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DIRECT LIQUEFACTION OF LOW-RANK COAL

Final Technical Report

for the period July 13, 1994 – November 30, 1995

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EXECUTIVE SUMMARY

A multistep direct liquefaction process specifically aimed at low-rank coals (LRCs) has been developed at the Energy & Environmental Research Center (EERC). The process consists of a preconversion treatment to prepare the coal for solubilization, solubilization of the coal in the solvent, and polishing using a phenolic solvent or solvent blend to complete solubilization of the remaining material. The product of these three steps can then be upgraded during a traditional hydrogenation step.

This project addressed two research questions necessary for the further development and scaleup of this process: 1) determination of the recyclability of the solvent used during solubilization and 2) determination of the minimum severity required for effective hydrotreatment of the liquid product. The project was performed during two tasks: the first consisting of ten recycle tests and the second consisting of twelve hydrotreatment tests performed at various conditions.

Different solvents have proven to be more effective in different steps during the process. It is important that the solvent(s) chosen for the Task 1 testing 1) have the hydrogen-donor characteristics needed during the pretreatment and solubilization steps, 2) have the characteristics of the phenolic solvent during the polishing step, and 3) be easily separable from heavier streams for recycling purposes. To meet these criteria, a composite feed solvent was prepared for the ten Task 1 recycle tests using equal quantities of phenolic solvent (cresylic acid) and a light fraction of hydrogenated coal-derived anthracene oil (HAO61). In the first test, the composite solvent was combined with the feed coal, and the slurry was pretreated, solubilized, and polished. The polished liquid product was combined with a vehicle solvent and distilled to remove water, solubilization solvent equal to the amount added in the polishing step, and oxygenated, light, coal-derived liquids. The solubilization solvent was recycled to the pretreatment step for the next test. This scheme was repeated for all ten multistep tests.

The Task 1 data show that the system is operationally stable. An electrical power outage resulted in a distillation error during one of the tests. Even though some solvent was not removed for recycle and was added back during a later test as additional solvent, little change was observed in product quality. Excess recycle solvent averaging about 17 wt% was produced during the Task 1 tests. During recycle, the solvent maintained its hydrogen-donor capability and appeared to approach a viable lineout composition of 32 to 34 wt% cresol (or equivalent).

The Task 2 hydrotreatment severity tests were performed to determine the lowest-severity hydrotreatment conditions that would produce high-quality liquid product. To accurately predict the conditions in as few a number of tests as possible, the tests were performed according to a statistically designed experimental matrix. The analytical and mass balance data from the Task 2

tests were used to calculate various product quality indicators which were analyzed using regression analysis. The result of the analysis was a set of mathematical equations describing the combined effects of the operating parameters on each product quality indicator. The equations were plotted over the range of operating conditions. The plots for each product quality indicator were compared to determine the lowest-severity set of operating conditions that would produce high-quality liquid product. It was determined that the lowest-severity conditions were a temperature of 678 K (405°C), a pressure of 2.07×10^4 kPa (3000 psig), and a reaction time of 60 minutes. A verification hydrotreatment test was performed at these operating conditions.

The product slate of the verification test was found to be similar to those of tests performed during earlier EERC direct liquefaction research in that in both cases, approximately 80 wt% of the moisture- and ash-free (maf) lignite fed to the pretreatment step went toward the production of distillate product and only 20 wt% of the maf coal went toward the production of gases. The verification test was performed at considerably less severe hydrotreatment conditions than the earlier tests, indicating that high-quality liquid products can be produced at low-severity conditions using the EERC multistep direct liquefaction process. The hydrotreatment temperature at which the verification test was performed was at the lower end of the valid range of the predictive equations. The effect of lowering the temperature below 678 K (405°C) cannot be determined. It is possible that an even lower temperature might effectively hydrotreat the liquid product from the multistep process.

This project showed that the solvent could be recycled during the preconversion, solubilization, and polishing steps of the multistep process and that lower-severity conditions can be used to successfully hydrotreat the product of the multistep process. The success of this project indicates that additional studies should be performed to evaluate the liquid-phase reactions taking place during batch tests in which the gas flow is continuous (i.e., the gas effects would be negligible). In addition, the entire multistep process (including hydrotreatment) should be evaluated during continuous unit operations.

DIRECT LIQUEFACTION OF LOW-RANK COAL

1.0 INTRODUCTION

Direct liquefaction research at the Energy & Environmental Research Center (EERC) has, for a number of years, concentrated on developing a direct liquefaction process specifically for low-rank coals (LRCs) through the use of hydrogen-donating solvents and solvents similar to coal-derived liquids, the water/gas shift reaction, and lower-severity reaction conditions. The underlying assumption of all of the research was that advantage could be taken of the reactivity and specific qualities of LRCs to produce a tetrahydrofuran (THF)-soluble material that might be easier to upgrade than the soluble residuum produced during direct liquefaction of high-rank coals. A multistep approach was taken to produce the THF-soluble material, consisting of 1) preconversion treatment to prepare the coal for solubilization, 2) solubilization of the coal in the solvent, and 3) polishing to complete solubilization of the remaining material. The product of these three steps could then be upgraded during a traditional hydrogenation step.

To provide a preliminary comparison between the EERC process and existing direct liquefaction processes, product slurry produced during solubilization (Step 2) and polishing (Step 3) steps (i.e., without the Step 1 pretreatment) was catalytically hydrotreated to equilibrium based upon hydrogen uptake. The hydrotreatment was performed in this manner to define the practical upper limit of the product's hydrotreatability. The results were positive, and further tests were performed incorporating the pretreatment step (Step 1). Steps 1 through 3 (pretreatment, solubilization, and polishing) were performed in an integrated fashion. The products were catalytically hydrotreated to demonstrate the maximum hydrotreatability of the solubilized slurry and to provide products that could be compared to the products of existing processes.

The results of the EERC's research indicated that additional studies to more fully develop this process were justified. Two areas were targeted for further research: 1) determination of the recyclability of the solvent used during solubilization and 2) determination of the minimum severity required for hydrotreatment of the liquid product. This project addressed these two areas.

2.0 GOALS AND OBJECTIVES

The project goals were to determine the recyclability of the solvent used during solubilization and to determine the minimum hydrotreatment severity required to upgrade the liquid product of the multistep EERC process.

The project was performed during two tasks. The first task consisted of ten recycle tests. Lignite was solubilized via the pretreatment, solubilization, and polishing steps. The product of these three steps was combined with a vehicle solvent and the resulting stream distilled to remove water, solubilization solvent, and oxygenated, light, coal-derived liquids. The overheads were further distilled to separate the water and light oil streams. The light oil was then recycled for use as the solubilization solvent in the next test sequence. The analyses of the products of these tests were used to characterize the recycle solvent stream and to calculate mass and material balances.

The second task consisted of a series of twelve hydrotreatment tests at various conditions. The tests were performed according to a statistically designed experimental matrix to enable the identification and evaluation of the most effective low-severity hydrotreatment conditions. Analyses of the products of these tests were used to characterize the hydrotreated product and to calculate mass and material balances.

3.0 EQUIPMENT

The EERC's time-sampled, batch autoclave system was used during this project. The system is capable of close-coupled multistage operation. It can be configured to multiple designs with reactor sizes ranging from 1 to 8 L. Maximum operating conditions are 5.173×10^4 kPa and 783 K (7500 psig and 510°C). System control and data acquisition are computerized, with the operators and computers located at a control panel separated from the high-pressure/high-temperature (HPT) system by a steel barricade.

4.0 TASK 1 - SOLVENT RECYCLABILITY

The Task 1 work effort included readying the equipment for operation, preparation of an appropriate composite solvent, and the Task 1 testing. The following sections detail these activities. Table 1 summarizes the tests performed during this task.

4.1 Preparation of HPT Equipment

The HPT equipment was readied for the testing. All of the system components were checked, and instrumentation was calibrated and equipment repairs made as necessary. Activities in this work effort included the following:

- An autoclave was refurbished and pressure tested.
- New o-rings were installed.
- Valves were rebuilt and hydrostatically tested.
- The charger was rebuilt.
- The cold traps were refurbished.
- The pressure transducers were recalibrated.
- The wiring was replaced on the thermocouples, and they were recalibrated.
- A new oil filter was installed in the hydraulic system.
- A new dry-volume meter was installed.

TABLE 1

Summary of Task 1 Tests

Run No.	Description	Mass Balance, %
N596	Autoclave Bay 2 calibration	NA[a]
N597	Bay 2 shakedown	100.7
N598	Redistillation of composite solvent	99.4
N599	Test 1 pretreatment and solubilization steps[b]	98.8
N600	Test 1 polishing step[b]	98.6
N601	Distillation of HAO61	98.9
N602	Repeat of Test 1 pretreatment and solubilization steps	96.0
N603	Repeat of Test 1 polishing step	98.3
N604	Fractionation of N601 overheads	99.5
N605	Distillation of simulated feed slurry	103.5
N606	Test 1 distillation of polished product	97.9
N607	Test 2 pretreatment and solubilization steps	98.6
N608	Verification of gas charge and recovery procedures	NA
N609	Test 2 polishing step	98.7
N610	Test 2 distillation of polished product	98.7
N611	Test 3 pretreatment and solubilization steps	91.6
N612	Test 3 polishing step	99.2
N613	Test 3 distillation of polished product	97.9
N614	Test 4 pretreatment and solubilization steps	98.7
N615	Test 4 polishing step	99.1
N616	Test 4 distillation of polished product	98.1
N617	Test 5 pretreatment and solubilization steps	99.3
N618	Test 5 polishing step	99.0
N619	Test 3 redistillation of bottoms from N613	97.9
N620	Test 5 distillation of polished product	99.6
N621	Test 6 pretreatment and solubilization steps	99.8
N622	Test 6 polishing step	98.8
N623	Test 6 distillation of polished product	97.2
N624	Test 7 pretreatment and solubilization steps	99.1
N625	Test 7 polishing step	98.8
N626	Test 7 distillation of polished product	97.3
N627	Test 8 pretreatment and solubilization steps	99.7
N628	Test 8 polishing step	98.9
N629	Test 8 distillation of polished product	97.4
N630	Test 9 pretreatment and solubilization steps	99.8
N631	Test 9 polishing step	98.2
N632	Test 9 distillation of polished product	96.3
N633	Test 10 pretreatment and solubilization steps	100.4
N634	Test 10 polishing step	98.8
N635	QA/QC liquid product check sample	NA
N636	QA/QC feed slurry check sample	NA
N637	Test 10 distillation of polished product	97.1

[a] Not applicable.

[b] Runs in which CH_4 was inadvertently used as the reducing gas.

- The quench was cleaned out, a new liner installed, and the head torqued.
- The gas-handling system was tested.
- The accumulators were calibrated.
- A new gas line for the letdown system was fabricated and installed.
- A new condenser coil was installed on the distillation unit, and high-temperature valves were used to replace the unit's existing valves.
- Two data-logging programs were written for the distillation unit and the autoclave system.
- The existing gas-sampling system was modified to permit collection of the product gas in a single vessel.
- The gas collection procedures for the new system were verified using both wet- and dry-test meters.
- The scale used to weigh the quench vessel was refurbished.
- A leak in the quench was repaired.
- The autoclave system in Bay 2 was pressure-tested.
- The Fluke Hydra data bucket and CO and H_2 volumes were calibrated.
- The autoclave system in Bay 2 was shaken down. The gas balance, liquid balance, and overall mass balance for the shakedown test were 103.88%, 99.09%, and 100.74%, respectively.

4.2 Preparation of Composite Feed Solvent

The EERC multistep direct liquefaction process consists of three solubilization steps (pretreatment, solubilization, and polishing) followed by a traditional hydrotreatment step. The pretreatment step consists of a 60-min soak at 448 K (175°C) in a hydrogen-donating solvent such as hydrogenated coal-derived anthracene oil (HAO61) in the presence of argon gas and H_2S. The solubilization step consists of heating the pretreated coal/solvent slurry at 648 K (375°C) for 60 min under 6.89×10^3 kPa (1000 psi) CO (cold-charge pressure). Any remaining carbonaceous material is solubilized during the polishing step, which is performed at 708 K (435°C) in the presence of a phenolic solvent such as cresylic acid (POH) and 6.89×10^3 kPa (1000 psg) H_2 (cold-charge pressure). The resulting solubilized slurry is then combined with a heavier vehicle solvent; the excess phenolic (POH) solvent and oxygenated coal-derived liquids (CDLs) are removed during distillation; and the solubilized slurry is upgraded during a traditional catalytic hydrotreatment step.

The fact that different solvents are more effective in different steps during the process means that an appropriate composite solvent is needed for the performance of the testing during this project. The composite solvent must 1) have the hydrogen-donor characteristics needed during the pretreatment and solubilization steps, 2) have the characteristics of the phenolic solvent used during the polishing step, and 3) be easily separable from heavier streams for recycling purposes.

The first step in the production of an appropriate composite solvent was to determine that the starting solvents were completely distillable. Previously produced HAO61 was distilled during Run N585 to separate any nondistillable fraction from the portion which would be used as solvent. Nondistillable fractions were defined as those that were not distillable at approximately 590 K (317°C) and about 45 kPa (2.32 psi). The results of this distillation are summarized in Table 2.

TABLE 2

Summary of Bulk Distillation of HAO61

Feed, kg	Distillable Overheads, kg	Nondistillable Bottoms, kg	% Distillable	% Recovery
14.852	13.584	1.280	91.50	100.08

A bulk sample of POH was distilled during Run N586. Virtually all of this solvent was found to be distillable at conditions of 406 K (133°C) and 10.2 kPa (1.47 psi). Table 3 presents the results of the POH bulk distillation.

