TESTING OF ADVANCED LIQUEFACTION CONCEPTS IN HTI RUN ALC-1: COAL CLEANING AND RECYCLE SOLVENT TREATMENT

Gary A. Robbins, Richard A. Winschel, and Francis P. Burke
CONSOL Inc., Research & Development,
4000 Brownsville Road, Library, PA 15129

Francis J. Derbyshire, Edwin N. Givens, University of Kentucky,
Center for Applied Energy Research (CAER),
3572 Iron Works Pike, Lexington, KY 40511-8433

Jianli Hu, Theo L. K. Lee, Hydrocarbon Technologies, Inc. (HTI),
1501 New York Avenue, Lawrenceville, NJ 08648

James E. Miller, Howard P. Stephens, Sandia National Labs,
Department 6212, 1515 Eubank SE, Albuquerque, NM 87185-0709

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

INTRODUCTION

In 1991, the Department of Energy initiated the Advanced Liquefaction Concepts Program to promote the development of new and emerging technology that has potential to reduce the cost of producing liquid fuels by direct coal liquefaction. Laboratory research performed by researchers at CAER, CONSOL, Sandia, and LDP Associates in Phase I is being developed further and tested at the bench scale at HTI. HTI Run ALC-1, conducted in the spring of 1996, was the first of four planned tests. In Run ALC-1, feed coal ash reduction (coal cleaning) by oil agglomeration, and recycle solvent quality improvement through dewaxing and hydrotreatment of the recycle distillate were evaluated. Improvements in liquefaction process performance will be compared to previous results from Wilsonville pilot plant and HTI bench scale runs. Implications of these results for liquefaction economics will be evaluated.

RUN OBJECTIVES

There were four main objectives for Run ALC-1: 1) provide a baseline operating period with Black Thunder Mine subbituminous coal, 2) demonstrate liquefaction of low ash coal produced by oil agglomeration of Black Thunder Mine coal at low pH, 3) demonstrate liquefaction of Black Thunder Mine coal with dewaxing and hydrotreatment of distillate solvent, and 4) operate with extinction recycle of 343 $°C^+$ material, such that a hydrotreated light distillate would be the intended net product. An additional objective was to exploit the advantages of the low-ash coal concept by decreasing the fresh catalyst make-up rate with the lower-ash agglomerated feed.

ACCOMPLISHMENTS

HTI's bench liquefaction Run ALC-1 consisted of 25 days of operation. Major accomplishments were:

- Oil agglomeration reduced the ash content of Black Thunder Mine coal by 40%, from 5.5% to 3.3% (MF, SO_3-free ash basis)

- Excellent coal conversion of 98% was obtained with oil agglomerated coal, about 3% higher than the raw Black Thunder Mine coal, increasing the potential product yield by 2-3% on an MAF coal basis.

- Agglomerates were liquefied with no handling problems.

- Fresh catalyst make-up rate was decreased by 30%, with no apparent detrimental operating characteristics, both when agglomerates were fed and when raw coal was fed (with solvent dewaxing and hydrotreating).

- Recycle solvent treatment by dewaxing and hydrotreating was demonstrated, but steady-state operation was not achieved.

- There was some success in achieving extinction recycle of the heaviest liquid products.

Performance data have not been finalized; they will be fully evaluated when they become available in the near future.

