponding PFL samples.

Catalyst Aging Effects. The two sets of samples analyzed from condition 1 (days 5 and 9) provide an illustration of the effects of catalyst aging. For both the PFL and first-stage oils, the sample taken later in the run contains more resid and more preasphaltenes and is more aromatic. In addition, both the resid and distillate fractions are more aromatic and have higher concentrations of phenolics. These observations, which are consistent with other CTSL runs analyzed earlier, appear to indicate deactivation. Hydrogenation, cracking and deoxygenation activities are all directly or indirectly affected.

First-Stage Temperature. The first three sets of operating conditions in Run I-13 were used to test the effect of first-stage temperature. Condition 1 used 750°F, condition 2 used 725°F and condition 3 used 775°F. All other operating conditions were constant except for catalyst age. A comparison of first-stage oil properties is shown below. Complete data for these and the PFL samples are given in Tables 2 through 8.

						Phenolic Conc., meq/g	
Condition	Period	First-Stage Temp., °F	Resid Content, wt %	Preasph., wt % of Resid	Aromaticity, %	Dist.	Resid
1	9	750	50.5	9.8	15.0	0.24	0.84
2	12	725	54.8	14.7	16.0	0.29	1.13
3	15	775	49.2	8.2	17.7	0.29	0.85

As the first-stage temperature was reduced between conditions 1 and 2 from 750 to 725°F, the PFL and first-stage oils became less highly upgraded. The effects of the reduced temperature on oil properties were similar to catalyst aging effects. For example, resid and preasphaltenes contents increased and the oils became more aromatic and more phenolic.

The increase in first-stage temperature between conditions 2 and 3 from 725 to 775°F had the opposite effect on several properties. Resid and preasphaltenes contents were reduced and resid phenolic concentration was reduced. However, distillate phenolic contents were unchanged and the oils became more aromatic.

A comparison of the data from days 9 and 15 illustrates the sum of the effects of increasing the first-stage reactor temperature from 750 to 775°F and catalyst aging on oil properties. The oils from these two periods have similar resid and preasphaltenes contents which indicates that the higher temperature offset catalyst aging effects for these parameters. The samples from period 15 are significantly more aromatic and more phenolic than those from period 9. This is as would be expected based on catalyst aging alone. In other CTSL runs examined, higher first-stage temperature decreased phenolic concentration. Its effect on aromaticity, particularly at the low space velocity used here, is not clearly defined. Obviously, however, the increased first-stage temperature did not offset catalyst aging effects on the phenolics concentrations.

The effect of first-stage temperature on oil properties can also be observed by comparing the oils from conditions 4 and 5. These two sets of operating conditions were identical except that condition 5 used a lower first-stage temperature (750 vs 775°F). The oils produced at the two conditions are not greatly different. Most of the observable differences are those expected from catalyst aging. The first-stage oils produced at the lower temperature (condition 5) are somewhat less aromatic than those produced at the higher temperature (condition 4). Since this is opposite the effect expected from catalyst aging, we can attribute the difference to the lower first-stage temperature. This would appear at first to be a hydrogenation equilibrium effect; however, changes in coal and resid conversion must be considered before such a conclusion can be confirmed. Interestingly, even though the first-stage oils were more hydrogenated at condition 5, the PFL oils from conditions 4 and 5 showed no difference in aromaticity. This would be expected if the second stage, which was at constant conditions, controlled the aromaticity of the PFL. At conditions 1, 2 and 3, the aromaticity of the PFL did respond to first-stage temperature changes. However, in that case, overall space velocity was greater than in conditions 4 and 5 because of the higher solvent/coal ratio.

Reduced Solvent/Coal Ratio. Beginning with condition 4, the solvent/coal ratio was reduced from 1.6 to 1.1. All other operating conditions except catalyst age remained unchanged from condition 3. The reduction in solvent/coal ratio corresponds to about a 23% relative increase in first-stage feed coal concentration. Since coal space velocity was unchanged, the lower solvent/coal ratio resulted in a lower overall space velocity, i.e., longer residence time. The net effect on oil properties was almost negligible. There were small but experimentally significant increases in aromaticity and phenolic concentrations, but these may merely reflect catalyst aging. Changes in the other measured parameters approached experimental error.

HRI requested that we examine the effect of solvent/coal ratio (S/C) on the difference between the properties of the first- and second-stage oils. At otherwise constant conditions (including constant coal space velocity), a reduction in S/C reduces overall space velocity. The reduced space velocity may either increase or decrease the difference between the properties of the first- and second-stage oils because the products from each stage should more closely approach equilibrium. HRI expected that the reduced space velocity would increase the difference (7). The only comparison of this type available in these data is between conditions 3 and 4 of Run I-13. This comparison is shown below.

	Δ, First-Stage Oil - PFL	
Property	Condition 3 (S/C = 1.6)	Condition 4 (S/C = 1.1)
Resid content, wt %	2.7	4.8
Preasphaltenes, wt % of resid	2.1	2.5
H-aromaticity, % - distillate	-1.1	-1.6
- resid	-2.7	-3.5
Phenolic content, meq/g - distillate	0.09	0.14
- resid	0.09	0.15
Microautoclave conversion, wt % MAF	2.3	3.6

For each property, the absolute value of the difference is greater at the lower solvent/coal ratio (condition 4), as expected. However, all differences are small. Experimental errors are compounded in such comparisons because each comparison relies on four measurements. It would appear that only the difference in phenolic content reduction is experimentally significant.

Second-Stage Temperature. Conditions 4 and 6 were nearly identical except for catalyst age and second-stage temperature. The later set of conditions used 815°F; up from the 800°F used earlier. Condition 6 also used a higher boiling recycle oil. The oils produced at the higher temperature contain slightly less resid and are more aromatic but otherwise have properties similar to the oils produced in condition 4. This indicates that the increased reactor temperature offset any effects of catalyst aging on resid conversion and on the removal of phenolics. The increased aromaticity is the expected result of both catalyst aging and the higher reactor temperature.

Reduction in Coal Space Velocity. Between conditions 6 and 7 of Run I-13, coal space velocity was reduced from 0.67 to 0.50 (relative to Run I-11). This resulted in small decreases in phenolic concentrations and substantial increases in aromaticities for both the first-stage and PFL oils. The decreased phenolic concentrations would be expected to result from the longer residence time at the low space velocity. The increased aromaticities could result from either reactor, e.g., the second-stage, being at dehydrogenating conditions; however, it is more likely that catalyst aging and the additional conversion of heavy material are responsible for the increased aromaticities.

Start-up Oil and Filter-Cake Extract. The start-up oil used for Runs I-13 through I-15 was a distillate oil from the Wilsonville pilot plant. It is very highly hydrogenated as evidenced by its very low aromaticity (Table 4) and its low phenolic concentration (Table 7). Most Wilsonville hydrotreated distillate ($850°F^-$) recycle solvents from Illinois 6 coal give about 80-85% conversion in the modified equilibrium microautoclave test, whereas most hydrotreater feed distillates (850°F$^-$) give about 67-74% conversion (11,13). Two potential start-up oils for Run I-13, also obtained from the Wilsonville pilot plant, gave 71% conversion at these conditions. The 75% conversion obtained with this oil (Table 8) indicates that it is a poorer donor solvent than most Wilsonville distillate (850°F$^-$) recycle solvents produced from bituminous coal.

The one filter-cake extract sample analyzed was used as make-up oil for the recycle solvent during conditions 6 and 7 of Run I-13. This material is the toluene extractable portion of the filter cake produced during pressure filtration (Figure 1). HRI removes the toluene by distillation before using the extract as a recycle oil. About 4.8 wt % toluene remained with the sample sent to us. It was removed by rotary evaporation prior to further analysis by Conoco. The filter-cake extract contains a low level of resid. Its distillate and resid fractions have properties close to those of the corresponding fractions of the PFL from periods 9 and 12. The one exception is that filter-cake extract, being a toluene extract, is low in preasphaltenes.

CTSL Run I-14

CTSL Run I-14 (HRI #227-33) was made during February and March, 1986. The run lasted fourteen days and used three sets of operating conditions (Table 1). The major purpose of Run I-14 was to test the effects of omitting catalyst from the second-stage reactor. Therefore, Run I-14 was operated with a catalytic first stage and a thermal second stage without reducing coal throughput. The first portion of the run was operated at conditions essentially the same as the demonstration run, Run I-11 (HRI #227-20). The recycle oil used in condition 1 simulated a hydroclone overflow material. It consisted of a combination of PFL and unfiltered atmospheric-still bottoms at flow rates of 0.8 and 1.8 lbs/lb coal, respectively. All other periods of this and other runs discussed in this report used a solids-free recycle oil with PFL as the major component. The middle of the run used different temperatures, a lower space velocity and a solids-free recycle. The last portion of the run used the highest second-stage temperature tested at conditions called "thermal cracking" by HRI. HRI reported good operability at all conditions (7). Conoco analyzed one first-stage inventory oil and one PFL from each set of operating conditions for a total of six samples.

Oil Quality Changes in Thermal Reactor. Differences between first-stage and PFL samples taken at any one set of operating conditions reflect the additional upgrading that occurs in the second stage. This difference is particularly interesting for Run I-14 because the second stage was operated at thermal, i.e., non-catalytic conditions. Most of the differences observed are qualitatively the same as observed at catalytic/catalytic conditions. For example, at all three sets of operating conditions, the whole PFL sample and its two fractions are more aromatic than the corresponding first-stage oil. In addition, each PFL resid contains a substantially lower concentration of preasphaltenes and a reduced level of phenolics. PFL resid content is lower than the corresponding first-stage resid content only for the two conditions that used second-stage temperatures of 825 and 840°F (conditions 1 and 3). For condition 2, which used high first-stage and low second-stage temperatures, the PFL sample contains slightly more resid than the first-stage sample. Apparently, this is a result of reduced second-stage resid conversion at these conditions. Though phenolic concentrations were lower in the PFL resids than the first-stage resids, there was little difference in the phenolic concentrations in the distillate oils from the two stages. This is the first time we have observed this for CTSL samples. This observation clearly demonstrates the importance of catalysis for removal of distillate phenolics. As in most other cases, the first-stage oils are slightly better donor solvents than the corresponding PFL as measured by microautoclave tests.

Oil Properties at Catalytic/Thermal vs Catalytic/Catalytic Conditions. Condition 1 of Run I-14 was essentially identical to the operating conditions used in Run I-11, also called the demonstration run or Run 227-20, except that the second stage was at thermal conditions in Run

I-14. Since coal throughput was the same, total space velocity based on catalyst was doubled in Run I-14. The properties of oils from Run I-11 and from condition 1 of Run I-14 can be compared to observe the effect of operating the second stage at thermal conditions. Conoco reported analyses of PFL samples from Run I-11 (227-20) earlier (8). The corresponding PFL we analyzed from Run I-14 (period 7) is significantly less upgraded than PFL samples taken at about the same point (period 6) of Run I-11.

Run	Period	Resid, wt %	Preasph., wt % of Resid	Aromaticity, %	Phenolic Conc., meq/g		Microautoclave Coal Conv., wt % MAF
					Dist.	Resid	
I-11	6	38.2	5.6	22.8	0.18	0.62	83.2
	14	46.9	7.7	25.9	0.33	1.00	79.3
	18	51.0	11.9	26.5	0.38	1.04	74.8
I-14	7	51.1	7.3	24.8	0.70	1.24	76.2

The Run I-14 sample contains much more resid, is much more aromatic, has a very much greater concentration of phenolics, and performs significantly worse in the microautoclave test. Most of the measured parameters changed nearly linearly with run time or catalyst age in Run I-11 (8). Conoco's earlier report concerning Run I-11 (8) included a set of equations relating various oil properties and run period. Substituting the values for the PFL from period 7 of Run I-14 into these equations showed that similar oil properties were attained between periods 11 and 19 of Run I-11. Therefore, it would appear that with only one catalytic reactor, oil properties deteriorate about twice as rapidly as they did in the demonstration run. An exception to this observation is phenolic concentration. The PFL sample from period 7 of Run I-14 has a significantly greater concentration of phenolics than even the last PFL sample from Run I-11 (period 25). The equations discussed above predict that similar concentrations of distillate phenolics would have been attained on period 35 and Run I-11. Once again the importance of catalysis for removal of distillate phenolics is evident.

