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A Characterization and Evaluation of Coal Liquefaction Process Streams

Annual Technical Progress Report
July 1 through September 30, 1998

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ABSTRACT

This is the first Annual Technical Report of activities under DOE Contract No. DE-AC22-94PC93054. Activities from the first three quarters of the fiscal 1998 year were reported previously as Quarterly Technical Progress Reports (DOE/PC93054-57, DOE/PC93054-61, and DOE/PC93054-66). Activities for the period July 1 through September 30, 1998, are reported here.

This report describes CONSOL's characterization of process-derived samples obtained from HTI Run PB-08. These samples were derived from operations with Black Thunder Mine Wyoming subbituminous coal, simulated mixed waste plastics, and pyrolysis oils derived from waste plastics and waste tires. Comparison of characteristics among the PB-08 samples was made to ascertain the effects of feed composition changes. A comparison also was made to samples from a previous test (Run PB-06) made in the same processing unit, with Black Thunder Mine coal, and in one run condition with co-fed mixed plastics.

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Section 1

EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM HTI RUN PB-08

In support of the Hydrocarbon Technologies Inc. (HTI) bench unit program, CONSOL analyzed samples from the five run conditions of HTI's Run PB-08. The five-condition run had three objectives, which were to study the processing of oils derived from mild pyrolysis of scrap tires, waste plastics, and waste lube oils; to investigate the feasibility of integrating waste plastic and rubber pyrolysis with direct coal liquefaction; and to evaluate the economics of such a process.

A clear distinction can be made in the characteristics of process samples derived from operations with different feed compositions. Pyrolysis oils derived from plastics and tires result in better overall distillate yields than in coal-only or coal and mixed plastics conditions. The analyses show that the distillate portions of the process-derived samples from co-processing of pyrolysis oils with Black Thunder Mine coal are lower in phenolic -OH contents and have a lower ash content, but higher insoluble organic matter (IOM) content than those derived from coal co-fed with mixed plastics. The distillate portion of the pressure filter liquids (PFL) and the O-6 Bottoms samples from conditions which fed pyrolysis oils have much poorer solvent quality than either coal-only or coal-plastics conditions. The introduction of a coal-derived carrier oil in the waste plastics/rubber tire pyrolysis operation resulted in a material with properties intermediate between those of coal only derivation and those derived from coal co-fed with waste plastics/rubber tire pyrolysis oil manufactured with waste lube oil as a carrier.

A comparison was made of sample characteristics from Run PB-08 and those of a previous run (PB-06) for coal alone, coal and mixed plastics, and coal and a pyrolysis oil derived from mixed plastics conditions. Coal-alone conditions were comparable. Limited data were available from Run PB-06 for coal and mixed plastics conditions. However, the component distribution for the first-stage slurry for Run PB-06 has over twice as much distillate and only 2/3 as much IOM as the corresponding Run PB-08 sample. In the coal and pyrolysis oil conditions compared, the whole samples from Run PB-06 are more aromatic than those obtained from Run PB-08. The pyrolysis oils produced at HTI and used for Condition 4 of Run PB-08 do not appear to have as large a component of the undecomposed plastics. This may be attributable to the pyrolysis oil being derived partially from waste tires and lube oil, rather than 100% plastics as was the oil used in Run PB-06.

FUTURE WORK

Analyses will be completed for HTI Runs PB-02 and PB-03. A compilation of all data on jet fuel cuts of direct liquefaction net product oils acquired over this and previous DOE contracts will be completed. These data will be released as a Topical Report.

Section 2

INTRODUCTION

This is the Annual Progress Report for activities under DOE Contract No. DE-AC22-94PC93054. This report covers the period July 1 through September 30, 1998. Activities for the preceding nine months of the 1998 fiscal year are available in References 1-3.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project builds on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods are obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. The data obtained from this study are used to guide process development and to develop an improved data base on coal and coal liquids properties. A sample bank, established and maintained for use in this project, is available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) was examined. From the literature and experimental data, a kinetic model of resid conversion was constructed and is being refined. Such a model will provide insights to improve process performance and the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS PERIOD

- Fifty-nine samples from five run conditions of HTI Run PB-08 were received (Table 2). Proton NMR spectroscopy, phenolic -OH determination by Fourier transform infrared spectroscopy, and vacuum distillation were employed. Component distributions were determined, hot decalin extractions were performed on selected samples, and solvent quality tests were completed for appropriate samples. A discussion of the results is presented in the Results and Discussion Section of this report.

- CONSOL completed a second generation of the resid reactivity models originally constructed under subcontract by the University of Delaware.

- A journal article authored by S. Wang, H. Huang, K. Wang, M.T. Klein, and W. H. Calkins (University of Delaware) entitled "Kinetics of Coal Liquefaction Distillation Resid Conversion" was published in Energy & Fuels. A copy of this paper is appended to this report (Appendix I).

ACTIVITIES IN PROGRESS

- Characterization work on samples from HTI PB-02 and PB-03 continues.

- A draft of the topical report fulfilling the Task 2.1 obligation was issued to DOE for review.

- Compilation of coal-derived jet fuel properties is continuing. A Topical Report describing the data is being drafted.

- Samples from the NEDO pilot plant in Kashima, Japan continue to be sought.

- The computer code for the improved Resid Reactivity model will be submitted to the Department of Energy/FETC.

- A summary report describing the CONSOL improvements made to the University of Delaware Resid Reactivity computer model is being drafted.

Section 3

RESULTS AND DISCUSSION

INTRODUCTION AND BACKGROUND

HTI Bench Run PB-08 (also known as Run 227-105) was designed to study the processing of oils derived from mild pyrolysis of scrap tires, waste plastics, and waste lube oils; to investigate the feasibility of integrating waste plastic and rubber tire pyrolysis with direct coal liquefaction; and to evaluate the economics of such processes. Run PB-08 was made in HTI's bench unit 227 configured with two equal-volume back-mixed reactors with internal recirculation (Figure 1). A dispersed catalyst, phosphorous-promoted Fe/Mo GelCat^{TM}, was used in both reactors. A water-soluble promoter was added to the iron-based GelCat^{TM} catalyst to improve dispersion of the metals in the feed blend.[4] An interstage vapor/liquid separator was employed. A short residence time coiled preheater was used to raise the feed slurry to 140 °C below the first-stage reactor temperature prior to introduction to the reactor. The in-line fixed-bed hydrotreater packed with Criterion C-411 catalyst was operational for all five operating conditions. In addition to the overhead from the second stage separator, the first stage separator overhead liquid also was fed to the hydrotreater. The coal feed was Black Thunder Mine Wyoming subbituminous coal procured by HTI originally for Run POC-2.

Process variables, including reactor temperatures (Reactor 1: 435 °C/Reactor 2: 449 °C), space velocity, and catalyst loading were held constant throughout the five-condition test. Different co-feeds with the Black Thunder Mine coal were introduced for each run condition (Table 1). Condition 1 was made in a coal-only mode. In Condition 2, 70 wt % coal was co-fed with a mixture of high density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS) (44, 28, and 28%, respectively) comprising the remaining 30 wt %. In Condition 3, the 343 °C$^+$ fraction of a pyrolysis oil derived from scrap tires and waste motor oil was blended with coal in a 30:70 (oil:coal) wt % ratio. A 343 °C$^+$ fraction of a pyrolysis oil derived from a 50:50 mixture of rubber tires and plastics (a waste lube oil was used as a carrier oil) and Black Thunder Mine coal were co-fed in Condition 4. The oil:coal ratio was 30:70 wt %. Co-fed with the coal in Condition 5 was a 343 °C$^+$ fraction of a pyrolysis oil derived from a 50:50 mixture of rubber tires and coal-derived oil. In this Condition, the oil had been produced with a coal-derived carrier oil (the 524 °C⁻ fraction of the pressure filter liquid (PFL)). The oil:coal ratio was 30:70 wt %. The three pyrolysis oils were produced off-line.[4]

In support of HTI Run PB-08, CONSOL received 59 samples for analyses from five periods representing the five run conditions (Table 2). Five of the samples were feed coals. These were reserved in the event their analysis was warranted because of unusual findings from the analysis of the process samples. Ten of the samples were the aqueous layer from the separator vessels and four samples were obtained from the first-stage knock-out vessel. These also were reserved for analyses if required. No analyses of the feed coal, the SOH water samples, or the knock-out samples were performed.

COMPARISON OF SAMPLE ANALYSES FOR PB-08 CONDITIONS

ALL CONDITIONS

Process performance for Conditions 1-5 is provided in Table 3. The in-line hydrotreater was operating through all conditions in PB-08. This resulted in the second-stage SOH product oils having undetectably low levels of phenolic -OH (Table 4) and low levels (1.6-5.2%) of hydrogen aromaticity (Table 5). In comparison, the analyses of the first-stage SOH samples, obtained prior to hydrotreatment, have 1.07-1.72 meq/g phenolic -OH and 9.8-19.9% hydrogen aromaticity.

COAL-ONLY AND COAL AND PLASTICS CONDITIONS

A comparison between Conditions 1 and 2 demonstrates the effects of the addition of mixed plastics on direct coal liquefaction. One obvious consequence is that the feed slurry, the pressure filter solids (PFS), and the pressure filter liquids (PFL) from Condition 2 contain entrained plastics (Table 11).

Other effects are evident in comparison of samples from different plant locations. The component distribution of the first-stage slurry (Table 6) shows that it has a greater distillate content and much less IOM for the coal-only period. The O-6 bottoms distillate contents are equivalent. However, the solvent quality of the O-6 bottoms is better for the Condition 1, coal-only period (Table 7). The ash contents of the O-6 bottoms and first-stage slurry samples are unexpectedly high for Condition 2 sample (Table 6). After filtration, the pressure filter liquids distillate content is greater for the plastics plus coal condition and the ash content is significantly lower (0.1 vs. 8.4 wt %). HTI indicated there were filtration problems in Period 5 of Condition 1.[1] This is likely the reason for a high ash content in the PFL. The aromatic proton content of the pyridine-soluble portion of the feed slurry and first-stage (also called "interstage") slurry is significantly lower for the coal-only period (26.2 vs. 30.4%, and 28.4 vs. 32.6%, respectively, Table 5). This is reversed in the O-6 bottoms, PFS, and PFL samples. This may be a result of analyzing the pyridine solubles, because the high density polyethylene (HDPE) and polypropylene (PP) in the sample may not dissolve in the pyridine solution as well as does the polystyrene.

All process streams, with the exception of the first-stage SOH sample from Condition 2, have phenolic -OH contents within 0.1 meq/g of each other for Conditions 1 and 2, with no consistent bias evident for samples of either condition (Table 4).

The ash contents of the first-stage slurry, O-6 bottoms, and pressure filter solids are greater for Condition 2 samples than for Condition 1 samples, even though only 70% of the feed is ash-containing coal. It may be possible that the plastics co-fed with the coal contain ash. Plastics samples were not obtained for analysis. It is recommended that the ash content of the plastics be determined.