RUN PLAN AND OPERATING HISTORY FOR ALC-1

All Conditions

The run plan, as finalized and executed for Run ALC-1, is shown in Table 1. The fresh catalyst addition rates for Conditions 1 and 2 were set to match the level used in Run CMSL-9, Condition 6 (100 ppm Mo, 10000 ppm Fe, as ppmw MF coal). The fundamental recycle strategy planned for Run ALC-1 was to recycle to extinction all materials that boil above 343 °C, except for the rejected washed pressure filter cake. In practice, equipment and operability constraints did not allow this. Space velocity was the principal "handle" used to control the reaction severity to avoid build-up or deficit of the recycle stream, while maintaining extinction recycle. The objective was to send the entire distillate product to the in-line hydrotreater to produce a light (entirely 343 °C$^-$), high-quality product at all conditions, including the baseline Condition 1. However, distillation inefficiencies resulted in some 343 °C$^-$ material being recycled, some 343 °C$^+$ material being taken as product, and a portion of the distillate not being hydrotreated. The solids rejection device was the pressure filter, allowing enough flexibility to recycle high concentrations of resid while maintaining a low resid-to-solids ratio in the reject pressure-filter cake (PFC). Relative to vacuum distillation, pressure filtration provides a better simulation of a plant with solvent deashing (e.g., ROSE-SR). The pressure-filter cake was washed with toluene to minimize rejection of solubles; this increased the solids content of the pressure-filter cake from ca. 60% to approximately 80%. The vacuum distillation unit, required for some of the conditions, had a cutpoint initially set to 524 °C. The cutpoint was decreased for the conditions when agglomerates were fed. The continuous atmospheric still (or atmospheric flash separator - see footnote "e" in Table 1) cutpoint was specified as 329 °C to provide a 371 °C$^-$ product and ease of operation of the pressure filter. The recycle solvent (including buffers) to MF coal ratio was set at 1.60. The recycle solids to MF coal ratio was set at 20%. This is higher than in either Run CMSL-9 Condition 6 or Run PB-01, Condition 2. The Run ALC-1 conditions provide for high catalyst and unconverted coal recycling rates, which should improve coal conversion, yet allow operation despite the high solids content in the recycle stream.

Condition 1

Solids recycle was performed by recycling toluene-washed PFC. The entire continuous atmospheric still bottoms (CASB) stream was filtered, and the recycle stream consisted of pressure-filter liquid (PFL) and a portion of the toluene-washed PFC. The vacuum still was not required for Condition 1. The recycle strategy was as follows. Toluene-washed PFC was recycled until the target recycle solids concentration (0.2 solids to MF coal ratio) was attained. Once this target was attained, the excess washed PFC was rejected. The balance of the recycle consisted of PFL. To accomplish extinction recycle of PFL, if there was more PFL than needed for recycle, then the space velocity was to be decreased to convert the excess. If there was not enough PFL to meet recycle requirements, then space velocity was to be increased to produce more. Thus, the space velocity was to be determined by performance at each set of operating conditions, including Condition 1. The initial space velocity was 670 kg MF coal/h/m^3. The effectiveness of this strategy was hindered by two operating constraints. First, the 12-hour cycle time for PFC extraction with toluene delayed achievement of the target recycle solids concentration until the fourth day of operation, requiring a one-day extension of Condition 1. Second, about two days were required after an adjustment was made to observe the effects of a change in conditions; there also was a lag of eight or more hours in the availability of lab analyses and material balance data. For these reasons, the first space velocity change was not made until early in Condition 2. In order to shorten the solids recirculation time, it was decided near the end of Condition 1 to recycle unwashed PFC directly, and to shorten the period of PFC extraction with toluene from 12 hours to 4 hours (with a slight reduction in extraction efficiency). The small amount of extracted oil from the toluene wash was recycled, and any additional PFL left on the washed PFC was credited as product.

Conditions 2, 3, and 4

These conditions used oil agglomerated coal as the feedstock. For these conditions, it was necessary to reduce the quantity of distillate in the recycle by an amount equal to the agglomerating oil fed with the coal. All of the PFL was sent to the vacuum still, and all the vacuum still bottoms (VSB) and enough of the vacuum still overhead (VSOH) were recycled as necessary to meet total recycle requirements. Any extra VSOH, which should approximately equal the distillate agglomerating oil added with the coal, was drummed out. To best simulate steady-state operation, this should match the amount and boiling range of the agglomerating oil. The recycle strategy remained the same as in Condition 1.

Early in Condition 2, the slurry viscosity became too high, and the recycle was temporarily changed to PFL, rather than VSB plus VSOH, to keep the system operating. In order to maintain a mixable and pumpable slurry feed blend, but recycle the heaviest resid and distillate components, it was necessary to use a low (413 °C) vacuum still cutpoint, take the 413 °C$^+$ portion of the PFL as slurry blending solvent for recycle, and the 413 °C$^-$ portion of the PFL as agglomerating oil equivalent. Recycle of PFL, and the subsequent decrease in the vacuum still cutpoint from 524 °C to 413 °C with VSOH and VSB recycle, resulted in a lighter recycle and heavier product than desired. Since there was an excess of PFL coming into Condition 2, the space velocity was also decreased from 670 kg MF coal/h/m^3 to 561 kg MF coal/h/m^3 early in Condition 2.