A similar comparison is available between condition 2 (period 10) of Run I-14 and condition 3 (period 15) of Run I-13. Once again the only major difference in operating conditions was that Run I-14 was operated with a thermal second stage. It would appear based on space velocities and period numbers that similar amounts of coal had been processed by period 10 of Run I-14 and period 15 of Run I-13. The PFL and first-stage sample from Run I-14 are both less highly upgraded than the corresponding samples from Run I-13. PFL properties are compared below.

Run	Period	Resid, wt %	Aromaticity, %	Phenolic Conc., meq/g Dist.	Phenolic Conc., meq/g Resid	Microautoclave Coal Conv., wt % MAF
I-13	15	46.5	19.3	0.20	0.71	81.0
I-14	10	54.3	25.2	0.57	0.98	76.9

Once again, the oils produced at catalytic/thermal conditions contain more resid, are more aromatic and much more phenolic, and perform much more poorly in the microautoclave test.

Effects of Reactor Temperature Changes. Condition 2 used a different recycle, lower space velocity, higher first-stage temperature and lower second-stage temperature then condition 1. The temperature changes would tend to shift the chemistry of the process in such a way that more reaction would occur in the first stage (catalytic) and less in the second stage (thermal). In fact, the first-stage oils from condition 2 contain less resid, preasphaltenes and phenolics than those from condition 1. However, only the reduction in phenolics carried through the second-stage reactor to the PFL. The PFL produced at condition 2 had about the same amount of preasphaltenes and more resid than the PFL from condition 1, even though the second-stage feed, i.e., the first stage oil, contained significantly less of this material. In the absence of catalyst, the second stage provides very little removal of phenolics. The PFL phenolic contents were lower in condition 2 than in condition 1 only because the second-stage feed, i.e., the first-stage oil, contained lower amounts.

Thermal Cracking Conditions. Condition 3 of Run I-14 was called "thermal cracking" conditions by HRI (5). The second-stage was operated at high temperature (840°F) without catalyst. Other than the higher second-stage temperature and more advanced catalyst age in condition 3, operating conditions 2 and 3 were identical. PFL properties are compared below for these two periods.

Cond.	Period	Resid, wt %	Aromaticity, % Whole	Aromaticity, % Dist.	Aromaticity, % Resid	Phenolic Conc., meq/g Dist.	Phenolic Conc., meq/g Resid	Microautoclave Coal Conv., wt % MAF
2	10	54.3	25.2	24.1	31.3	0.57	0.98	76.9
3	14	49.9	34.4	25.0	41.9	0.58	0.91	64.5

The PFL produced at condition 3 contained less resid and was much more aromatic than the PFL from condition 2. The lower resid content would indicate improved resid conversion at condition 3. The greatly increased aromaticities of the PFL and of its resid fraction at condition 3 could partly arise from increased coal conversion, but the magnitude is such as to suggest that the oils may have been dehydrogenated in the second stage. This is consistent with the greatly reduced solvent quality (measured by microautoclave test) of the PFL from condition 3 relative to both the PFL from condition 2 and to the first-stage oil from condition 3. The higher second-stage temperature used in condition 3 had virtually no effect on PFL distillate phenolic concentration. This is in direct contrast to the large response of phenolic concentration to temperature routinely observed with catalyst present. Comparing the oils from conditions 2 and 3, the first-stage oils showed the same differences as the PFLs except that the magnitude was smaller.

CTSL Run I-15

CTSL Run I-15 (HRI #227-34) was made in March, 1985. The run lasted 13 days and used two operating conditions (Table 1). The major purpose of this run was to test the effects of catalyst cascading on product yields. Catalyst cascading is a concept to reduce required catalyst addition rates in the CTSL process. Cascading would be accomplished by using the withdrawn spent catalyst from the first (low T) stage as the replacement catalyst in the second (high T) stage instead of replacing it with fresh catalyst. To perform catalyst cascading, catalyst addition/withdrawal capability is required for both reactors. Since HRI's bench unit is not suitable for continuous catalyst replacement, cascading was simulated in Run I-15 by charging the second stage with spent first-stage catalyst recovered from Runs I-12 (80%) and I-13 (20%). The average age of the cascaded catalyst was 34 days. Therefore, at the start of Run I-15, average total catalyst age was 17 days (14). Constant operating conditions, identical to Run I-13, were used for the first nine days of operation. The last three days used higher reactor temperatures, lower space velocity and a lower solvent/coal ratio in order to convert heavy oil to extinction. Conoco analyzed 4 PFL and 2 first-stage samples.

Oil Properties and Catalyst Age. Since the first nine days of Run I-15 were operated at constant conditions, changes in oils properties can be related to catalyst aging effects. This assumes that effects caused by the replacement of start-up oil are small. We obtained three PFL samples taken during the first nine days of Run I-15. As expected based on other runs analyzed, resid and preasphaltenes contents increased, aromaticities of the whole PFL and of its distillate and residual fraction increased and phenolic contents increased for both the resid and distillate fractions with catalyst age. The observed changes in oil properties with catalyst age are consistent with catalyst deactivation effects. Hydrogenation, cracking and deoxygenation functions all appear to be directly or indirectly reduced with age.

Heavy-Oil Extinction Conditions. Beginning on day 10 of Run I-15, operating severity was increased to provide for extinction of heavy oil. Both reactor temperatures were increased (25°F first stage, 15°F second stage), space velocity was reduced, recycle solvent/coal ratio was reduced and recycle-oil cut point was increased. For the first-stage oils, the change in conditions reduced resid, preasphaltenes and phenolic concentrations. The oil produced at condition 2 gave much poorer performance in the microautoclave test. Resid aromaticity increased significantly and distillate aromaticity decreased slightly. The decreased first-stage distillate aromaticity was accompanied by a large increase in paraffinic hydrogen (alkyl beta plus gamma). The large difference in the behavior of the first-stage resid and distillate (comparing conditions 1 and 2) is quite unusual and may indicate a bad sample. The PFL sample from condition 2 has an unusually high resid content and is the only sample found to contain any significant amount of solids. This sample, therefore, appears to have certain anomolous properties. Other than resid content, the PFL samples showed generally the same behavior from the change in operating conditions as the first-stage oils except that the aromaticities of both the distillate and resid increased substantially. Preasphaltene concentration in the resid decreased, and aromaticity increased substantially for the whole PFL and both of its fractions. Phenolic concentration decreased in the resid and stayed unchanged in the distillate.

Comparison of PFL and First-Stage Oils. Differences between first-stage and PFL samples taken at any one set of operating conditions reflect the additional upgrading that occurs in the second-stage reactor. In this regard, Run I-15 was qualitatively similar to other catalytic/catalytic CTSL runs analyzed. PFL samples contain less resid and less of the resid is preasphaltenes. Aromaticity is higher in the whole PFL sample and in its two functions and phenolic concentration is lower in both the PFL distillate and resid. The one exception to this generalization is the PFL sample from condition 2 which contains more resid than the corresponding first-stage sample. As discussed above, this particular PFL sample appears to have certain anomolous properties, but the increased resid content may merely reflect the efficient N_2 stripping used at this condition..

Catalyst Cascading vs Fresh Catalyst. The first nine days of Runs I-13 and I-15 were operated at essentially identical conditions except that Run I-15 simulated catalyst cascading. The second-stage catalyst charged to Run I-15 was previously aged as first-stage catalyst in earlier runs. The effects of simulated catalyst cascading can be observed by comparing oil properties from the first nine days of the two runs. Direct comparisons are available in the data tables for PFL samples taken on days 5 and 9 and for first-stage samples taken on day 10A from both runs.

For each of the three comparisons, the samples from Run I-15 are less highly upgraded. The differences are those commonly observed from catalyst aging. Run I-15 samples contain substantially more resid and the resid contains more preasphaltenes. The whole samples from Run I-15 and their distillate and resid fractions are significantly more aromatic. Run I-15 samples also are substantially richer in phenolics.

Figure 2 compares properties of the PFL samples over the first nine days of the two runs. Based on the trends of the measured parameters with period number (catalyst age) for the two runs, most properties of the PFLs from Run I-15 reach the same values as those reached on day 9 of Run I-13 by about days 5 to 7. This would indicate that for most of the oil properties measured, by about days 5 to 7 with catalyst cascading, the oil characteristics had deteriorated to the same point as day 9 with fresh catalyst in both reactors. Phenolic concentrations in the oils deteriorated even faster. By about day 3 with catalyst cascading, phenolic concentrations had increased to the same point as day 9 with fresh catalyst. These results agree qualitatively with HRI's reported 975°F$^+$ conversion results (15). Those data show that with catalyst cascading (Run I-15), 975°F$^+$ conversion declined by day 3 to the same point it was on day 9 with fresh catalyst in both reactors (Run I-13).

Another comparison is available to show the effects of catalyst cascading. The same operating conditions were in use for condition 2 (period 13) of Run I-15 and condition 7 (period 27) of Run I-13. Both periods used N_2 stripping as part of the "heavy-oil extinction" conditions. HRI reports (7) that the stripping was more efficient in Run I-15 and that the PFL product, therefore, would be expected to be heavier. Of course, by period 27 of Run I-13 more than twice as much coal had been processed as by period 13 of Run I-15.

Run	Period	Preasph., wt % of Resid	Aromaticity, %		Phenolic Conc., meq/g	
			Dist.	Resid	Dist.	Resid
I-13	27	5.4	21.8	36.3	0.24	0.63
I-15	13	4.6	22.6	35.2	0.25	0.57

Both the distillate and resid fractions of the PFL samples from the two runs have very similar properties. However, the high resid content of this PFL of Run I-15 (presumably resulting from very efficient N_2 stripping) affects the analyses of the whole (undistilled) sample. This indicates that the major second-stage product, the PFL, has properties on day 13 when using cascaded catalyst similar to those produced on day 27 when using fresh catalyst.

Interestingly, the samples taken at these conditions from the first stage, which used fresh catalyst in both runs, are more upgraded in Run I-15 relative to Run I-13 as evidenced by lower concentrations of preasphaltenes, aromatics and phenolics.

Run	Period	Resid, wt %	Preasph., wt % of Resid	Aromaticity, %		Phenolic Conc., meq/g	
				Dist.	Resid	Dist.	Resid
I-13	27C	47.5	10.4	16.9	30.0	0.33	0.90
I-15	14A	47.5	5.6	12.3	29.0	0.28	0.81

This is consistent with the lower first-stage catalyst age.

Taken as a whole, these data suggest that, in the catalyst cascading experiment, oil properties deteriorated to any one point in about half the time as when using fresh catalyst in both reactors. It should not be surprising that oil properties deteriorated more quickly in the cascading test. However, it is not obvious to the authors that this test using second-stage catalyst aged to 34 days is the best simulation of cascading. Assuming that Run I-15 was a good model for catalyst cascading, overall catalyst addition rates with catalyst cascading will clearly be greater than 50% of the replacement rate required without cascading.

