

## EXPLORATORY RESEARCH ON NOVEL COAL LIQUEFACTION CONCEPT

Susan D. Brandes, Richard A. Winschel, Francis P. Burke  
CONSOL Inc., Research and Development, 4000 Brownsville Road,  
Library, PA 15129

Francis J. Derbyshire, Geoffrey M. Kimber,  
Richard K. Anderson, Scott D. Carter  
University of Kentucky Center for Applied Energy Research,  
3572 Iron Works Pike, Lexington, KY 40511-8433

Michael Peluso, LDP Associates, 32 Albert E. Bonacci Dr.  
Hamilton Square, NJ 08690

### INTRODUCTION AND SUMMARY

A novel direct coal liquefaction technology is being investigated. The chemistry employed is based on the use of hydride ion donation rather than free-radical/hydrogen atom donation to effect an initial solubilization of coal at low temperature in the first stage of a two-stage process. The program explores not only the initial solubilization step, but integration of the subsequent processing steps with the first stage to produce distillate products. Figure 1 presents a conceptual design for the proposed process. As depicted in this particular process design, decoupling of the steps is possible because little, if any, recycle of products to the first stage is anticipated. Thus, in the work conducted to date, each key element of the process concept was explored independently.

A systematic study was conducted on a laboratory scale to determine conditions for the first-stage reaction which produce high coal conversions at low-severity conditions. Variables tested were residence time, reaction temperature, solvent type, solvent-to-coal ratios, hydride ion sources, hydride ion reagent-to-coal ratios, autogenic reaction pressure, and coal rank. Coal conversions to THF-soluble material greater than 92 wt % (MAF basis) at 350 °C and 60 min have been obtained with lignite and bituminous coal and over 90 wt % with subbituminous coal. Analyses of the first-stage products show them to be enriched in hydrogen over the feed coal. Low reaction temperatures minimize the production of hydrocarbon gases from the coal.

An interstage filtration step is used to remove ash and unreacted coal from the first-stage products. The low temperature required to effect the solubilization in the first stage results in a minimization of retrograde reactions; thus, there is little refractory material to be filtered from the first-stage products. Filtration rates of first-stage products were found to be very fast; cake resistivities are on the order of  $10^{10}$  m/kg, and filter cake solids contents are as high as 50%.

In the integrated process, a second-stage catalytic reactor will be used to upgrade the first stage filtrate. Preliminary upgrading studies were performed using a conventional two-stage liquefaction distillation resid to establish conditions and choose an

appropriate catalyst. Subsequent work with the first-stage hydride reaction products indicate that they are more reactive than the conventional two-stage direct liquefaction resid. Resid conversion of 67 wt % was achieved after one hour at 440 °C with Molyvan L catalyst, much higher than the 35 wt % resid conversion obtained with conventional two-stage-liquefaction resid under the same hydrotreating conditions.

To evaluate the process steps and the feasibility of the integrated process, an engineering/economic evaluation is being conducted concurrently using the laboratory-scale results.

## **EXPERIMENTAL**

### **First-stage solubilization**

Experimental work is being conducted in a 45 mL shaken microautoclave and a one-liter stirred autoclave. Variables explored are residence time at reaction temperature, temperature, solvent, solvent/dry coal ratio, hydride ion source, hydride ion reagent/dry coal ratio, autogenic pressure, and coal rank. Pressures are varied by increasing total reactor charge or by increasing the percentage of water in the feed. Products are analyzed by gas chromatography, <sup>1</sup>H-NMR spectrometry, and GC/MS. Elemental analyses are obtained for select products to obtain elemental balances.

### **Filtration**

Filtration work is conducted in one of two cylindrical filter test units. One is 1.9 cm diameter, 15 cm long; the other is 3.8 cm diameter, 45.7 cm long. The filter in each apparatus is a glass fiber with ca. 1 μm pores. In the smaller apparatus, the fiber filter is sandwiched between two perforated steel plates. In the larger apparatus, the filter is supported from underneath by a perforated steel plate. Samples are distilled at 115-150 °C prior to filtration to remove lower boiling material, including water. The filter is heated to 250-300°C and pressurized at 2 to 30 psig. Samples up to 70 g have been filtered in the larger apparatus.

### **Hydrotreating**

Microautoclave hydrotreating of the first-stage reaction products is carried out in 50 mL reactors. The feed sample size is limited to 3 g to assure ample hydrogen for hydrotreating. Total pressure (cold) is 1450 psi, and 2 mol % H<sub>2</sub>S is added to each run as a catalyst sulfiding agent. Total pressure is monitored as the reactions proceed. Product gases are analyzed by gas chromatography; upgraded products are characterized by vacuum distillation (ASTM D-1160) to determine conversion to 566 °C distillate. Simulated distillation is used to confirm the D-1160 cut point temperature and to obtain a boiling curve for the upgraded products. Variables examined include catalyst, catalyst pretreatment conditions, reaction temperature, residence time at reaction temperature, and solvent.