COAL-ONLY AND COAL AND PYROLYSIS OIL CONDITIONS

The addition of pyrolysis oils which are 86 to 89 % distillate (Table 6) in Conditions 3, 4, and 5 directly affects all process streams in the same way, they all contain more distillate than samples from the coal-only Condition 1. A comparison of PFS samples for the coal only and pyrolysis oil-fed conditions shows the ash contents are 23-25% for the coal plus pyrolysis oil conditions as compared to 26% for the coal only condition, but the IOM is 9-14% (abs.) higher for the conditions in which pyrolysis oils were co-fed. The plastics content of the Condition 3 sample (coal co-fed with the 343 $^\circ C^+$ fraction of a pyrolysis oil derived from scrap tires and waste motor oil) is much greater than the plastics content of the other two conditions which co-fed a pyrolysis oil (Table 11).

The aromaticity of the pyrolysis oils is low (Table 5). Consequently, the feed slurry for the coal only condition (1) is much more aromatic than that of the coal plus pyrolysis oil conditions (3, 4, and 5) which are a 30:70 mixture of oil and coal. The difference in aromaticity of the O-6 bottoms and the PFLs is more apparent in the distillate portions of the samples (Table 8). The distillate portion of these samples from Condition 1 have significantly better solvent quality than the distillates of samples obtained from Conditions 3, 4, and 5 (Table 7).

The phenolic -OH contents of the feed slurries for Conditions 3 and 5 were similar to that of the Condition 1 slurry. However, the distillates of the first-stage slurry, the O-6 Bottoms, PFLs, and the first-stage SOH oil all contain less phenolic -OH than the corresponding sample from Condition 1.

COAL AND PYROLYSIS OIL CONDITIONS

Total conversion for Conditions 3 through 5 varied between 92.5 and 94.1% (Table 3). The resid conversion also was virtually unaffected by the type of pyrolysis oil. C_4-524 °C distillate yield may be a little better for Condition 4 at 69.2% vs. 66.7 and 65.8%. This is reflected in the higher distillate content of the PFL for Condition 4 (Table 6). The solvent quality of the whole O-6 bottoms samples (Table 7) for all three conditions is about the same.

The IOM contents of the first-stage slurry oil, O-6 bottoms, PFL, and PFS samples from Condition 3 are greater than those from Conditions 4 and 5 (Table 6). The plastics content of the Condition 3 whole feed slurry and pressure filter solids and the pressure filter liquid resid samples (Table 11) also are greater.

The introduction of a coal-derived carrier oil to the pyrolysis unit resulted in an oil (L-932) with a higher aromatic hydrogen content than the waste tire (L-931) and the waste tire and plastics (L-933) derived oils generated with a waste lube carrier oil (Table 5). The use of this oil in Condition 5 resulted in essentially the same total conversion, resid conversion, and distillate yield (Table 3), but the selectivity for C_1-C_3 gases was much higher and, consequently, the hydrogen efficiency was lower. Its use in Condition 5 resulted in all but the first-stage slurry samples having a higher aromatic hydrogen content than the process samples from Conditions 3 and 4. This resulted in improved solvent quality of the distillates of both the O-6 bottoms sample and the PFL sample, likely due to the better solubilizing properties of the aromatics (Table 7). The phenolic -OH content of all Condition 5 whole and distillate samples is greater than for the corresponding samples from Conditions 3 or 4. This likely reflects a contribution from the coal-derived carrier oil.

COMPARISON OF RUN PB-08 AND RUN PB-06

COMPARISON OF COAL-ONLY CONDITIONS

Comparison of several of the Run PB-08 conditions can be made with Run PB-06, which was completed in 1997.[1] Condition 1 of Run PB-08 and Condition 5 of Run PB-06 were operated with Black Thunder Mine subbituminous coal. Iron/molybdenum/phosphorous-promoted GelCat^{TM} catalyst was used in both runs and, in both run conditions, the in-line hydrotreater was operated. Recycle/solvent ratio was 1.5 in Run PB-06 Condition 5 and 1.2 for Condition 1 of Run PB-08. Process performance for Run PB-06 Condition 5 and Run PB-08 Condition 1 are given in Table 3. Space velocity was slightly higher for Run PB-08 Condition 1 than Run PB-06 Condition 5 (640 vs. 626 $kg/h/m^3$). However, yields and process performance are essentially the same with coal conversion for both runs at 94 wt % MAF feed. 524 $°C^+$ resid conversion was 88 wt % (Run PB-06) and 84 wt % (Run PB-08) and C_4-524°C yield was 60 and 63 wt % MAF feed for Runs PB-08 and PB-06, respectively. From this comparison, the operation of the 227 unit in Runs PB-06 and PB-08 were considered by HTI to be comparable[4.] This continuity in operation allows for comparisons of other conditions of the two runs in which the feeds included materials other than just coal (see below).

COMPARISON OF CONDITIONS WITH COAL AND PLASTICS CO-FEEDS

Using the limited data available, a comparison can be made between Run PB-08 Condition 2 and Run PB-06 Condition 2. Run PB-08 Condition 2 was operated with Black Thunder Mine coal and a mixture of three plastics, (high density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS)) in a 70:30 (coal:plastics) ratio. The ratio of HDPE/PP/PS was 44/28/28 wt %. The recycle ratio was 1.2 kg/kg MF feed. In Run PB-06 Condition 2, in addition to these three plastics, polyvinyl chloride also was incorporated in the plastics mixture. The ratio of HDPE/PP/PS/PVC in Run PB-06 was 40/30/25/5 wt %, the ratio of coal to plastics mixture was 67:33, the recycle ratio was 1.5 kg/kg MF feed. Phosphorous-promoted iron-based GelCat™ was not used in Run PB-06 condition 2.

Process performance for Run PB-08 Condition 2 and Run PB-06 Condition 2 can be seen in Table 3. HTI attributes the better performance in Run PB-08 (higher resid conversion and C_4-524 °C distillate yield) to the addition of promoters to the iron-based GelCat^{TM} catalyst.[4]

The component distribution of the hot decalin extraction of the feed slurries from Condition 2 of PB-08 and PB-06 are presented in Table 11. The percent of the sample recoverable as plastics is greater for Run PB-06. The amount of soluble materials recovered from the two runs is a small amount greater for Run PB-06 (46% vs. 40 and 45%). The major difference between the two runs is the amount of component reporting to the insolubles fraction (37.5% for Run PB-06 and 45% for Run PB-08). Additionally, if normalized to a plastics-free mixture, the amount of insolubles in Run PB-08, Condition 2 Period 8B (~51%) is about 6% less than that of the coal-only period (Condition 1). This is not the case for the sample from Run PB-06, in which the normalized plastics-free insolubles component is 12 wt % (abs.) less than the coal only period. The first-stage slurry for Run PB-06 contains more than twice as much distillate and only 2/3 as much IOM as the corresponding Run PB-08 sample (Table 6). Unfortunately, no component analyses are available for second-stage products (O-6 bottoms or PFLs) from Run PB-06 to make a comparison.

COMPARISON OF CONDITIONS WITH COAL AND PYROLYSIS OIL CO-FEEDS

Condition 3 of Run PB-06 co-fed with Black Thunder Mine coal a pyrolysis oil produced in a fixed-bed reactor. Prior to Run PB-08, HTI acquired technology from the University of Wyoming to produce pyrolysis oils. This off-line pyrolysis unit was employed to make three different pyrolysis oils for Run PB-08 (L-931, L-932, and L-933). The analyses of the oil used in Run PB-06 and the oils used in Run PB-08 are presented in Table 10. The oil used in Run PB-06 was mixed plastics-derived. The oil used in Run PB-08 Condition 3 was waste tire-derived (pyrolyzed with waste lube oil (L-931)). The oil used in Condition 4 was waste tire plus plastics-derived, pyrolyzed with waste lube oil (L-933), and the oil used in Condition 5 was waste tire-derived, but the pyrolyzing carrier oil was coal-liquefaction-derived process oil (L-932). The three oils produced for PB-08 have a higher H/C ratio than the oil used in Run PB-06.

A comparison can be made between operations in Condition 3 of Run PB-06 and Condition 4 of Run PB-08 (Table 3). Both conditions used an oil that was at least 50% plastics-derived. The oil used in Run PB-08, Condition 4, is lower boiling than that used in Run PB-06, Condition 3. HTI concludes that the pyrolysis technology used to produce the oils for Run PB-08 is superior to the fixed-bed type of pyrolysis operation employed for production of the Run PB-06 oils. Total conversion and resid conversion are comparable; however, distillate yield was greater in Run PB-08 and hydrogen efficiency was 1.5 times better. All whole samples from Run PB-06 are more aromatic than those obtained from Run PB-08, Condition 4 (Table 12). The more aromatic feed slurry may be due to a higher concentration of intact aromatic structure from the pyrolyzed plastics. Alternatively, the non-aromatic contribution from the lube oil in Run PB-08 or better hydrogenation and/or cracking activity of the catalyst in Run PB-08 may be responsible for the lower aromaticity of the Run PB-08 samples. Based on the available data, a distinction among these possibilities cannot be made. The component distribution (Table 11) of the feed slurry for Run PB-06 Condition 3 shows that it has 5 times as much plastics than the feed slurry for Condition 4 of Run PB-08. It was argued previously that a some of the plastics become entrained or dissolved in the pyrolysis oils derived from plastic and do not decompose in the pyrolysis process.[1] The pyrolysis oils produced at HTI and used for Condition 4 of Run PB-08 do not appear to have as large a component of the undecomposed plastics. This may be attributable to the pyrolysis oil being derived from waste tires and lube oil, which were not present in the oil used in Run PB-06, or to the different pyrolysis processes used.

Section 4

EXPERIMENTAL

The experimental procedures used to produce results presented in this report were described previously.[5-7]

Section 5

CONCLUSIONS

Conclusions are provided in the Results and Discussion section of the report.

Section 6

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TABLE 1

HTI RUN PB-08 PLANNED RUN CONDITIONS[4]

Condition	**1**	**2**	**3**	**4**	**5**
Period	**1-5**	**6-8**	**9-11**	**12-14**	**15-17**
Work-Up Period	5	8	11	14	17
Temperature, K-1, °C	435	435	435	435	435
Temperature, K-2, °C	449	449	449	449	449
In-line Hydrotreater, °C	379	379	379	379	379
Space Velocity, kg feed/h/m^3	640	640	640	640	640
Recycle Solvent/MF Feed[b], kg/kg	1.2	1.2	1.2	1.2	1.2
Feed Coal	BTM[a]	BTM[a]	BTM[a]	BTM[a]	BTM[a]
Dispersed Catalyst Fe/Mo GelCat^{TM}/P-promoter, ppm	1000/100/100	1000/100/100	1000/100/100	1000/100/100	1000/100/100
Feed Composition Flow rate, g/h					
Coal	1425	1000	1000	1000	1000
Plastics[c]		385			
Pyrolysis Oil[d]			385		
Pyrolysis Oil[e]				385	
Pyrolysis Oil[f]					385

a. BTM = Black Thunder Mine Wyoming subbituminous coal.
b. Recycle consisted of a mixture of pressure filter liquids (PFL) and O-6 separator bottoms.
c. HDPE/PP/PS = 44/28/28 wt %.
d. 343 °C^+ distillation cut of waste tire pyrolyzed with waste lube oil.
e. 343 °C^+ distillation cut of waste tire plus plastics pyrolyzed with waste lube oil
f. 343 °C^+ distillation cut of waste tire pyrolyzed with coal-liquefaction process-derived oil.