Catalytic Hydrogenation in Second Stage. The oils produced from the high temperature second stage are consistently more aromatic than those produced from the lower temperature first stage. This observation holds true for the whole oils and their distillate and resid fractions for all CTSL runs examined to date by Conoco. At first, this may appear to be a thermodynamic equilibrium effect such that the degree of hydrogenation decreases with increasing temperature. For all CTSL runs examined before the current set, the first- and second-stage catalyst aged simultaneously. This left the possibility open that the increased aromaticity resulted from first-stage catalyst deactivation. This observation is therefore not necessarily inconsistent with the hypothesis that the degree of hydrogenation of the second-stage oils is controlled by thermodynamic equilibrium. However, the comparison discussed in the report between the "normal" catalytic/catalytic and the simulated catalyst cascading modes (Runs I-13 vs I-15) demonstrates that aromaticity increases with second-stage catalyst age. Also, the comparison between the "normal" catalytic/catalytic and the catalytic/thermal modes (Runs I-11 vs I-14) demonstrates that the increase in aromaticity through the second stage is greatest in the absence of catalyst. Therefore, the increases in oil aromaticity in the second stage at the majority of operating conditions tested do not appear to result from thermodynamic equilibrium effects. Instead, it would appear that the increase in aromaticity through the second stage results from the additional conversion to lighter products that occurs in that stage.

PHENOL MATERIAL BALANCE

This section describes a material balance of total phenolics in coal liquids around three of the sample separation procedures used at Conoco. The objectives of the work were twofold: first, to determine if the phenol data provided by our Fourier-Transform Infrared (FTIR) spectroscopic analysis method were useable on a material balance basis, and second, to determine if the sample workup procedures adversely affected sample characteristics or composition. These objectives are important in evaluating the accuracy of the FTIR analysis and of the other sample workup procedures and in exploring the potential for broader application of these data.

The separation procedures used were distillation to an 850°F (equivalent) endpoint, pressure filtration of vacuum bottoms to recover THF-soluble resid, and preparative liquid column fractionation (LCF) to obtain resid fractions (oils, asphaltenes, and preasphaltenes). Three daily composite samples from Wilsonville Run 249 (all from 8/13/86) were used: 1) a first-stage solvent (V-131B), 2) a first-stage product/second-stage feed (V-1064), and 3) a second-stage product (V-1067), a portion of which is recycled as the first-stage solvent.

Conclusions

- The phenol material balances for the distillation and distillation/pressure filtration procedures were 103-110% and 105-115%, respectively.

- The phenol material balance for the liquid column fractionation (LCF) procedure was 83-120%.

- All material balance values were within experimental reproducibility of the determination of phenolic OH content.

- Phenolic concentration data obtained by the FTIR procedure appear to be suitable for material balance purposes. The sample separation procedures give no evidence of detrimental changes to the samples.

- The asphaltene resid fractions were found consistently to have higher phenolic concentrations than the corresponding preasphaltene fractions.

- Some difficulty was noted in obtaining accurate phenol concentrations of the V-1067 whole sample. The high ash content and low phenolic content produced a noisy spectrum and a baseline interference that resulted in a slightly low phenol concentration using the automated software.

Procedure

Each daily composite sample was distilled to an 850°F equivalent endpoint (320°C pot/270°C column/5 torr). Pressure filtration of the distillation residue (pot bottoms), followed by rotary evaporation of the solvent, was used to obtain the THF-soluble resid for subsequent analysis. These procedures have been described in detail (8). A portion of each THF-soluble resid sample was separated by a preparative liquid column fractionation (LCF) procedure into oils (hexane soluble), asphaltenes (benzene soluble/hexane insoluble), and preasphaltenes (pyridine soluble/benzene insoluble) fractions. Details of the preparative LCF procedure have been given elsewhere (11). The phenolic OH concentration of each sample (whole, distillate, distillation bottoms, THF-soluble resid, oils, asphaltenes, and preasphaltenes) was determined in THF solution by an FTIR procedure which has been described previously (8,11).

Results and Discussion

The phenolic concentration, phenol concentration reproducibility, component distribution, and solubility fractionation data for the samples are given in Tables 9 through 12, respectively. These data were used to generate phenol material balances for the distillation/pressure filtration procedures and for the LCF procedure. For each balance, the phenolic OH contribution from each component was summed to give a calculated net phenol concentration. This was compared with the measured phenol concentration for the unfractionated sample to give a percentage recovery balance. The equations below give the calculations used for each balance.

Distillation balance:

$$C_{net} = C_d \times f_d + C_b \times f_b, \quad \text{Balance} = \frac{C_{net} - C_{whole}}{C_{whole}} \times 100\%$$

Distillation/pressure filtration balance:

$$C_{net} = C_d \times f_d + C_r \times f_r, \quad \text{Balance} = \frac{C_{net} - C_{whole}}{C_{whole}} \times 100\%$$

LCF Balance:

$$C_{net} = C_o \times f_o + C_a \times f_a + C_p \times f_p, \quad \text{Balance} = \frac{C_{net} - C_r}{C_r} \times 100\%$$

where C is phenol concentration and f is weight fraction. Subscript abbreviations are: d for distillate, b for distillation bottoms, r for THF-soluble resid, o for oils, a for asphaltenes and p for preasphaltenes. Note that the distillation/pressure filtration phenol balance assumes that IOM does not contribute to the net phenolic concentration. Since the methods used do not permit the phenolic content of IOM to be measured, such an assumption is necessary. The phenol material balance results are shown in Tables 13 and 14. Balance results are 103-110% for distillation (Table 13), 105-115% for distillation/pressure filtration (Table 13) and 83-120% for LCF (Table 14). In all cases, the absolute phenol balance error is less than the measurement error for the whole sample or soluble resid. Thus the balances are within the experimental error of the measurements. The higher errors in the LCF balances probably result from the small sample weights involved. Weights of component fractions ranged from 3 to 200 mg and some weight error due to solvent retention is possible.

In spite of the assumption that IOM does not contribute to the phenol concentration (which might tend to lower the calculated net phenol concentration), the balance results for distillation/pressure filtration are higher than the distillation balance in two cases. It is likely that the presence of ash in the V-1064 and V-1067 whole and distillation bottoms samples results in some error in the phenol concentrations in those samples. The spectra of the ashy V-1067 samples were quite noisy and baseline interferences from the ash resulted in slightly low phenolic concentration values by the automated software for the V-1067 whole sample. This was partially corrected by manual treatment of the data for that sample. The assumption that IOM does not contribute to the phenol concentration did not appear to adversely affect the results, in part because the IOM makes up such a small part (less than 6%) of the total sample. It is likely that other samples might give worse results under that assumption. A better assumption for such purposes might be to assume that the IOM has the same phenolic concentration as the preasphaltenes or as the THF-soluble resid.

It is not surprising that the phenol concentration results for distillates are more reproducible than those for the other sample types (Table 10). Since the THF soluble resids do not contain IOM and ash, it is expected that phenol concentration results for them should be more reproducible than those for the whole or distillation bottoms samples. However, the opposite effect was observed (Table 10). Perhaps the effect observed here is not true in general.

One surprising result from this set of experiments is that the asphaltene resid fractions consistently contained more phenols than the corresponding preasphaltene fractions (Table 9). It is generally assumed that preasphaltenes are higher in molecular weight and contain more functional groups than the corresponding asphaltenes. It is possible that these preasphaltenes contain relatively higher concentrations of nitrogen and other functionalities. It is also possible that the lower solubility of preasphaltenes in THF results in a portion of the sample not being detected. This would cause the determined phenolic contents of preasphaltenes to be lower than the actual values; however, this would belie the close balance closures observed.

In general, it appears that the phenol concentration data from the FTIR method are suitable for use on a balance basis, and that the sample separation procedures do not adversely affect sample composition or characteristics within the reproducibility of the method. Some caution is noted for phenol determination of ashy samples, but even those results appear fairly good in the case reported here. It is possible that adaptation or improvement of the FTIR method could yield better results for ashy samples.

ANALYSIS OF PURDUE PRODUCTS FROM POTASSIUM/CROWN-ETHER/ COAL REACTIONS

Conoco previously analyzed (12), by Fourier-Transform infrared (FTIR) spectroscopy, various samples from experiments performed by Purdue Research Foundation on reactions of coal with potassium dissolved in crown ether. The purpose of Purdue's experiments was to use solvated electrons to cause chemical cleavage of alkyl and ether linkages in the coal, producing soluble moieties for structural characterization. By conducting these selective reactions at low temperature, it was hoped that these structural data would bear a direct relationship to the original parent coal structure. Purdue's work was performed under DOE Contract FG22-84PC70792 and is described elsewhere (16,17). The sample previously analyzed by Conoco included feed coals, alkali extracts, unextractable products and their acetylated and methylated derivatives. Here we report on analyses of two types of tetrahydrofuran (THF) soluble products made from Illinois 6 bituminous coal using these reactions.

Purdue's work-up scheme (16,17) following reaction consists of extracting the reaction products with THF to produce a material called "THF-1". The residue is then extracted with water which is highly basic because of the potassium. The residue from the water extraction is acidified with HCl and re-extracted with THF to give a material called "THF-2". The final unextracted material forms the feed for another reaction cycle with potassium/crown ether. Reaction cycles may be repeated numerous times.

The following four samples were supplied by Dr. Ramani Narayan of Purdue:

J1-20B-THF-1
J1-20C-THF-1
J1-20B-THF-2
J1-20C-THF-2

The last digit in the sample number indicates that the sample is either "THF-1" or "THF-2" material. The letters B and C indicate that the material was produced in the second and third reaction cycle, respectively. All four samples were analyzed by gas chromatography/mass spectrometryy (GC/MS) and FTIR to provide compositional details. FTIR spectra were obtained on films cast from THF solution. GC/MS, which will only detect volatile species with boiling points up to about 500°C, was operated as described elsewhere (8) using a 30m crosslinked methyl silicone capillary column. Analyses are reported below for each of the four samples.

No evidence was found for the presence of homologous series of alkylnaphthalenes, alkyltetralins or alkyldecalins as indicated in Reference 17. In Reference 17, the alkylnaphthanes and their hydrogenated derivatives were identified in the THF-1 fractions by chemical ionization tandem mass spectrometry (CI/MS/MS). According to Dr. Narayan (18), this technique, as used, is not very sensitive to paraffins. Based on our GC/MS results, these compounds, if present, are at trace levels in the 500°C$^-$ portions of these samples. The near absence of aromatic C-H stretch peaks in the FTIR spectra of these samples corroborates this conclusion. Dr. Narayan (18) reports that the samples he supplied to us for analysis may not be typical of his work. These samples were produced at unusually low potassium-to-crown ether ratios (0.5 vs 1.5). As a result, the reaction may not have proceeded as completely as normally. Also, Dr. Narayan (18) now believes that the identified naphthalenes and hydronaphthalenes may be products of higher molecular weight species that decompose during the CI/MS/MS analysis.

Sample THF-1, Second Cycle (J1-20B-THF-1)

The major single component apparent in the GC/MS analysis of this sample is butylated hydroxy toluene (BHT, a THF preservative). Other major components include a probable triterpane eluting between the C_{25} and C_{26} n-paraffins, an unknown, a methyl biphenyl isomer and benzophenone. The n-paraffins from C_{20} through C_{38} are quite prominent. The probable triterpane appears to be a tricyclic saturate of formula $C_{23}H_{42}$ or $C_{24}H_{44}$. The FTIR spectrum (Figure 3) of the whole sample indicates a highly aliphatic material; the aromatic C-H peak near 3050 cm^{-1} is nearly absent. This is consistent with the observed absence of a high concentration of alkylnaphthalenes. A prominent carbonyl peak near 1700 cm^{-1} is apparent.

Sample THF-1, Third Cycle (J1-20C-THF-1)

The GC/MS chromatogram of this sample is much more complex than the above sample. The single major peak is the probable triterpane ($C_{23}H_{42}$ or $C_{24}H_{44}$) found above. BHT, a methyl biphenyl isomer and pyrene are fairly prominent peaks. The series of n-paraffins from C_{14} through C_{35} (maximum at C_{26}) is very prominent. Other components were not identified. The FTIR spectrum (Figure 4) is similar to the above sample except that the aliphatic C-H stretch bands near 2900 cm^{-1} are much more intense.