TABLE 3

Summary of Bulk Distillation of POH

Feed, kg	Distillable Overheads, kg	Nondistillable Bottoms, kg	Loss, kg	% Distillable	% Recovery
0.954	0.934	0.016	0.002	98.11	99.79

The distillable HAO61 was redistilled during Run N587 to identify fractions that were lighter or heavier than the POH. (This was necessary so that the POH, light HAO61, and light CDLs could be separated from the heavier HAO61 vehicle solvent during the distillation between the polishing and hydrotreatment steps.) The mixture of components in the HAO61 did not distill into distinct light and heavy cuts so a middle cut of approximately 10 wt% was removed by distillation from the distillable HAO61 during Run N593. The light fraction was defined as the material that was removed at an overhead temperature of about 464 K (191°C) or less at a pressure of 7.7 kPa (1.12 psi). The light fraction made up 33.84 wt% of the total HAO61 stream.

The HAO61 that remained as bottoms during the distillation to remove the light material was redistilled to remove a middle fraction. The middle fraction was defined as the material that distilled over at an overhead temperature of between 464 K (191°C , the upper limit of the light

fraction) and about 479 K (206°C) at a pressure of 7.2 kPa (1.04 psi). The middle fraction made up 13.4 wt% of the total HAO61 stream.

The composite solvent was prepared for use during the testing on this project as follows. The solubilization solvent consisted of equal quantities of POH and the HAO61 light fraction. The HAO61 heavy fraction was added to the product slurry of the polishing step to serve as the vehicle solvent for the hydrotreatment step. The entire mixture was distilled to remove the POH, HAO61 light fraction, and light CDLs. The light materials were recycled back to the pretreatment and polishing steps. This solvent scheme is summarized in the block diagram shown in Figure 1.

The final step in testing the composite solvent was to verify that the POH and HAO61 light fraction could be reproducibly separated from the HAO61 heavy fraction. The light and heavy fractions of the HAO61 were combined with POH in the proportion that would be present during the distillation that follows the polishing step. (In preparing this mixture, POH was added to simulate light CDLs.) This mixture was distilled during Run N591 and the products combined and redistilled during Run N592. This process was repeated during Runs N594 and N595, at which point the composite solvent had been distilled a total of four times. The mass balance information gathered during the composite solvent distillations is summarized in Table 4. Table 4 shows that the mass balance closures were very close to 100%.

Table 4 also shows that less light material (cresylic acid [POH] and the light fraction of coal-derived, hydrogenated anthracene oil [HAO61]) was collected than was expected for these runs. The distillations were all performed at an overhead temperature of about 460 K (187°C). To quantitatively remove all light material, the distillation should have been performed at an overhead temperature closer to 479 K (206°C), the upper limit of the HAO61 middle fraction (which had

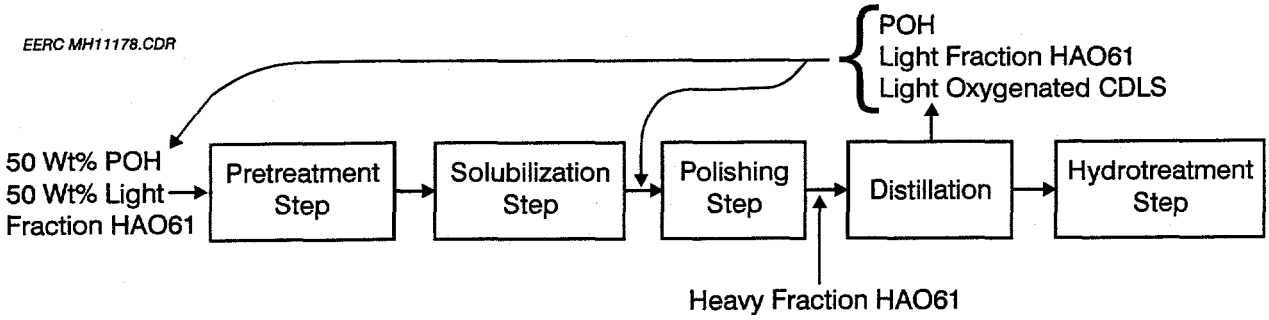

Figure 1. Block diagram summarizing the composite solvent scheme.

TABLE 4

Summary of Composite Solvent Distillation

Run No.	HAO61 Heavy Fr., kg	HAO61 Light Fr., kg	POH, kg	Total Fed, kg	Distilled Heavy Fr., kg	Distilled Light Fr., kg	Total Out, kg	Distillation Losses, kg	% of Distillate	% Recovery
P591	0.372	0.250	0.372	0.830	0.472	0.374	0.848	0.002	0.2	102.2
P592				0.822	0.458	0.364	0.822	0.0	0.0	100.0
P594	0.400	0.272	0.400	1.056	0.616	0.452	1.070	0.002	0.2	101.3
P595				1.069	0.594	0.470	1.066	0.002	0.2	99.7
P598				1.048	0.402	0.638	1.042	0.006	0.6	99.4

been removed). The distillation of the composite solvent was then repeated (Run N598) at an overhead temperature closer to 479 K (206°C) to be certain that the light material could be quantitatively recovered from the HAO61 heavy fraction. During N598, the solvent cuts from Run N595 were combined and distilled at an overhead temperature of approximately 476 K (203°C). The recovery results of this distillation are shown in Table 4. As the table shows, the quantity of light fraction collected during Run N598 was nearly identical to the quantity present in the composite solvent. The results of this distillation verified that the composite solvent could be reproducibly and quantitatively fractionated if the overhead temperature was kept close to 479 K (206°C).

4.3 Preparation of Additional HAO61 Heavy Fraction

Additional HAO61 solvent heavy fraction was needed to complete all ten of the Task 1 solvent recyclability tests. To provide the needed solvent fraction, HAO61 solvent was fractionated during Runs N601 and N604. The fractionation was performed in two steps: separating the non-distillable material from the distillable material and then fractionating the distillable material into light, middle, and heavy oil fractions. The separation of distillable from nondistillable material was performed at an overhead temperature of about 558 K (285°C) and a pressure of about 15.24 kPa (2.21 psig). The distillable material made up 90.52 wt% of the total as-received HAO61 stream. The overheads from this separation were fractionated into light, middle, and heavy oils by vacuum distillation at about 13.55 kPa (1.96 psig) pressure. The target pressure of 8.47 kPa could not be maintained. The distillation was, therefore, performed at conditions as close as possible to those of Run N593, the original HAO61 fractionation test. Vitron® hoses and heads were installed on the distillation unit to enable the target pressure to be attained during future distillations. The light oil fraction made up 36.01 wt% of the total stream while the middle oil fraction made up 13.16 wt%. Samples of each fraction were analyzed for comparison to the products of N593. Table 5 summarizes the HAO61 fractionation, and Table 6 compares the analyses of the N604 and N593 tests. As Table 6 shows, the N604 products were virtually identical to those of N593.

TABLE 5

Summary of HAO61 Fractionation

N601	Separation of distillable and nondistillable material Performed at 15.24 kPa (2.21 psig) and 558 K (285°C) Results: Nondistillable material = 9.48 wt% of material fed Distillable material = 90.52 wt% of material fed (target = 90 wt%) Mass balance = 98.94%
N604	Fraction of distillable material from N601 Performed at 13.55 kPa (1.96 psig) and 518 K (245°C) Results: Heavy fraction = 50.83 wt% of material fed Middle fraction = 13.16 wt% of material fed (target = 13.04 wt%) Light fraction = 36.01 wt% of material fed (target = 35.8 wt%) Mass balance = 99.54%

TABLE 6

Comparison of N593 and N604 Distillation Products

Analysis	N593 Light Fr.	N604 Light Fr.	N593 Heavy Fr.	N604 Heavy Fr.
Carbon, wt%	90.59	90.35	91.86	91.58
Hydrogen, wt%	8.45	8.47	6.74	6.86
Nitrogen, wt%	0.56	0.70	0.63	0.72
Sulfur, wt%	0.02	0.00	0.16	0.19
Water, wt%	0.05	0.04	0.04	0.02
Distillation[a]				
IBP	313.8	313.8	410.4	402.6
5%	349.9	352.6	415.4	414.9
10%	354.9	356.0	421.0	420.4
20%	363.2	363.2	427.6	425.4
30%	372.1	371.5	432.6	430.4
40%	377.6	377.6	437.6	434.9
50%	384.3	386.0	443.2	441.0
60%	391.5	393.8	449.9	447.6
70%	399.9	404.3	458.2	454.3
80%	410.4	414.3	469.3	464.3
90%	426.5	431.5	479.9	478.8
95%	442.6	448.8	491.5	493.2
Max. Temp., K	444.3	449.9	494.3	496.0
% Residuum	1.70	1.40	1.65	1.83
% Distillable	96.39	97.11	97.34	97.06
% Loss	1.90	1.50	1.01	1.10

[a] Distillation data are in K unless otherwise noted.

4.4 Distillation of a Simulated Product Slurry

A simulated product slurry was prepared and distilled during Run N605 to verify that the water, POH, and HAO61 light fraction could be separated from the coal and/or coal-derived liquids (CDLs)–HAO61 heavy fraction following the polishing step. The slurry contained 0.175 kg POH, 0.176 kg HAO61 light fraction, 0.351 kg HAO61 heavy fraction, and 0.295 kg Freedom lignite. Following water removal, the distillation was performed at 7.79 kPa (1.13 psig), 478 K (204.8°C) overhead temperature, and a 496 K (222.7°C) pot temperature. A 103.52% material balance was achieved.

4.5 Task 1 – Operations

Task 1 consisted of ten multistep tests. In the first test, feed coal and solubilization solvent were pretreated under CO in the presence of H_2S for 60 min. The pretreated slurry was solubilized under CO and H_2S for 60 min. The product of the solubilization step was polished with additional solvent in the presence of H_2 for 20 minutes. The polished product slurry was combined with a vehicle solvent and distilled to remove water, solubilization solvent equal to the amount added in the polishing step, and oxygenated light CDLs. If hydrotreatment were part of this task, the

bottoms from this distillation would go to the hydrotreatment step. The solubilization solvent was recycled to the pretreatment step for the next test. This scheme was repeated for all ten multistep tests. The run conditions for each of the ten tests are summarized in Table 7. A detailed description of each test is given in the subsections that follow.

4.5.1 Test 1

Test 1 was attempted as Runs N599 and N600. The N599 feed consisted of 0.35 kg Freedom lignite slurried in 0.7 kg of a 50:50 mixture of POH and HAO61 light fraction. The feed gas was supposed to be CO with H_2S used as the reaction promoter. The pretreatment was carried out for 30 min at 1.03×10^4 kPa (1500 psig) and 422 K (149°C). Following pretreatment, the temperature was increased and the solubilization step performed. Solubilization took place at 2.84×10^4 kPa (4125 psig) and 646 K (373°) for 60 min. The unit was quenched and the product recovered. The autoclave was filled with solids, an occurrence that had never happened during previous research using this particular process. Because Freedom lignite had never been used in the process before, it was decided to continue the sequence by performing the polishing step in case it was a coal-specific problem. Analytical tests were performed and operating conditions evaluated in an effort to determine why the solubilization step had not worked well. Run N600 was performed as the polishing step for the product slurry of Run N599. Approximately 0.176 kg of a 50:50 mixture of POH and HAO61 light fraction was placed in the autoclave. The unit was charged to 6.21×10^3 kPa (900 psig) H_2 and heated to 733 K (460°C). The N599 product slurry was charged to the system, held at run conditions for 20 min, and quenched.

Analysis of the N599 product gas revealed an extremely high concentration of methane. The newly delivered CO feed gas tank was sampled and found to be filled with methane. Further analyses of the products of either N599 or N600 were not performed. Preliminary data reduction was performed to check operator performance. The system was thoroughly cleaned and prepared for a second attempt at the data point. Approximately 2 weeks of operating time were lost to the gas supplier's mistake.

A second attempt at Test 1 was made during Run N602. For this run, 0.35 kg of Freedom lignite was slurried with 0.7 kg of a 50:50 mixture of POH and HAO61 light fraction and charged to the autoclave with CO and H_2S, which served as the reaction promoter. Pretreatment was performed at 425 K (152°C) and 9.67×10^3 kPa (1402 psig) for 35 min. The conditions were then increased to 650 K (377°C) and 2.40×10^4 kPa (3478 psig) for 60 min for the solubilization step. The unit was then quenched and the product recovered and sampled. The overall material balance for the test was 95.97%.

The N602 product slurry was polished during Run N603. The product slurry was charged to a preheated autoclave containing 0.179 kg of the start-up solvent and 6.21×10^3 kPa (900 psig) cold-charge pressure H_2. The unit was operated for 20 minutes at reaction conditions of 714 K (441°C) and 3.18×10^4 kPa (4605 psig). The reaction was quenched and the product collected and sampled. An overall material balance of 98.29% was achieved for the run.