## **RESULTS AND DISCUSSION**

### **First-stage solubilization**

Solubilization tests were conducted in the 45 mL microautoclave with five different coals of three different ranks, six different residence times, three temperatures, three hydride ion sources, four solvents, and a range of hydride reagent-to-coal ratios,

solvent-to-coal ratios, and autogenic pressures. The ranges studied for each of these variables are given in Table 1.

Coal conversion was found to be dependent on temperature, residence time, coal rank, hydride ion-to-coal ratio, and autogenic pressure. Coal conversions greater than 90 wt % can be obtained by the selection of these variables within the ranges given in Table 1. Table 2 is a list of microautoclave tests chosen to show the different combinations of values of these variables which produced high coal conversions.

Mass and elemental balance data were obtained for four tests made with Black Thunder coal which gave coal conversions greater than 85 wt % at 350 °C, 150 min, 375 °C, 150 min, and 400 °C, 45 min. The elemental analyses of the soluble resid products (488 °C<sup>+</sup> material) from these tests show them to be enriched in hydrogen relative to the feed coal; the H/C ratios are 0.80 for the feed coal, 0.99 for a run made at 350 °C, 0.92 for a run made at 375 °C, and 0.89 for a run made at 400 °C.

One-liter stirred autoclave tests were made to produce large quantities of material for interstage filtration and second-stage hydrotreating studies. To date, tests completed are replicates of smaller microautoclave runs. Coal conversions in the two reactors were comparable.

### **Filtration**

Preliminary filtration tests with first-stage products were made to establish operating conditions and procedures. Three duplicate pairs of microautoclave product samples produced from Freedom Mine, North Dakota lignite were filtered. In one test the filter apparatus was held horizontally while the sample was warmed to 250 °C. Nitrogen gas was bubbled through the filter. The apparatus was returned to vertical and filtration then proceeded under 30 psi of N<sub>2</sub> pressure; the sample filtered in less than 10 s. Solids were retained on the walls of the heated filter apparatus and the filter cake did not cover the entire area of the filter. The duplicate sample was introduced into the filter apparatus that was held vertically as it was warmed; no gas was bubbled through the filter. Again, filtration was very rapid and no material was left on the filter walls. The vertical orientation was adopted for all subsequent tests.

Filtration tests were performed with microautoclave product samples made with Black Thunder subbituminous coal (Table 3) at various solvent-to-coal ratio and temperature. Cake resistivities were found to be between  $2 \times 10^{10}$  and  $25 \times 10^{10}$  m/kg. Coal conversions, determined from the THF-solubility of the filter cakes, compared well with those values obtained by THF filtration of the entire product from duplicate microautoclave tests (Table 3). Runs 26, 52 and 53 gave similar coal conversions (about 88 wt %) based on ash enrichment indicating that the solvent-to-coal ratio used in the first-stage reaction does not greatly influence coal conversion at these conditions and that it can be adjusted to maximize filterability of the first-stage products. The filter cakes when cooled are brittle solids and have ca. 40-50 wt % THF-insolubles. Little difference in yields was found in the samples produced at 375 °C and 400 °C; therefore, the filtrates from microautoclave runs made at 375 °C and 400 °C from Black Thunder Mine coal were composited. This filtrate composite was used in second stage

hydrotreating tests (see below).

Filtration tests were made with products of the one-liter stirred autoclave. Products from tests made with Black Thunder Mine coal were filtered in the larger (3.8 cm diameter) filter. These materials filter very rapidly. The filter cake represents about 15 wt % of the 115 °C<sup>+</sup> first-stage product; 50 wt % of the filter cake is THF-insoluble. Filtrates were distilled to increase their 566 °C<sup>+</sup> resid content to ca. 70%, comparable to the Wilsonville deashed resid being used in hydrotreating experiments (see below).