Sample THF-2, Second Cycle (J1-20B-THF-2)

GC/MS showed the volatile portion of this material to consist of about 95% crown ether (18-crown-6), about 1% each of BHT and benzophenone and traces of a methylbiphenyl isomer and the probable triterpane ($C_{23}H_{42}$ or $C_{24}H_{44}$) discussed above. FTIR (Figure 5) indicates that the whole sample is perhaps 80% crown ether.

Sample THF-2, Third Cycle (J1-20C-THF-2)

This sample is very similar to the previous one. GC/MS indicates that the volatile portion consists of about 90% crown ether, about 1% each of BHT and benzophenone, a series of n-paraffins and two unknowns at about 5% and 1% concentration, respectively. FTIR (Figure 6) indicates that the whole sample is perhaps 80% crown ether.

ANALYSIS OF PENN STATE MICROAUTOCLAVE TSL SAMPLES

Conoco has conducted cooperative work with the Pennsylvania State University concerning their program on coal pretreatment for two-stage liquefaction (Contract No. DE-FG22-84PC7003). Some of this work was reported (11). In this quarter, we analyzed a set of twenty-eight two-stage liquefaction (TSL) oils produced by Penn State in microautoclave experiments.

Prof. F. J. Derbyshire supplied Conoco with a set of samples consisting of the hexane-soluble and hexane-insoluble/tetrahydrofuran-soluble portions of the products from two-stage catalytic liquefaction tests. The sample set included those made with bituminous and subbituminous coals, with and without pretreatment, using three solvents (650 x 850°F, 850°F$^+$ and the 50/50 blend) for a total of twenty-four products. The 650 x 850°F and 850°F$^+$ solvent and the hexane-soluble and hexane-insoluble/tetrahydrofuran-soluble portion of the 850°F$^+$ solvent were also supplied for a total of four solvent samples. Penn State's report on the production of these samples is given in Reference 19. Conoco analyzed each by ^{1}H-NMR, FTIR (for phenols) and elemental composition (C, H, N and S). All unused samples were returned. The original analytical data are shown in Table 15. The sample designation code is as follows: C-catalytic run without pretreatment, D-catalytic run with pretreatment, 2-asphaltene and 3-oil. Wyoming subbituminous coal (PSOC 1401) was used in Runs 68, 69, 72, 73, 80 and 81; the remainder used Ohio #5 bituminous coal (PSOC 1266). Three solvents (different fractions of a Lummus ITSL oil) were used: 850°F$^+$ resid was used in Runs 80, 81, 84, and 85, 650 x 850°F distillate was used in Runs 64, 65, 68 and 69 and a 50/50 blend of these two was used in Runs 60, 61, 72 and 73. Analyses of the distillate and resid feed solvents and of the oils and asphaltenes fractions of the feed solvents are also shown in Table 15.

The ^{1}H-NMR analyses showed that most of these samples were contaminated with tetrahydrofuran (THF) and butylated hydroxytoluene

(BHT). The contamination was severe enough that many of the analytical results would not well represent the oil properties. To improve the utility of these data, calculations were performed to "back-out" the effects of the contaminants from the results. This was done as follows.

The amounts of THF and BHT in each sample were determined from the ^{1}H-NMR and hydrogen analyses as

$$\text{wt \% THF} = \frac{^1\text{H-NMR area from THF}}{\text{total } ^1\text{H-NMR area}} \text{ \% H in total sample} \times \text{\% H in THF}$$

$$\text{wt \% BHT} = \frac{^1\text{H-NMR area from BHT}}{\text{total } ^1\text{H-NMR area}} \text{ \% H in total sample} \times \text{\% H in BHT}$$

^{1}H-NMR data were corrected by ignoring the area due to THF and BHT during integration. Concentrations of phenolics, C, H, N and S were each corrected as

$$\text{correct conc. of species in sample} = \frac{C_T - XC_B - YC_{THF}}{1 - X - Y}$$

where C_T is the concentration of the species in the total sample, C_B is the concentration of the species in pure BHT, C_{THF} is the concentration of the species in pure THF, X is the weight fraction of BHT in the total sample and Y is the weight fraction of THF in the total sample. Corrected data are shown in Table 16. The contamination and the correcting calculation will somewhat reduce the accuracy of the analyses. Interpretation of these data will be performed by Penn State and reported under their contract.

Section 3

EXPERIMENTAL

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

Section 4

REFERENCES

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15. McLean, J. B., Comolli, A. G., Johanson, E. S. and Smith, T. O., "Status of HRI's Catalytic Two Stage Liquefaction Program", Presented at the 1986 EPRI Coal Liquefaction Contractors' Conference, Palo Alto, CA, May, 1986.

16. Narayan, R., "Guest Molecules in Coal. Third Quarterly Report, April 1 - June 30, 1985", DOE Contract FG22-84PC70792, June, 1985.

17. Narayan, R., "Guest Molecules in Coal. Fourth Quarterly Report, July 1 - September 30, 1985", DOE Contract FG22-84PC70792, August, 1985.

18. Narayan, R., personal communication with authors, October 31, 1986.

19. Derbyshire, F. J., "Current Activities", Presented at the Technical Review Meeting on Coal Pretreatment and Two Stage Liquefaction, Library, PA, August 14, 1986.

TABLE 1

OPERATING CONDITIONS
HRI CTSL RUNS I-12, 13, 14, 15

Condition No.	Days	Temperature, °F		S.V. (a)	Recycle (b)	S/C (c)
		1st Stage	2nd Stage			
Run I-12 (227-30)						
SH	16-17	700	700	No coal	-	No coal
5	17-20	750	825	1.0	PFL	2.6
Run I-13 (227-32)						
1	1-9	750	800	0.67	PFL	1.6
2	10-12	725	800	0.67	PFL	1.6
3	13-15	775	800	0.67	PFL	1.6
4	16-18	775	800	0.67	PFL	1.1
5	19-20	750	800	0.67	PFL	1.1
6	21-24	775	815	0.67	PFL (e)	1.1
7	25-27	775	815	0.50	PFL (e)	1.1
Run I-14 (227-33)						
1	1-7	750	825	1.0	HOF	2.5 (f)
2	8-10	775	800	0.67	PFL	1.6
3	11-14	775	840	0.67	PFL	1.6
Run I-15 (227-34)						
1	1-9	750	800	0.67	PFL	1.6
2	10-13	775	815	0.50	PFL (e)	1.1

Feed Coal: Illinois 6, Burning Star #2 mine.

Start-up oil: Run I-12 used H-Coal fractionater bottoms from Illinois 6 coal run, Runs I-13 to I-15 used Wilsonville solvent.

Pressure: 2500 psig

Catalyst (g)	1st Stage	2nd Stage
Run I-12	Fresh Amocat 1C	Fresh Amocat 1A
Run I-13	Fresh Amocat 1C	Fresh Amocat 1C
Run I-14	Fresh Amocat 1C	None
Run I-15	Fresh Amocat 1C	Recovered Amocat 1C (d)

(a) Coal space velocity, relative to Run I-11 (227-20) which used 68 lbs MF/h/ft^3 settled first-stage catalyst.

(b) PFL - pressure filter liquid, solids-free. HOF - simulated hydroclone overflow, contains solids.

(c) Solvent to coal ratio, additional solvent added through buffer pumps increases ratio by about 0.3 for Run I-12, 13 and 14 and 0.3-0.5 for Run I-15.

(d) Catalyst recovered from first-stage of Runs I-12 (80%) and I-13 (20%), avg. age is 34 days.

(e) Recycle oil consisted of PFL and filter-cake extract. PFL cut-point increased (by using N_2 stripping during distillation) in an attempt to recycle heavy oil to extinction.

(f) Solvent/coal ratio = 2.5, oil/solids ratio = 1.8

(g) 1/16" extrudates, Amocat 1C is Ni/Mo, Amocat 1A is Co/Mo, both on alumina.

Source: References 3 to 7.

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TABLE 2

DISTILLATION RESULTS
HRI CTSL Runs I-12, 13, 14, 15

				wt % of Sample	
Run	Condition	Run Period	Sample Number	850°F Distillate	Resid
I-12	Hydrogenated Solvent				
	SH	17ABC	4613	59.5	40.4
	Pressure-Filter Liquid				
	5	20	4614	45.9	53.9
I-13	Pressure-Filter Liquids				
	1	5	4629	60.6	39.3
	1	9	4631	53.3	46.5
	2	12	4633	49.1	50.4
	3	15	4635	53.3	46.5
	4	18	4637	53.2	46.7
	5	21	4639	49.2	50.6
	6	24	4641	55.6	44.3
	7	27	4643	54.7	45.2
	First-Stage Samples				
	1	6A	4630	51.3	48.3
	1	10A	4632	49.2	50.5
	2	13A	4634	44.8	54.8
	3	16A	4636	50.4	49.2
	4	19A	4638	49.0	51.5
	5	22A	4640	47.1	52.2
	6	25A	4642	49.8	49.7
	7	27C	4644	52.1	47.5
	Filter-Cake Extract (a)				
			4645	62.5	36.9
I-14	Pressure-Filter Liquids				
	1	7	4653	48.7	51.1
	2	10	4655	45.5	54.3
	3	14	4657	49.9	49.9
	First-Stage Samples				
	1	8A	4654	42.1	57.4
	2	11A	4656	46.9	52.6
	3	15A	4658	44.7	54.9
I-15	Pressure-Filter Liquids				
	1	2	4662	65.8	33.8
	1	5	4663	56.8	42.9
	1	9	4664	48.4	51.3
	2	13	4666	40.5	59.0 (b)
	First-Stage Samples				
	1	10A	4665	43.4	56.1
	2	14A	4667	51.5	47.5

(a) 4.8 wt % toluene removed prior to analysis.
(b) includes 0.6% IOM and 0.3% ash, absolute.

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TABLE 3

SOLUBILITY FRACTIONATION ANALYSES OF RESIDS
HRI CTSL Runs I-12, 13, 14, 15

Run	Condition	Run Period	wt % of Pyridine-Soluble Resid		
			Oils	Asphaltenes	Preasphaltenes
I-12	Hydrogenated Solvent				
	SH	17ABC	79.5	17.2	3.3
	Pressure-Filter Liquid				
	5	20	68.6	21.1	10.3
I-13	Pressure-Filter Liquids				
	1	5	80.4	17.4	2.2
	1	9	77.8	16.2	6.0
	2	12	71.0	20.5	8.4
	3	15	76.8	17.1	6.1
	4	18	75.4	18.7	5.9
	5	21	73.9	22.3	3.8
	6	24	78.1	18.1	3.8
	7	27	77.8	16.8	5.4
	First-Stage Samples				
	1	6A	76.3	17.1	6.6
	1	10A	70.8	20.4	9.8
	2	13A	65.7	19.6	14.7
	3	16A	73.7	18.2	8.2
	4	19A	72.1	19.4	8.4
	5	22A	68.5	20.1	11.3
	6	25A	69.2	19.0	11.8
	7	27C	71.0	18.6	10.4
	Filter-Cake Extract				
			81.3	17.8	0.9
I-14	Pressure-Filter Liquids				
	1	7	71.8	20.9	7.3
	2	10	75.7	18.5	5.8
	3	14	73.0	20.1	6.9
	First-Stage Samples				
	1	8A	63.2	18.2	18.6
	2	11A	70.0	18.9	11.0
	3	15A	69.5	18.6	11.9
I-15	Pressure-Filter Liquids				
	1	2	82.8	13.6	3.6
	1	5	76.6	17.4	6.0
	1	9	70.8	20.5	8.7
	2	13	78.3	17.1	4.6
	First-Stage Samples				
	1	10A	68.3	20.1	11.6
	2	14A	75.4	19.0	5.6