The polished product from N603 was distilled during N606 to remove the light fractions for use as Test 2 solvent feed. The N603 product slurry was combined with 0.79 kg of HAO61 heavy fraction (which would serve as the vehicle solvent for the product going into the hydrotreatment

TABLE 7

Run Conditions for Task 1 Tests

Processing Step	Test Number 1	2	3	4	5	6	7	8	9	10
Pretreatment	N602	N607	N611	N614	N617	N621	N624	N627	N630	N633
Temperature, K (°C)	425 (152)	426 (153)	424 (151)	425 (152)	422 (149)	423 (150)	424 (151)	421 (148)	424 (151)	424 (151)
Pressure, kPa × 10^3 (psig)	9.67 (1402)	9.63 (1397)	9.74 (1412)	9.82 (1424)	10.05 (1458)	10.16 (1474)	10.07 (1461)	9.82 (1424)	10.18 (1477)	10.14 (1471)
Time, min	35	30	30	30	30	31	30	30	30	30
Gas	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO
Additive	H_2S	H_2S	H_2S	H_2S	H_2S	H_2S	H_2S	H_2S	H_2S	H_2S
Solubilization	N602	N607	N611	N614	N617	N621	N624	N627	N630	N633
Temperature, K (°C)	650 (377)	650 (377)	646 (373)	645 (372)	645 (372)	647 (374)	647 (374)	647 (374)	647 (374)	647 (374)
Pressure, kPa × 10^3 (psig)	23.98 (3478)	24.27 (3520)	24.55 (3560)	23.72 (3440)	23.38 (3391)	24.08 (3493)	23.78 (3449)	23.03 (3340)	22.53 (3267)	22.24 (3226)
Time, min	60	60	60	60	60	60	60	60	60	60
Polishing	N603	N609	N612	N615	N618	N622	N625	N628	N631	N634
Temperature, K (°C)	714 (441)	713 (440)	717 (434)	720 (437)	721 (438)	725 (442)	726 (443)	726 (443)	723 (440)	717 (434)
Pressure, kPa × 10^3 (psig)	31.75 (4605)	31.30 (4540)	31.54 (4575)	29.61 (4294)	27.59 (4001)	28.99 (4204)	28.59 (4147)	27.49 (3987)	25.93 (3761)	24.30 (3525)
Time, min	20	20	20	20	20	20	20	20	20	20
Gas	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2
Additive	Feed Solvent	RS-606	RS-610	RS-613	RS-616	RS-620	RS-623	RS-626	RS-629	RS-632
Distillation	N606	N610	N613	N616	N620	N623	N626	N629	N632	N637
Temperature, pot, K (°C)	494 (221)	492 (219)	492 (219)	494 (221)	494 (221)	496 (223)	496 (223)	495 (222)	495 (222)	495 (222)
Pressure, kPa × 10^3 (psig)	0.008 (1.19)	0.007 (1.10)	0.007 (1.10)	0.007 (1.09)	0.008 (1.10)	0.007 (1.09)	0.007 (1.09)	0.007 (1.09)	0.007 (1.10)	0.007 (1.08)

step). The water fraction was easily separated from the product slurry. A light oil fraction was removed at 8.23 kPa (1.19 psig), an overhead temperature of 471 K (198.2°C), and a pot temperature of 494 K (221°C). The overall material balance for the Test 1 distillation was 97.86%. After samples were taken for analysis, the light oil fraction was used as the feed solvent for Test 2.

4.5.2 Test 2

Approximately 0.325 kg of Freedom lignite was slurried with 0.65 kg of the light oil fraction from the Run N606 distillation. The autoclave was charged with slurry, CO, and H_2S. Run N607 consisted of a 30-min pretreatment performed at 9.63×10^3 kPa (1397 psig) and 426 K (153°C), followed by solubilization at 2.43×10^4 kPa (3520 psig) and 650 K (377°C). The unit was quenched and the product recovered. An overall material balance of 98.62% was achieved for this run.

The product slurry from Run N607 was polished during Run N609. The slurry was hot-charged to an autoclave containing 0.162 kg of recycle solvent and H_2. The polishing step was performed at an average temperature of 713 K (440°C) and 3.13×10^4 kPa (4540 psig) for 20 min. The reaction was quenched and product recovered. A material balance of 98.74% was achieved for the polishing step.

The N609 product slurry was combined with HAO61 heavy fraction and distilled during Run N610. Water was removed and the distillation performed at end-point conditions of 7.55 kPa (1.10 psig) and 492 K (219°C) to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 3.

4.5.3 Test 3

Test 3 was performed as Runs N611, N612, and N613. During Run N611, approximately 0.342 kg of moisture- and ash-free (maf) Freedom lignite was slurried with 0.65 kg of the recycle solvent obtained from the Run N610 distillation. The autoclave was charged with slurry, CO, and H_2S, which served as the reaction promoter. The pretreatment was performed at 424 K (151°C) and 9.73×10^3 kPa (1412 psig) for 30 minutes. The conditions were then increased to 646 K (373°C) and 2.45×10^4 kPa (3560 psig) for 60 min for the solubilization step. The unit was quenched and the product recovered and sampled. The overall material balance for the test was 99.0%.

The N611 product slurry was polished during Run N612. The product slurry was charged to a preheated autoclave containing 0.171 kg of recycle solvent and H_2. The polishing step was performed at average conditions of 707 K (434°C) and 3.15×10^4 (4575 psig) for 20 min. The reaction was quenched and the product recovered. The polishing step overall material balance was 99.2%.

The N612 polished product slurry was combined with 0.82 kg HAO61 heavy fraction and distilled during Run N613. Water was removed and the distillation performed at end-point conditions of 7.58 kPa (1.10 psig) and 492 K (219°C) to separate the light oil fraction from the

heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 4. A mass balance of 97.9% was attained for the Test 3 distillation step.

An unexpected electrical power outage occurred prior to Run N613. The equipment was preliminarily tested to be sure that it still operated, but the pressure transducer calibration was not tested. Because it was no longer in calibration, the distillation was not performed at the correct conditions, and approximately 20% of the light organics remained in the bottoms. This changed the composition of the recycle organics used as the solvent in the Test 4 feed slurry. The bottoms from the N613 distillation were redistilled during N619, and the appropriate light material was collected for readdition to the system.

During analysis it was noted that some light organic material was removed with the aqueous phase during distillation. This material was phenolic in nature and made up approximately 10% to 16% of the aqueous stream. The organics were gravity-separated for readdition to the system with the additional light organics collected during the N619 distillation.

4.5.4 Test 4

Runs N614, N615, and N616 made up Test 4. The pretreatment and solubilization steps were performed as Run N614. Approximately 0.300 kg of maf Freedom lignite was slurried with 0.590 kg of recycle solvent obtained from the N613 distillation. The slurry was cold-charged to the autoclave with CO and H_2S, the reaction promoter. The pretreatment was performed at 425 K (152°C) and 9.82×10^3 kPa (1424 psig) for 30 min. Solubilization was performed at 645 K (372°C) and 2.37×10^4 kPa (3440 psig) for 60 min. After the unit was quenched, the product was recovered and sampled. The overall material balance for these two integrated steps was 98.7%.

The N614 product slurry was charged to a preheated autoclave containing 0.151 kg recycle solvent and H_2 for Run N615. The average polishing conditions were 710 K (437°C) and 2.96×10^4 kPa (4294 psig) for 20 minutes. The reaction was quenched and product recovered. An overall material balance of 99.1% was achieved for the polishing step.

The polished product slurry from N615 was combined with 0.68 kg HAO61 heavy fraction and distilled during Run N616. Water was removed from the organics and the distillation performed at the end-point conditions of 7.52 kPa (1.09 psig) and 494 K (221°C) pot temperature to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 5. An overall mass balance of 98.1% was achieved for the Test 4 distillation.

4.5.5 Test 5

Test 5 was performed as Runs N617, N618, and N620. During Run N617, approximately 0.249 kg of maf Freedom lignite was slurried with 0.493 kg of the recycle solvent obtained from the Run N616 distillation. The autoclave was charged with slurry, CO, and H_2S, which served as the reaction promoter. The pretreatment was performed at 422 K (149°C) and 1.01×10^4 kPa (1458 psig) for 30 minutes. The conditions were then increased to 645 K (372°C) and 2.34×10^4 kPa (3391 psig) for 60 minutes for the solubilization step. The unit was quenched and the product recovered and sampled. The overall material balance for the test was 99.3%.

The N617 product slurry was polished during Run N618. The product slurry was charged to a preheated autoclave containing 0.127 kg of recycle solvent and H_2. The polishing step was performed at average conditions of 711 K (438°C) and 2.76×10^4 kPa (4001 psig) for 20 min. The reaction was quenched and the product recovered and sampled. The polishing step overall material balance was 99.0%.

The N618 polished product slurry was combined with 0.59 kg HAO61 heavy fraction and distilled during Run N620. Water was removed and the distillation performed at end-point conditions of 7.58 kPa (1.10 psig) and 494 K (221°C) pot temperature to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 6.

4.5.6 Test 6

The additional light organics obtained from the N619 distillation (i.e., the redistillation of the N613 distillation bottoms) as well as the light oil removed from the aqueous phase separated during distillation were added to the N620 recycle solvent. Approximately 0.524 kg of this mixture was combined with 0.266 kg maf Freedom lignite to form the feed slurry for Run N621, the pretreatment and solubilization steps for Test 6. The slurry was cold-charged to the autoclave with CO and H_2S, the reaction promoter. The 30-min pretreatment step was performed at 423 K (150°C) and 1.02×10^4 kPa (1474 psig). The solubilization step was performed at 647 K (374°C) and 2.41×10^4 kPa (3493 psig) for 60 min. An overall mass balance of 99.8% was achieved for this run.

The resulting product slurry was polished during Run N622. In this run, the slurry was hot-charged into an autoclave containing H_2 and 0.13 kg recycle solvent. The polishing step lasted 20 minutes and was performed at 715 K (442°C) and 2.90×10^4 kPa (4204 psig). After the reaction was quenched, the product was recovered and sampled. The polishing step overall mass balance was 98.8%.

The polished product slurry was distilled during Run N623. Water was removed and the distillation was performed at end-point conditions of 496 K (223°C) pot temperature and 7.52 kPa (1.09 psig) to separate the light oil fraction from the heavier fraction. The lighter organic fraction was recycled for use as the feed solvent for Test 7. A mass balance of 97.2% was calculated for the distillation step.

4.5.7 Test 7

Runs N624, N625, and N626 made up Test 7. The pretreatment and solubilization steps were performed as Run N624. Approximately 0.258 kg of maf Freedom lignite was slurried with 0.497 kg of recycle solvent obtained from the N623 distillation. The slurry was cold-charged to the autoclave with CO and H_2S, the reaction promoter. The pretreatment was performed at 424 K (151°C) and 1.01×10^4 kPa (1461 psig) for 30 min. Solubilization was performed at 647 K (374°C) and 2.38×10^4 kPa (3449 psig) for 60 min. After the unit was quenched, the product was recovered and sampled. The overall material balance for these two integrated steps was 99.1%.

The N624 product slurry was charged to a preheated autoclave containing 0.129 kg recycle solvent and H_2 for Run N625. The average polishing conditions were 716 K (443°C) and 2.86 × 10^4 kPa (4147 psig) for 20 min. The reaction was quenched and product recovered and sampled. An overall material balance of 98.8% was achieved for the polishing step.

The polished product slurry from N625 was combined with 0.57 kg HAO61 heavy fraction and distilled during Run N626. Water was removed from the organics and the distillation performed at the end-point conditions of 7.52 kPa (1.09 psig) and 496 K (223°C) pot temperature to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 8. An overall mass balance of 97.3% was achieved for the Test 7 distillation.

4.5.8 Test 8

Runs N627, N628, and N629 made up Test 8. The pretreatment and solubilization steps were performed as Run N627. Approximately 0.232 kg of maf Freedom lignite was slurried with 0.456 kg of recycle solvent obtained from the N626 distillation. The slurry was cold-charged to the autoclave with CO and H_2S, the reaction promoter. The pretreatment was performed at 421 K (148°C) and 9.82 × 10^3 kPa (1424 psig) for 30 min. Solubilization was performed at 647 K (374°C) and 2.37 × 10^4 kPa (3440 psig) for 60 min. After the unit was quenched, the product was recovered and sampled. The overall material balance for these two integrated steps was 99.7%.

The N627 product slurry was charged to a preheated autoclave containing 0.114 kg recycle solvent and H_2 for Run N628. The average polishing conditions were 716 K (443°C) and 2.75 × 10^4 kPa (3987 psig) for 20 min. The reaction was quenched and product recovered and sampled. An overall material balance of 98.9% was achieved for the polishing step.

The polished product slurry from N628 was combined with 0.51 kg HAO61 heavy fraction and distilled during Run N629. Water was removed from the organics and the distillation performed at the end-point conditions of 7.52 kPa (1.09 psig) and 495 K (222°C) pot temperature to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 9. An overall mass balance of 97.4% was achieved for the Test 8 distillation.

4.5.9 Test 9

Test 9 was performed as Runs N630, N631, and N632. During Run N630, approximately 0.214 kg of maf Freedom lignite was slurried with 0.424 kg of the recycle solvent obtained from the Run N629 distillation. The autoclave was charged with slurry, CO, and H_2S, which served as the reaction promoter. The pretreatment was performed at 424 K (151°C) and 1.02 × 10^4 kPa (1477 psig) for 30 min. The conditions were then increased to 647 K (374°C) and 2.25 × 10^4 kPa (3267 psig) for 60 min for the solubilization step. The unit was quenched and the product recovered and sampled. The overall material balance for the test was 99.8%.

The N630 product slurry was polished during Run N631. The product slurry was charged to a preheated autoclave containing 0.105 kg of recycle solvent and H_2. The polishing step was performed at average conditions of 713 K (440°C) and 2.59 × 10^4 kPa (3761 psig) for 20 min.

The reaction was quenched and the product recovered and sampled. The polishing step overall material balance was 98.2%.

The polished product slurry from Run N631 was combined with 0.47 kg HAO61 heavy fraction and distilled during Run N632. Water was removed from the organics and the distillation performed at the end-point conditions of 7.6 kPa (1.1 psig) and 495 K (222°C) pot temperature to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Test 10. An overall mass balance of 96.3% was achieved for the Test 9 distillation step.

4.5.10 Test 10

Runs N633, N634, and N637 made up Test 10. The pretreatment and solubilization steps were performed as Run N633. Approximately 0.191 kg of maf Freedom lignite was slurried with 0.325 kg of recycle solvent obtained from the N632 distillation. The slurry was cold-charged to the autoclave with CO and H_2S, the reaction promoter. The pretreatment was performed at an average temperature of 424 K (151°C) and an average pressure of 1.01×10^4 kPa (1471 psig) for 30 min. Solubilization was performed at 647 K (374°C) and 2.22×10^4 kPa (3226 psig) for 60 min. After the unit was quenched, the product was recovered and sampled. The overall material balance for these two integrated steps was 100.4%.

The N633 product slurry was charged to a preheated autoclave containing 0.097 kg recycle solvent and H_2 for Run N634. The average polishing conditions were 707 K (434°C) and 2.43×10^4 kPa (3525 psig) for 20 min. The reaction was quenched and product recovered. An overall material balance of 98.8% was achieved for the polishing step.

The polished product slurry from N634 was combined with 0.43 kg HAO61 heavy fraction and distilled during Run N637. Water was removed from the organics and the distillation performed at the end-point conditions of 495 K (222°C) pot temperature and 7.45 kPa (1.08 psig) to separate the light oil fraction from the heavier fraction. An overall mass balance of 97.1% was achieved for the Test 10 distillation.

