SOLVENT RECYCLABILITY IN A MULTISTEP DIRECT LIQUEFACTION PROCESS

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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 can then be upgraded during a traditional hydrotreatment 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 products' 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 develop this process more fully 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. The current project was funded to investigate these two areas.

PROJECT OBJECTIVES

The project objectives are to determine both 1) the recyclability of the solvent used during solubilization and 2) the minimum hydrotreatment severity required to upgrade the liquid product of the multistep EERC process.

The project is being performed as two tasks. The first task consists of ten solvent recycle tests in which lignite is solubilized via the pretreatment, solubilization, and polishing steps. The product of these three steps is combined with a vehicle solvent, and the resulting stream distilled to remove water, solubilization solvent, and oxygenated light coal-derived liquids. The water is then separated from the light solvent stream, and the solubilization solvent is reused as the solubilization solvent for the next recycle test. The analyses of the products of the tests are used to characterize the recycle solvent stream and to calculate mass and material balances.

The second task consists of a series of twelve hydrotreatment tests at various conditions. The tests will be 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 will be used to characterize the hydrotreated product and to calculate mass and material balances.

This paper discusses only the results of the Task 1 recyclability tests performed to date.

PROGRAM APPROACH

Task 1 consists of ten multistep tests. In the first test, feed coal and solubilization solvent were pretreated and solubilized. The product of the solubilization step was polished with additional solvent, combined with a hydrogen-donor vehicle solvent, and distilled to remove water, solubilization solvent equal to the amount added in the polishing step, and oxygenated light coal-derived liquids (CDLs). If hydrotreatment had been part of this task, the bottoms from this distillation would have gone to the hydrotreatment step. The distillation overheads were further distilled to separate the water from the solubilization solvent and light CDLs. The solubilization solvent was recycled to the pretreatment and polishing steps for the next test. This sequence is being repeated until ten multistep tests have been performed, each utilizing the solubilization solvent removed in the distillation of the previous test. To date, five tests have been completed.

The purpose of this task is to monitor both the changes occurring in the solubilization solvent as it is recycled in the multistep process and the changes in product slate resulting from the recycle of the solvent. Analyses were selected to enable this information to be determined. The feed coal was subjected to moisture, ash, and elemental (C, H, N, and S) analyses, while the solubilization solvent undergoes ash, Karl Fischer water, elemental (C, H, N, and S), THF solubility, and ASTM D1160 distillation analyses. Oxygen contents are determined by difference. Liquid products are analyzed using the same analyses as were applied to the solubilization solvent. Gaseous products are analyzed by gas chromatography. Changes in the recycled solubilization solvent stream are determined by speciation of this stream using mass spectroscopy (MS) analysis. Complete speciation was scheduled to be performed after the first, third, seventh, and tenth multistep tests. Complete mass and material balances are being performed for all multistep tests.

ACCOMPLISHMENTS

Preparation of a Composite Solvent

During development of the multistep process, it was found that different solvents were more effective in different steps. A hydrogen-donating solvent is needed during the pretreatment and solubilization steps, while phenolic solvent is needed during the polishing step. Providing these solvents at appropriate times during the previous testing was not difficult since no attempt was made to recycle any of the solvent. The multistep process is of virtually no practical value if it must be performed in a batch mode on a commercial scale; therefore, a solvent must be procured that meets the requirements of each step, yet is recyclable.

The original process development work was performed using hydrogenated coal-derived anthracene oil (HAO61) in the polishing and solubilization steps and cresylic acid (POH) in the polishing step. A composite solvent was prepared from these materials as follows. The HAO61 was distilled to remove a middle fraction equal to 13.4 wt% of the HAO61 stream. (Removing this middle fraction makes it easier to separate the HAO61 into light and heavy fractions for use in different parts of the process.) The light fraction of the HAO61 was defined as the material that distilled over at an overheads' temperature of about 464 K (191°C) or less at a pressure of 7.7×10^3 N/m^2 (1.12 psi). It made up 33.8 wt% of the total HAO61 stream. The light fraction of the HAO61 was combined with an equal part of cresylic acid to form the pretreatment/solubilization solvent. Additional light material was added to the polishing step. Following polishing, the HAO61 heavy fraction (the material that did not distill at 479 K [206°C] and 7.2×10^3 N/m^2 [1.04 psi]) was added to the product slurry to serve as the vehicle solvent for the hydrotreatment step. The entire mixture was distilled to remove water, POH, HAO61 light fraction, and light CDLs produced from the coal. The water is separated from the light organics, which are then recycled back to the pretreatment and polishing steps. The overall solvent scheme is summarized in the block diagram shown in Figure 1.