In Condition 3 (also feeding agglomerates), the make-up catalyst rate was cut by 30%, relative to Conditions 1 and 2. A second vacuum still cutpoint of 343 °C was added, so that recycle of light material could be avoided. The 343 x 413 °C stream became the source of agglomerating oil equivalent and recycle distillate.

In Condition 4, conditions were maintained the same as in Condition 3, except that the space velocity was decreased to 400 kg MF coal/h/m^3, in order to reduce the yield of 343 °C$^+$ material. One batch of agglomerates fed during this condition out of the 10 batches fed during Run ALC-1 seemed to result in higher slurry viscosity, but did not cause any operating problem.

Condition 5

The transition was made back to raw Black Thunder Mine coal in Condition 5. For this condition, which includes dewaxing and hydrotreating, it was decided to keep the catalyst make-up rate at 70% of the Condition 1 value, and to set the space velocity at 481 kg MF coal/h/m^3 reactor. The entire PFL stream was vacuum distilled at 524 °C to produce VSOH for dewaxing/hydrotreating. The recycle strategy remained the same as in Condition 1.

RESULTS

Preparation of Agglomerated Coal

A total of 35 exploratory laboratory agglomeration tests and 10 large-scale runs were performed to prepare 590 kg of agglomerated coal for Run ALC-1. The agglomerating oil used to prepare the ALC-1 feed was heavy recycle distillate (V-1074) from the Wilsonville pilot plant end-of-run inventory from Run 263; its analysis is shown in Table 2. Analyses of the agglomeration feed coal (Black Thunder Mine coal) and product agglomerates are also provided in Table 2. To produce each typical batch of agglomerates, 51 kg as-received coal was slurried in ca. 68 L of water (43% slurry concentration) in CONSOL's 189 L agglomeration vessel, the slurry was heated to 70 °C, acidified with concentrated sulfuric acid (1.45 L, or 2.5 kg dose) to a pH of ca. 0.3, and allowed to condition for 60 minutes at high shear mixing conditions. Next, 15.4 kg of the agglomerating oil (ca. 33 wt % MF coal dose) was added to the vessel, at which time a phase inversion took place, as indicated by a change in appearance and consistency of the slurry. Addition of the oil significantly changed the mixing characteristics of the vessel contents, and about 5 min usually were required to restore complete mixing action. These changes coincide with formation of microagglomerates of ca. 0.2 mm in diameter. The high shear mixing continued for a total of 90 minutes after oil addition, at 70 °C, until the spherical agglomerates grew to be predominately 2-4 mm in diameter. The contents of the vessel were discharged over 50-mesh screens and rinsed with cool water. Because of the size growth, the agglomerates were retained on the screen, and the rejected mineral matter washed through the screen. The agglomerates were dried for about 4 days indoors in the open air, or in ovens with a nitrogen purge at 60 °C or lower. The rejected mineral matter included a substantial amount of gypsum created by precipitation of sulfate from sulfuric acid with calcium ions leached from the coal. One of the advantages of agglomeration at low pH is selective rejection from the feed coal of calcium, a potential catalyst poison and source of oolite deposits. At the same time, however, agglomeration selectively retains pyrite, a potential liquefaction catalyst. The ash elemental analyses (Table 2) demonstrate these changes that result from oil agglomeration at low pH. On a mass basis, about 75% of the calcium in the coal was removed. About 0.5% sulfur was added to the oil-free agglomerates.

Agglomeration at low pH produced a consistent ash rejection of 42% $\pm$3% in the ten batches, the product ash content being decreased to 3.3% $\pm$ 0.1% from a 5.5% ash feed coal (MF ash-SO_3-free and oil-free basis). Organic recovery was nearly quantitative. As a percent of the whole agglomerate (average of all 10 runs $\pm 1\sigma$), the agglomerates are composed of 7.5% $\pm$1.2% moisture, 23.4% $\pm$0.3% agglomerating oil, 2.4% $\pm$0.1% SO_3-free ash, and 66.7% $\pm$1.0% MAF coal (69.0% $\pm$1.1% MF coal). Other average and composite sample analyses for the agglomerate products are provided in Table 2.