TABLE 2

SAMPLE ACQUISITION SCHEDULE
HTI RUN PB-08

Condition	**1**	**2**	**3**	**4**	**5**
Sample	**Acquisition Period**[a]				
Feed Coal	5A	8A	11A	14A	17B
Feed Slurry	5A	8A,8B	11A	14A	17A
Pressure Filter Liquid	5B	8B	11B	14B	17B
Pressure Filter Solid	5B	8B	11B	14B	17B
First Stage Slurry[b]	6A	9A	11B	15A	17B
0-6 Bottoms	5B	8B	11B	14B	17B
First Stage SOH[c] (Oil)	5B[d]	8B	11B	14B	17B
First Stage SOH (water)	5B	8B	11B	14B	17B
Second Stage SOH (Oil)	5B	8B	11B	14B	17B
Second Stage SOH (water)	5B	8B	11B	14B	17B
First Stage Knock-out	-	8B	10B, 11B	14B	17B
Pyrolysis Oils	-	-	L-931	L-933	L-932

a. Periods are 24 h long. The designation A or B indicates which of the two 12 h shifts during the period the sample was obtained.

b. The First Stage slurry sample was taken following the end of the run condition. It represents the preceding run period. (Also called Interstage)

c. SOH = separator overhead

d. Contains knock-out oil

TABLE 3

PROCESS PERFORMANCE FOR PB-08 CONDITIONS 1-5 AND PB-06 CONDITIONS 2,3, AND 5

	PB-08[4]					**PB-06[1]**		
Condition **Mass Balance Period** **Material Recovery, %**	**1** **5** **98**	**2** **8** **98**	**3** **11** **104**	**4** **14** **98**	**5** **16** **101**	**2** **9** **98**	**3** **15** **97**	**5** **23** **104**
Normalized Yields, % MAF Feed								
C_1-C_3	10.75	6.44	5.83	5.45	8.13	7.9	8.8	12.5
C_4-C_7	5.65	5.06	4.35	3.66	7.99	3.4	8.1	6.9
IBP-177 °C	10.50	15.39	9.89	10.74	9.41	22.1	13.6	20.7
177-260 °C	13.29	9.60	9.35	10.17	8.86	5.3	6.8	11.1
260-343 °C	17.83	17.89	14.60	15.66	14.66	7.9	7.4	14.6
343-399 °C	8.03	11.43	14.43	15.94	13.83			
399-454 °C	3.03	4.44	7.59	7.21	6.05	16.3	15.	8.2
454-524 °C	2.39	3.70	6.45	5.79	4.97	4.3	7	1.3
524 °C$^+$	9.63	10.49	10.47	8.81	11.13	16.3	5.6	5.5
Unconverted Feed	6.15	6.72	7.45	7.35	5.92	9.2	18.5	6.1
H_2O	13.04	10.72	10.17	10.44	8.46	7.9	9.0	12.2
COx	7.08	3.01	3.34	3.20	4.93	3.2	8.2	7.5
NH_3	0.81	0.46	0.41	0.43	0.46	0.4	3.2	1.0
H_2S	0.14	0.02	0.24	0.10	0.26	-0.14	0.4	-0.05
							0.1	
Process Performance, % MAF Feed								
Coal Conversion(a)	93.9	90.3	89.3	89.4	91.5			
Total Conversion	93.9(b)	93.2(b)	92.5(b)	92.6(b)	94.1(b)	91	91	94
Residuum Conversion	84.3	82.7	74.7	76.9	75.6	75	73	88
C_4-524 °C Yield	60.3	67.5	66.7	69.2	65.8	59	57	63
H_2 Consumption	7.05	4.60	4.43	4.44	4.80	3.9	5.4	7.5
H_2 Efficiency, kg dist/kg H_2	8.6	14.7	15.1	15.6	13.7	15.1	10.6	8.4
C_1-C_3 Gas Selectivity (c)	17.8	9.5	8.74	7.88	12.36	13.3	15.4	19.8

(a) Data offered by HTI (Reference 4)

(b) Calculated by CONSOL based on the assumption that there was 100% conversion of co-feeds.

(c) Defined as a percentage of C_1-C_3 light gas yield, relative to the C_4-524 °C distillate yield.

TABLE 4

PHENOLIC -OH CONTENT OF HTI BENCH RUN PB-08 SAMPLES

Condition	**1**	**2**	**3**	**4**	**5**
Sample	**Phenolic -OH, meq/g (peak location, cm^{-1})**				
	Whole Oils				
1st Stage SOH Oil	1.72 (3308)	1.20 (3309)	1.22 (3311)	1.46 (3309)	1.07 (3309)
2nd Stage SOH Oil	ND[a]	ND	ND	ND	ND
1st Stage knock-out	ND[a]	ND	ND	ND	ND
	THF-Soluble Portion of Samples				
1st Stage Slurry[b] 454°C- Distillate	0.93 (3306)	0.85 (3306)	0.55 (3306)	0.60 (3305)	0.72 (3305)
1st Stage Slurry[b] 454°C+ Resid	0.96 (3292)	1.03 (3292)	1.01 (3292)	1.03 (3292)	1.04 (3292)
0-6 Bottoms 454°C- Distillate	0.90 (3305)	0.80 (3305)	0.70 (3305)	0.61 (3306)	0.72 (3305)
0-6 Bottoms 454°C+ Resid	0.85 (3293)	0.84 (3293)	0.92 (3292)	0.93 (3293)	0.87 (3292)
Feed Slurry	0.56 (3284)	0.68 (3293)	0.53 (3294)	0.40 (3296)	0.59 (3296)
Pressure Filter Liquid (PFL) 454°C- Distillate	0.85 (3305)	0.71 (3307)	0.54 (3306)	0.45 (3307)	0.68 (3305)
Pressure Filter Liquid (PFL) 454°C+ Resid	0.86 (3292)	0.76 (3294)	0.89 (3293)	0.73 (3291)	0.86 (3294)
Pressure Filter Solid (PFS)	0.88 (3294)	0.91 (3294)	0.96 (3293)	0.95 (3291)	0.91 (3294)

a. ND = none detected.
b. Also called interstage sample.

TABLE 5

^{1}H-NMR ANALYSES OF RUN PB-08 WHOLE SAMPLES(a)

	Period	Cond. Arom	Uncond. Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
SOH 1stG +KO Oil(b)	5B	6.8	10.0	10.3	12.4	14.6	28.8	17.1
SOH 1st Stg Oil(b)	8B	8.9	11.0	9.9	9.5	12.5	28.6	19.6
SOH 1st Stg Oil(b)	11B	4.6	6.3	7.5	9.0	15.5	36.0	21.1
SOH 1st Stg Oil(b)	14B	3.5	6.3	6.5	8.8	14.0	38.1	22.8
SOH 1st Stg Oil(b)	17B	4.8	7.2	7.8	9.8	14.4	34.9	21.1
SOH 2nd +KO Oil(b)	5B	0.6	2.3	4.5	4.5	23.5	36.8	27.7
SOH 2nd Stg Oil(b)	8B	1.8	3.4	5.2	4.6	21.0	35.8	28.3
SOH 2nd Stg Oil(b)	11B	1.0	1.3	3.7	3.4	20.4	40.7	29.6
SOH 2nd Stg Oil(b)	14B	0.6	1.0	3.2	3.2	20.6	41.9	29.4
SOH 2nd Stg Oil(b)	17B	0.7	1.4	3.7	3.7	21.5	41.2	27.8
PFL	5B	23.0	10.3	16.9	10.6	11.8	18.7	8.7
PFL	8B	17.8	8.7	14.0	9.7	12.0	26.0	11.9
PFL	11B	10.9	7.5	9.2	7.7	11.0	35.4	18.2
PFL	14B	10.2	6.8	8.4	7.2	10.4	38.4	18.7
PFL	17B	14.6	10.9	11.0	9.3	11.6	27.5	15.2
O-6 Btms(c)	5B	21.4	11.4	15.9	11.1	11.9	18.6	9.8
O-6 Btms(c)	8B	10.3	5.7	16.1	11.4	13.1	28.7	14.7
O-6 Btms(c)	11B	11.7	8.3	9.8	7.8	11.3	34.1	17.0
O-6 Btms(c)	14B	9.5	4.6	9.2	6.7	11.9	40.0	18.1
O-6 Btms(c)	17B	17.6	8.3	12.5	9.5	11.3	27.6	13.2
L-931 Pyrolysis Oil	Cond 3	1.8	2.4	4.9	5.3	15.1	45.4	25.1
L-932 Pyrolysis Oil	Cond 4	7.0	3.8	7.3	7.2	14.2	39.1	21.3
L-933 Pyrolysis Oil	Cond 5	1.5	1.5	3.1	3.9	12.5	48.8	28.6
1st Stg Slurry (d)	6A	21.8	6.6	18.0	10.1	12.6	20.8	10.1
1st Stg Slurry (d)	9A	19.1	13.5	14.1	10.4	11.7	18.3	12.8
1st Stg Slurry (d)	11B	13.6	7.2	10.4	7.8	11.2	32.2	17.5
1st Stg Slurry (d)	15A	9.2	5.8	7.5	7.0	11.5	38.3	20.7
1st Stg Slurry (d)	17B	10.8	6.5	9.2	7.5	11.4	37.6	17.0
Feed Slurry	5A	20.4	5.8	15.2	9.3	11.9	25.4	12.0
Feed Slurry	8A	19.4	11.0	13.8	8.6	13.1	22.5	11.5
Feed Slurry	11A	11.1	4.7	8.9	6.5	13.3	37.0	18.6
Feed Slurry	14A	10.3	4.2	8.8	6.2	12.9	39.5	18.2
Feed Slurry	17B	12.7	5.6	10.6	7.8	12.8	33.7	16.8
P.F. Solids (c)	5B	27.2	7.1	16.9	10.3	12.0	17.9	8.5
P.F. Solids (c)	8B	23.2	5.8	16.0	9.4	12.8	22.3	10.4
P.F. Solids (c)	11B	19.6	5.8	13.5	8.7	12.5	27.9	11.9
P.F. Solids (c)	14B	18.9	6.2	14.3	9.0	12.6	26.2	12.8
P.F. Solids (c)	17B	19.4	7.7	14.4	9.7	11.6	24.9	12.3

(a) Samples dissolved in 99.8 % $CDCL_3$ and filtered prior to obtaining NMR spectrum
(b) SOH samples were not filtered prior to obtaining NMR spectra
(c) Dissolved in 99.96 % d_5-pyridine and filtered prior to obtaining NMR spectrum.
(d) Also called interstage sample

TABLE 6

COMPONENT DISTRIBUTION - HTI RUNS PB-08 AND PB-06 SAMPLES

Sample	**Component, %**	**Condition**				
		1	**2**	**3**	**4**	**5**
		Run PB-08				
Pyrolysis Oils	Distillate[a]	-	-	85.5	89.4	88.0
	Resid, THFS[a]	-	-	14.2	10.0	11.6
	IOM	-	-	0.1	0.1	0.2
	Ash	-	-	<0.1	0.1	<0.1
First-Stage Slurry[b]	Distillate	27.7	19.4	36.5	35.7	33.6
	Resid, THFS	45.6	43.9	38.7	43.9	43.2
	IOM	15.8	22.8	14.9	12.2	13.8
	Ash	9.8	12.2	7.8	6.2	7.2
O-6 Bottoms	Distillate	39.5	39.5	47.8	46.1	50.2
	Resid, THFS	38.7	39.9	34.3	39.2	39.1
	IOM	10.1	4.0.	10.5	8.6	6.2
	Ash	10.2	15.8	6.4	5.6	4.0
Pressure Filter Liquid	Distillate	37.6	45.5	55.7	64.8	52.9
	Resid, THFS	42.3	40.6	39.6	33.1	44.2
	IOM	10.1[c]	13.2	4.3	1.5	1.8
	Ash	8.4[c]	0.1	<0.1	<0.1	0.1
Pressure Filter Solid	Distillate	ND[d]	ND	ND	ND	ND
	Resid, THFS	54.5	40.1	40.9	45.5	47.5
	IOM	20.0	32.7	34.4	31.5	29.3
	Ash	25.6	27.2	24.7	23.0	23.2
		Run PB-06				
First-Stage Slurry	Distillate		51.1	31.3		
	Resid		27.5	44.8		
	IOM		14.0	13.9		
	Ash		3.9	5.1		

a. Distillation cut point 454°C; THFS = tetrahydrofuran solubles.
b. Also called interstage.
c. May be due to problems encountered with filtration in Condition 1, Period 5.[1]
d. ND = not determined.