### **Hydrotreating**

Second-stage hydrotreating tests are being carried out with a Wilsonville deashed resid (Run 258A) and filtered products of both the first-stage microautoclave tests and one-liter autoclave tests. Work with the Wilsonville resid was performed to provide a basis for comparison to the materials produced in this program. Operating conditions were established using the Wilsonville resid. Three catalysts were tested: supported Ni/Mo on alumina catalyst Akzo AO60, molybdenum naphthenate, and homogeneous catalyst Molyvan L. Resid conversions for the Wilsonville resid were determined at different hydrotreating temperatures and catalyst loadings (Table 4). Recycle of catalyst and hydrotreated-product resids was investigated. Resid conversion for a single pass at 440 °C and 60 min with 1000 ppm Mo was 32 wt %. When make-up resid was added, but no fresh catalyst, resid conversion on the second pass was 25 wt %. In another experiment fresh catalyst (100 ppm Mo) and make-up resid were added; resid conversion on the second pass was 33 wt %. In a fourth experiment, 10 wt % of the feed was hydrotreated with 1000 ppm Mo (on a total feed basis); after venting the reactor, the remaining 90 wt % of the feed was added and a second 60 min reaction at 440 °C was carried out. Overall resid conversion was 36 wt %. These data indicate that the recycled Mo catalyst is still quite active on the second pass.

Work with filtered first-stage reaction products was begun with a composite sample made from a number of microautoclave tests made with Black Thunder Mine coal which gave similar coal conversions. Four tests were completed with this composite sample (Table 5). Both temperature and catalyst loading affect resid conversion.

Hydrotreatment at 440 °C for 60 min with 1% Mo of filtered and distilled first-stage reaction products from a one-liter autoclave run made with Black Thunder coal at 350 °C for 150 min gave an average resid conversion of 65 wt %. This conversion is much higher than the 35 wt % obtained for a conventional two-stage liquefaction resid (Wilsonville 258A, deashed resid) under the same hydrotreating conditions. The implication is that the first-stage reaction produces a much more reactive product than the recycled resid from the two-stage liquefaction process.

### **Engineering/Economic Evaluation**

A review of the technical and patent literature on hydride transfer agents is ongoing. An annotated bibliography is being compiled and is continually updated. Overall process design and economic data are being evaluated. In an effort to elucidate the chemical mechanisms of the proposed process, elemental analyses of microautoclave material balance tests were begun.

## PLANNED WORK

The program will continue to be concentrated on evaluating the effects of low-severity, first-stage reaction conditions on coal conversions, exploring the effect of changing first-stage conditions on filtration performance, exploring conditions for hydrotreatment of first-stage products, and determining the hydrotreated product quality. The technical and patent literature review will continue. An economic evaluation will be focused on the design of a pilot-scale facility when the parameters for each reaction step are defined.

Figure 1. A Conceptual Process Design for a Two-Stage Coal Conversion System with Hydride Ion Donation-Promoted First-Stage Solubilization, Interstage Filtration, and Second-Stage Hydrotreating.

**TABLE 1. VARIABLES INVESTIGATED IN FIRST-STAGE SOLUBILIZATION TESTS**

<b>Variable</b>	
coal (coal rank)	Freedom Mine, North Dakota lignite - low sodium Freedom Mine, North Dakota lignite - high sodium Glenharold Mine, North Dakota lignite Black Thunder Mine, Wyoming subbituminous Ohio 11 Mine, Kentucky bituminous
residence time, min	0, 30, 45, 60, 120, 150
temperature, °C	350, 375, 400
solvent	Wilsonville Run 262E, V1074 Wilsonville Run 262E, V1074, 488 °C- distillate Lummus 3LCF7 pasting solvent 454 °C- distillate tetralin
solvent/dry coal ratio, w/w	0 - 4.4 (majority of tests made at 1.5 - 2.2)
hydride ion source	Hydride reagents "A", "B", and "C"
hydride ion reagent/dry coal ratio, relative	0 - 6.9 (majority of tests made at 1.0 and 1.5)

estimated pressure, psi	1120 - 3400
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**TABLE 2. SELECTED COAL SOLUBILIZATION TESTS, 45 mL MICROAUTOCLAVE**

Run No.	Coal (a)	Solvent (b)	Time, min	Temp, °C	HI/Coal (c)	Pressure (d), psia	Coal Conversion(e)
11	FM-LS	D	45	400	1.1	1201	90.4
5	FM-LS	D	45	375	1.4	2705	91.0
18	FM-LS	D	45	400	1.4	2811	90.4
60	FM-LS	D	150	375	1.4	-	92.4
90c	FM-HS	D	150	400	1.1	2679	91.4
78	GH	D	60	400	0.9	1790	91.9
84	GH	D	60	400	1.1	-	91.4
94	GH	W	60	350	1.5	3312	92.7
94b	GH	W	60	350	1.5	3312	92.4
96	GH	D	60	350	1.5	3323	93.0
98	GH	W	60	350	1.0	3207	90.1
26	BT	D	45	400	1.5	-	90.1
27	BT	D	45	400	1.8	2603	90.2
28	BT	D	45	400	2.0	-	90.9
30	BT	D	45	400	3.2	3399	90.6
34	BT	D	45	400	1.7	2262	90.7
35	BT	D	45	400	2.0	2143	91.4
76b	BT	D	150	375	1.0	2154	90.5
105	O	W	60	350	1.0	3016	91.2
111	O	W	60	350	1.5	1123	90.1
112	O	W	60	375	1.5	1282	93.3
116	O	W	60	400	1.5	1458	93.5