Run Operations Summary

Run ALC-1 was operated for 25 days, from April 19 through May 14, 1996. Only preliminary results are available. Reporting, additional evaluation of results, and sample characterization will be complete in the near future.

As the run progressed, various changes in equipment and operating conditions were made. These adjustments to the planned operations were made primarily to:

- shorten equipment cycle times (e.g., toluene wash of PFC)
- improve filtration (ca. 343x 399 °C diluent was added, the feed was split to two filters)
- prepare manageable feed slurry blend
- decrease yield of 524°C$^+$ resid and 343 x 524°C range liquid

A more detailed description of these adjustments will be provided in the run report. In general, this run was more complicated than most bench runs made at HTI. It involved several untried concepts, more equipment, more unit operations, and consequently more streams than are typically used. One limitation encountered was that distillation cutpoints were not as clean as was desired. This resulted in more light material being recycled and more heavy material reporting to product than intended. Operational aspects of this run are being evaluated in order better plan future runs under this program.

Preliminary Yield and Performance Results

The preliminary yield and performance data for Run ALC-1 are given in Table 3. The reader should be aware that these data have not been finalized and may be subject to revision. The results are briefly discussed below, organized according to run condition.

Condition 1, Baseline with Raw Coal

The baseline condition shows a coal conversion of 95%, a C_4-524 °C^- distillate yield of 69%, and a (distillate plus 524 °C^+ resid) liquid yield of 73%, somewhat higher than that observed in Run CMSL-9, Condition 6, or in Run PB-01, Conditions 1-3. A lower space velocity would be needed to achieve extinction of the 343 °C^+ material (yield of ca. 20%) or 524 °C^+ material (yield of ca. 4%).

Condition 2, Agglomerated Coal, Standard Catalyst Make-Up Rate

Coal conversion increased from ca. 95% with raw coal in Condition 1 to about 98% with the agglomerated coal. Distillate yield was 56%, and liquid yield was 71%. Overall, there were no slurry preparation problems or other operating issues that arose because of agglomerate characteristics. There were some difficulties associated with distillation to make an appropriate VSOH/VSB split for slurry preparation and compensation for agglomerating oil foreign to the run. Although space velocity was reduced during this condition, there was still a 26% yield of 343 °C^+ material. Distillation inefficiencies contributed to a high yield of 524 °C^+ material. This was a factor in deciding to extend testing of agglomerates into Condition 4.

Condition 3, Agglomerated Coal, Decreased Catalyst Make-Up Rate

The catalyst make-up rate was decreased by 30%, apparently without any negative consequences. For this condition and Condition 4, some distillation changes were made, in order to decrease the recycle of lighter ≈343 °C^- material, in favor of increased recycle of heavier material. Coal conversion remained high at 98%, and there were no operating difficulties. Distillate yield was ca.61%, and liquid yield was ca. 71%.

Condition 4, Agglomerated Coal, Decreased Catalyst Make-Up Rate

For this condition, the space velocity was decreased. Otherwise, conditions were the same as in Condition 3. Coal conversion remained at 98%, the distillate yield increased to 66%, and the liquid yield decreased slightly to 70%. The preliminary distillate and resid yields from Condition 4 of Run ALC-1 are a little lower than in Condition 1, but the distillate product made in Condition 4 is a little lighter. Relative to Conditions 1 and 5, in which raw coal was fed, preliminary results from Conditions 2 through 4, in which agglomerates were fed, showed higher coal conversion, the same or lower hydrogen consumption, the same or lower distillate yield, and higher yields of gas, H_2S, and water. Sulfate retained on the agglomerates may account for the higher yield of H_2S and some of the water. However, the water yield is too high to be accounted for by sulfate alone.

Condition 5, Dewaxing and Hydrotreating of Recycle Distillate

Dewaxing and hydrotreating were successfully demonstrated during Condition 5, but steady state was not achieved because of slow filtration and other delays in getting fresh dewaxed/hydrotreated distillate. Overall time to recycle material was long because of the large number of unit operations required. Coal conversion returned to 95%, distillate yield was 65% (includes the material removal as wax), and liquid yield was 72%.