4.6 FT-IR Speciation Tests

Detailed analyses were performed to determine more accurately the changes in composition of the light solvent as it was recycled during the Task 1 testing. Two types of tests were performed. The first analysis determined the relative aromatic concentration in the recycle solvent, providing an indication of the ability of the solvent to maintain its hydrogen donor characteristics during processing. Fourier transform infrared spectroscopy (FT-IR) was used to determine the relative aromatic concentrations. Samples of the recycle solvent were dissolved in carbon tetrachloride at a concentration of 20.0 mg recycle solvent/mL carbon tetrachloride. The infrared absorbance of the sample was determined at 3037 cm^{-1}, corresponding to the frequency for the aromatic C–H stretching band. The results of this analysis are presented in Table 8.

TABLE 8

Relative Aromatic Concentrations in Recycle Solvent

Test Number	C–H Absorbance
1	0.35
4	0.34
7	0.36
10	0.35

The second test determined the cresol (or equivalent) concentration in the solvent. Samples of the recycle solvent were dissolved in dioxane at a concentration of 20.0 mg recycle solvent/mL dioxane. The infrared absorbance of the samples was determined at 3345 cm^{-1}, the frequency for the phenolic OH that is exclusively hydrogen-bonded to dioxane. Table 9 shows the results of this analysis.

TABLE 9

Cresol Concentrations in Recycle Solvent

	Cresol Concentration	
Test Number	mg/mL	wt% of Sample
1	8.3	42
4	7.5	38
7	7.0	35
10	6.7	34

4.7 Discussion of Results

The material balances for the Task 1 solvent recyclability tests are presented in Table 10. The recoveries for each of the steps are similar. The liquid balance for the pretreatment/ solubilization step ranged from 90.4% to 91.7% and from 95.9% to 97.7% for the polishing step. The overall mass balances for the pretreatment/solubilization step ranged from 96.0% to 100.4%, for the polishing step from 98.2% to 99.2%, and for the distillation step from 96.3% to 99.6%. The consistency of the mass balances is indicative of the operational stability of the system. Overall mass balances of at least 96.0% indicate that significant leaks or spills that might have skewed the data did not occur. The data appear to reliably describe the multistep process.

Table 11 shows the distillate yields and solvent balances for each of the Task 1 tests. During the original distillation, some of the distillable material from Test 3 was not collected. The distillation bottoms were redistilled, and the additional material collected was added to the recycle solvent stream used in the Test 6 feed slurry. The table shows that as a result of the lower fraction of light distillate present in Tests 4 and 5, the solvent recovery dropped from approximately 15% excess solvent to about 5% excess solvent. Excess solvent was produced in each of the tests, with an average excess solvent production for all tests of 16.81 wt%. Excluding the low solvent balances for Tests 4 and 5, the average excess solvent produced is 19.48 wt%.

TABLE 10

Mass and Material Balances for Task 1 Tests

	Gas Balance, %	Liquid Balance, %	Overall Mass Balance, %
Test 1			
Pretreatment/Solubilization	122.6	91.4	96.0
Polishing	169.5	97.3	98.2
Distillation	NA[a]	NA	97.9
Test 2			
Pretreatment/Solubilization	135.8	91.7	98.6
Polishing	197.9	97.3	98.7
Distillation	NA	NA	98.7
Test 3			
Pretreatment/Solubilization	140.9	91.7	99.0
Polishing	205.6	97.7	99.2
Distillation	NA	NA	97.9
Test 4			
Pretreatment/Solubilization	132.1	91.6	98.7
Polishing	220.0	97.2	99.1
Distillation	NA	NA	98.1
Test 5			
Pretreatment/Solubilization	131.8	91.0	99.3
Polishing	196.1	97.2	99.0
Distillation	NA	NA	99.6
Test 6			
Pretreatment/Solubilization	138.9	90.8	99.8
Polishing	222.1	96.7	98.8
Distillation	NA	NA	97.2
Test 7			
Pretreatment/Solubilization	133.7	90.8	99.1
Polishing	219.4	96.7	98.8
Distillation	NA	NA	97.3
Test 8			
Pretreatment/Solubilization	133.8	90.5	99.7
Polishing	212.7	96.7	98.9
Distillation	NA	NA	97.4
Test 9			
Pretreatment/Solubilization	131.5	90.4	99.8
Polishing	210.6	95.9	98.2
Distillation	NA	NA	96.3
Test 10			
Pretreatment/Solubilization	129.8	90.7	100.4
Polishing	183.4	96.9	98.8
Distillation	NA	NA	97.1

[a] Not applicable.

TABLE 11

Distillate Yields and Solvent Balances for Task 1 Tests

	Hydrotreatable Solubles, wt% maf[a]			
Test No.	Liquid Basis[b]	Gas Basis[c]	Solvent Yield, wt% maf	Solvent Balance, %
1	79.52	87.02	42.01	116.42
2	71.23	86.49	68.17	127.75
3	86.00	86.08	46.27	118.57
4	86.02	85.00	13.67	105.47
5	82.61	83.08	17.12	106.80
6	83.35	79.63	49.53	120.00
7	79.57	83.83	39.52	115.84
8	72.86	79.86	44.88	118.07
9	75.90	79.44	45.03	117.96
10	81.60	81.69	47.20	121.22
Average	79.87	83.21	41.34	116.81

[a] Weight percentage of moisture- and ash-free coal fed to the system.
[b] Yield calculated from liquid stream mass balance data.
[c] Yield calculated by subtracting the gas yield from unity.

The product yield structures of the ten Task 1 tests are shown in Table 12. The values are expressed in weight percentages equivalent to the quantity of maf lignite fed to the pretreatment/solubilization step of each test. Approximately 20 wt% of the maf lignite fed to the system went toward the production of gaseous products and water while about 80 wt% of the maf lignite went toward the production of liquid products. The table shows that, in general, the product slates for each test are fairly consistent.

Tables 8 and 9 presented the results of the FT-IR detailed speciation tests. As seen in Table 9, the cresol concentration appears to be approaching a constant value of approximately 32 to 34 wt% of the recycle solvent stream. This is easily seen in Figure 2, a plot of the cresol concentration in the sample for each test. The recycle cresol concentration agrees with that attained during direct liquefaction research performed in 1983 at the EERC which indicated that solvent lineout occurred at about 32 wt% phenolics after 40 passes through the system (1). Table 8 shows that the number of aromatic C–H bonds did not change significantly during the test sequence, indicating that the solvent maintained its hydrogen-donor capabilities.

4.8 Conclusions

Several conclusions can be drawn from the Task 1 test results:

- The data reliably describe the first steps of the EERC multistep direct liquefaction process.

TABLE 12

Yield Structures for Task 1 Solvent Recyclability Tests[a]

	Test Number									
	1	2	3	4	5	6	7	8	9	10
Gas Out										
CO	-38.79	-39.06	-37.58	-38.91	-37.77	-36.87	-38.37	-37.99	-38.86	-35.13
H_2	0.98	1.25	0.68	0.97	1.35	0.23	0.07	0.22	0.41	0.79
CO_2	71.78	72.16	70.32	72.32	71.15	73.14	72.70	75.38	76.68	70.01
C1-C3	3.07	3.38	3.39	3.85	3.98	4.81	5.03	5.23	5.49	2.95
H_2S	-1.70	-1.71	-1.22	-0.76	0.06	0.38	-1.08	-0.73	-0.67	0.03
H_2O	-14.58	-9.68	-21.25	-22.83	-21.32	-23.53	-18.08	-14.24	-19.09	-19.03
Total Gas + Water	20.76	26.34	14.34	14.64	17.45	18.16	20.27	27.87	23.96	19.62
Liquid Out										
Liquid to HT Step[b]	79.52	71.23	86.00	86.02	82.61	83.35	79.57	72.86	75.90	81.60
Ash	-0.29	2.42	-0.36	-0.67	-0.06	-1.50	0.15	-0.72	0.14	-1.22
Total Liquids	79.23	73.65	85.64	85.35	82.55	81.85	79.72	72.14	76.04	80.38
Total, All Products	99.99	99.99	99.98	99.99	100.00	100.01	99.99	100.01	100.00	100.00

[a] Product slates given are based upon percentage of maf coal fed to the pretreatment/solubilization step. Positive values indicate production of a component; negative values indicate a consumption.

[b] Liquid products that will be hydrotreated during the hydrotreatment step.

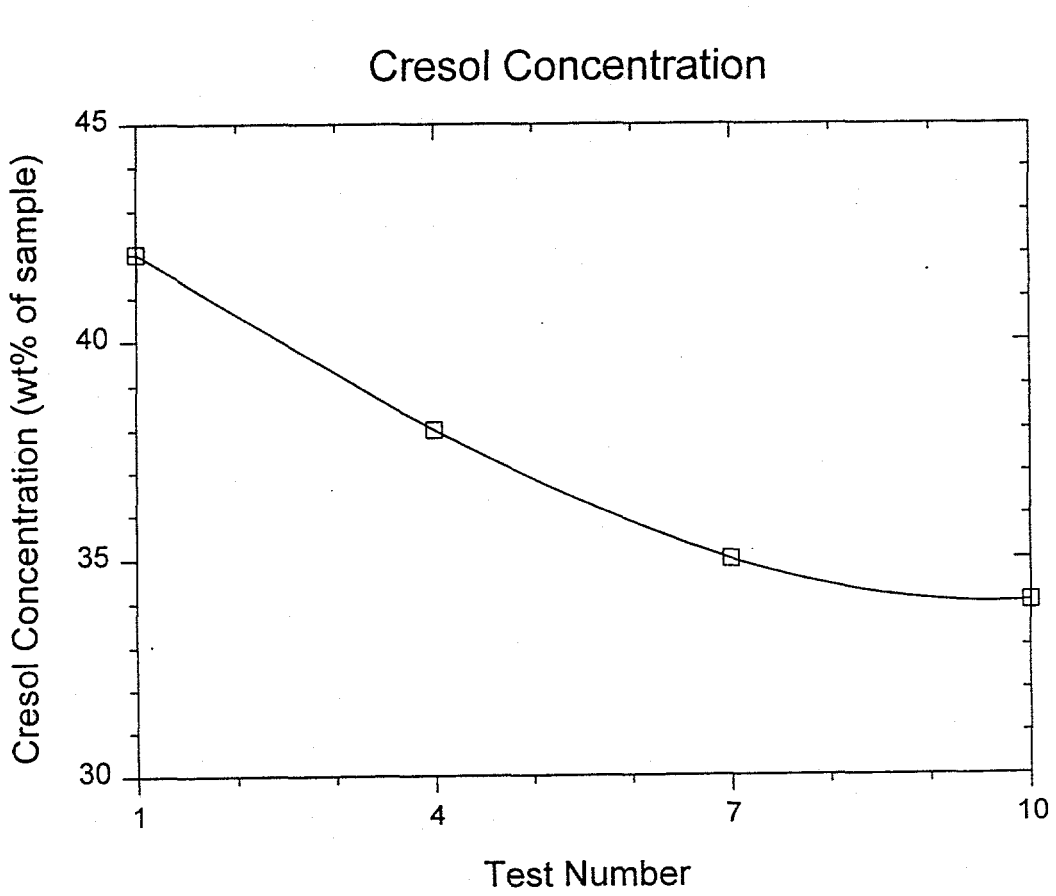

Figure 2. Cresol concentration in recycle solvent as a function of test number.

- The system is operationally stable. Even when some solvent was not removed for recycle (as in Test 3) or was added back as additional solvent (as in Test 6), little change in product quality was observed.
- Excess solvent was produced for each multistep test.
- Product yield structures were fairly constant for all tests.
- The process produces recycle solvent consisting of approximately 32 to 34 wt% cresol (or equivalent).
- The recycle solvent maintains its hydrogen-donor capability.

In general, the Task 1 testing showed that it is possible to produce a consistent, viable recycle solvent stream using the EERC multistep direct liquefaction process.

5.0 TASK 2 - HYDROTREATMENT SEVERITY STUDY

The purpose of the Task 2 study was to determine the lowest-severity hydrotreatment conditions that produce high-quality liquid product. Because funding availability limited the

number of tests that could be performed, a statistical approach to data collection was chosen because it would result in the prediction of the lowest-severity conditions with a relatively small number of tests.

5.1 Experimental Matrix Development

The Task 2 testing took place according to a statistically designed experimental matrix. This method of testing was chosen because statistical strategies generally achieve the experimental goal in a smaller number of experiments, provide the greatest degree of reliability to the conclusions, and minimize the risk of overlooking something of practical importance. The results of such an experimental matrix can be statistically analyzed to develop mathematical equations describing the process. A factorial design consisting of 10 tests was employed to test the effects of three factors (temperature, pressure, and residence time) on product quality. Maximum and minimum conditions of each factor were used for eight of the tests. Two tests were performed at center point conditions to permit a determination of lack of fit of the equations. The matrix was randomized to minimize skewing of data that can occur when one variable is held constant for several tests in a row. The equations developed from analysis of the results of the ten factorial tests were used to determine the lowest-severity hydrotreatment conditions that would result in a desirable product slate. The test matrix is presented in Table 13, while Table 14 summarizes all of the runs performed during Task 2.