- a. Coals:FM-LS: Freedom Mine, North Dakota lignite, low sodium  
 FM-HS: Freedom Mine, North Dakota lignite, high sodium  
 GH: Glenharold Mine, North Dakota lignite  
 BT: Black Thunder Mine, Wyoming subbituminous  
 O: Ohio 11 Mine, Kentucky bituminous

- b. Solvent: W = Wilsonville Run 262E V1074 composite distillate 343C x 565 °C  
 D = Wilsonville Run 262E V1074 composite distillate 343C x 510 °C cut

- c. Relative value
- d. Estimated pressure at reaction temperature
- e. Coal conversion to THF-solubles on moisture and S<sub>0</sub>-free-ash-free basis

**TABLE 3. FILTRATION TEST DATA, BLACK THUNDER COAL TESTS (a)**

First-Stage Reaction					Filtration				
Run No.	Temp., °C	Hydride Ion/Dry Coal (b)	Solvent(c)/ Dry Coal, w/w	Coal Conversion(d), wt % THF Soluble	Temp., °C	Pressure, psig	Cake Resistivity, m/kg x 10 <sup>0</sup>	Cake THF-insols, wt % feed	Coal Conversion, wt% (e)
22c	350	1.0	2.1	63.0	260	29.5	2	39.1	56.2
21a	375	1.0	2.0	80.1	258	9.7	19	42.4	78.7
21d	375	1.0	2.0	80.1	250	9.4	10	43.5	73.2
26a	400	1.5	2.1	90.1	250	2.5	4	41.9	89.4
26b	400	1.5	2.1	90.1	252	10.6	5	49.8	88.4
52a	400	1.5	1.0	ND(f)	255	10.2	25	52.6	87.7
53a	400	1.5	1.5	ND(f)	250	9.9	11	49.2	88.2

- a. Residence time: 45 min
- b. Relative ratio
- c. Wilsonville Run 262E, V1074 343C x 510 °C
- d. Determined on duplicate tests
- e. Determined by ash enrichment, SQ-free ash-free basis
- f. ND = not determined



**TABLE 4. SECOND-STAGE HYDROTREATING DATA DEASHED RESID, WILSONVILLE RUN 258A, 60 MIN RUNS, 1450 PSI (COLD), 2 mol % H<sub>2</sub>S**

Sample No.	Reaction Temp, °C	Mo Conc., ppm	H/C & CO <sub>x</sub> Gas Yield, wt % MAF Feed	1050 °F, wt % MAF Feed	1050 F <sup>+</sup> Resid, wt % MAF Feed	H <sub>2</sub> Consumed, mg/g MAF Feed	Resid Conv., wt % MAF Resid
Blank R6-51-1	-	-	-	27.2	72.8	-	-
R5-339-1	400	1000	0.8 0	36.2	63.0	8	17
R6-92-1 (duplicate of R5-339-1)	400	1000	1.4 0.1	28.5	70.0	7	8
R6-95-3	400	10000	1.7 0	25.3	73.0	19	4
R6-92-2	420	1000	2.8 0.1	37.9	59.2	11	22
R6-99-2	420	1000	2.8 0.1	35.4	61.7	11	19
R6-51-2	440	1000	6.2 0.1	42.3	51.4	25	32
R6-99-1	440	10000	6.6 0.1	38.3	55.0	23	27
R6-106-1 (duplicate of R6-99-1)	440	10000	7.1 0.1	43.3	49.5	40	35

**TABLE 5. SECOND-STAGE HYDROTREATING DATA MICROAUTOCLAVE PRODUCTS, COMPOSITE FILTRATE, 60 MIN RUNS, 1450 PSI (COLD), 2 MOL% H<sub>2</sub>S**

Sample No.	Reaction Temp, °C	Mo Conc., ppm	H/C & CO <sub>x</sub> Gas Yield, wt % MAF Feed	1050 °F, wt % MAF Feed	1050 F <sup>+</sup> Resid, wt % MAF Feed	H <sub>2</sub> Consumed g/g MAF Feed	Resid Conv., wt % MAF Resid
R6-94-1	400	1000	4.1 0.7	27.1	68.1	20	6
R6-93-2	400	10000	4.8 0.5	33.7	61.0	25	15
R6-95-1	440	1000	10.1 0.9	46.4	42.7	33	41
R6-93-1	440	10000	11.4 0.6	54.1	33.9	40	53