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TABLE 4

PROTON DISTRIBUTIONS OF WHOLE SAMPLES
HRI CTSL Runs I-12, 13, 14, 15

			Proton Distributions, %						
Run	Condition	Run Period	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
I-12	Hydrogenated Solvent								
	SH	17ABC	14.9	5.3	18.1	9.9	19.4	20.6	11.8
	Pressure-Filter Liquids								
	5	20	21.7	4.7	19.0	9.9	17.1	17.8	9.9
I-13	Pressure-Filter Liquids								
	1	5	9.9	4.4	13.4	8.3	21.2	26.3	16.5
	1	9	12.2	4.7	14.7	8.6	20.5	23.9	15.6
	2	12	13.3	4.8	15.7	9.1	20.0	23.0	14.1
	3	15	14.3	5.0	15.8	9.0	19.5	22.4	14.1
	4	18	16.5	3.9	17.1	8.8	19.9	21.6	12.3
	5	21	16.1	4.8	16.3	9.0	18.9	22.0	12.9
	6	24	18.0	4.9	16.7	9.3	17.8	21.0	12.3
	7	27	21.7	5.0	17.0	9.1	16.7	19.1	11.4
	First-Stage Samples								
	1	6A	8.7	5.2	14.1	8.9	21.0	25.8	16.3
	1	10A	11.3	3.7	16.6	8.9	22.2	23.9	13.3
	2	13A	11.4	4.6	16.3	9.2	20.2	23.8	14.5
	3	16A	13.7	4.0	17.4	9.2	20.8	22.1	12.9
	4	19A	14.4	4.4	17.0	9.2	20.0	21.9	13.1
	5	22A	11.7	6.2	14.5	9.4	19.1	23.5	15.5
	6	25A	14.9	5.3	16.8	9.6	19.0	21.6	12.9
	7	27C	15.5	6.0	16.0	9.7	18.3	20.8	13.6
	Filter-Cake Extract								
			11.6	5.5	13.1	8.4	19.5	25.4	16.5
	Start-Up Oil (#4646)								
			2.5	5.0	10.5	7.9	24.5	30.2	19.4
I-14	Pressure-Filter Liquids								
	1	7	19.2	5.6	18.0	10.1	17.5	18.7	11.0
	2	10	20.2	5.0	18.5	9.8	17.7	18.3	10.5
	3	14	28.3	6.1	17.4	9.9	14.1	14.8	9.3
	First-Stage Samples								
	1	8A	16.5	5.8	18.4	10.3	17.8	19.5	11.7
	2	11A	16.8	5.3	17.8	9.9	18.6	19.7	12.0
	3	15A	21.2	5.3	19.0	10.0	17.1	17.2	10.1
I-15	Pressure-Filter Liquids								
	1	2	8.1	4.0	13.4	8.1	22.9	27.5	16.0
	1	5	12.3	4.1	15.2	8.7	20.9	24.4	14.5
	1	9	15.2	4.5	16.6	8.9	19.4	22.3	13.1
	2	13	23.9	4.9	17.3	8.8	16.0	17.9	11.1
	First-Stage Samples								
	1	10A	12.9	4.7	16.6	9.4	20.0	22.5	13.8
	2	14A	14.4	4.0	13.5	8.3	16.2	27.0	16.7

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

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TABLE 5

PROTON DISTRIBUTIONS OF 850°F⁻ DISTILLATES
HRI CTSL Runs I-12, 13, 14, 15

			Proton Distributions, %						
Run	Condition	Run Period	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
I-12	Hydrogenated Solvent								
	SH	17ABC	9.9	7.2	17.5	9.8	21.0	23.0	11.6
	Pressure-Filter Liquid								
	5	20	13.7	7.4	16.8	10.5	18.6	21.7	11.4
I-13	Pressure-Filter Liquids								
	1	5	6.6	4.9	12.6	8.0	23.3	28.1	16.5
	1	9	7.2	5.7	12.4	8.1	22.3	27.4	17.0
	2	12	7.6	5.4	13.0	8.3	22.1	27.0	16.5
	3	15	8.9	5.7	14.4	8.8	21.7	25.6	14.9
	4	18	9.5	6.1	14.9	8.9	21.7	24.7	14.2
	5	21	9.2	6.2	13.7	8.8	20.7	26.1	15.3
	6	24	13.1	5.5	16.1	9.0	19.8	24.1	12.5
	7	27	15.3	6.5	15.6	9.1	18.2	22.7	12.7
	First-Stage Samples								
	1	6A	5.7	5.3	13.2	8.3	23.0	28.1	16.4
	1	10A	6.4	5.4	13.6	8.4	22.8	27.0	16.3
	2	13A	6.3	5.3	13.0	8.8	21.6	28.6	16.3
	3	16A	7.3	6.2	14.1	9.0	22.2	25.8	15.4
	4	19A	8.2	5.8	14.6	9.3	22.0	25.5	14.6
	5	22A	7.4	5.9	13.9	9.2	21.7	26.8	15.1
	6	25A	9.6	6.1	15.2	9.3	21.1	24.9	13.8
	7	27C	10.2	6.7	15.1	9.6	20.5	24.1	13.8
	Filter-Cake Extract								
		8.1	5.3	11.4	7.6	20.6	28.9	18.1	
I-14	Pressure-Filter Liquids								
	1	7	11.9	7.6	15.8	10.7	18.8	22.6	12.7
	2	10	13.1	7.1	17.0	10.1	19.1	21.7	11.8
	3	14	20.5	8.1	16.9	10.7	15.7	18.0	9.9
	First-Stage Samples								
	1	8A	9.6	7.3	15.2	10.3	20.1	23.7	13.8
	2	11A	10.3	7.1	15.9	10.3	20.2	23.3	12.8
	3	15A	13.7	7.8	16.7	10.4	18.6	20.7	12.1
I-15	Pressure-Filter Liquids								
	1	2	5.2	4.6	11.9	7.8	23.2	29.7	17.6
	1	5	7.6	5.3	13.3	8.4	21.8	27.4	16.1
	1	9	9.1	5.4	14.5	8.7	21.6	26.0	14.8
	2	13	17.2	5.4	17.2	9.0	18.4	21.8	11.1
	First-Stage Samples								
	1	10A	6.9	6.1	12.9	8.8	21.4	26.9	17.0
	2	14A	8.0	4.5	11.5	7.8	17.4	32.5	18.2

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TABLE 6

PROTON DISTRIBUTIONS OF 850°F$^+$ RESIDS
HRI CTSL Runs I-12, 13, 14, 15

			Proton Distributions, %						
Run	Condition	Run Period	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
I-12	Hydrogenated Solvent								
	SH	17ABC	23.2	4.3	22.2	9.5	17.5	15.2	8.1
	Pressure-Filter Liquid								
	5	20	29.0	4.6	21.3	9.9	15.0	13.2	7.1
I-13	Pressure-Filter Liquids								
	1	5	17.1	3.2	18.0	8.3	20.1	21.3	12.1
	1	9	19.9	2.8	19.9	9.1	19.8	18.8	9.7
	2	12	21.9	3.2	21.8	9.4	18.3	16.8	8.5
	3	15	23.4	3.8	20.3	9.1	17.5	16.7	9.2
	4	18	24.8	4.0	20.3	9.2	16.9	16.1	8,7
	5	21	24.0	4.9	20.0	9.3	16.6	15.9	9.2
	6	24	28.5	3.3	21.3	9.1	15.9	14.6	7.4
	7	27	32.7	3.6	20.6	8.9	14.5	12.9	6.8
	First-Stage Samples								
	1	6A	14.9	3.6	19.1	9.1	20.7	21.0	11.7
	1	10A	17.3	3.6	20.8	9.4	19.8	18.9	10.2
	2	13A	19.0	3.7	23.2	10.1	17.1	17.8	9.1
	3	16A	20.8	3.7	21.8	9.5	18.6	16.8	8.9
	4	19A	21.0	4.3	20.8	9.4	18.3	16.7	9.4
	5	22A	21.0	3.5	23.0	9.8	18.4	16.2	8.2
	6	25A	22.9	3.9	22.0	9.7	17.4	15.7	8.2
	7	27C	25.5	4.5	21.5	9.5	16.3	14.5	8.3
	Filter-Cake Extract								
			18.9	4.9	16.6	8.5	18.1	20.3	12.7
I-14	Pressure-Filter Liquids								
	1	7	27.5	5.3	21.4	9.8	15.2	13.3	7.4
	2	10	26.9	4.4	20.8	9.7	16.1	14.2	7.8
	3	14	36.2	5.7	19.9	9.4	12.6	10.3	5.8
	First-Stage Samples								
	1	8A	22.7	4.8	23.3	10.3	16.8	14.3	7.8
	2	11A	23.7	4.8	21.0	9.9	16.6	15.2	8.7
	3	15A	28.4	4.8	21.9	9.7	15.4	12.6	7.2
I-15	Pressure-Filter Liquids								
	1	2	14.7	2.7	19.5	9.0	22.1	23.1	8.8
	1	5	19.7	2.9	20.4	9.2	19.6	18.8	9.4
	1	9	22.6	3.3	20.9	9.3	18.1	17.4	8.5
	2	13	32.2	3.0	20.7	8.8	15.3	13.5	6.6
	First-Stage Samples								
	1	10A	18.6	3.9	21.2	9.7	19.2	18.1	9.4
	2	14A	25.4	3.6	20.6	9.2	16.7	16.4	8.1

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

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TABLE 7

PHENOLIC CONTENTS OF DISTILLATES AND THF-SOLUBLE RESIDS
HRI CTSL Runs I-12, 13, 14, 15

Run	Condition	Run Period	Phenolic Concentration, meq/g	
			850°F Distillate	850°F$^+$ Resid
I-12	Hydrogenated Solvent			
	SH	17ABC	0.20	0.65
	Pressure-Filter Liquid			
	5	20	0.45	0.99
I-13	Pressure-Filter Liquids			
	1	5	0.08	0.39
	1	9	0.11	0.57
	2	12	0.19	0.94
	3	15	0.20	0.71
	4	18	0.23	0.73
	5	21	0.32	0.91
	6	24	0.25	0.70
	7	27	0.24	0.63
	First-Stage Samples			
	1	6A	0.19	0.66
	1	10A	0.24	0.84
	2	13A	0.29	1.13
	3	16A	0.29	0.85
	4	19A	0.32	0.88
	5	22A	0.36	1.04
	6	25A	0.35	0.93
	7	27C	0.33	0.90
	Filter-Cake Extract			
			0.13	0.50
	Start-up Oil			
			0.07	----
I-14	Pressure-Filter Liquids			
	1	7	0.70	1.24
	2	10	0.57	0.98
	3	14	0.58	0.91
	First-Stage Samples			
	1	8A	0.61	1.36
	2	11A	0.57	1.13
	3	15A	0.61	1.16
I-15	Pressure-Filter Liquids			
	1	2	0.09	0.50
	1	5	0.17	0.69
	1	9	0.24	0.87
	2	13	0.25	0.57
	First-Stage Samples			
	1	10A	0.34	0.96
	2	14A	0.28	0.81

Peak maxima between 3302 and 3330 cm^{-1} for all distillates and between 3291 and 3303 cm^{-1} for all resids.