The Task 1 testing began following preparation of the composite solvent and distillations performed to determine that the solvent could be reproducibly fractionated into the light and heavy fractions.

Test Description

For each test, the following run sequence was performed. Freedom lignite was slurried with the solubilization solvent (which consisted of a 50:50 mixture of POH and HAO61 light fraction for the first test and recycle solvent for the other tests) in a 2:1 solvent-to-coal ratio. The feed slurry was cold-charged to the reactor. The autoclave was charged with CO and H_2S, which serves as the reaction promoter. The reactor was heated to a temperature of approximately 423 K (150°C) and a pressure of about 9.65×10^6 N/m^2 (1400 psig) for the pretreatment, which lasted 30 minutes. The temperature and pressure were then increased to about 648 K and 2.414×10^7 N/m^2 (375°C and 3500 psig, respectively) for 60 minutes. (All pressures are at

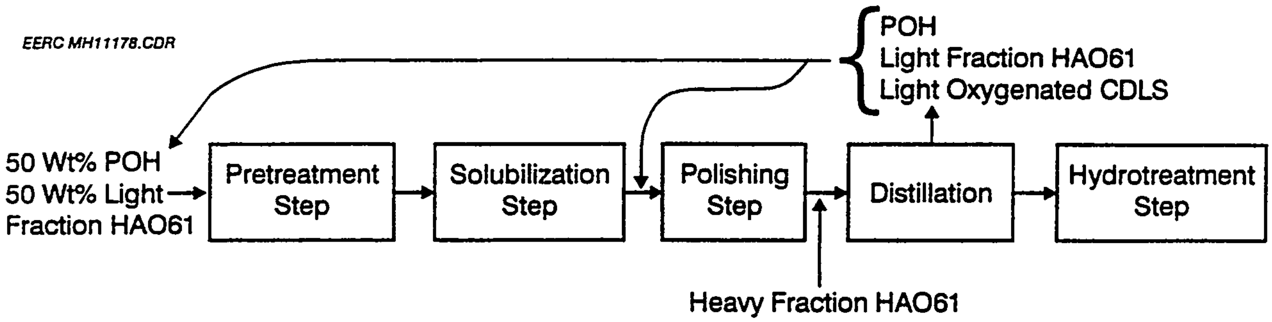

Figure 1. Block diagram showing the location of various solvent fractions during the multistep direct liquefaction process.

reaction temperature and are equivalent to 6.898×10^6 N/m^2 [1000 psig] at room temperature.) The unit was quenched and the product recovered and sampled.

The solubilized product slurry was then charged to a preheated autoclave containing start-up solvent and H_2. The unit was operated at reaction conditions of 713 K and 3.10×10^7 N/m^2 (440°C and 4500 psig) for 20 minutes during the polishing test. The reaction was quenched and the product collected and sampled.

The polished product slurry was combined with HAO61 heavy fraction (which would serve as the vehicle solvent for the product going into the hydrotreatment step) and then distilled. The water was removed first, and a light oil fraction was collected as the overhead material resulting from distillation at 8.2×10^3 N/m^2 (1.19 psig), an overhead temperature of 471 K (198.2°C), and a pot temperature of 494 K (221°C). After samples were taken for analysis, the light oil fraction was used as the feed solvent for the next test.

The conditions at which Tests 1 through 5 were performed are summarized in Table 1.