TABLE 7

MICROAUTOCLAVE COAL CONVERSIONS[a]
HTI RUN PB-08 SAMPLES

Sample		Condition				
		1	2	3	4	5
Pyrolysis Oils	Whole	-	-	27.9	47.3	36.4
O-6 Bottoms	Distillate[b]	83.4	75.5	55.1	51.7	65.6
	Whole	62.9	55.9	69.9	69.4	66.9
PFL	Distillate	85.5	77.3	50.0	49.2	66.4
	Whole	70.2	82.0	61.0	72.7	70.3

a. Test Conditions: 398 °C, 30 min, 9 g sample, 6 g Old Ben Mine coal

b. 454 $^\circ C^-$ fraction of whole sample

TABLE 8

^{1}H-NMR ANALYSES OF RUN PB-08 DISTILLATE SAMPLES[a]

	Period	Cond. Arom.	Uncond Arom.	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
PFL	5B	16.3	10.1	13.2	11.6	11.6	23.9	13.4
PFL	8B	13.6	7.7	12.4	9.6	11.9	29.4	15.5
PFL	11B	8.1	4.8	8.1	6.9	11.4	40.6	20.0
PFL	14B	7.4	4.2	8.3	6.5	12.6	43.0	17.9
PFL	17B	12.7	5.9	11.8	8.7	12.8	33.5	14.5
O-6 Btms[b]	5B	16.6	9.6	14.3	11.4	12.2	24.1	11.9
O-6 Btms[b]	8B	12.9	7.9	12.0	9.7	11.9	30.6	15.0
O-6 Btms[b]	11B	9.5	4.7	10.5	7.6	12.9	37.0	17.7
O-6 Btms[b]	14B	8.3	4.8	9.0	7.4	12.3	40.1	18.2
O-6 Btms[b]	17B	13.0	6.3	11.7	9.1	12.6	32.3	15.0
L-931 Pyrolysis Oil	Cond 3	1.8	2.0	5.3	5.5	15.6	45.3	24.5
L-932 Pyrolysis Oil	Cond 4	7.6	3.5	7.1	6.9	13.7	39.3	21.9
L-933 Pyrolysis Oil	Cond 5	1.2	1.8	3.3	4.2	13.2	48.6	27.6
1st Stg Slurry[c]	6A	16.3	7.5	13.8	11.2	12.4	26.5	12.2
1st Stg Slurry[c]	9A	16.1	7.4	14.5	10.2	13.0	24.8	14.1
1st Stg Slurry[c]	11B	8.8	4.7	9.2	7.8	12.7	37.2	19.6
1st Stg Slurry[c]	15A	7.9	4.8	8.4	7.0	12.5	39.5	19.8
1st Stg Slurry[c]	17B	11.0	6.5	10.0	8.8	12.4	32.4	18.9

a. Samples dissolved in 99.8 % $CDCL_3$ and filtered prior to obtaining NMR spectrum.
b. Dissolved in 99.96 % d_5-pyridine and filtered prior to obtaining NMR spectrum.
c. Also called interstage sample.

TABLE 9

^{1}H-NMR ANALYSES OF RUN PB-08 RESID SAMPLES[a]

		Cond. Arom.	Uncond. Arom.	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
PFL	5B	29.0	12.6	16.7	10.8	11.2	11.6	8.1
PFL	8B	28.0	12.4	16.6	9.9	11.4	14.0	7.8
PFL	11B	24.7	10.2	14.8	9.5	11.0	20.0	9.8
PFL	14B	24.4	8.1	15.2	8.8	11.8	22.1	9.5
PFL	17B	30.2	11.0	17.5	10.1	11.2	13.3	6.7
O-6 Btms[b]	5B	31.4	10.3	19.1	10.3	11.5	11.5	6.0
O-6 Btms[b]	8B	28.4	11.2	18.3	9.6	11.2	13.5	7.7
O-6 Btms[b]	11B	27.6	12.0	16.8	9.9	11.0	14.7	8.0
O-6 Btms[b]	14B	25.6	11.6	16.2	9.7	11.1	17.0	8.9
O-6 Btms[b]	17B	29.2	11.8	16.5	10.6	10.4	14.0	7.5
L-931 Pyrolysis Oil	Cond 3	3.4	3.2	7.7	5.8	15.3	42.3	22.3
L-932 Pyrolysis Oil	Cond 4	7.3	3.4	7.1	5.9	14.1	42.4	19.7
L-933 Pyrolysis Oil	Cond 5	2.4	2.1	4.9	4.2	13.6	50.2	22.6
1st Stg Slurry[c]	6A	24.8	11.0	17.3	10.7	12.0	15.7	8.6
1st Stg Slurry[c]	9A	27.3	10.9	18.1	10.6	12.3	13.9	6.9
1st Stg Slurry[c]	11B	21.5	8.4	14.8	9.4	12.8	22.3	10.8
1st Stg Slurry[c]	15A	23.1	11.5	15.5	9.8	11.3	19.0	9.7
1st Stg Slurry[c]	17B	24.6	11.3	16.6	10.5	9.6	18.6	8.8

a. Samples dissolved in 99.8 % $CDCL_3$ and filtered prior to obtaining NMR spectrum.
b. Dissolved in 99.96 % d_5-pyridine and filtered prior to obtaining NMR spectrum.
c. Also called interstage sample.

TABLE 10

PROPERTIES OF PYROLYSIS OILS[a]

Condition	**Run PB-08**[4]			**Run PB-06**[1]
	3	**4**	**5**	**3**[c]
HTI Identification No.	L-931	L-933	L-932	
Gravity, API	26.1	29.0	NA	6.2
IBP, °C	319	278	NA	NA
FBP, °C	500	515	520	NA
Elemental Analysis, wt %				
C	86.23	86.30	87.72	88.88
H	12.40	13.08	11.23	9.33
S	0.912	0.470	0.887	1.14
N	0.14	0.16	0.51	0.17
H/C	1.73	1.82	1.54	1.26
Distillation, wt %[b]				
IBP-343 °C	4.57	4.70	20	NA
343 - 454 °C	76.24	78.69	65	NA
454-524 °C	15.73	16.33	15	NA
524°C+	0.0	0.0	0.0	43.1[d]
Loss	0.46	0.22	0.0	NA

a. Provided by HTI[1,4]
b. ASTM D-1160, by simulated distillation
c. Obtained from simulated waste plastics, but contains an unidentified contribution from pyrolyzed L-814 make-up oil.
d. 524°C$^+$ resid, wt %

NA = not available

TABLE 11

HOT DECALIN EXTRACTIONS OF PB-08 CONDITIONS 1-5 FEED SLURRY, PRESSURE FILTER LIQUID, PRESSURE FILTER SOLID WHOLE SAMPLES, AND PFL RESIDS, AND PB-06 CONDITIONS 2 AND 3 WHOLE FEED SLURRY SAMPLES

	Condition	Period	Insols, %	Sols, %	Plastics, %	Recovery, %
Whole Samples						
Run PB-06						
Feed Slurry	2	10A[a]	37.5	46	16.5	99.8
Feed Slurry	3	15A	22.3	71.5	6.2	100.6
Run PB-08						
Feed Slurry	1	5B	56.5	43.3	0.14	97
Feed Slurry	2	8A	43.8	45.2	11.00	103.5
Feed Slurry	2	8B	46.5	40.5	12.90	98.3
Feed Slurry	3	11B	41.3	55.2	3.50	99.1
Feed Slurry	4	14B	36.7	62.1	1.20	97.1
Feed Slurry	5	17B	41.9	57.7	0.41	97.7
PFS	1	5B	42.6	57.1	0.26	100.0
PFS	2	8B	63.7	31.8	4.50	99.0
PFS	3	11B	61.7	37.7	0.57	97.0
PFS	4	14B	57.6	42.3	0.11	99.9
PFS	5	17B	56.5	44.0	0.16	96.9
Resids						
PFL	1	5B	30.4	69.5	0.1	103.4
PFL	2	8B	2.9	76.8	20.4	101.7
PFL	3	11B	0.6	90.2	9.2	101.7
PFL	4	14B	0.1	97.5	2.5	102.6
PFL	5	17B	4	95.6	0.5	102.3

a. Sample believed to represent the period which immediately precedes the run period.

TABLE 12

COMPARISON OF PB-08 CONDITION 4 AND PB-06 CONDITION 3 AROMATIC HYDROGEN CONTENT[a] OF THF SOLUBLES FROM WHOLE SAMPLES

Sample	**PB-08 Condition 4, %**	**PB-06 Condition 3, %**
SOH First-Stage Oil	9.8	13.1
SOH Second-Stage Oil	1.6	2.2
Pressure Filter Liquid	17.0	36.5
O-6 Bottoms	14.1	37.9
First-Stage Slurry[b]	15.0	32.7
Feed Slurry	14.5	30.3
Pressure Filter Solids	25.1	41.1

a. Sum of condensed and uncondensed aromatic proton content.
b. Also called interstage sample.