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TABLE 8

MICROAUTOCLAVE TESTS WITH WHOLE SAMPLES
HRI CTSL Runs I-12, 13, 14, 15

Run	Condition	Run Period	THF Coal Conversion wt % MAF
I-12	Hydrogenated Solvent		
	SH	17ABC	86.7
	Pressure-Filter Liquid		
	5	20	65.9 (a)
I-13	Pressure-Filter Liquids		
	1	5	80.6
	1	9	83.4
	2	12	85.0
	3	15	81.0
	4	18	79.9
	5	21	79.0
	6	24	78.2
	7	27	75.7
	First-Stage Samples		
	1	6A	84.6
	1	10A	85.8
	2	13A	84.0
	3	16A	83.3
	4	19A	83.5
	5	22A	82.8
	6	25A	80.8
	7	27C	81.3
	Filter Cake Extract		78.9
	Start-up Oil		75.4
I-14	Pressure Filter Liquids		
	1	7	76.2
	2	10	76.9
	3	14	64.5
	First-Stage Samples		
	1	8A	79.9
	2	11A	77.9
	3	15A	74.5
I-15	Pressure Filter Liquids		
	1	2	78.6
	1	5	83.0
	1	9	75.8 (a)
	2	13	71.8
	First-Stage Samples		
	1	10A	84.2
	2	14A	72.8

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

(a) Questionable result, could not be retested.

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TABLE 9

PHENOLIC OH CONCENTRATIONS
Phenolic Material Balance Experiments

Sample Type	Phenolic OH Concentration, meq OH/g Sample		
	V-131B	V-1064	V-1067
Whole*	0.21	0.87	0.20
Distillate*	0.13	1.00	0.14
Distillation Bottoms*	0.37	0.81	0.29
THF-Soluble Resid*	0.36	1.03**	0.40
Oils	0.26	0.71	0.38
Asphaltenes	1.13	1.40	0.96
Preasphaltenes	1.07	1.05	0.80

* Values given are averages of two determinations. Others given are single determinations unless otherwise indicated.

** Average of three determinations.

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TABLE 10

PHENOLIC CONCENTRATION REPRODUCIBILITY
Phenolic Material Balance Experiments

Sample Type	Phenolic Concentration, meq/g							Std. Dev. for Sample Type
	V-131B		V-1064			V-1067		
Trial No.	1	2	1	2	3	1	2	
Whole	0.22	0.20	0.89	0.84	-	0.22	0.17	0.03
Distillate	0.13	0.13	1.00	1.00	-	0.14	0.13	0.01
Distillate Bottoms	0.36	0.38	0.81	0.81	-	0.25	0.33	0.03
THF-Soluble Resid	0.36	0.36	1.15	0.96	0.98	0.40	0.40	0.07

Pooled Standard Deviation = 0.05 meq/g

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TABLE 11

COMPONENT DISTRIBUTIONS OF WHOLE SAMPLES
Phenolic Material Balance Experiments

Component, wt %	V-131B		V-1064		V-1067	
Distillate	56.7		47.8		46.7	
Soluble Resid	41.9	42.8	42.1	51.6	39.9	52.3
IOM	0.5		4.9		5.5	
Ash	0.4		4.6		6.9	
Total	99.5		99.4		99.0	

TABLE 12

SOLUBILITY FRACTIONATION OF THF-SOLUBLE RESID
Phenolic Material Balance Experiments

Component, wt %	V-131B	V-1064	V-1067
Oils	95.1	58.6	82.7
Asphaltenes	3.0	25.1	11.3
Preasphaltenes	1.9	16.3	6.0
LCF wt Recovery	96.5%	109.2%	105.7%

/ls

TABLE 13

PHENOLIC BALANCE DATA FOR DISTILLATION AND PRESSURE FILTRATION PROCEDURES

Phenolic Material Balance Experiments

	Phenolic Concentration, meq/g		
	V-131B	V-1064	V-1067
Whole Sample	0.21	0.87	0.20
Distillation Balance			
Distillate	0.07	0.48	0.07
Distillation Bottoms	0.16	0.42	0.15
Total	0.23	0.90	0.22
Balance	110%	103%	110%
Distillation/Pressure Filtration Balance			
Distillate	0.07	0.48	0.07
Resid*	0.15	0.43	0.16
Total	0.22	0.91	0.23
Balance	105%	105%	115%

* Corrected for IOM and ash, assuming no IOM contribution to phenols.

/ls

TABLE 14

PHENOLIC BALANCE DATA FOR PREPARATIVE LCF PROCEDURE
Phenolic Material Balance Experiments

	Phenolic Concentration, meq/g		
	V-131B	V-1064	V-1067
THF-Soluble Resid	0.36	1.03	0.40
Oils	0.25	0.42	0.32
Asphaltenes	0.03	0.35	0.11
Preasphaltenes	0.02	0.17	0.05
Total	0.30	0.94	0.48
Balance	83%	91%	120%

/ls

TABLE 15

ANALYSIS OF PENN STATE MICROAUTOCLAVE TSL SAMPLES
UNCORRECTED

Sample I.D.	Elemental, wt %					Phenolic Concentration, meq/g	Contaminants, wt %	
	C	H	N	S	O (Diff)		THF	BHT
650°-850°F Dist.Solvent	82.02*	9.62	0.28	0.06	8.02*	0.66	-	-
850°F$^+$ Resid Solvent	90.63	7.34	0.76	0.15	1.12	0.66	-	-
809-87-B-2 (Solvent Oils)	69.90*	5.48	3.77*	NES	20.85*	1.50	1.48	7.79
-3 (Solvent Asph.)	88.37	10.52	0.41	0.15	0.55	0.42	-	-
809-60-C-2	84.42	5.84	1.49	0.40	7.85	2.03	5.57	-
-3	89.60	9.42	0.29	0.10	0.59	0.52	-	4.84
809-61-D-2	84.40	5.97	1.48	0.40	7.75	2.96	5.75	-
-3	89.12	9.55	0.31	0.09	0.93	0.51	-	3.68
809-64-C-2	81.81*	5.93	1.59	0.42	10.25*	2.34	4.38	2.23
-3	88.30	10.44	0.28	0.07	0.91	0.59	-	3.73
809-65-D-2	83.43	6.09	1.68	0.39	0.41	2.54	3.12	2.74
-3	88.01	10.66	0.31	0.06	0.96	0.59	-	3.71
809-68-C-2	80.46*	6.31	1.43	0.56	11.24*	3.22	-	6.25
-3	82.06*	9.92	0.32	0.08	7.62*	0.69	-	4.82
809-69-D-2	79.17*	6.27	1.57	0.40	12.59*	3.05	0.73	5.35
-3	87.70	10.57	0.33	0.08	1.32	0.65	-	4.17
809-72-C-2	82.02*	5.97	1.19	0.39	10.43*	2.36	2.58	2.96
-3	NES	NES	NES	NES	NES	NES	NES	NES
809-73-D-2	82.83*	6.03	1.28	0.22	9.64*	2.25	-	4.20
-3	89.30	9.55	0.70	0.10	0.35	0.57	-	3.94
809-80-C-2	84.48	5.81	1.14	0.32	8.25	1.62	3.71	3.14
-3	91.43*	8.33	0.73	0.12	0.61*	0.52	-	7.79
809-81-D-2	84.60	6.04	1.18	0.13	8.05	1.96	5.06	2.27
-3	88.23	8.39	0.41	0.15	2.82	0.58	-	5.15
809-84-C-2	85.78*	6.10	1.29	0.31	6.52*	1.50	4.61	2.57
-3	91.48*	8.05	0.79	0.15	-0.47*	0.77	5.00	0.59
809-85-D-2	84.93*	5.80	1.54	0.27	7.46*	2.60	5.48	2.76
-3	90.30*	8.14	0.68	0.18	0.70*	0.80	2.78	3.36

NES - Not enough sample

* - Result appears to be in error

/ls

TABLE 16

ANALYSIS OF PENN STATE MICROAUTOCLAVE TSL SAMPLES CORRECTED FOR THF AND BHT CONTAMINATION

	Proton Distribution							Elemental, wt %					Phenolic
Sample I.D.	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	C	H	N	S	O (Diff.)	Concen., meq/g
850°F$^-$ Resid Solvent	30.3	3.4	18.1	8.6	15.0	17.5	7.1	90.63	7.34	0.76	0.15	1.12	0.66
650°-850°F Dist. Solvent	10.3	5.4	11.8	8.4	14.8	34.9	14.4	82.02*	9.62	0.28	0.06	8.02*	0.66
809-87-B-2 (Solvent oils)	35.4	6.6	17.4	11.2	11.6	11.2	6.6	76.96*	6.03	4.16*	NES	12.85*	1.26
-3 (Solvent Asph.)	10.3	4.0	12.4	10.4	15.4	33.9	13.6	88.37	10.52	0.41	0.15	0.55	0.42
809-60-C-2	29.4	7.4	23.0	11.2	13.1	10.6	5.4	89.36	6.18	1.58	0.42	2.46	2.15
-3	16.5	4.7	16.0	8.5	15.4	27.8	11.1	90.03	9.34	0.25	0.05	0.33	0.32
809-61-D-2	26.6	8.7	24.4	11.6	13.9	10.8	4.0	89.51	6.33	1.57	0.42	2.17	3.14
-3	15.5	4.6	15.9	8.2	15.6	28.1	12.1	89.42	9.50	0.28	0.06	0.74	0.36
809-64-C-2	26.4	8.0	23.0	11.1	12.8	12.6	6.2	82.54*	6.34	1.70	0.45	8.97*	2.40
-3	11.3	4.8	14.4	8.7	15.4	32.6	12.9	88.58	10.42	0.25	0.03	0.72	0.44
809-65-D-2	26.5	7.2	24.6	11.7	12.9	11.2	6.0	88.58	6.46	1.78	0.41	2.77	2.57
-3	10.4	4.6	13.7	8.6	15.6	33.1	14.0	88.27	10.65	0.28	0.02	0.78	0.44
809-68-C-2	24.7	7.1	20.9	11.0	12.6	16.8	6.8	80.41*	6.00	1.46	0.53	11.60*	3.13
-3	10.6	5.5	12.8	8.6	15.5	33.0	14.0	82.10*	9.87	0.29	0.03	7.71*	0.49
809-69-D-2	20.5	7.5	23.4	11.7	14.6	15.2	7.1	84.24*	6.67	1.67	0.43	6.99*	2.99
-3	9.9	5.5	12.7	8.7	15.3	33.8	14.1	87.98	10.56	0.30	0.04	1.12	0.48
809-72-C-2	27.9	9.8	20.1	9.5	12.0	14.1	6.6	86.79*	6.31	1.26	0.41	5.23*	2.36
-3	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES
809-73-D-2	26.3	6.6	22.5	10.5	11.5	15.7	7.0	82.90*	5.82	1.29	0.19	9.80*	2.15
-3	15.2	5.4	14.8	8.7	15.0	28.9	11.9	89.63	9.49	0.69	0.06	0.13	0.41
809-80-C-2	32.0	10.2	19.4	9.3	11.3	12.2	5.6	90.64	6.23	1.22	0.34	1.57	1.59
-3	25.4	5.6	16.3	8.2	14.2	20.3	10.1	92.30*	8.11	0.71	0.05	-1.17*	0.18
809-81-D-2	29.7	6.1	21.4	10.0	13.6	13.2	6.0	91.24	6.51	1.27	0.14	0.84	2.00
-3	22.7	6.3	16.9	8.4	14.0	20.6	11.0	88.61	8.25	0.38	0.10	2.66	0.36
809-84-C-2	30.9	10.4	19.0	9.1	11.6	12.9	6.2	92.36*	6.56	1.39	0.33	-0.64*	1.49
-3	24.0	6.9	15.0	8.9	13.2	22.5	9.6	96.86*	8.52	0.84	0.16	-6.38*	0.79
809-85-D-2	29.7	8.2	23.1	9.9	12.3	10.9	6.0	92.49*	6.31	1.68	0.29	-2.07*	2.70
-3	22.1	6.8	17.8	8.7	13.0	22.1	9.5	96.16*	8.67	0.72	0.19	-5.74*	0.69