TABLE 13

Task 2 Experimental Matrix

Test No.	Temperature	Pressure	Residence Time, min
1	Multistep test to produce solubilized slurry for hydrotreatment		
2	698 K (425°C)	1.724×10^4 kPa (2500 psig)	73
3	718 K (445°C)	1.324×10^4 kPa (1920 psig)	112
4	698 K (425°C)	1.724×10^4 kPa (2500 psig)	73
5	718 K (445°C)	1.324×10^4 kPa (1920 psig)	34
6	678 K (405°C)	1.324×10^4 kPa (1920 psig)	112
7	678 K (405°C)	2.124×10^4 kPa (3080 psig)	34
8	718 K (445°C)	2.124×10^4 kPa (3080 psig)	112
9	678 K (405°C)	2.124×10^4 kPa (3080 psig)	112
10	678 K (405°C)	1.324×10^4 kPa (1920 psig)	34
11	718 K (445°C)	2.124×10^4 kPa (3080 psig)	34
12	Verification test at conditions indicated by statistical analysis		

TABLE 14

Summary of Task 2 Tests

Run No.	Description	Mass Balance, %
N638	Test 1 – Hydrotreatment Feed Preparation	NA[a]
N639	Catalyst Preparation	99.0
N640	Catalyst Preparation	96.4
N641	Test 2	96.9
N642	Test 3	95.2
N643	Catalyst Preparation (possible feed gas contamination)	NA
N644	Catalyst Preparation	96.1
N645	Test 4	97.9
N646	Test 5	98.3
N647	Catalyst Preparation	96.4
N648	Test 6 (thermocouple failed)	NA
N649	Test 6	98.6
N650	Test 7	99.9
N651	Test 8 (stirrer leaked)	NA
N652	Test 10	98.7
N653	Test 11 (head leaked)	89.2
N654	Catalyst Preparation	97.8
N655	Test 9	98.5
N656	Test 11	98.7
N657	Blank Run	99.4
N658	Test 8	95.1
N659	Catalyst Preparation	98.8
N660	QA/QC Check Sample	NA
N661	Temperature and Pressure Calibration	NA
N662	Test 12	98.5

[a] Not applicable.

5.2 Task 2 Operations

5.2.1 Test 1, Hydrotreatment Feed Preparation

The liquid product from Task 1 Tests 1, 2, 4, and 6 were combined into a single sample to be used as the feedstock for the Task 2 tests. Preparation of the feed slurry was designated as Run N638. The composite sample was well mixed and sampled. The analysis of the composite feed is presented in Table 15.

TABLE 15

Analysis of Composite Feed for Hydrotreatment Severity Tests

Component	Analysis, wt%
C	87.85
H	6.42
N	1.08
S	0.40
Ash	2.83
THFI[a]	5.49

[a] Tetrahydrofuran insolubles.

5.2.2 Catalyst Preparation

Shell 424 catalyst was activated during several tests. Activation was performed by reaction with H_2S and H_2 for 180 min. Run conditions for these tests are given in Table 16.

TABLE 16

Catalyst Preparation Run Conditions

Run No.	Temperature, K (°C)	Pressure, kPa
N639	698 (425)	1.09×10^4
N640	698 (425)	1.16×10^4
N643	---[a]	---[a]
N644	699 (426)	1.15×10^4
N647	699 (426)	1.14×10^4
N654	698 (425)	9.80×10^3
N659	698 (425)	1.13×10^4

[a] Feed gas for run was possibly contaminated with nitrogen.

5.2.3 Test 2

Approximately 0.225 kg composite feed and 0.043 kg sulfided Shell 424 catalyst were charged to the 1-l autoclave for Run N641, the second matrix point. Hydrotreatment took place at an average temperature of 698 K (425°C) and an average pressure of 1.67×10^4 kPa (2419 psig) for 73 min. A liquid balance of 99.1%, a gas balance of about 44.3%, and an overall material balance of 96.9% were achieved for this test.

5.2.4 Test 3

Test 3 was performed as Run N642. Approximately 0.225 kg composite feed and 0.043 kg sulfided Shell 424 catalyst were charged to the 1-l autoclave. Hydrotreatment took place at an average temperature of 716 K (443°C) and an average pressure of 1.33×10^4 kPa (1930 psig) for 112 min. A liquid balance of 97.8%, a gas balance of 44.9%, and an overall material balance of 95.2% were achieved for this test.

5.2.5 Test 4

Test 4 was performed as Run N645. Approximately 0.219 kg composite feed and 0.044 kg sulfided Shell 424 catalyst were charged to the 1-l autoclave. Hydrotreatment took place at an average temperature of 698 K (425°C) and an average pressure of 1.71×10^4 kPa (2485 psig) for 73 min. A liquid balance of 100.3%, a gas balance of 41.8%, and an overall material balance of 97.9% were achieved for this test.

5.2.6 Test 5

Approximately 0.217 kg composite feed and 0.043 kg sulfided Shell 424 catalyst were charged to the 1-l autoclave during Run N646. Hydrotreatment took place at an average temperature of 715 K (442°C) and an average pressure of 1.34×10^4 kPa (1937 psig) for 34 min. A liquid balance of 100.0%, a gas balance of 39.1%, and an overall material balance of 98.3% were achieved for this test.

5.2.7 Test 6

Test 6 was originally attempted as Run N648. A thermocouple failed during this test, and the test was repeated as Run N649. Approximately 0.217 kg composite feed and 0.043 kg sulfided Shell 424 catalyst were charged to the 1-l autoclave. The hydrotreatment was performed at an average temperature of 679 K (406°C) and an average pressure of 1.33×10^4 kPa (1934 psig) H_2 for 112 min. A liquid balance of 99.9%, a gas balance of about 53.5%, and an overall material balance of 98.6% were achieved for this test.

5.2.8 Test 7

Test 7 was performed as Run N650. Approximately 0.213 kg composite feed and 0.043 kg sulfided Shell 424 catalyst were charged to the 1-l autoclave. Hydrotreatment took place at an average temperature of 677 K (404°C) and an average pressure of 2.12×10^4 kPa (3081 psig) H_2

for 34 min. A liquid balance of 102.2%, a gas balance of 47.4%, and an overall material balance of 99.9% were achieved for this test.

5.2.9 Test 8

The stirrer leaked during the first attempt at Test 8 (Run N651), resulting in a 78% liquid recovery. Because this value did not meet the quality assurance criterion of a material balance (≥95 wt%), the test was repeated as Run N658. The autoclave was charged with 0.204 kg composite feed and 0.041 kg sulfided Shell 424 catalyst. The hydrotreatment was performed at an average pressure of 2.11×10^4 kPa (3060 psig) H_2 and an average temperature of 715 K (442°C) for 112 min. A liquid balance of 99.6%, a gas balance of 37.1%, and an overall material balance of 95.1% were achieved for this test.

5.2.10 Test 9

Test 9 was performed as Run N655. The 1-l autoclave was charged with 0.211 kg composite feed and 0.042 kg sulfided Shell 424 catalyst. Hydrotreatment took place at an average temperature of 679 K (406°C) and an average pressure of 2.13×10^4 kPa (3089 psig) H_2 for 112 min. A liquid balance of 101.2%, a gas balance of 45.3%, and a material balance of 98.5% were achieved for the test.

5.2.11 Test 10

Test 10 was performed as Run 652. The autoclave was charged with 0.212 kg composite feed and 0.042 kg sulfided Shell 424 catalyst. The hydrotreatment was performed at an average temperature of 676 K (403°C) and an average pressure of 1.32×10^4 kPa (1921 psig) H_2 for 34 min. A liquid balance of 99.8%, a gas balance of 44.9%, and an overall material balance of 98.7% were achieved for this test.

5.2.12 Test 11

Test 11 was first attempted as N653. The autoclave developed a head leak halfway through the run; the resulting overall material balance was only 89.2%. The test was redone as Run N656. The 1-l autoclave was charged with 0.206 kg composite feed and 0.041 kg sulfided Shell 424 catalyst. The hydrotreatment was performed at an average temperature of 712 K (439°C) and an average pressure of 2.10×10^4 kPa (3048 psig) H_2 for 34 min. A liquid balance of 101.0%, a gas balance of 48.2%, and an overall material balance of 98.7% were achieved for this test.

5.3 Statistical Analysis of Results

The analytical and mass balance data from the Task 2 tests were used to calculate various product quality indicators, including the saturated molar H:C ratio of the hydrotreated product; the percent improvement in saturated molar H:C ratio of the product over that of the solubilized feed slurry; the distribution of product as pot residue, middle oil, light oil, and cold trap liquids; the hydrogen consumption of the hydrotreatment step; the yield of hydrocarbon gases from the hydrotreatment step; and the ratio of hydrocarbon gas yield to hydrogen consumption. These values were combined with the operating parameters (i.e., temperature, pressure, and residence

time) to form the data set that was statistically analyzed. The data set is presented in Table 17. The operating parameters were the independent variables, and the product quality indicators were the dependent variables during the statistical analysis. The operating parameters were read by the Statistical Analysis System (SAS) computer program used for the statistical analyses as functions equaling approximately -1, 0, or 1. These functions were defined as presented in Table 18.

The product quality indicators were analyzed using regression analysis. The effect on product quality of each operating parameter or combination of parameters was determined for each indicator by using both backwards elimination and stepwise regression analyses. During a regression analysis, the degree of effect of all independent variables and their combinations on the dependent variable is determined. When the backwards elimination procedure is employed, the independent variable having the least (statistically) significant effect on the dependent variable is dropped. The procedure is repeated until the remaining independent variables are all considered to significantly affect the dependent variable. The stepwise procedure is the reverse of the backwards elimination procedure, in that independent variables are added until one is found not to be statistically significant. The mathematical equation indicated by both regression procedures describes the combined effect of the independent variables on a given dependent variable. Each equation was checked for statistical lack of fit to the data. All of the equations were found to fit the data at a 90% confidence interval.

The ranges and center points of each operating parameter are given in Table 19. Spreadsheets were constructed for each product quality indicator by inputting values of the operating parameters over their ranges and calculating the value of a given product quality indicator using the mathematical equation derived during statistical analysis. Nonsignificant operating parameters were held constant at their center point values during these calculations. The calculated product quality indicators were plotted to show what the values would be at various operating conditions that were not actually tested. Two sets of plots were produced: three-dimensional surface plots and contour plots. Trends are easier to see on the three-dimensional surface plots, while specific conditions resulting in specific indicator values are more easily seen on the contour plots. The various trends indicated by the statistical analysis are discussed in the following subsections, accompanied by the three-dimensional surface plots.

5.3.1 Saturated Molar H:C

The goal of coal liquefaction is to add hydrogen to the organic components to produce a lighter product. The first step in determining the quantity of hydrogen added during the processing is to calculate the saturated molar hydrogen-to-carbon ratio for both the feed and products. The equation describing the saturated molar H:C as a function of the operating parameters was found during statistical analysis to be:

$$\text{Saturated molar H:C} = 0.31269683 + 0.015402\,X_1 + 0.03127663\,X_3 + 0.01165106\,X_2X_3$$

The equation shows that hydrogen addition to the coal structure depends upon the reaction time, the pressure, and the interaction of the temperature and the pressure. Several different plots of the equation were made to show the changes in saturated molar H:C as the operating parameters were changed. The plots are presented in Figure 3 and show that the saturated molar H:C increases linearly with an increase in either reaction time or pressure, although the pressure has a

TABLE 17

Task 2 Statistical Analysis Data Set

Run No.	Reaction Time, min	Temp., K	Pressure, kPa	Saturated Molar H:C	H:C Improvement, %	Pot Residue, wt% of product	Middle Oil, wt% of product	Light Oil, wt% of product	Cold-Trap Liquids, wt% of product	H_2 Consumed, wt%	HC Gas Yield, wt%	HC Gas Yield:H_2 Consumed
N641	73	698	1.67×10^4	0.3119	42.29	12.25	74.18	8.10	5.47	2.53	1.52	0.6012
N642	112	716	1.33×10^4	0.2737	24.86	16.22	62.05	12.31	9.42	4.31	3.92	0.9106
N645	73	698	1.71×10^4	0.3213	46.56	11.66	75.77	9.36	3.21	3.05	1.18	0.3859
N646	34	715	1.34×10^4	0.2599	18.56	11.51	78.05	7.67	2.77	2.33	1.10	0.4728
N649	112	679	1.33×10^4	0.3083	40.63	16.26	72.61	6.76	4.37	1.69	0.82	0.4850
N650	34	677	2.12×10^4	0.3109	41.80	10.58	80.60	5.50	3.32	3.35	0.30	0.0895
N652	34	676	1.32×10^4	0.2779	26.77	12.96	82.74	2.72	1.58	1.03	0.31	0.3046
N655	112	679	2.13×10^4	0.3585	63.54	10.57	76.86	8.32	4.25	3.28	0.60	0.1818
N656	34	712	2.10×10^4	0.3305	50.73	10.29	68.75	15.97	4.99	3.35	1.04	0.3119
N658	112	715	2.11×10^4	0.3635	65.80	8.32	50.01	30.77	10.90	6.21	3.18	0.5127

TABLE 18

Definition of Independent Variables Used During Statistical Analysis

Variable	Definition
X_1	(Reaction Time in Minutes - 73)/39
X_2	(Temperature in °C - 423)/20
X_3	(Pressure in psig - 2505)/584

TABLE 19

Center Point Conditions and Valid Range of Mathematical Equations

Variable	Valid Range	Center Point
X_1 (reaction time)	34–112 min	73 min
X_2 (temperature)	678–718 K (405°–445°C)	698 K (425°C)
X_3 (pressure)	1.32×10^4 - 2.12×10^4 kPa (1920–3080 psig)	1.72×10^4 kPa (2500 psig)

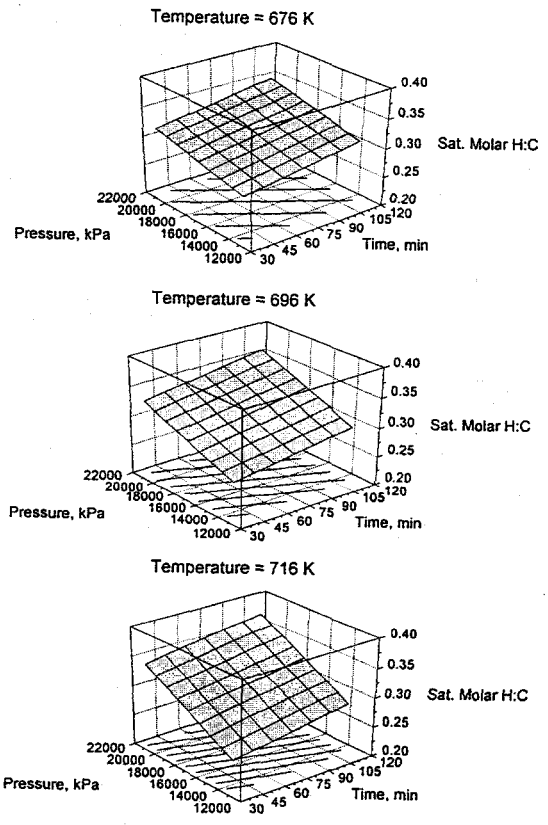

Figure 3. Plots showing the effect of operating parameters on the saturated molar H:C ratio.

greater effect than the reaction time. The change in H:C ratio increases as the temperature is increased. The largest saturated molar H:C of 0.37 occurs at a pressure of about 2.10×10^4 to 2.14×10^4 kPa (3050 to 3100 psig), a temperature of about 716 K (443°C), and a reaction time of at least 110 min.