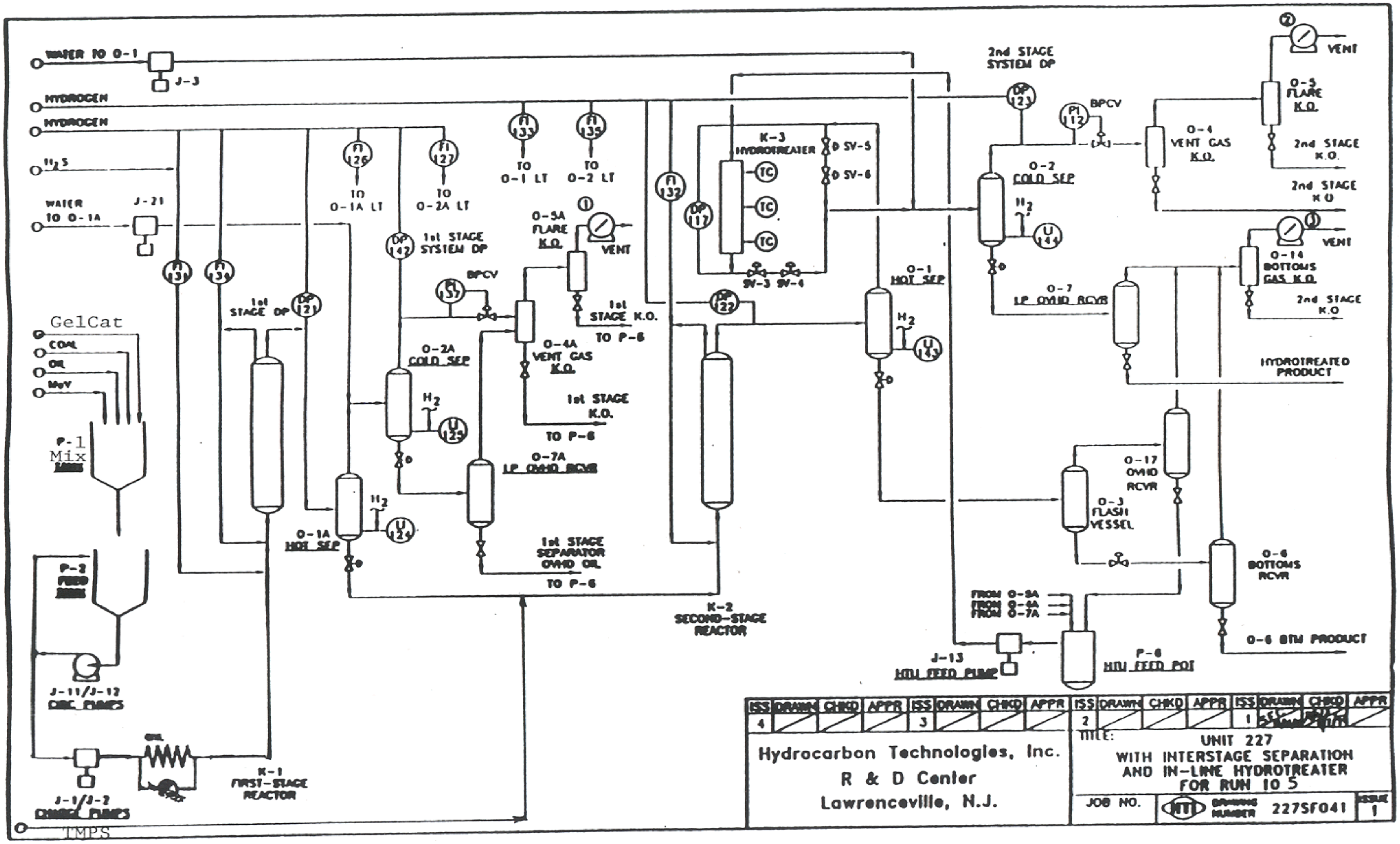

Figure 1. Process Flow Diagram of Bench-Scale Liquefaction Unit (Unit 227), as Configured for Run PB-08.[4]

APPENDIX I

KINETICS OF COAL LIQUEFACTION DISTILLATION RESID CONVERSION

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Kinetics of Coal Liquefaction Distillation Resid Conversion

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The objectives of this study were to understand the characteristics of coal liquefaction resids from the direct two-stage coal liquefaction process, the reactivity of these resids in hydroconversion, and the relationship between resid reactivity and resid composition. A suite of 15 distillation resids obtained from two-stage pilot plant liquefaction runs were extensively characterized. An empirical direct liquefaction test was developed to determine the relative resid reactivity in hydroconversion and was applied to these resids. The kinetics of hydrocracking of two of the resids were also investigated in more detail. The presence of about 10−15% of an unconvertible component in the resids was indicated and isolated. The source of this unconvertible component is being investigated.

Introduction

The direct coal liquefaction process was invented by Bergius in Germany in 1910. Since that time, a great deal of work has been done on the process in Germany, the United States, and various other countries, increasing the understanding of the reactions involved and changing the ideas of how the process should be carried out. The present concept for a direct liquefaction process to produce liquid fuels from coal is a closed-coupled integrated two-stage liquefaction system. This concept included two reaction stages with a number of possible variations. For most of the recent runs at Wilsonville, it consisted of two ebulating bed-catalyzed stages or a combination of a thermal (noncatalytic) and a subsequent catalyzed stage. Various temperatures in the two stages have also been experimented with. The reaction product, which is only partially converted, must be fractionated in a series of atmospheric and vacuum distillation stages and a final solvent deashing stage to separate the fuel-grade product from the gases and heavy liquids and any unconverted coal and coal ash produced. Since conversion of the coal to distillable material is only around 30% per pass through the system, considerable material consisting of a mixture of some high-boiling components, deasher effluent, and product distillate must be recycled to the process and used as the principal solvent which is fed with fresh coal to the first stage of the process. Experience has shown that recycling of some of the heavy product to the liquefaction reaction actually results in higher conversion to fuel-grade product than if the process was carried out in a single-stage batch process without recycling.[1,2] This recycle stream contains a considerable amount of high-boiling material (bp > 454 °C (850 °F)) which is not suitable for processing in a conventional petroleum refinery.

Since this high-boiling material represents an important component of coal liquefaction products, a number of workers have investigated the conversion of these materials to lower boiling products. Benito and Martinez examined the catalytic hydrocracking of a residue from deasphalting a syncrude obtained by direct coal liquefaction of a subbituminous Spanish coal.[3] Mochida et al. investigated the hydrocracking of an Australian subbituminous coal liquefaction residue.[4] Martinez et al. studied the kinetics of hydroconversion of coal residues.[5,6] It was, therefore, of interest to know the behavior of resids from the two-stage process of coal liquefaction performed in the Wilsonville pilot plant during recycle.[7] This was approached in the following stages: (1) by developing an empirical method for the evaluation of resid conversion and resid reactivity; (2) by measuring the kinetic parameters that define the resid reactivity based on hydroconversion experiments; (3) by correlating chemical and physical characteristics of resids with resid reactivity.

This report was written to document the work aimed at these latter objectives. Mathematical models of coal resids and the kinetics of hydroconversion will be published separately

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10.1021/ef980102z CCC: $15.00

Experimental Section

Apparatus. A laboratory-scale reactor (short contact time batch reactor, SCTBR) was developed capable of running reactions up to 450 °C and 2500 psi at well-defined reaction times from a few seconds to 30 min or longer. This reactor system is described in detail in two papers.[8,9]

In operation, both the empty 30 cm^3 reactor and the preheater are immersed in a fluidized sand bath and brought up to reaction temperature. High-pressure gas (hydrogen or in some cases nitrogen) provides the driving force to deliver the reaction mixture of solvent, resid, and catalyst from a blow case through the preheater into the reactor. The process stream enters the reactor within 5−8 °C of the desired reaction temperature in approximately 0.3 s. The mixture then comes up to full reaction temperature within about 30 s in the hot reactor. Hydrogen or nitrogen gas bubbled through the reaction mixture from the bottom provided the necessary agitation. Temperature control was within ± 2 °C. Discharging and quenching of the reaction mixture was carried out in a similar way and a similar time frame by changing the valve settings and forcing the reactor contents with high-pressure gas through the precooler (immersed in a water bath) into the product receiver.

A limitation of this equipment is that in the normal experiments the product is blown out of the reactor into the receiver. This leaves a small amount of the reaction product adhering to the walls of the reactor, particularly the preheater and precooler walls. A small amount of the reaction mixture is also left in the blow case. This precludes obtaining an accurate material balance with small samples, as normally between 80% and 90% of the reaction product is recovered.

It is possible to recover essentially all of the product by washing the system out with a solvent, evaporating the solvent, and measuring the residue. This was shown to work but was extremely time-consuming and normally no more accurate than using an ash tracer method. Also, by this method, some of the product is exposed to a slightly different thermal history than the rest of the sample.

It is also important that a representative sample of the product be obtained for conversion determination. This was shown to be the case in resid hydroconversion by putting the reaction mixture through the reactor at room temperature and comparing the ash content of that product with the original sample. It was found that during hydroconversion, the ash component remains with the undissolved solid residue and not with the oil or liquefied components.

The thermogravimetric analyzer used for proximate analysis determination was a model 51 TGA (TA Instruments, New Castle, DE).

The concentration of tetralin and tetralin derivatives present in the process streams was determined using a HP 5880A gas chromatograph equipped with a HP 5 cross-linked PhMe silicone capillary column.

A GC/MS gas chromatograph with an electron ionization detector (GCD Series G1800A) equipped with a GC column HP-1 with a cross-linked methyl silicone gum of 50 m × 0.2 μm film thickness was used to examine the solvents and products not containing resids.

Materials Studied. Thirteen resids were prepared by CONSOL Inc. from liquefaction runs made at the Wilsonville, AL, pilot plant, and two resids were made from runs from the Hydrocarbon Research Institute bench-scale unit. The feed coals for these runs were Wyodak−Anderson subbituminous coal and Illinois No. 6 and Pittsburgh high-volatile bituminous coals. Samples were taken from several points in the Wilsonville process. The resids were produced from whole process oils by distillation in a 1 in. × 3 ft jacket-heated Vigreux column to an end point of 320 °C pot/270 °C column/5 Torr (454 °C or 850 °F atm equivalent).

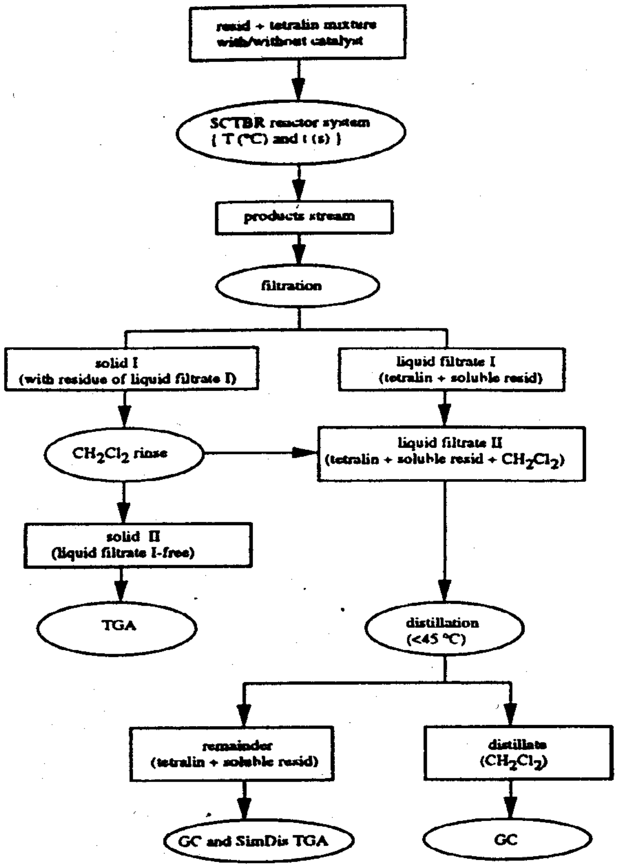

Figure 1. Scheme of reaction product workup.