NES - Not enough sample

* - Result appears to be in error

/ls

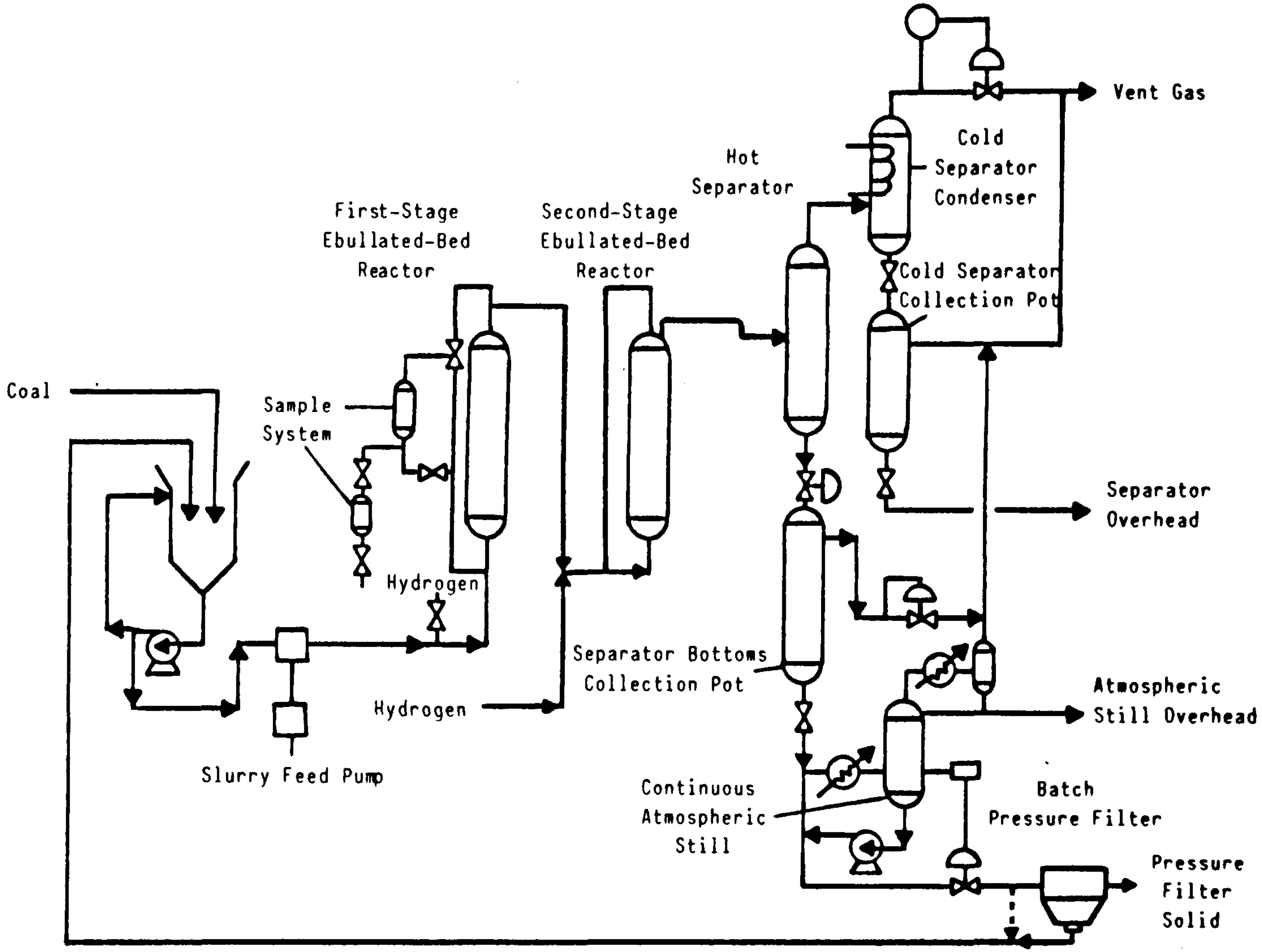

Figure 1. HRI Ebullated-Bed Bench Unit 227. Source: Reference 1.

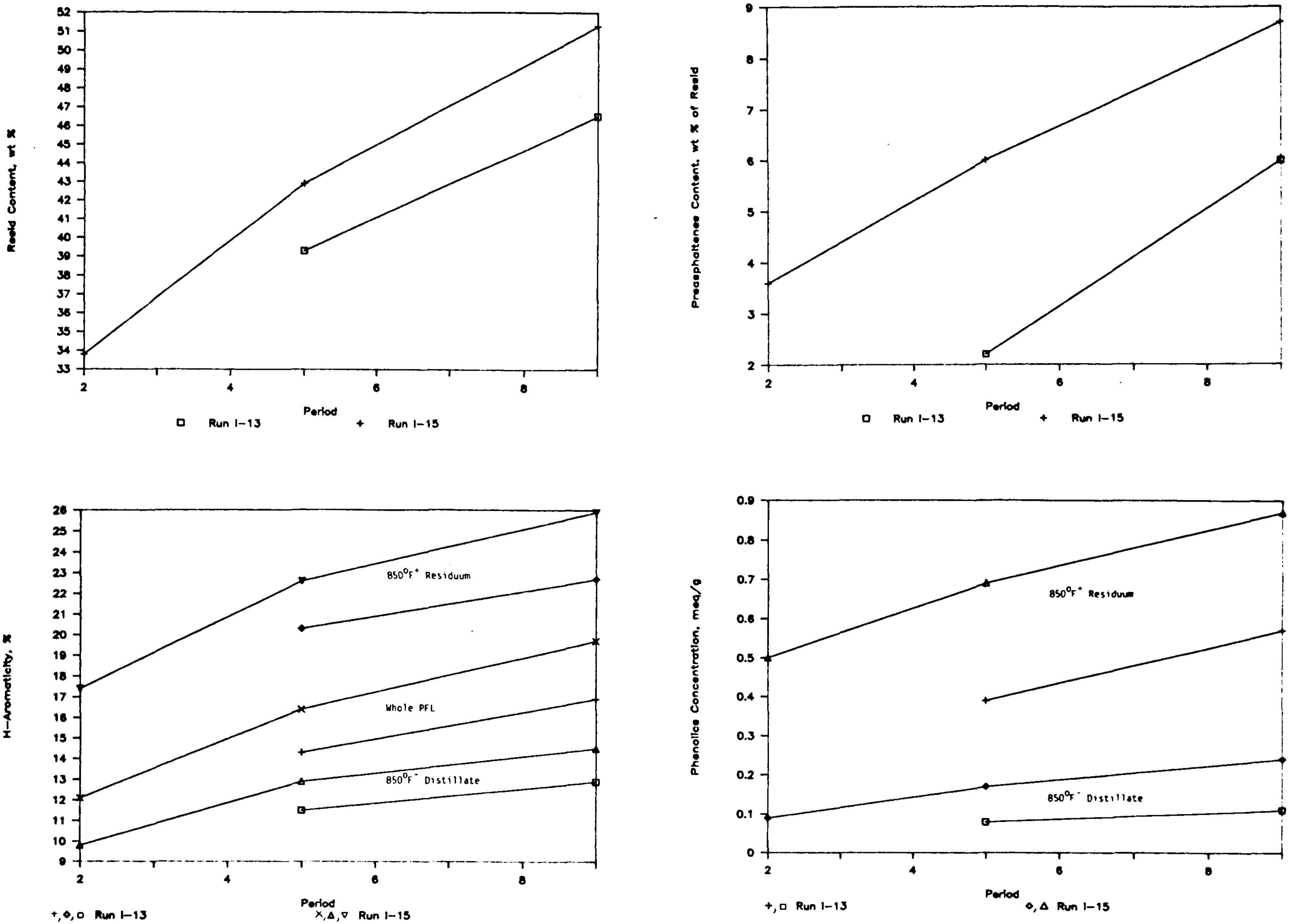

Figure 2. PFL Properties vs Run Period - HRI CTSL Runs I-13 and I-15.

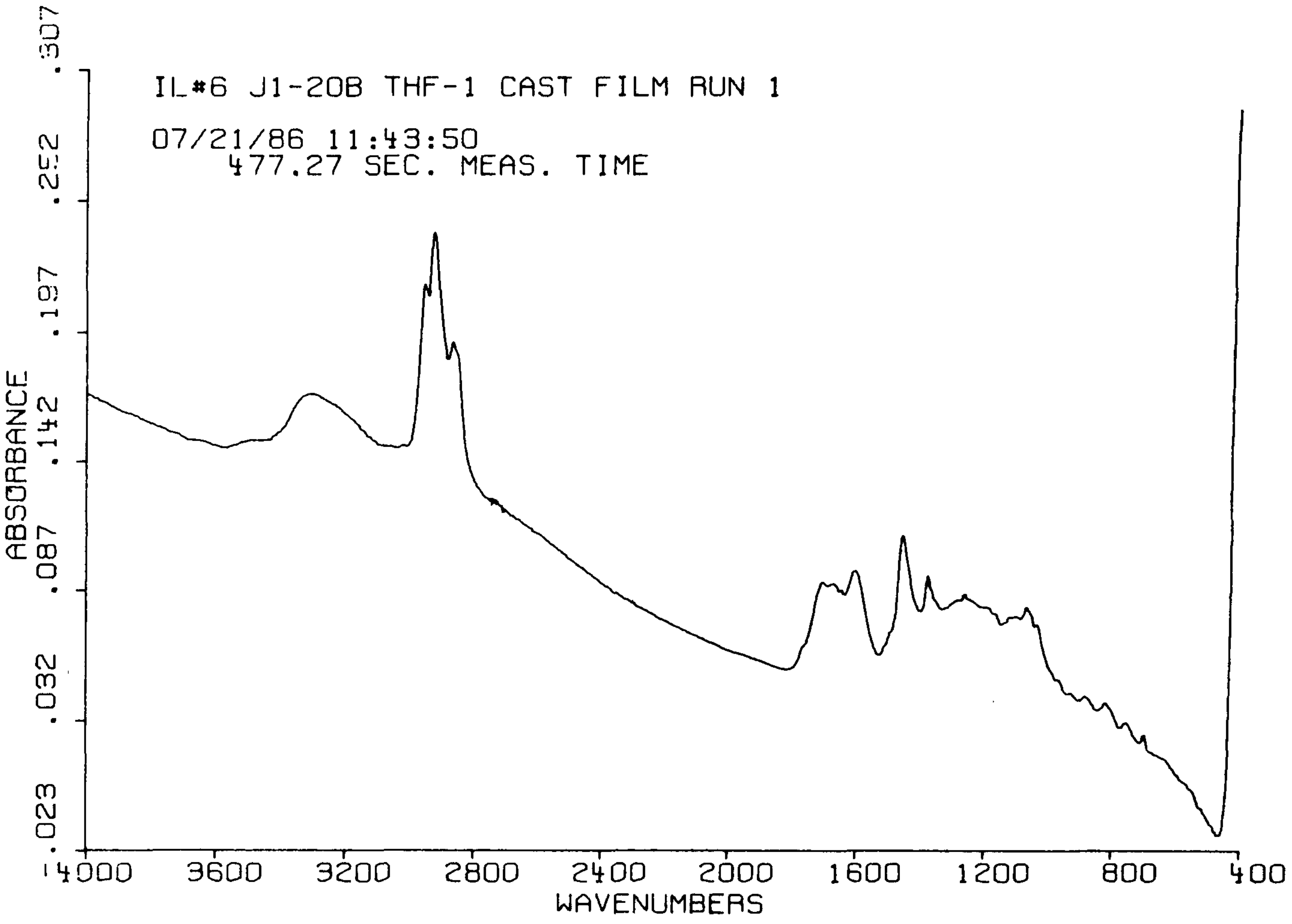

Figure 3. FTIR Spectrum of Purdue Sample #J1-20B-THF-1.