Discussion of Results

The first two tests went as planned. An electrical power outage unexpectedly occurred prior to the distillation step during Test 3. 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 material balances for Tests 1 through 5 are presented in Table 2. These data show that recoveries for the gas and liquid fractions for each of the steps are similar. The liquid balance for the pretreatment/solubilization step ranged from 91.0% to 91.7%. The polishing step liquid balance ranged from 97.2% to 97.7%. Overall mass balances for the pretreatment/solubilization step ranged from 96.0% to 99.3%, for the polishing step 98.2% to 99.2%,

TABLE 1

Run Conditions for Task 1, Tests 1 Through 5

			Test Number		
Processing Step	1	2	3	4	5
Pretreatment	N602	N607	N611	N614	N617
Temp., K	425	426	424	425	422
Pressure, N/m^2 × 10^6	9.7	9.6	9.7	9.8	10.1
Time, min	35	30	30	30	30
Gas	CO	CO	CO	CO	CO
Additive	H_2S	H_2S	H_2S	H_2S	H_2S
Solubilization	N602	N607	N611	N614	N617
Temp., K	650	650	646	645	645
Pressure, N/m^2 × 10^6	24.0	24.3	24.5	23.7	23.4
Time, min	60	60	60	60	60
Polishing	N603	N609	N612	N615	N618
Temp., K	714	713	707	710	711
Pressure, N/m^2 × 10^6	31.8	31.3	31.5	29.6	27.6
Time, min	20	20	20	20	20
Gas	H_2	H_2	H_2	H_2	H_2
Additive	Feed Solvent	RS-606[a]	RS-610	RS-613	RS-616
Distillation[b]	N606	N610	N613	N616	N620
Temp., pot, K	494	492	492	494	494
Pressure, N/m^2 × 10^6	0.008	0.008	0.008	0.008	0.008

[a] Recycle solvent from distillation step of prior test.

[b] Water was removed first; listed conditions indicate the cutoff point for separation of light organic materials from the hydrotreatment step feed.

and for the distillation step 97.9% to 99.6%. The consistency of the mass balances for each step proves that the system is operationally stable. The fact that the mass balances are at least 95% indicates that adequate amounts of material were collected for analysis and subsequent tests and that the data, therefore, reliably describe the process.

The solvent balance from the Test 3 distillation was reduced because some of the distillable material was not collected. After calibration of the pressure transducer during Test 4, the Test 3

TABLE 2

Mass and Material Balances for Task 1, Tests 1 Through 5

	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

[a] Not applicable.

TABLE 3

Distillate Yields and Solvent Balances for Task 1, Tests 1 Through 5

Test No.	Hydrotreatable Solubles, wt% maf[a] Liquid Basis[b]	Hydrotreatable Solubles, wt% maf[a] Gas Basis[c]	Solvent Yield, wt% maf	Solvent Balance, %
1	76.90	72.54	42.01	116.42
2	80.50	78.88	68.17	127.75
3	77.42	73.55	46.27	118.57
4	73.79	70.03	13.67	105.47
5	80.20	77.99	17.12	106.80

[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.

distillation was repeated and the recovery results used to calculate the actual Test 3 solvent balance. This value is shown in Table 3, which summarizes the solvent balance and yields of hydrotreatable solubles and distillate for Tests 1 through 5. As the table shows, solvent balances of over 115% were attained for Tests 1 through 3. The lower balances shown by Tests 4 and 5 are probably due to the improper recycle solvent composition. The additional material removed during the redistillation of the Test 3 hydrotreatment feed was added to the recycle solvent stream that will be used in the Test 6 feed slurry.

The yields of hydrotreatable soluble material noted in Table 3 were calculated two different ways: from the liquid stream mass balance data and by subtracting the gas yield from unity. The reliability of the data is high since the numbers are similar and exhibit a consistent 4% difference between values calculated by both methods.

During analysis it was noted that some light organic material was removed with the aqueous phase during distillation. This material is phenolic in nature and makes up about 10% to 16% of the aqueous stream. The organics were gravity-separated and added to the recycle solvent stream that will be used in the Test 6 feed slurry. The organics will be separated from the aqueous stream and added to the recycle solvent during the remaining tests.

CONCLUSIONS

- The process remained both operationally and chemically constant, even though the recycle solvent composition was abruptly changed and some of the light solvent was not returned to the recycle stream.

- This work was performed using a composite solvent that had not been previously used in the multistep process. Although the solvent was prepared using information gathered during previous process development work, it is possible that, as it recycles, the solvent will not remain hydrogen-enriched enough to be optimally effective in the pretreatment and solubilization steps. If not enough hydrogen is available, light organic material could be removed from the hydrotreated product stream and recycled to the pretreatment step.

FUTURE PLANS

The Task 1 solvent recyclability tests and the Task 2 hydrotreatment severity tests will be completed. The next step in the process development would be optimization of the process on a batch scale, followed by one or more continuous demonstration tests.