Chemicals Used. Tetralin (99%; Aldrich) was used as the solvent. Molybdenum naphthenate (6.8% molybdenum; Shepherd Chemical Co.) and methyl disulfide (99%; Aldrich) were used for the principal catalyst system. Shell 324 Ni/Mo on alumina catalyst obtained from Wilsonville via CONSOL was used in a limited number of experiments, but its high ash content made conversion determination by ash tracer measurement imprecise.

Resid Conversion Reactions. All hydroconversion reactions were run as mixtures of tetralin T (the hydrogen-donor solvent) and resid R over a range of T/R ratios, hydrogen pressures, temperatures, and catalyst concentrations. In some cases, the reactions were run under nitrogen instead of hydrogen to determine the effect of hydrogen-donor alone. In each reaction, 5−10 g of resid were used together with added tetralin to make up the desired T/R ratio.

Product Workup Procedure. The reaction products were worked up by separating the solids from the liquids by filtration according to the scheme shown in Figure 1. The solid filter cake was washed with cold methylene chloride, which went into the filtrate along with the product liquids. The filtrate was then distilled at low temperatures (ca. 45 °C) to remove the methylene chloride. The solid filter cake was dried in a vacuum oven at room temperature.

Analytical Methods. Conversion. The conversion to tetralin soluble liquid was determined on the filter cake using

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(8) Huang, H.; Calkins, William, H.; Klein, M. T. A Novel Laboratory Scale Short Contact Time Batch Reactor System for Studying Fuel Processes. 1. Apparatus and Preliminary Experiments. *Energy Fuels* 1994, *8*, 1304−1309.

(9) Huang, H.; Fake, D. M.; Calkins, W. H.; Klein, M. T. A Novel Laboratory Scale Reactor System for Studying Fuel Processes from the Initial Stages. 2. Detailed Energy and Momentum Balances. *Energy and Fuels* 1994, *8*, 1310−1315.

Table 1. Selected Properties of the Resids[a]

resid	feed coal	no.	stream	f_a	VM wt %	FC wt %	ash wt %	T_{peak} °C	peak height, wt % min (daf)
resid L	Wyodak–Anderson Black Thunder	W4	V 1067	34	51.3	48.7	19.1	470.7	4.59
resid K	Wyodak–Anderson Black Thunder	W5	R 1235	24.6	53.6	46.4	17.2	464.8	4.6
resid H	Wyodak–Anderson Black Thunder	W6	V 131B	33.3	57.1	42.9	15.2	475.3	4.67
resid F	Wyodak–Anderson Black Thunder	W10	V 1067	24.3	55.2	44.8	17.5	461.5	4.36
resid E	Wyodak–Anderson Black Thunder	W11	R 1235	26	53.4	46.6	15.6	454.4	4.24
resid G	Wyodak–Anderson Black Thunder	W12	V 131B	25.9	55.7	44.3	15.9	462.2	5.02
resid I	Illinois No. 6 Burning Star No. 2	W7	V 1067	30.4	61.5	38.5	15.9	480.1	6.44
resid M	Illinois No. 6 Burning Star No. 2	W8	R 1235	29.4	59.9	40.3	13.7	481.8	6.16
resid D	Illinois No. 6 Burning Star No. 3	W9	V 131B	29.2	70.9	29.1	9.9	490.5	6.83
resid J	Pittsburgh Ireland	W1	V 1067	31.6	57.6	42.4	10.2	490.1	7.2
resid B	Pittsburgh Ireland	W2	R 1235	33.3	61.1	38.9	8.7	493.6	7.43
resid C	Pittsburgh Ireland	W3	V 131B	31.5	61	39	8.5	490.2	6.23
resid A	Wyodak–Anderson Black Thunder	W	V 131B	38.9	51.8	48.2	17	472.1	4.75
resid N	Wyodak–Anderson Black Thunder	HR1		20.6	90.6	6	0.4	451.5	0.12
resid O	Wyodak–Anderson Black Thunder	HR1		18.8	89.1	8.2	2.8	449.2	0.18

[a] V 1067 = interstage stream. R 1235 = second-stage product stream. V 131B = recycle stream. W = Wilsonville. HRI = Hydrocarbon Research Institute. T_{peak} and peak height = peak temperature and peak value of derivative curve of TGA.

Table 2. Experimentally Determined Elemental Weight Percent of 15 Coal Resids

	resid A	resid B	resid C	resid D	resid E
hydrogen wt %	5.61	6.18	6.50	6.57	6.59
carbon wt %	88.30	90.00	90.92	88.39	85.34
sulfur wt %	1.74	1.50	1.24	1.05	1.74
nitrogen wt %	1.19	1.15	1.04	1.05	0.99
oxygen wt %	3.16	1.18	0.30	2.94	5.34
phenolic OH wt %	0.80	0.92	0.69	0.78	0.82
	resid F	resid G	resid H	resid I	resid J
hydrogen wt %	6.75	6.77	6.35	6.53	6.38
carbon wt %	86.03	85.84	87.43	88.14	90.10
sulfur wt %	1.94	1.73	1.53	1.54	1.49
nitrogen wt %	0.93	0.93	1.10	1.11	1.05
oxygen wt %	4.35	4.73	3.59	2.68	0.98
phenolic OH wt %	1.25	0.85	0.69	0.92	0.70
	resid K	resid L	resid M	resid N	resid O
hydrogen wt %	5.89	6.25	6.59	8.55	8.36
carbon wt %	86.61	86.77	87.44	90.34	89.06
sulfur wt %	1.82	1.95	1.57	0.34	0.21
nitrogen wt %	1.09	1.10	1.19	0.66	0.31
oxygen wt %	4.59	3.93	3.21	0.10	2.05
phenolic OH wt %	0.95	0.69	0.88	0.50	0.22

thermogravimetric analysis (TGA) by an ash balance calculation. The conversion to tetralin-soluble material was determined using the formula:

$$X\ (\text{daf wt }\%) = 1/1 - A_0 \times (1 - A_c/A_s) \times 100\%$$

where A_o and A_s are the weight fractions of ash (derived from the mineral matter) in a control sample and the liquefaction residue, respectively.

The boiling range of the tetralin-soluble material had to be measured to determine what portion of the liquid was converted to a material boiling below 454 °C (850 °F) since the original resids boiled above 454 °C. A boiling-range method, SimDis TG, was developed based on thermogravimetric analysis (TGA) to accomplish this.[10] This value had to be corrected for the amount of tetralin and tetralin-derived material in the liquid product. This was determined by gas chromatography using 1-methylnaphthalene (99% from Aldrich) as an internal standard.

As a control to the resid hydroconversion experiments, tetralin and tetralin with sulfided molybdenum naphthenate were exposed for 30 min at 420 °C in 1500 psi of hydrogen without the resid being present. GC/MS on the products of these experiments showed no buildup of high-boiling materials from the tetralin, however, there was 15–22% of the tetralin converted to the expected low-boiling isomerization products methylindane, some naphthalene, and what was tentatively identified as tetrahydromethylnaphthalene. These were corrected for in the boiling-range measurements.

Resid Characterization. Proximate analysis by thermogravimetric analysis (TGA) and the aromaticity (f_a) of the 15 resids studied are shown in Table 1. Elemental analysis and phenolic hydroxyl contents are shown in Table 2. Table 3 shows the osmotic molecular weights of the samples and a breakdown of the resids by component types (saturates, resins, asphaltenes, and preasphaltenes) by SARA analysis.[11] Table 4 shows the breakdown of the samples into distribution by proton type by ^{1}H NMR.

Determination of the Boiling Range of the Liquid Products. Since the objective of the project was in part, to determine the conversion of resids boiling above 454 °C (850 °F) to lower boiling material, under the hydroconversion conditions in the liquefaction process, it was necessary to develop a method for determining the boiling range of the derived liquids. This had to be done on very small samples. While there is a simulated distillation analysis[12,13] based on

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(10) Huang, H.; Wang, K.; Klein, M. T.; Calkins, W. H. A Novel Method for the Determination of the Boiling Range of Liquid Fuels by Thermogravimetric Analysis. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 40 (3), 485–491.

(11) Ali, M. F.; Bukhari, A.; Hasan, M. Structural Characterization of Arabian Crude Oil Residue. *Fuel Sci. Technol. Int.* **1989**, *8*, 1179.

Table 3. Experimentally Determined Molecular Weights and Compound Class Mole Fractions of 15 Coal Resids

	resid A	resid B	resid C	resid D	resid E
molecular weight[a] wt %	488	543	474	394	612
SARA wt %					
saturates wt %	2.2	2.3	2.7	6.3	6.9
resins wt %	49.6	49.1	59.5	56.0	49.4
asphaltenes wt %	41.0	33.5	27.7	28.8	32.8
preasphaltenes wt %	7.2	15.1	10.1	8.9	10.9
	resid F	resid G	resid H	resid I	resid J
molecular weight[a] wt %	453	543	515	478	521
SARA wt %					
saturates wt %	10.9	9.0	6.3	3.6	7.8
resins wt %	49.1	47.8	51.7	57.9	42.8
asphaltenes wt %	30.7	34.5	33.3	28.2	38.6
preasphaltenes wt %	9.3	8.7	8.7	10.3	10.8
	resid K	resid L	resid M	resid N	resid O
molecular weight[a] wt %	446	540	445	385	356
SARA wt %					
saturates wt %	9.1	4.2	10.9	16.8	27.6
resins wt %	50.9	58.4	45.4	77.7	67.4
asphaltenes wt %	26.6	28.0	31.5	5.0	4.5
preasphaltenes wt %	13.4	9.4	12.2	0.5	0.5

[a] Molecular weight determined by vapor-phase asmomitry.

Table 4. Experimentally Determined Proton Distribution of 15 Coal Resids

	resid A	resid B	resid C	resid D	resid E
uncondensed arom wt %	7.6	2.6	5.4	3.8	3.7
condensed arom wt %	31.3	30.7	26.1	25.4	22.3
alkyl α wt %	9.5	10.2	9.4	9.6	9.3
cyclic α wt %	18.8	20.9	18.9	19.7	19.2
alkyl β wt %	11.9	13.4	14.6	16.8	20.9
cyclic β wt %	12.9	13.8	14.8	15.3	14.6
γ wt %	8.1	8.4	10.8	9.3	10.0
	resid F	resid G	resid H	resid I	resid J
uncondensed arom wt %	3.9	3.7	3.8	4.5	3.8
condensed arom wt %	20.4	22.2	29.5	25.9	27.8
alkyl α wt %	9.0	9.4	4.5	9.6	9.6
cyclic α wt %	18.6	18.1	21.5	19.9	21.2
alkyl β wt %	21.9	21.3	17.0	16.0	13.4
cyclic β wt %	15.3	15.2	14.3	14.7	15.5
γ wt %	10.8	10.1	9.3	9.3	8.7
	resid K	resid L	resid M	resid N	resid O
uncondensed arom wt %	4.3	6.8	4.9	5.9	4.3
condensed arom wt %	20.3	27.2	24.5	14.7	14.5
alkyl α wt %	9.4	8.8	9.6	9.6	8.0
cyclic α wt %	17.2	18.3	21.1	16.3	14.5
alkyl β wt %	21.2	16.6	15.6	24.2	30.0
cyclic β wt %	15.3	13.6	15.2	16.1	15.1
γ wt %	12.3	8.7	9.2	13.1	13.6

gas chromatography which requires only small samples, it is generally limited to samples boiling below about 350 °C because of the stability of the column packing. Also, the resid would tend to plug the GC column. For those reasons, a simulated distillation analytical method, referred to above, based on thermogravimetric analysis was developed.[10] It could be run either at atmospheric pressure or under vacuum.