5.3.2 Improvement in Saturated Molar H:C

The effectiveness of hydrogen addition during the hydrotreatment step can be easily determined by comparing the saturated molar hydrogen-to-carbon ratios of the product to the feed, i.e., the improvement in this ratio. The equation that was developed to describe the effect of the operating parameters on the improvement of the saturated molar H:C is:

$$\text{Improvement in H:C} = 0.42635712 + 0.07030996\, X_1 + 0.142578\, X_3 + 0.05308855\, X_2X_3$$

Since the saturated molar H:C is used in the calculation of the improvement of the H:C ratio, it would be expected that the equation would show that the improvement in H:C is affected by the pressure, the reaction time, and the interaction of the temperature and pressure. This is exactly what the equation indicates. Figure 4 shows the plots that were generated by applying this equation over the range of the operating parameters. The greatest improvement in saturated molar H:C during the hydrotreatment step is predicted to be about 60%. Such improvement requires that the hydrotreatment step be performed at a pressure higher than about 1.93×10^4 kPa (2800 psig) and a temperature of 716 K (443°C) for at least 60 min.

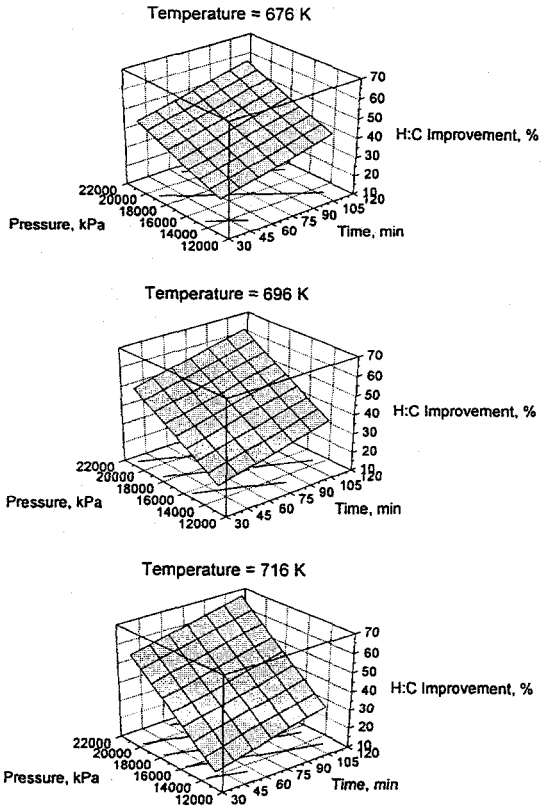

Figure 4. Plots showing the effect of operating parameters on the improvement in saturated molar H:C ration

5.3.3 Pot Residue

One important product quality indicator is the product's distillation characteristics. The fractions of the liquid product stream that appear as pot residue, middle oil, light oil, and cold-trap liquids were evaluated. The equation developed to describe the effect of the operating parameters on the production of pot residue is:

$$\text{Pot residue} = 0.12027092 + 0.00788226\,X_1 - 0.00586668\,X_2 - 0.02207834\,X_3 - 0.01262655\,X_2X_3$$

The production of pot residue material is affected by reaction time, pressure, temperature and the interaction between time and pressure. Pot residue production increases with reaction time at low pressures but actually decreases with reaction time at high pressures. The production of pot residue decreases with either increased pressure or increased temperature. Figure 5 is a plot of the predicted pot residue production over the entire range of operating conditions. Ideally, the production of pot residue should be minimized in order to maximize the production of the desired middle oil fraction. Figure 5 shows that the pot residue production can be minimized at 10% of the liquid product stream at either a pressure of 2.00×10^4 kPa (2800 psig), a reaction time longer than 30 min, and a temperature of 716 K (443°C) or at a pressure of 2.14×10^4 kPa (3100 psig) and a temperature of 676 K (403°C) for a reaction time longer than 105 min.

5.3.4 Middle Oil

The middle oil fraction of hydrotreated product was determined and statistically analyzed. The equation describing the effect of the operating parameters on the production of middle oil is:

$$\text{Middle oil} = 0.72328574 - 0.05616614\,X_1 - 0.07465351\,X_2 - 0.02673068\,X_3 - 0.02842754\,X_1X_2 - 0.03439456\,X_2X_3$$

Middle oil production is affected by reaction time, temperature, and pressure as well as the reaction time–temperature and temperature–pressure interactions. Figure 6 shows the plot of the middle oil production equation over the range of operating conditions. As the figure shows, middle oil production decreases when reaction time is lengthened or when temperature is increased. Increasing pressure enhances these changes. Middle oil is the preferred product of the hydrotreatment step and can be maximized at about 80 wt% of the liquid product stream if the hydrotreatment step is performed at a temperature less than 708 K (435°C) and a pressure of about 1.32×10^4 kPa (1920 psig) for 60 min or less. If the temperature is kept between about 678 and 683 K (405° to 410°C), the same middle oil production can be accomplished by operation at a pressure of 2.13×10^4 kPa (3090 psig) for less than 80 min.

5.3.5 Light Oil

The fraction of liquid product made up by light oil was statistically analyzed. The equation that was developed to describe the effect of the operating parameters on the production of light oil is:

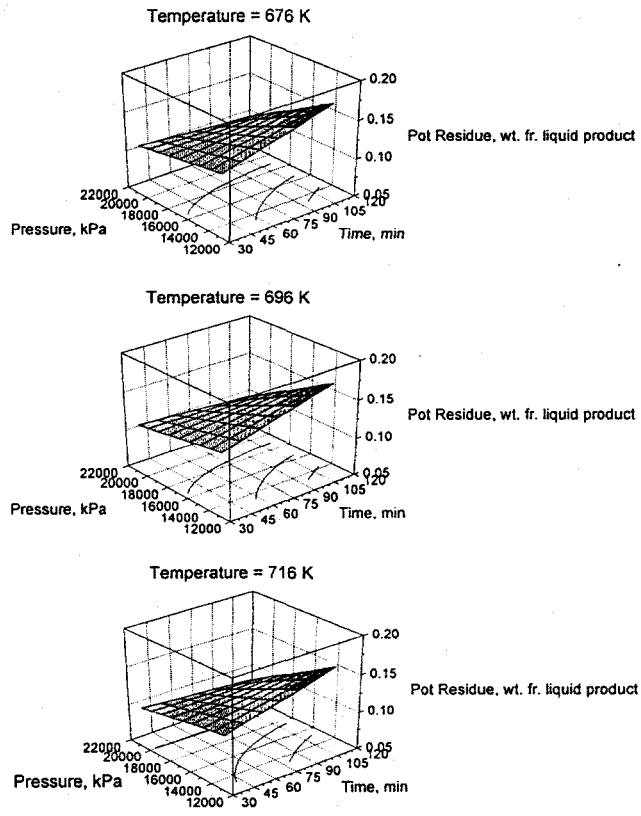

Figure 5. Plots showing the effect of operating parameters on the production of pot residue.

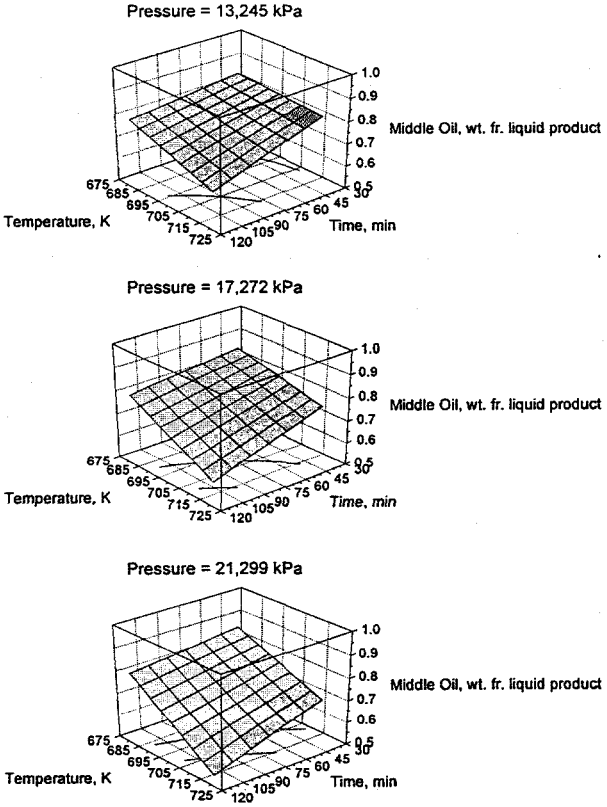

Figure 6. Plots showing the effect of operating parameters on the production of middle oil.

$$\text{Light oil} = 0.10783603 + 0.02915696X_1 + 0.06067492X_2 + 0.04190558\,X_3 + 0.03497495\,X_2X_3$$

The equation shows that the light oil production is affected by the reaction time, temperature, pressure, and the interaction between the temperature and the pressure. The equation was plotted over the range of operating conditions. The resulting plots are shown in Figure 7. The figure shows that light oil production increases as temperature increases. At low temperatures, there is very little change in light oil production as pressure is increased, while at high temperatures, a significant increase in light oil production can be seen to correspond with an increase in pressure. Lengthening the reaction time also increases light oil production. Light oils can be minimized to make up about 5 wt% of the hydrotreated liquid product stream if reaction time is limited to about 35 min at a pressure of 2.14×10^4 kPa (3100 psig) and a temperature of about 683 K (410°C). If the temperature is increased to about 703 K (430°C), the pressure can be decreased to about 1.31×10^4 kPa (1900 psig) to accomplish the same light oil production.

5.3.6 Cold-Trap Liquids

The cold-trap liquids make up the rest of the liquid product stream. The equation describing the effect of hydrotreatment operating conditions on cold-trap liquid production is:

$$\text{Cold trap liquids} = 0.04923549 + 0.01917977\,X_1 + 0.01942403\,X_2 + 0.01242015\,X_1X_2$$

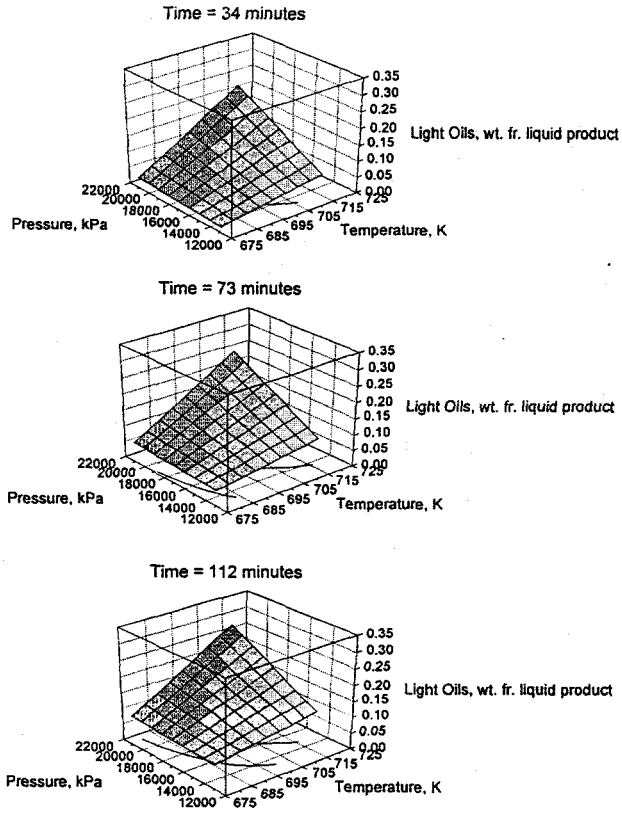

Figure 7. Plots showing the effect of operating parameters on the production of light oil.

The production of cold-trap liquids is affected by the reaction time, temperature, and the interaction between these two parameters. The equation was plotted over the range of operating conditions, and the resulting plot is shown in Figure 8. As the plot shows, the cold-trap liquid production increases slightly with temperature at short reaction times. The increase in production with increase in temperature is much greater at longer reaction times. Similarly, cold-trap liquid production increases with time only slightly at low temperatures, but to a much greater degree at higher temperatures. Cold-trap production can be minimized to less than 3 wt% of the liquid product stream when hydrotreatment takes place either at a temperature of less than 698 K (425°C) for less than 40 min or at a temperature of about 678 K 405°C for less than 75 min.

