

# SOLVENT RECYCLABILITY AND HYDROTREATMENT SEVERITY IN DIRECT LIQUEFACTION OF LOW-RANK COAL

Melanie D. Hetland and John R. Rindt  
University of North Dakota  
Energy & Environmental Research Center  
PO Box 9018  
Grand Forks, ND 58202-9018  
(701) 777-5000

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## INTRODUCTION

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.

Research was performed to address two 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 research was performed during two tasks, the first consisting of ten recycle tests and the second consisting of hydrotreatment tests performed at various conditions.

## EQUIPMENT

The EERC's time-sampled, batch autoclave system was used during these studies. The system is capable of close-coupled multistage operation. It can be configured to multiple designs with reactor sizes ranging from 1-8 L. Maximum operating conditions are 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 system by a steel barricade.

## COMPOSITE SOLVENT

Different solvents have proven to be more effective in different steps during the multistep 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 recycle tests using equal quantities of phenolic solvent (cresylic acid) and a light fraction of hydrogenated coal-derived anthracene oil (HAO61).

The solvent recycling scheme is summarized in Figure 1. The solubilization solvent initially consisted of equal parts of phenolic solvent and HAO61 light fraction. Heavy fraction HAO61 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 phenolic solvent, HAO61 light fraction, and light coal-derived liquids (CDLs). The light materials were then recycled to the pretreatment and polishing steps.

## SOLVENT RECYCLABILITY TESTS

Ten solvent recyclability tests were performed. In the first test, feed coal and composite solvent were pretreated at 175°C under 1000 psig (cold-charge pressure) CO in the presence of H<sub>2</sub>S for 60 min. The pretreated slurry was solubilized at 375°C under 1000 psig (cold-charge pressure) CO and H<sub>2</sub>S for 60 min. The product of the solubilization step was polished with additional phenolic solvent under 1000 psig (cold-charge pressure) H<sub>2</sub> for 20 min at 435°C. 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.

Material balances were calculated for all of the processing steps during the solvent recyclability tests. The recoveries for each of the steps were 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 process.

Table 1 shows the distillate yields and solvent balances for each of the solvent recyclability tests. During the original distillation, some of the distillable material from the third test was not collected because of a pressure transducer problem caused by an unexpected power outage. The distillation bottoms were redistilled, and the additional material collected was added to the recycle solvent stream used in the sixth test feed slurry. The table shows that as a result of the lower fraction of light distillate present in the fourth and fifth tests, 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 16.8 wt%. Excluding the low solvent balances for the fourth and fifth tests, the average excess solvent produced was 19.48 wt%.

Detailed analyses were performed to determine the changes in composition of the light solvent as it was recycled during the recyclability tests. Two types of analyses were performed. The first 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 for this analysis. Table 2 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. The second analysis determined the cresol (or equivalent) concentration in the solvent. The results of this analysis are plotted in Figure 2. As is easily seen from the plot, the cresol concentration appears to be approaching a constant value of approximately 32%-34% wt% of the recycle solvent stream. This 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.

Several conclusions can be drawn from the solvent recyclability test results:

- 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%-34 wt% cresol (or equivalent).
- The recycle solvent maintains its hydrogen donor capability.

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

#### HYDROTREATMENT SEVERITY TESTS

The purpose of the hydrotreatment severity study was to determine the lowest-severity hydrotreatment conditions that produce high-quality liquid product. A statistical approach to data collection was used so as to predict the lowest-severity conditions in a relatively small number of tests. The results of this type of experimental matrix can be statistically analyzed to develop mathematical equations describing the process. A factorial design consisting of ten tests was employed to test the effects of temperature, pressure, and residence time on product quality. Maximum or minimum conditions of each factor were tested for eight of the tests; tests were performed at temperatures of either 405° or 445°C, at pressures of either 1920 or 3080 psig, and at reaction times of either 34 or 112 min. Two tests were performed at center point conditions (425°C, 2500 psig, and 73 min) to determine 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 liquid product from solvent recyclability Tests 1, 2, 4, and 6 were combined into a single sample to be used as the feedstock for the hydrotreatment severity tests. For each test, composite feed and sulfided Shell 424 catalyst were hydrotreated at experimental matrix-specified conditions.

The analytical and mass balance data from the hydrotreatment severity tests were used to calculate various product quality indicators, including the saturated molar H-to-C ratio of the hydrotreated product; the percent improvement in saturated molar H-to-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.

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.

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 their values would be at various operating conditions that were not actually tested.

The plots showed that a high hydrotreatment temperature (about 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 min. The plots also showed that an increase in pressure improves total liquid yield.

The various plots were compared to determine the lowest-severity set of conditions that would result in the optimum values for the majority of the product quality indicators. The lowest-severity conditions were determined to be: 405°C temperature, 3000 psig pressure, and 60 min reaction time. A test was performed at these conditions to verify the accuracy of the predictions. The predicted values for each of the product quality indicators are compared with the actual values calculated for the test in Table 3. The data show that the equations predicted the product quality indicator values fairly accurately.

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 405°C cannot be determined. Therefore, it is possible that an even lower temperature might effectively hydrotreat the liquid product from the multistep process.

Interpretation of the hydrotreatment severity data led to the following 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 solvent recyclability test sequence produced solubilized material that could be as effectively hydrotreated as the product of batch tests using optimal solvents for each test.
- 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 400°C while maintaining desired product quality and yield.

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

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TABLE 1

Distillate Yields and Solvent Balances for Task 1 Tests				
Hydrotreatable Solubles, wt% maf <sup>a</sup>				
Test No.	Liquid Basis <sup>b</sup>	Gas Basis <sup>c</sup>	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

<sup>a</sup> Weight percentage of moisture- and ash-free coal fed to the system.

<sup>b</sup> Yield calculated from liquid stream mass balance data.

<sup>c</sup> Yield calculated by subtracting the gas yield from unity.

TABLE 2

Relative Aromatic Concentrations in Recycle Solvent	
Test Number	C-H Absorbance
1	0.35
4	0.34
7	0.36
10	0.35

TABLE 3

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 <sub>2</sub> Consumption	0.1268	0.1822

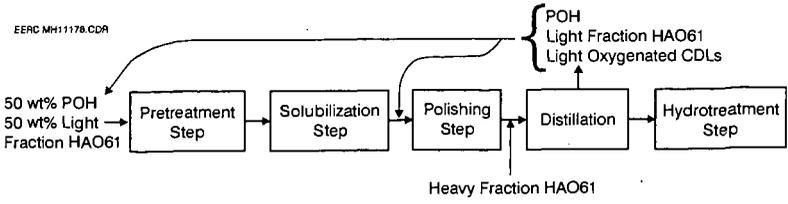


Figure 1. Block diagram summarizing the composite solvent scheme.

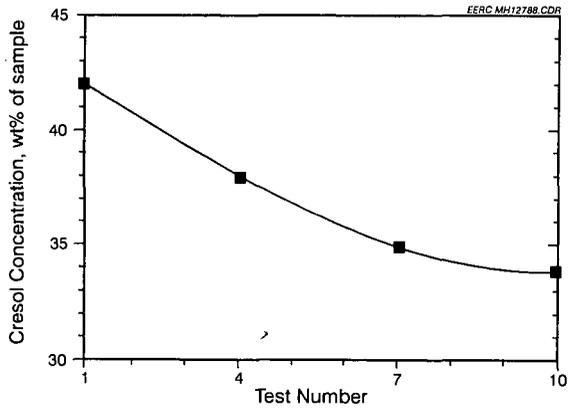


Figure 2. Cresol concentration in recycle solvent as a function of test number.

MDH/djs