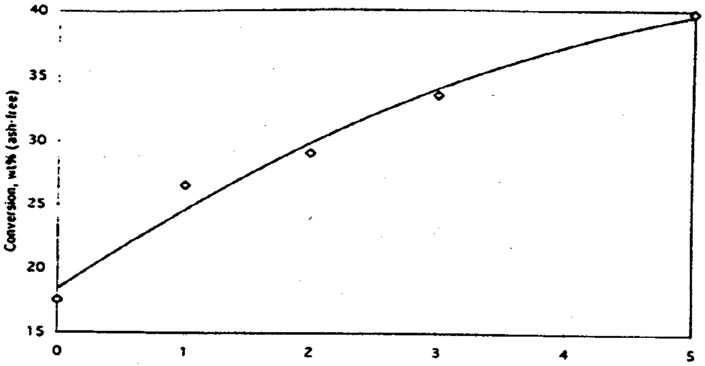

Figure 2. Effect of catalyst concentration (sulfided molybdenum naphthenate) on the conversion of resid A (420 °C, 1500 psi of hydrogen, 30 min).

Development of an Empirical Method for the Evaluation of Resid Conversion and Reactivity. Preliminary experiments in hydroconversion of resid A were performed in order to explore the affects of reaction variables such as temperature, tetralin-to-resid ratio, and time on the conversion of this resid. These experiments were done with and without catalyst and in some cases with hydrogen and in others in a nitrogen atmosphere. Resid A was produced from Wyodak–Anderson subbituminous coal and taken from the recycle solvent stream; it is representative of solvent being recycled to the process. The resid produced from it represents the high-boiling components of that process stream. It consists of a combination of three process streams: a portion of the second-stage flashed bottoms product, heavy distillate, and the deashed resid from the solvent deashing (Rose) unit.

Molybdenum naphthenate (6.8% molybdenum; Shepherd Chemical Co.) was the soluble catalyst used in most of this work. The catalyst was prepared by dissolving the molybdenum naphthenate in tetralin. The catalyst was then sulfided by reacting the solution with the appropriate amount of methyl disulfide for complete sulfidation. This catalyst contributed very little ash to the system, making an ash-based conversion method valid. Sulfidation appeared to be complete after the process stream passed through the preheater.

Establishing a Standard Set of Hydroconverion Conditions. To establish a set of standard conditions for running the hydroconversion of the 15 resid samples, a procedure had to be established. To achieve the greatest accuracy in the conversion kinetics, it was important to use as high a resid-to-tetralin ratio as possible. Ratios of less than 1/3, however, resulted in lower recoveries and higher than 1/3 resulted in a more dilute reaction product and somewhat lower precision. For that reason, a R/T ratio of 1/3 was selected.

Experiments were run using 0.9%, 2.0%, 3.0%, and 5.0% sulfided molybdenum naphthenate (as % Mo of the resid) to select a catalyst level. Figure 2 shows the strong effect of catalyst concentration on conversion. Hydrogen pressure was also shown to have a very significant effect on conversion (see Figure 3). With these results, "standard" conditions of 30 min at 420 °C at a 3:1 tetralin-to-resid ratio, 3 wt % sulfided molybdenum naphthenate catalyst, and 1500 psig of hydrogen pressure were selected for determination of the relative reactivity to hydroconversion of the coal-derived vacuum resids. A time of 30 min was selected to approximate the reaction time in the Wilsonville reactors.

Results and Discussion

Tables 5 and 6 show the conversions to material boiling below 454 °C (850 °F) for the thermal and 3%

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(12) *ASTM Standard Annual Book of ASTM Standards*; American Society of Testing and Materials: Philadelphia, PA, 1983; Vol.05.03, pp 442–455.

(13) *ASTM Standard Annual Book of ASTM Standards*; American Society of Testing and Materials: Philadelphia, PA, 1983; Vol 05.02, pp 791–799.

Table 5. Conversion of Thermal Hydroprocessing of Resid[a]

resid			solid residue		liquid residue			conversion to 850 °F, wt %
sample	name	ash wt %	ash wt %	TSF wt %	tetralin	RSF	850 °F+	
resid A	W258V-131B	17.0	50.1	79.7	88.2	11.8	9.6	15.0
resid B	W259R-1235	8.7	33.5	81.0	88.0	12.0	9.6	15.9
resid C	W259V-131B	8.5	35.0	82.7	86.2	13.8	10.8	17.7
resid D	W261V-131B	9.9	45.8	87.1	87.9	12.1	9.7	17.1
resid E	W262R-1235	15.6	43.5	76.0	88.4	11.6	8.6	19.6
resid F	W262V-1067	17.5	47.8	76.9	87.4	12.6	9.7	17.7
resid G	W262V-131B	15.9	46.5	78.3	88.7	11.3	8.7	18.2
resid H	W260V-131B	15.2	46.6	79.5	87.7	12.3	9.0	21.3
resid I	W261V-1067	15.9	50.8	81.8	88.9	11.1	8.5	19.4
resid J	W259V-1067	10.2	38.7	82.0	86.4	13.6	11.5	12.9
resid K	W260R-1235	17.2	49.0	78.4	86.9	13.1	9.8	19.7
resid L	W260V-1067	19.1	51.3	77.6	89.2	10.8	8.3	17.8
resid M	W261R-1235	13.7	45.6	81.1	90.1	9.9	7.9	16.0
resid N	HTI POC-01, O-43	0.4	33.0	99.2	80.6	19.4	14.1	27.0
resid O	HTI POC-02, O-43	4.1	38.0	93.1	70.6	29.4	22.4	22.1

[a] Thermal: 420 °C; 30 min; 1500 psig of H_2. Catalytic: 420 °C; 30 min; 1500 psig of H2; 3 wt % Mo. Control: 25 °C; 10 min; 1500 psig of H_2. TSF: tetralin-soluble fraction of resid, wt % (daf basis). RSF: resid-soluble fraction in tetralin, wt %. 850 °F+: fraction of boiliing above 850 °F.

Table 6. Conversion of Catalytic Hydroprocessing of Resid[a]

resid			solid residue		liquid residue			conversion wt %
sample	name	ash wt %	ash wt %	TSF wt %	tetralin	RSF in tetralin	850 °F+	
resid A	W258V-131B	17.0	51.5	80.7	82.5	17.5	9.9	35.0
resid B	W259R-1235	8.7	40.0	85.6	79.8	20.2	11.2	38.1
resid C	W259V-131B	8.5	41.4	86.8	81.4	18.6	11.5	33.1
resid D	W261V-131B	9.9	54.9	91.0	77.9	22.1	14.1	32.9
resid E	W262R-1235	15.6	44.2	76.6	80.6	19.4	11.3	32.1
resid F	W262V-1067	17.5	49.4	78.3	79.6	20.4	10.7	37.4
resid G	W262V-131B	15.9	48.3	79.8	79.2	20.8	11.5	35.8
resid H	W260V-131B	15.2	50.9	82.7	75.6	24.4	11.3	44.6
resid I	W261V-1067	15.9	56.6	85.5	76.2	23.8	11.9	42.7
resid J	W259V-1067	10.2	43.8	85.4	76.5	23.5	11.9	42.1
resid K	W260R-1235	17.2	52.1	80.8	78.1	21.9	12.4	35.2
resid L	W260V-1067	19.1	53.5	79.5	79.1	20.9	11.7	35.0
resid M	W261R-1235	13.7	53.7	86.3	80.2	19.8	11.7	35.3
resid N	HTI POC-01, O-43	0.4	36.4	99.3	67.9	32.1	16.7	47.6
resid O	HTI POC-02, O-43	4.1	48.3	95.4	70.2	29.8	19.1	34.3

[a] Thermal: 420 °C; 30 min; 1500 psig of H_2. Catalytic: 420 °C; 30 min; 1500 psig of H_2; 3 wt % Mo. Control: 25 °C; 10 min; 1500 psig of H_2. TSF: tetralin-soluble fraction, wt % (daf basis) RSF: resid-soluble fraction in tetralin, wt %. 850 °F+: fraction of boiling above 850 °F.

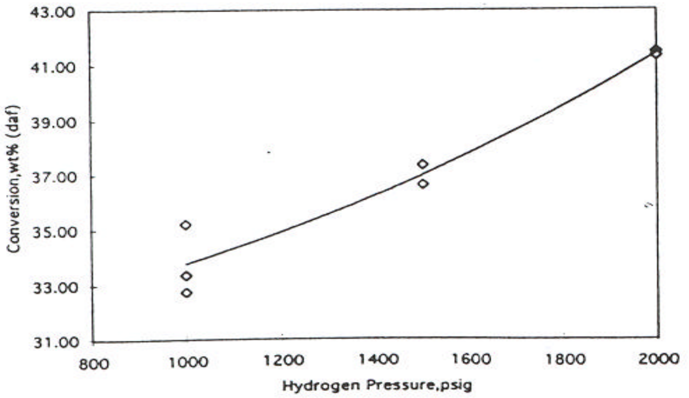

Figure 3. Influence of hydrogen pressure on the conversion of catalyzed resid (sulfided molybdenum naphthenate).

sulfided molybdenum naphthenate catalyzed runs under standard conditions for all 15 resids. It is to be noted that significant conversion to lower boiling material occurs even in the absence of catalyst. However, in the presence of the 3% molybdenum catalyst, conversion to the lower boiling material at least doubled. To attain as much as 30–40% conversion, a significant amount of catalyst is required. Only a portion (76–86%) of the resid is solubilized in the hydroprocessing. A substantial amount of the resids are soluble in tetralin even at room temperature, and processing at over 400 °C increases the solubility but not completely. Table 6 shows that the presence of the catalyst in the hydroconversion process only increases the solubilization by 1–4 %. Thermogravimetric analysis on the undissolved solids shows no material boiling below 454 °C (850 °F). The hydroconversion of the resid apparently occurs only when the resid is actually dissolved in the tetralin.