5.3.7 Hydrogen Consumption

The amount of hydrogen gas that is consumed is related to the incorporation of hydrogen into the liquid product. The mathematical equation describing hydrogen consumption as a function of operating conditions is:

$$\text{Hydrogen consumption} = 0.0308566 + 0.00616869\,X_1 + 0.00946022\,X_2 + 0.00902330\,X_3 + 0.00583292\,X_1X_2$$

The equation indicates that the hydrogen consumption is affected by reaction time, temperature, pressure, and the interaction between reaction time and temperature. The hydrogen consumption increases with increases in either temperature or pressure. As reaction time is lengthened, the increase due to temperature is much more significant. These relationships can be seen in Figure 9, plots of the hydrogen consumption equation over the range of operating

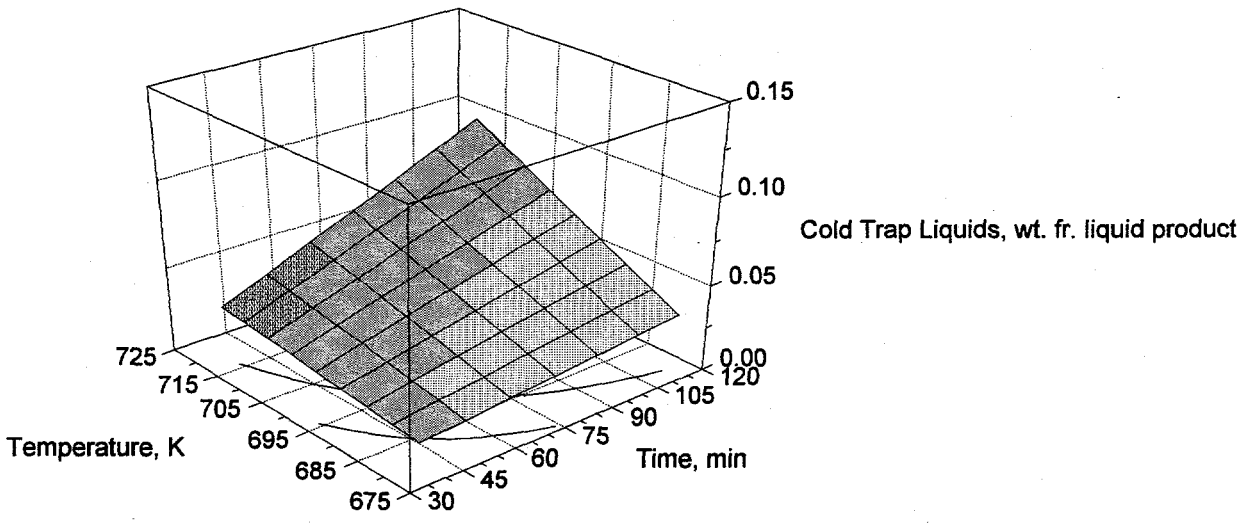

Figure 8. Plots showing the effect of operating parameters on the production of cold-trap liquids.

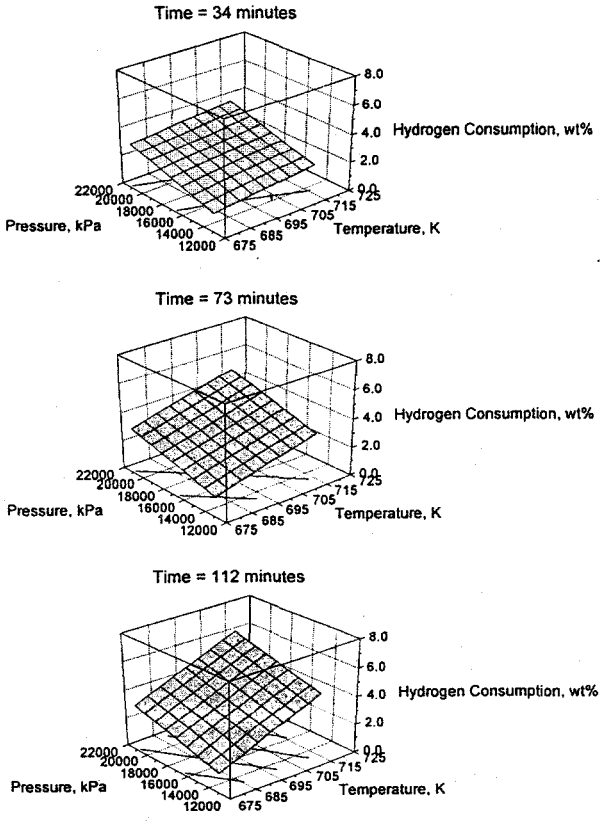

Figure 9. Plots showing the effect of operating parameters on hydrogen consumption.

conditions. The plots indicate that the maximum hydrogen consumption of about 6% can be attained when the pressure is at least 2.07×10^4 kPa (3000 psig), the temperature is greater than 713 K (440°C), and the reaction time is about 110 min.

5.3.8 Hydrocarbon Gas Yield

The goal of liquefaction processes is to maximize the production of liquid products while minimizing the production of gaseous products. Unfortunately, the severe conditions required to produce the desired liquid products can result in either cracking of the coal or reaction with hydrogen to hydrocarbon gases at the expense of liquid production. The mathematical equation describing the hydrocarbon gas yield in terms of the operating conditions is:

$$\text{Hydrocarbon gas yield} = 0.01346489 + 0.0066227\ X_1 + 0.00984582\ X_2 + 0.00575482\ X_1X_2$$

The equation shows that the hydrocarbon gas yield is affected by the reaction time, the temperature, and the interaction between time and temperature. The equation was plotted over the entire range of operating conditions and is shown in Figure 10. The figure shows that hydrocarbon gas production increases with time slightly at lower temperatures, but that the increase with longer reaction times is much more pronounced at higher temperatures. The same is true for temperature: at shorter reaction times, the hydrocarbon gas production increases only slightly with an increase in temperature and the increase is much greater at longer reaction times. The hydrocarbon gas yield

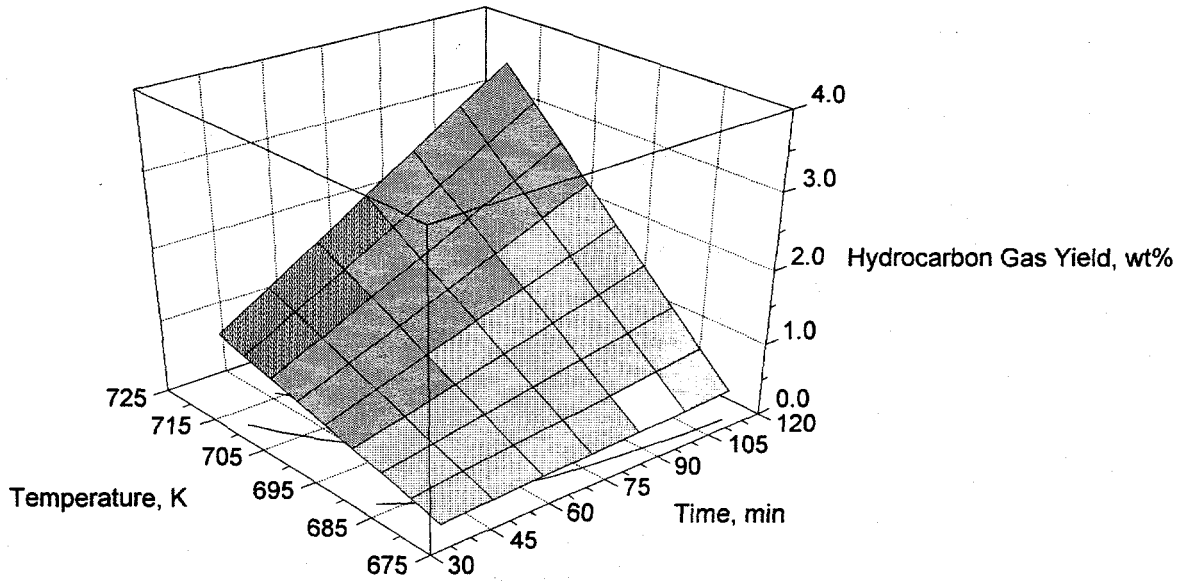

Figure 10. Plots showing the effect of operating parameters on the yield of hydrocarbon gases.

can be minimized at 0.5 wt% if the hydrotreatment is performed at a temperature less than 678 K (405°C) for at least 80 min. If the reaction time is shortened to 35 min, it is necessary to increase the temperature to 688 K (415°C) to obtain similar results.

5.3.9 Ratio of Hydrocarbon Gas Yield to Hydrogen Consumption

A simple index for determining that the hydrogen consumed during hydrotreatment resulted in the production of liquids rather than the production of hydrocarbon gas is the ratio of the yield of hydrocarbon gas to hydrogen consumption. The equation describing this ratio in terms of the operating conditions is:

$$\text{Hydrocarbon gas yield:hydrogen consumption} = 0.41828366 + 0.10597888\,X_1 + 0.1546914\,X_2 - 0.13796217\,X_3$$

The equation shows that this ratio is affected by reaction time, pressure, and temperature. The equation was plotted over the entire range of operating conditions and is shown in Figure 11. As the plot shows, the ratio increases linearly with increases in either reaction time or temperature. Increased pressure decreases the ratio of hydrocarbon gas yield to hydrogen consumption. Because liquid products are preferred, a small hydrocarbon gas-to-hydrogen consumption ratio is desired. The smallest ratio occurs at a pressure of 2.13×10^4 kPa (3089 psig), a temperature of less than 688 K (415°C), and a reaction time of less than 60 min.

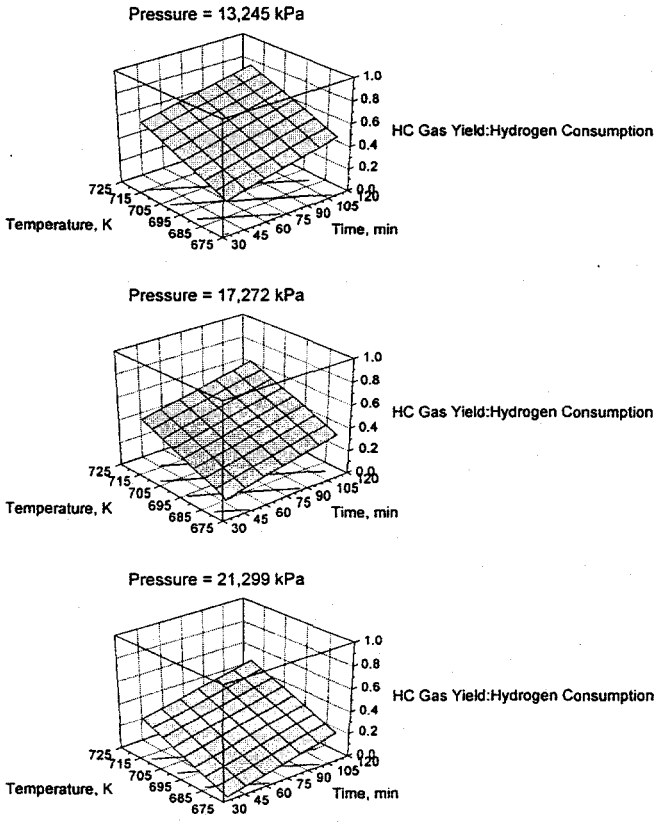

Figure 11. Plots showing the effect of operating parameters on the ratio of hydrocarbon gas yield to hydrogen consumption

5.4 Verification Test

Desired criteria were determined for each of the product quality indicators as follows:

- Saturated molar H:C ratio – maximize
- Improvement in saturated molar H:C ratio – maximize
- Pot residue fraction of product slurry – minimize
- Middle oil fraction of product slurry – maximize
- Light oil fraction of product slurry – minimize
- Cold-trap liquid fraction of product slurry – minimize
- Hydrogen consumption – maximize
- Hydrocarbon gas yield – minimize
- Hydrocarbon gas yield:hydrogen consumption – minimize

Comparing the various plots, the set of conditions that would meet most of the product quality indicator criteria at the lowest processing severity was determined to be:

Temperature = 678 K (405°C)
Pressure = 2.07×10^4 kPa (3000 psig)
Reaction time = 60 min

A verification test (Test 12) was performed at these conditions.

Test 12 was performed as Run 662. The autoclave was charged with 0.210 kg composite feed and 0.042 kg sulfided Shell 424 catalyst. The hydrotreatment was performed at an average temperature of 678 K (405°C) and an average pressure of 2.07×10^4 kPa (2998 psig) H_2 for 60 min. A liquid balance of 101.0%, a gas balance of 47.0%, and an overall material balance of 98.5% were achieved for the verification test.

5.5 Discussion of Results

The mathematical equations were used to predict the product quality indicator values at the verification test conditions. The predicted values are compared with the Run N662 actual values in Table 20. The data show that the equations predicted the product quality indicator values fairly accurately.

TABLE 20

Predicted and Actual Product Quality Indicator Values for the Verification Test

Product Quality Indicator	Predicted Value	Actual Value
Saturated Molar H:C	0.3252	0.3306
H:C Improvement, %	48.33	50.82
Pot Residue, wt% of product slurry	10.78	7.72
Middle Oil, wt% of product slurry	80.42	86.16
Light Oil, wt% of product slurry	5.23	1.43
Cold-Trap Liquids, wt% of product slurry	2.91	4.69
Hydrogen Consumption, %	2.97	1.96
Hydrocarbon Gas Yield, %	0.41	0.36
HC Gas Yield:H_2 Consumption	0.1268	0.1822

The hydrotreatment temperature at which the verification test was performed was at the lower end of the valid range of the predictive equations. The effect of lowering the temperature below 678 K (405°C) cannot be determined. Therefore, it is possible that an even lower temperature might effectively hydrotreat the liquid product from the multistep process. The hydrotreated product yield structures for the Task 2 tests are presented in Table 21.

5.6 Conclusions

- The mathematical equations derived during statistical analysis of the data effectively predicted the effects of changing the hydrotreatment operating parameters on product quality.

- The composite solvent used during the Task 1 test sequence produced solubilized material that could be as effectively hydrotreated as the product of batch tests using optimal solvents for each step.