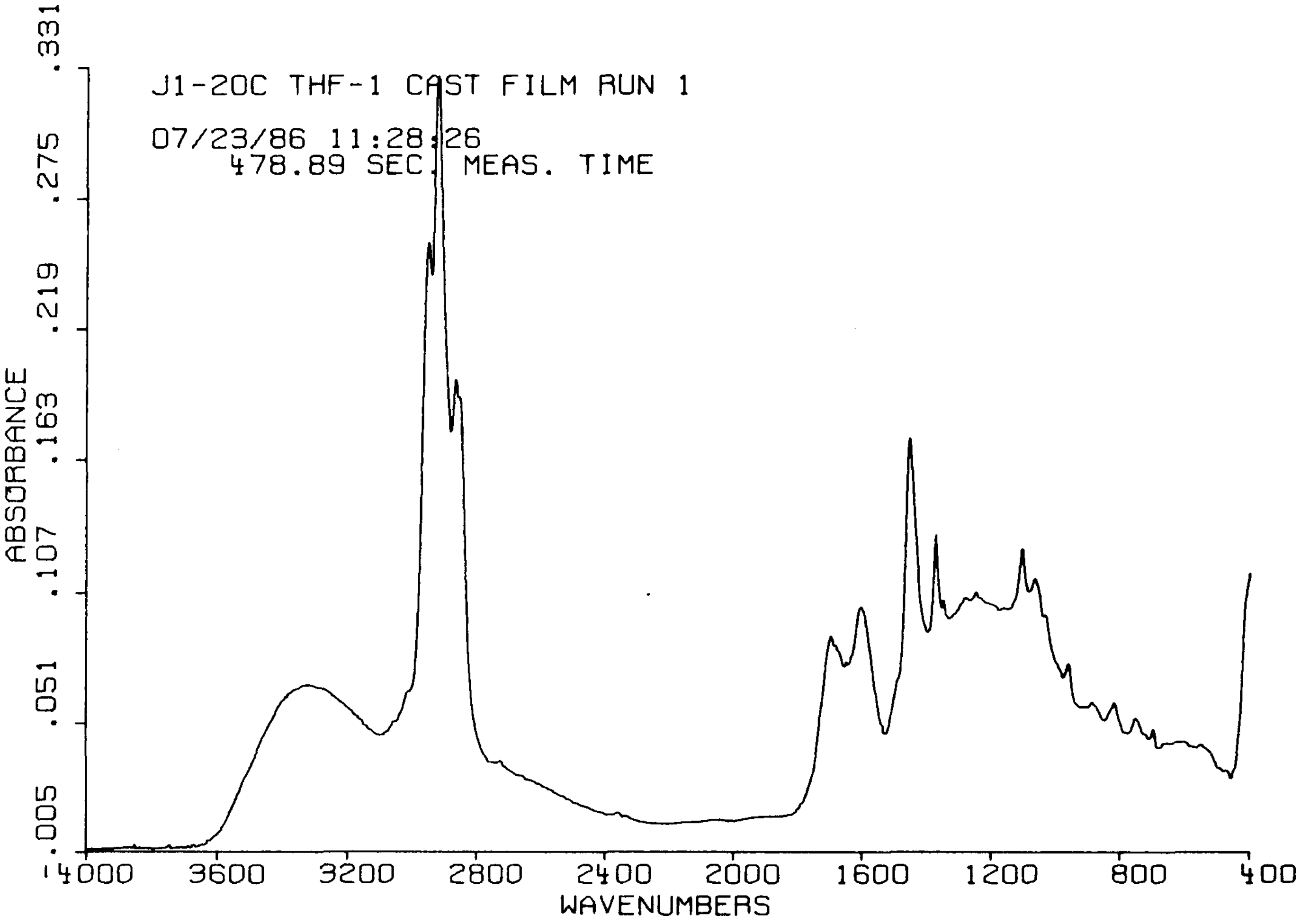

Figure 4. FTIR Spectrum of Purdue Sample J1-20C-THF-1.

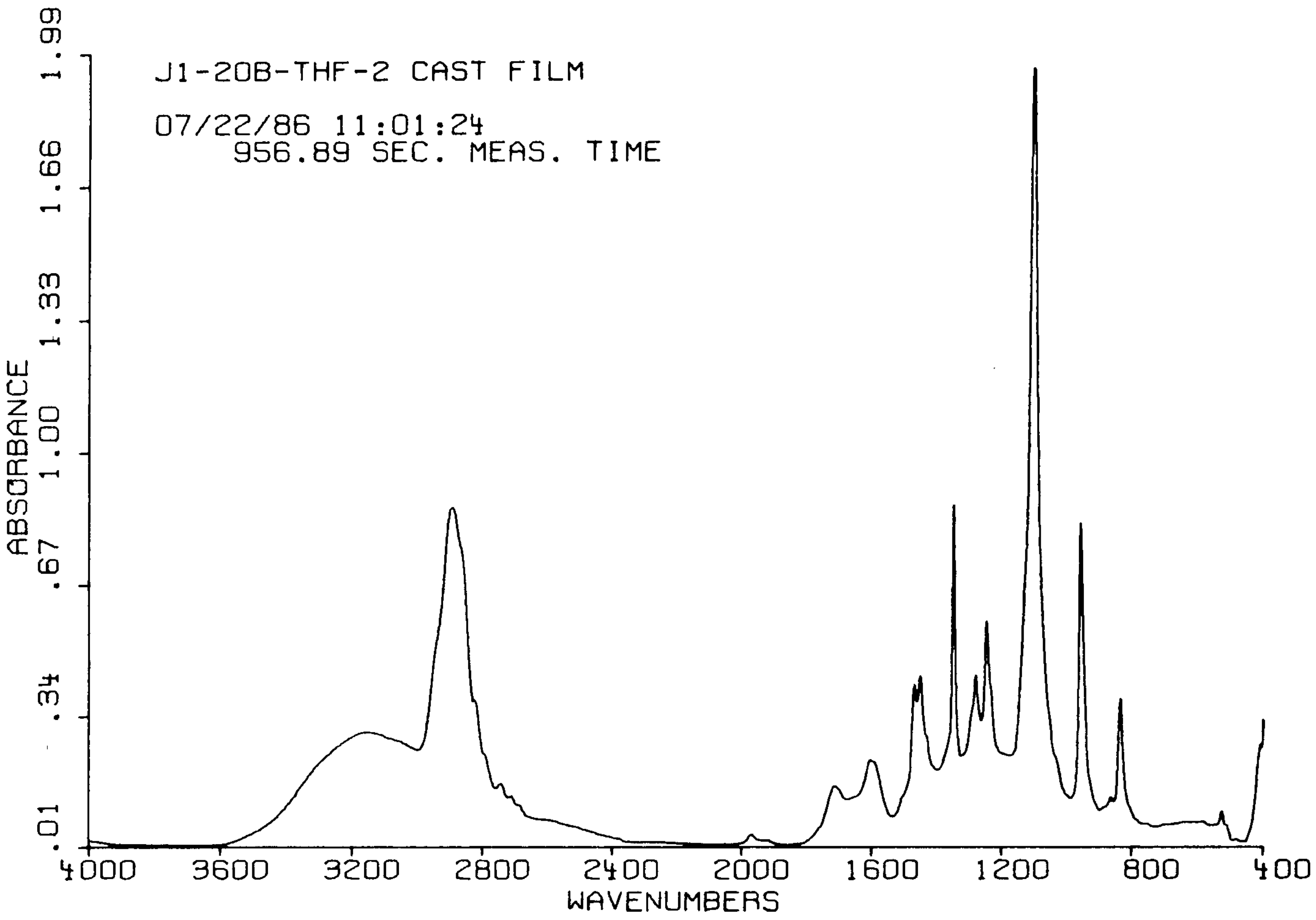

Figure 5. FTIR Spectrum of Purdue Sample J1-20B-THF-2.

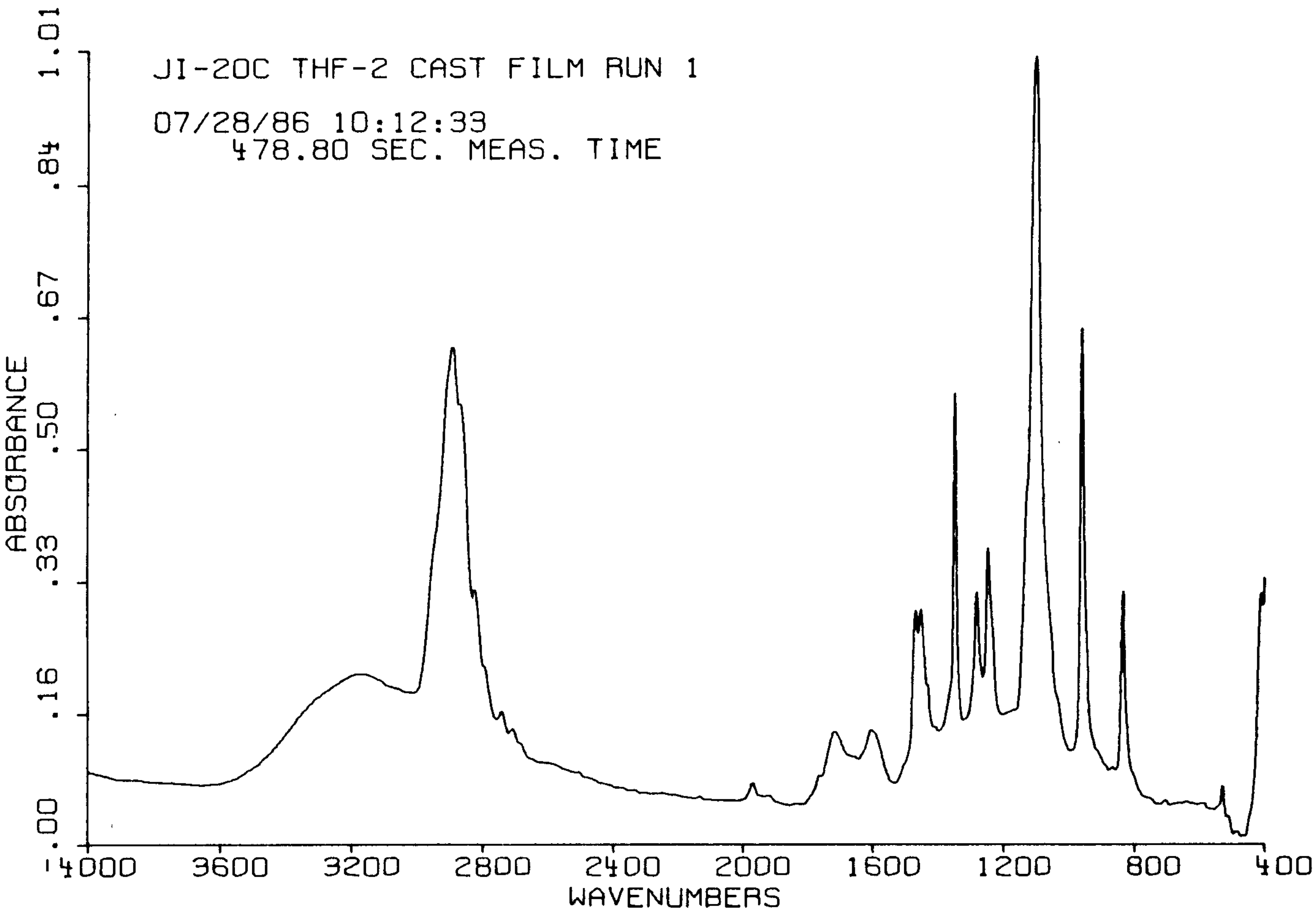

Figure 6. FTIR Spectrum of Purdue Sample J1-20B-THF-2.