As these tables show, there is considerable variation among the resids in terms of their reactivity and convertability to lower boiling products. As apparent from the steps involved, there are several separate determinations in computing conversion where experimental error can be expected to be involved. These taken together can lead to a conversion variation of ±0.04%. Since the variation between samples is considerably greater than that, this suggests that the conversion variation is real and is due to other unidentified causes in the process. In thermal hydroprocessing, there appears to be some correlation with the coal type, i.e., the lower rank coal produces resid giving the higher conversion to low-boiling material on hydropro-

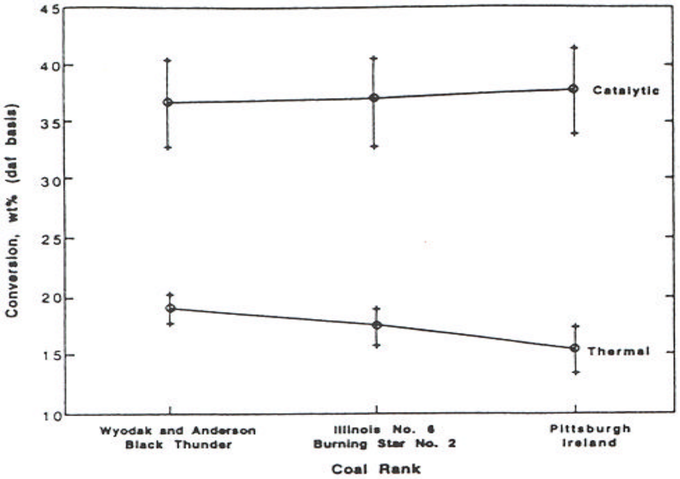

Figure 4. Thermal and catalyzed conversions of resids vs coal type and rank.

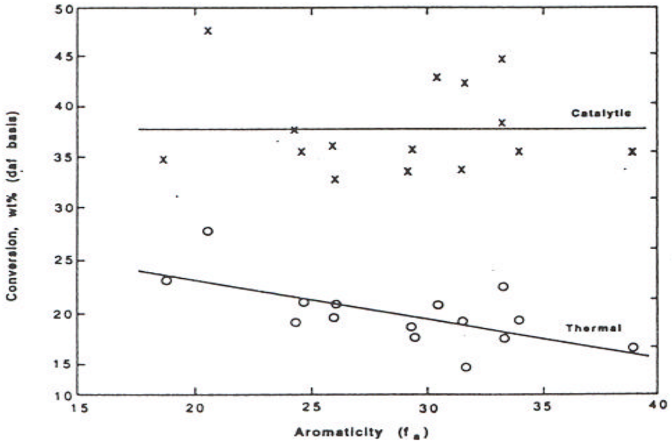

Figure 5. Thermal and catalyzed conversions of resids vs aromaticity (F_a %).

cessing in the absence of catalyst (Figure 4). On the other hand, if a catalyst is used, the resids from the three coals studied showed little or no difference in conversion under the conditions used. Apparently, the catalytic process overrides the thermal process or swamps it out.

Plots of the thermal and catalyzed conversions of resids vs the aromaticity (f_a) of the resid is shown in Figure 5. Those resids having a high aromaticity show lower conversions under thermal hydroprocessing conditions, while lower aromatic carbon containing resids show higher conversions in thermal hydroprocessing. No affect of resid aromaticity, however, is observable if a catalyst is used in the hydroliquefaction.

There appears to be no correlation of resid conversion vs wt % carbon content, hydrogen to carbon atomic ratio, or the presence of uncondensed aromatics. In none of these properties was there a clearly observable effect on the hydroconversion of resids C and H to low-boiling materials.

Kinetics of Resid Hydroconversion. Resid hydroconversion vs reaction time at two temperatures for resid C and H are shown in Figures 6 and 7. These resids were chosen as showing the highest and the lowest conversion of the resids studied under the standard conditions used. Clearly, there is at least one component of the resids which reacts rapidly, and after it is converted, the reaction becomes very slow indeed. Temperature also has a strong effect on reaction rate and conversion.

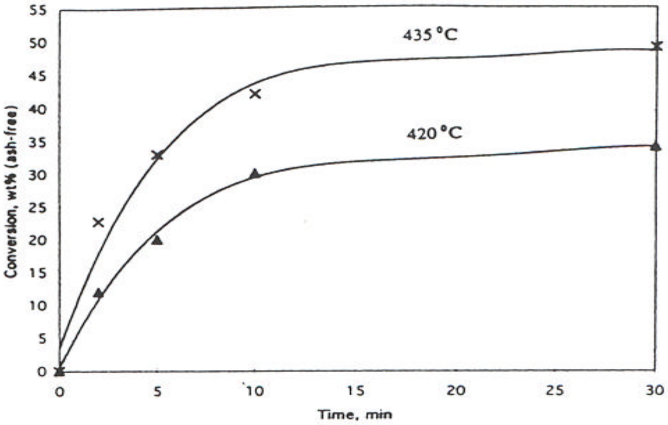

Figure 6. Conversion vs time for the catalyzed hydroprocessing of resid C (1500 psig of H_2, 3 wt % Mo, 3:1 tetralin:resid).

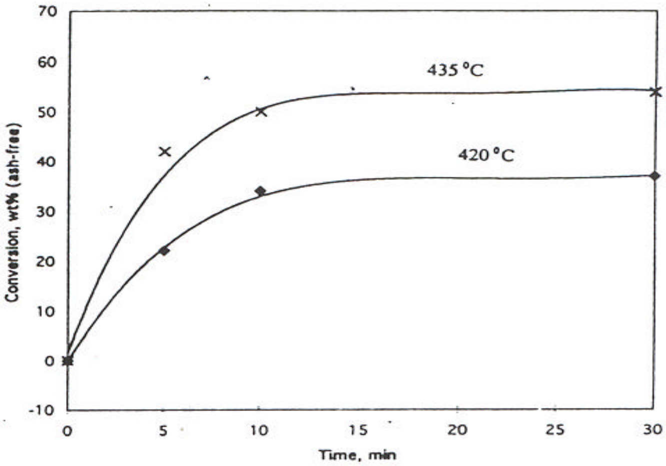

Figure 7. Conversion vs time for the catalyzed hydroprocessing of resid H (1500 psig of H_2, 3 wt % Mo, 3:1 tetralin:resid).

In an effort to get some idea of the mechanisms of the hydroconversion for resids C and H (representing the most- and least-reactive resids available), two kinetic assumptions were tried to explain the time vs conversion data: a first-order assumption and a second-order assumption (Figure 8). It was obvious from these plots for resid C that neither assumption can be interpreted as second order with confidence to resid hydroconversion (Figures 9 and 10). Benito, Callejas, and Martinez[6] found that the catalyzed conversion of coal residues to low-boiling material followed second-order kinetics. This is not inconsistent with the results obtained in this work if one considers only the early portion of the reaction. The data, however, are not sufficient to clearly identify the reaction order.

Presence of an Unconvertible Material in These Resids. Various samples of resids were washed with tetralin to extract the soluble components, and the solid

Kinetics of Catalyzed Hydroprocessing of Resid

First-order Assumption:

$$\frac{dX}{dt} = k \cdot (1 - X)$$

$$\ln(1 - X) = -k \cdot t$$

Second-order Assumption:

$$\frac{dX}{dt} = k \cdot (1 - X)^2$$

$$\frac{X}{1 - X} = k \cdot t$$

Figure 8. Kinetic equations of hydroprocessed resid.

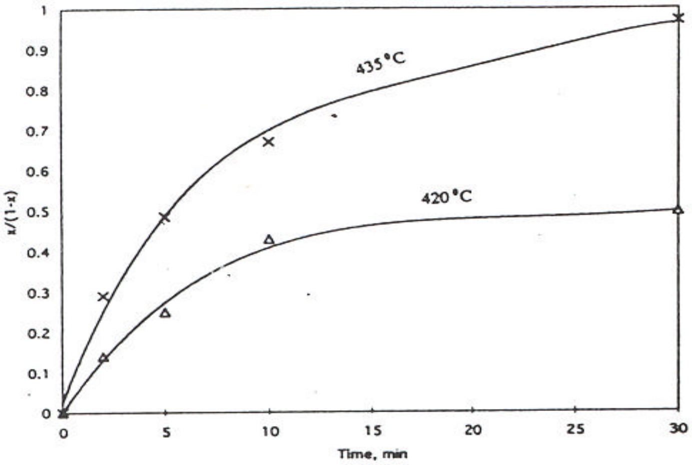

Figure 9. Kinetics of resid C (first-order assumption).

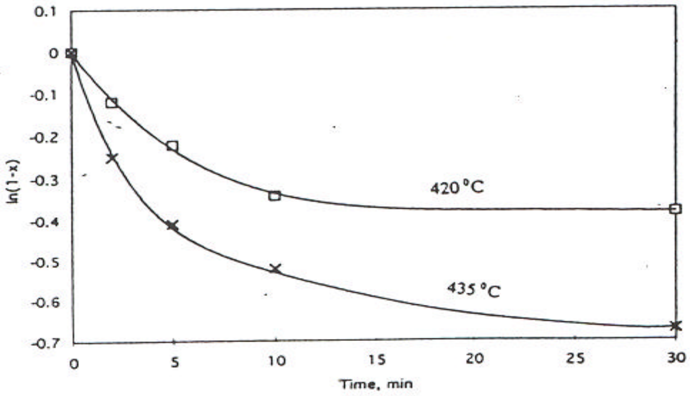

Figure 10. Kinetics of resid C (second-order assumption).

Table 7. Elemental Analysis of Solid Resid Residues

sample	original	cold tetralin washing	tetralin reflux	hydro-processing
sample no.	C161-0	C161-1	C161-2	C161-3
ultimate, day wt %				
C	82.16	65.01	52.87	44.34
H	5.93	3.21	1.83	1.56
N	0.90	1.21	1.01	0.69
S (total)	1.13	2.67	3.78	5.81
Ash	8.57	24.53	37.94	46.87
O (by diff)	1.31	3.37	2.57	0.82
H/C (atomic)	0.87	0.59	0.42	0.42

residues were exhaustively extracted with tetralin at the boiling point of tetralin in a Soxhlet extractor. The resulting solid residues were put through the reactor with tetralin and sulfided molybdenum naphthenate catalyst under the standard conditions. This material which represented some 10−15% of the resid showed only about 1% conversion to low-boiling material. Table 7 shows the elemental analysis of the extracted and unconvertible component in the resid. The low hydrogen to carbon atomic ratio suggests that the unconvertible material is a retrograde product of some sort, either present in the original coal or arising in the liquefaction process or the ensuing distillation processes.

Summary and Conclusions

The following conclusions can be drawn from these experiments: (1) With the appropriate catalyst and conditions approximating coal liquefactions, high-boiling coal-derived resids do break down to lower boiling products as they are recycled to the coal liquefaction process. (2) High catalyst activity and high hydrogen pressure are important to convert these refractory materials to lower boiling materials. (3) Solubilization of the resid in the processing solvent is necessary for the molecular breakdown. (4) There is considerable variation in the reactivity of the resids studied, even in the presence of sulfided molybdenum naphthenate catalyst. The causes of this variability may be, in part, due to the coal used in the production of the resid and, in part, due to higher aromaticity in some resids. However, these factors do not account for the very large variation in resid reactivity. (5) There is a significant portion of the resids examined that is unreactive and unconvertible to low-boiling material under the catalytic conditions investigated. The source of this unconvertible material is not known. It may arise from the original coal, from retrograde reactions in the liquefaction process, or from retrograde reactions during the product distillation or product workup. It represents a significant amount of inert material which is being recycled to the reactor, reducing the capacity of the process, thereby increasing the operating cost and investment.

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