TABLE 21

Yield Structures of Integrated Task 2 Hydrotreatment Tests[a]

	N641	N642	N645	N646	N649	N650	N652	N655	N656	N658	N662
Reaction Time, min	73	112	73	34	112	34	34	112	34	112	60
Temperature, K	698	716	698	715	679	677	676	679	712	715	678
Pressure, kPa × 10^{-4}	1.67	1.33	1.71	1.34	1.33	2.12	1.32	2.13	2.10	2.11	2.07
Gas Out											
CO, wt%	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
H_2, wt%	-9.48	-14.86	-11.03	-8.85	-6.93	-11.89	-4.92	-11.70	-11.86	-20.43	-9.63
CO_2, wt%	11.31	11.31	11.31	11.31	11.31	11.31	11.31	11.31	11.31	11.31	11.31
C1-C3, wt%	8.42	15.69	7.37	7.14	6.29	4.72	4.76	5.61	6.95	13.35	5.24
H_2O, wt%	6.74	6.81	10.78	6.63	6.82	6.63	6.58	7.07	8.62	6.54	8.45
Total, wt%	17.41	19.36	18.84	16.64	17.91	11.18	18.15	12.71	15.43	11.19	15.78
Liquid Out											
Solvent, wt%[b]	38.10	38.10	38.10	38.10	38.10	38.10	38.10	38.10	38.10	38.10	38.10
HT Oil, wt%[c]	37.26	35.48	35.97	38.23	36.91	43.75	36.72	42.28	39.39	43.80	39.10
Total Liquid, wt%	75.36	73.58	74.07	76.33	75.01	81.85	74.82	80.38	77.49	81.90	77.20
IOM[d], wt% (by difference)	7.24	7.06	7.08	7.02	7.07	6.97	7.03	6.91	7.08	6.91	7.02
Conversion, %	92.76	92.94	92.92	92.98	92.93	93.03	92.97	93.09	92.92	93.09	92.98

[a] Product slates given include all steps (pretreatment, solubilization, polishing, distillation, and hydrotreatment) and are based upon percentage of maf coal fed to the pretreatment step. The effect of the water-gas shift reaction was calculationally removed, resulting in hydrogen-equivalent values. Positive values indicate production of a component; negative values indicate a consumption.

[b] Average yield of excess solvent leaving the polishing step.

[c] Distillate material produced during the hydrotreatment (HT) step.

[d] Insoluble organic material.

- The products of the Task 2 hydrotreatment tests had more favorable yield structures (i.e., lower hydrocarbon gas yield, lower total gas yield, and higher liquid production) than did any of the products of the multistep tests performed during EERC research in 1992.

- High hydrotreatment temperature (about 713 K or 440°C) results in the production of hydrocarbon gases at the expense of the production of desirable liquid products, especially when reaction time exceeds 100 minutes.

- An increase in pressure improves total liquid yield. Because the production of appropriate distillate material is crucial to a favorable yield structure, it is doubtful that hydrotreatment reaction severity can be reduced by reducing operating pressure. Reductions in hydrotreatment severity must therefore come from reductions in either temperature or reaction time or both.

- Reaction time can probably be reduced to approximately 30 minutes without a substantial reduction in product quality.

- It may be possible to reduce hydrotreatment temperature to less than 673 K (400°C) while maintaining desired product quality and yield.

- The EERC multistep direct liquefaction process produces a liquid that requires less severe hydrotreatment conditions than are employed during traditional direct liquefaction processing.

The product slate of Run N662 (the verification test) is compared with the product slate of Run N562 in Table 22. Run N562 was the most successful integrated multistep test performed during previous EERC liquefaction research. As Table 22 shows, the yield structures for these two runs are similar even though the hydrotreatment conditions of Run N662 were considerably less severe than those of Run N562.

6.0 QUALITY ASSURANCE/QUALITY CONTROL

The success of this project depended upon obtaining high-quality data. A system of quality control checks was implemented to ascertain that accurate, precise data were collected.

6.1 Internal Quality Control Checks

6.1.1 Instrumentation Calibration

Process measurement instrumentation was calibrated during Runs N596 and N661. For both runs, the measurements taken by the thermocouples and the thermocouple testers were 99.9999% in agreement. Agreement of the pressure transducer measurement and the dead-weight tester was at least 99.99% for both calibration runs.

TABLE 22

Comparison of Selected Task 2 Results with EERC 1992 Research Results

	N562[a]	N562[b]	N563[a]	N563[b]	N564[a]	N564[b]	N566[a]	N566[b]	N650[b]	N662[b]
Pretreatment Temp., K	453	453	453	453	453	453	453	453	425	425
Solubilization Temp., K	648	648	626	626	648	648	626	626	648	648
Polishing Temp., K	708	708	706	706	731	731	734	734	713	713
Hydrotreatment Temp., K	698	698	698	698	698	698	698	698	677	678
Hydrotreatment Time, min	180	180	180	180	180	180	180	180	34	60
Hydrotreatment Press., kPa × 10^4	2.41	2.41	2.41	2.41	2.41	2.41	2.41	2.41	2.12	2.07
Gas Out										
CO, wt%	-65.92	0.00	-36.92	0.00	-63.20	0.00	-36.44	0.00	0.42	0.42
H_2, wt%	-1.50	-6.25	-0.93	-3.59	-5.46	-10.02	-2.64	-5.27	-11.89	-9.63
CO_2, wt%	114.26	10.84	93.05	35.04	116.00	16.70	93.65	36.39	11.31	11.31
C1-C3, wt%	11.53	11.53	13.50	13.50	11.70	11.70	14.38	14.38	4.72	5.24
H_2S, wt%	1.48	1.48	0.58	0.58	0.92	0.92	0.42	0.42	---[a]	---
H_2O, wt%	-42.57	-0.22	-34.12	-10.37	-42.27	-1.61	-35.32	-11.88	6.63	8.45
Total, wt%	17.27	17.27	35.16	35.16	17.68	17.68	34.04	34.04	11.18	15.78
Total Liquids Out, wt%	79.29	79.29	59.55	59.55	72.83	72.83	58.23	58.23	81.85	77.20
IOM, wt%	3.36	3.36	7.60	7.60	9.12	9.12	6.43	6.43	6.97	7.02
Conversion, %	96.64	96.64	92.40	92.40	90.88	90.88	93.57	93.57	93.03	92.98

[a] Product slates as originally reported in the final report (2).

[b] Product slates with the effect of the water-gas shift reaction calculationally removed to produce hydrogen equivalent values.

[c] Not measured.

6.1.2 Check Samples

Check samples were used to evaluate the accuracy and precision of the analytical data. Check samples were prepared from standard reference materials to simulate feed slurry, product gas, and liquid product samples. Two feed slurry check samples (N636 and N660) were prepared from known quantities of certified analysis cresylic acid solvent and as-received lignite. The as-prepared analyses, the accuracy requirements, and the as-analyzed results are presented in Table 23. The feed slurry check samples met the accuracy criteria for all analyses. It was reported in the July–September 1995 quarterly report that the Run N636 check sample did not meet the necessary criteria. It was found that the as-prepared calculations had been based upon the wrong coal analysis. The corrected as-prepared analysis appears in Table 23.

Two certified gas mixtures were submitted for gas chromatography (GC) analysis as gaseous product samples, N635 PG-1 and N635 PG-2. The as-analyzed results of these check samples are compared with the certified gas composition in Table 24. As the table shows, all analyses are within the $\pm 2\%$ accuracy limit.

Finally, a sample of cresylic acid was submitted as the liquid product check sample, N634. The as-analyzed results are compared to the cresylic acid analysis in Table 25. Table 25 shows that the liquid product check sample also met the project accuracy criteria.

TABLE 23

Analysis of Feed Slurry Check Samples

Component	As Prepared, wt%	Accuracy Requirements, wt%	As Analyzed, wt%
Check Sample N636			
C	62.54	±0.5	62.93
H	7.12	±0.5	7.14
N	0.46	±0.5	0.62
S	0.15	±0.5	0.29
Ash	2.63	±1.0	2.39
H_2O	15.95	±1.39	15.63
THFI[a]	29.90	---[b]	33.31
Check Sample N660			
C	62.61	±0.5	62.92
H	7.09	±0.5	6.97
N	0.47	±0.5	0.77
S	0.19	±0.5	0.20

[a] Tetrahydrofuran insolubility analysis.

[b] Cannot be calculated because of lack of accepted standard reference material.

TABLE 24

Analysis of Task 1 Gas Product Check Samples[a]

	Gas 1		Gas 2	
Component	N635 PG-1	Standard 1	N635 PG-2	Standard 2
Hydrogen			38.97	38.63
Carbon Dioxide	7.53	7.22	35.27	35.71
Propane	0.27	0.11		
Acetylene	0.15	0.20		
iso-Butane	0.10	0.10		
n-Butane	0.09	0.10		
Ethylene	0.18	0.18		
Ethane	0.30	0.31	0.96	0.97
Oxygen–Argon	0.40	0.35		
Nitrogen	84.24	84.83	15.60	15.59
Methane	6.65	6.50	0.94	0.90
Carbon Monoxide			8.26	8.20

[a] All values are in mol%.

TABLE 25

Analysis of Liquid Product Check Sample

Component	N634 Check Sample Analysis, wt%	Cresylic Acid Analysis, wt%	Accuracy Requirements, wt%
C	77.24	77.51	±0.5
H	7.66	7.52	±0.5
N	0.39	0.21	±0.5
S	0.0	0.0	±0.5
Ash	0.02	---[a]	±1.0
H_2O	1.11	0.28	±1.39
THFI[b]	0.03	---	---[c]

[a] Analysis not performed; sample is assumed to be ash-free and 100% tetrahydrofuran-soluble.

[b] Tetrahydrofuran insolubility analysis.

[c] Cannot be calculated because of lack of accepted standard reference material.

6.1.3 Center Point Samples

In addition to verifying that the analytical results met the precision and accuracy requirements set in the quality assurance objectives, it was also important to evaluate the precision of the high-temperature/high-pressure system. This evaluation was built into the experimental design of Task 2 via the inclusion of center points. Center points are tests performed at the midpoint of the range tested for each operating condition. Comparison of the center point sample results provides a measure of the variance of the system's ability to generate identical samples under identical conditions, i.e., the system's precision.

The analyses of the two Task 2 center point samples (N641 and N645) are compared in Table 26. The table presents the analytical instrumentation accuracy criteria. There is no absolute analysis for the product against which the results can be compared. If the center point samples were to bracket the absolute analysis (e.g., one was −0.5 wt% from the "real" carbon value and the other was +0.5 wt% from the "real" carbon value), the absolute difference between the two samples would be twice the accuracy criterion for that analysis. In other words, if the absolute difference between the center point analyses is less than twice the analytical accuracy criteria, the samples can be said to be identical. Table 26 shows that the center point samples are identical within analytical error.

TABLE 26

Comparison of Task 2 Center Point Samples

Component	N641	N645	Precision Criteria, wt%
C	89.51	90.33	±0.5
H	9.38	9.75	±0.5
N	0.63	0.61	±0.5
Karl Fischer H_2O	0.08	1.53	±3.9

6.2 Performance and System Audits

6.2.1 Readiness Audits

Readiness audits were performed by the project engineers prior to the initiation of testing for each task. During these audits, the engineers verified that all quality assurance measures were in place, that all personnel understood the technical procedures for the testing, that all personnel were suitably trained and qualified for their responsibilities with respect to the testing, and that the equipment had been tested for operational readiness.

6.2.2 *Technical Systems Audit*

A technical systems audit (TSA) was performed by the project engineers. The TSA consisted of a thorough qualitative evaluation of the ability of the technical, operations, and analytical personnel and systems, including the chain-of-custody protocol and data transfer schemes, to produce high-quality data meeting the quality assurance objectives of mass and material balances ≥95%. The technical systems were found to produce high-quality data and to be capable of flagging nonvalid results.

6.2.3 *Audit of Data Quality*

An audit of data quality was performed for each of the ten Task 1 tests. Each data point was examined to determine if it was a feasible number within the range of analytical and/or system error. All of the data were judged to be feasible. Each test was then evaluated with respect to meeting the quality assurance objectives of mass and material balances ≥95%. Tests that did not meet these criteria were repeated.

6.2.4 *Performance Evaluation Audit*

Direct liquefaction research has been performed at the EERC for over 25 years. During that time, thousands of data points have been gathered to show that both the equipment and operators are capable of attaining the required 95% mass and material balance closure; therefore, the ability of the system and operators to achieve the quality assurance goals was not tested as part of the performance evaluation audit (PEA). The PEA consisted instead of an evaluation of the analytical laboratory. A feed slurry check sample (Run N660) was prepared from known proportions of certified-analysis cresylic acid and a well-analyzed coal. The sample was analyzed by both the EERC Advanced Research Technologies (ART) laboratory (the laboratory that performed all of the routine analyses for this project) and the EERC Coal Analysis laboratory. The two laboratories used the same techniques to analyze the samples. The results of the analyses are presented in Table 27. As the table shows, both laboratories analyzed the sample within the tolerance limits, indicating that the analytical data generated by the ART laboratory is accurate.

TABLE 27

Comparison of ART and Coal Analysis Laboratories[a]

Component	As Prepared	Coal Analysis Laboratory	ART Laboratory	Acceptance Criteria
C	62.61	62.94	62.92	±0.5
H	7.09	7.00	6.97	±0.5
N	0.47	0.31	0.77	±0.5
S	0.19	---[b]	0.20	±0.5

[a] All values given in wt%.

[b] Analysis not performed.

7.0 PAPERS PRESENTED DURING THIS PROJECT

Two papers summarizing project work effort were prepared and presented over the course of this project:

- A paper entitled "Summary of Recent Low-Rank Coal Direct Liquefaction Research at the Energy & Environmental Research Center" was presented at the Coal Liquefaction and Gas Conversion Contractors' Review Conference in September 1994.

- A paper entitled "Solvent Recyclability in a Multistep Direct Liquefaction Process" was presented at the August 1995 Coal Liquefaction and Gas Conversion Contractors' Review Conference.

8.0 RECOMMENDATIONS

This project showed that the solvent could be recycled during the preconversion, solubilization, and polishing steps of the multistep process and that lower-severity conditions could be used to successfully hydrotreat the product of the multistep process. The success of this project indicates that the reactions taking place in the liquid phase of the process should be optimized during batch tests in which the gas flow is continuous (i.e., gas effects are negligible). Testing should be performed to better define the HAO61 recycle loop around the hydrotreatment step. Finally, the process should be evaluated during continuous unit operations.

9.0 REFERENCES

1. University of North Dakota Energy Research Center. "Low-Rank Coal Research: Direct Liquifaction," quarterly technical progress report for the period April–June 1983; DOE/UNDERC/QTR-83-2, 1983, p5–34.

2. Hetland, M.D.; Rindt, J.R. "Low-Rank Coal Direct Liquefaction," final technical progress report for the period July 1, 1989, through Dec. 31, 1992; EERC publication, 1993.