CONCLUSIONS

HTI's bench liquefaction Run ALC-1 consisted of 25 days of operation. Oil agglomeration reduced the ash content of Black Thunder Mine coal by 40%, from 5.5% to 3.3% (MF, SO_3-free basis). Agglomerated coal achieved excellent coal conversion of 98%, about 3% higher than the raw Black Thunder Mine coal, presumably because it allowed higher recycle of solids. This can result in 2-3% higher yields of products. There were no handling problems associated with feeding agglomerates. There were no apparent detrimental operating characteristics associated with operation at a 30% lower fresh catalyst rate, both when agglomerates were fed and when raw coal was fed (with solvent dewaxing and hydrotreating). Recycle solvent treatment by dewaxing and hydrotreating was demonstrated, but steady-state operation was not achieved. For a number of reasons, there was limited success in achieving extinction recycle of the heaviest liquid products.

FUTURE WORK

A complete evaluation of Run ALC-1 results will be made after June, when a draft report will be issued and a post-run review meeting is scheduled. Additional sample characterization will be performed by CONSOL. LDP Associates will evaluate the results of Run ALC-1 in light of process economic considerations. Run ALC-2 is scheduled for later this year. Preliminary planning for it will take place as the Run ALC-1 results are evaluated. The program also calls for two additional runs to take place in 1997.

ACKNOWLEDGMENTS

The limited space here does not permit us to name all those who contributed to this work, and to whom many thanks are owed. Several of CONSOL's technicians, engineers, chemists, and secretaries made significant contributions. The cooperation and hard work of HTI's staff of engineers, chemists, analysts, and operators was critical to this project. Our thanks go to all of these people. This project is funded by U.S. DOE under contract Nos. DE-AC22-91PC91040 and DE-AC04-94AL85000.

TABLE 1

RUN PLAN - Run ALC-1

Condition	**1**	**2**	**3**	**4**	**5**
Periods	**1-6**	**7-13**	**14-17**	**18-20**	**21-25**
Feed Coal Pretreatment					
Black Thunder Coal (a)	Raw	OA	OA	OA	Raw
Distillate Solvent Pretreatment	None	None	None	None	DW-HT(b)
Recycle Conditions					
Recycle Streams	PFL/PFC	PFC/VSB/ VSOH	PFC/VSB/ VSOH	PFC/VSB/ VSOH	PFC/VSB/ DWHT-VSOH
Recycle (incl. buffers) to MF Coal Ratio	1.60	1.60	1.60	1.60	<1.60(c)
Recycle (excl. buffers) to MF Coal Ratio	1.52	1.52	1.52	1.52	<1.52(c)
Recycle Solids/MF Coal Ratio	0.20	0.20	"Y"(d)	"Y" (d)	0.20
Target % Solids in Toluene-Washed PFC	~75	~75	~75	~75	~75
Still Cut Points, °C					
Continuous Atmospheric Still(e)	329	329	329	329	329
Vacuum Still	-	413	343, 413	343, 413	343, 524
Temperature, °C					
Pretreater	300	300	300	300	300
K-1	440	440	440	440	440
K-2	450	450	450	450	450
HTU	350-380	350-380	350-380	350-380	350-380
Space Velocity (Nominal)					
kg MF coal/h/m^3, each reactor	670	561	561	400	481
Catalyst Addition Rates					
Molyvan A (as Mo), ppm MF Coal	100	100	70	70	70
Fe-based (as Fe), ppm MF Coal	10000	10000	7000	7000	7000
H_2S, wt % MF Coal	3	3	3	3	3

a. OA = low-pH oil agglomeration product.

b. DW-HT: VSOH will be dewaxed using acetone at ca. -5 °C, then hydrotreated at conditions to be determined by HTI and other participants.

c. Reduced by yield of wax.

d. "Y" is same recycle ash/MF coal ratio as in the baseline Condition 1.

e. The Continuous Atmospheric Still quit working early in the run and was bypassed; an equivalent atmospheric flash separator provided the same function.

TABLE 2

COMPOSITION OF AGGLOMERATING OIL, FEED COAL, AND AGGLOMERATED COAL

	Agglomerating Oil (As-Det'd Basis)	Black Thunder Mine Coal, HTI No. 6213		Whole Agglomerates Run C1-C10 Average	Oil-Free Agglomerates Run C1-C10 Average (By Calculation from Whole Agglomerates)	Whole Agglomerates Run C2-C9 Composite
		Avg Drums 1-4 (a)	Lab Composite Drums 1-4 (b)			
Moisture, wt % As-Determined		9.91	9.70	7.54 ±1.22		6.91
Ash, wt % MF, Including SO_3		6.23	6.26	2.83 ±0.12		2.77
<u>Ultimate, wt % MF, SO_3-Free Ash Basis</u>						
Carbon	89.74	71.08	70.72	75.84 ±0.34	71.21 ±0.45	75.00
Hydrogen	8.81	4.69	4.74	6.13 ±0.10	5.23 ±0.14	6.07
Nitrogen	0.59	0.92	1.00	0.86 ±0.01	0.96 ±0.01	0.85
Sulfur	0.03	0.50	0.49	0.73 ±0.03	0.97 ±0.04	0.74
Oxygen (by Diff.)	0.84	17.32	17.82	13.88 ±0.43	18.33 ±0.59	14.83
Ash, SO_3-Free		5.50	5.23	2.56 ±0.11	3.30 ±0.14	2.51
SO_3, wt % of Ash		11.78	16.42	9.65 ±1.19		9.32
HHV, Btu/lb (MF)	17954	12069	11967	13644 ±89		13559
<u>Major Ash Elements, Oxide wt % of SO_3-Free Ash</u>						
Na_2O			1.75	0.41 ±0.04		0.40
K_2O			0.51	0.53 ±0.04		0.53
CaO			25.78	8.99 ±0.50		8.53
MgO			5.40	1.45 ±0.12		1.41
Fe_2O_3			6.66	8.87 ±0.60		9.61
TiO_2			1.45	2.51 ±0.08		2.57
P_2O_5			1.36	2.13 ±0.14		2.02
SiO_2			37.34	47.84 ±1.11		46.06
Al_2O_3			19.14	26.93 ±0.50		26.22
Total			99.40	99.65 ±1.06		97.34

(a) Drums 1-4 were the feed to agglomeration production Runs C1-C9.
(b) Lab composite was the feed to laboratory agglomeration tests.

TABLE 3

PRELIMINARY YIELD AND PROCESS PERFORMANCE DATA FROM HTI RUN ALC-1 (227-94) RESULTS AS OF 6/12/96

Date Period Coal Type or Agglom. Product No. Condition	4/24/96 6 Raw Coal 1	5/1/96 13 Aggl. C6 & C7 2	5/5/96 17 Aggl. C8 & C9 3	5/8/96 20 Aggl. C1 & C10 4	5/13/96 25 Raw Coal 5
Net Normalized Yields, wt % MAF Coal					
C_1-C_3 in Gases	10.10	12.51	11.47	13.00	10.07
C_4-C_7 in Gases	4.96	5.19	5.06	6.48	4.17
IBP-177 °C (IBP-350 °F)	13.04	13.27	13.93	15.96	12.01
177-260 °C (350-500 °F)	11.32	7.33	7.75	9.70	13.43
260-343 °C (500-650 °F)	23.44	19.76	23.60	23.88	29.96
343-454 °C (650-850 °F)	14.76	8.86	12.87	13.24	2.13
454-524 °C (850-975 °F)	1.26	1.50	-2.52	-3.75	-1.17
524 °C^+ (975 °F^+)	4.43	15.42	10.38	4.56	7.22
Unconverted Coal	5.04	2.31	2.42	2.51	5.28
Water Yield by Material Balance	13.66	17.90	17.20	17.01	13.40
COx	5.93	2.79	4.44	4.27	6.59
NH_3	0.64	0.28	0.36	0.65	1.04
H_2S	-1.13	-0.28	0.03	-0.09	-1.13
Unnormalized Wax Product					4.70
Process Performance, wt % MAF Coal					
Hydrogen Consumption	7.45	6.85	7.00	7.43	7.69
Coal Conversion (SO_3 free)	94.96	97.69	97.58	97.49	94.72
524 °C^+ Conversion	90.53	82.27	87.20	92.93	87.49
C_4-524 °C Distillate	68.78	55.92	60.70	65.52	65.22
524 °C^+ Resid Yield, MAF	4.43	15.42	10.38	4.56	7.22

NOTE: Agglomerating oil is accounted as a non-fresh feed stream in Conditions 2-4.