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IN HTI RUN ALC-1: COAL CLEANING AND
RECYCLE SOLVENT TREATMENT**

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

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INTRODUCTION AND RUN OBJECTIVES

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.

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: 1) oil agglomeration reduced the ash content of Black Thunder Mine coal by 40%, from 5.5% to 3.3% (MF, SO₃-free ash basis); 2) 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; 3) agglomerates were liquefied with no handling problems; 4) 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); 5) recycle solvent treatment by dewaxing and hydrotreating was demonstrated, but steady-state operation was not achieved; and 6) there was some success in achieving extinction recycle of the heaviest liquid products. Performance data have not been finalized; they will be available for full evaluation 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 matched those used in Run CMSL-9, Condition 6. 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). The pressure-filter cake was washed with toluene to minimize rejection of solubles. 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 recycle solvent (including buffers) to MF coal ratio was set at 1.60 and the recycle solids to MF coal ratio was set at 20% to provide for high catalyst and unconverted coal recycling rates, which should improve coal conversion, yet allow operation with the high solids content in the recycle stream.

Condition 1

The entire continuous atmospheric still bottoms (CASB) stream was filtered, and the recycle strategy was as follows. Toluene-washed pressure-filter cake (PFC) was recycled until the target recycle solids concentration was attained. Once this target was attained, the excess washed PFC was rejected. The balance of the recycle consisted of pressure-filter liquid (PFL). To accomplish extinction recycle of PFL, if there was more PFL than needed for recycle, 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 effectiveness of this strategy was hindered by two operating constraints. First, the 12-hour cycle time for PFC extraction with toluene resulted in a two-day delay in achievement of the target recycle solids concentration. Second, an inherent lag of about two days was required to observe the effects of a change in conditions. These factors delayed the first space velocity change 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).

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 PFL was temporarily recycled in place of VSB plus VSOH to keep the system operating. The long-term solution was to decrease the vacuum still cutpoint from 524 °C to 413 °C with recycle of VSOH and VSB. Recycle of PFL, and the subsequent decrease in the vacuum still cutpoint, 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 decreased 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/m³, 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/m³ 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 (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% ±3% in the ten batches, the product ash content being decreased to 3.3% ± 0.1% from a 5.5% ash feed coal (MF ash-SO₃-free and oil-free basis). Organic recovery was nearly quantitative. As a percent of the whole agglomerate (average of all 10 runs ±1σ), the agglomerates are composed of 7.5% ±1.2% moisture, 23.4% ±0.3% agglomerating oil, 2.4% ±0.1% SO₃-free ash, and 66.7% ±1.0% MAF coal (69.0% ±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. 343 x 399 °C diluent was added, the feed was split to two filters); prepare manageable feed slurry blend; and decrease yield of 524 °C⁺ resid and 343 x 524 °C range liquid.

These adjustments will be described in more detail 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 distillation efficiency, resulting in lighter recycle and heavier product than intended. Operational aspects of this run are being evaluated in order to 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 as follows. The baseline condition (Condition 1, with raw coal) shows a coal conversion of 95%, a C₄-524 °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%). In Condition 2, with agglomerated coal and 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. In Condition 3, also with agglomerated coal, 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%. For Condition 4, 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, H₂S, and water. Dewaxing and hydrotreating of recycle distillate were 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, SO₃-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

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TABLE 1. RUN PLAN - RUN ALC-1

Condition/Periods	1/1-6	2/7-13	3/14-17	4/18-20	5/21-25
Pretreatment (a) of Black Thunder Coal/Distillate Solvent	Raw/None	OA/None	OA/None	OA/None	Raw/DW-HT
Recycle Conditions(b) Recycle Streams	PFL/PFC	PFC/VSB/ VSOH	PFC/VSB/ VSOH	PFC/VSB/ VSOH	PFC/VSB/ DWHT-VSOH(c)
Recycle Solids/MF Coal Ratio	0.20	0.20	"Y"(d)	"Y"(d)	0.20
Still Cut Points, °C CAS(e)/ Vacuum Still	329/ -	329/413	329/343, 413	329/343, 413	329/343, 524
Temperature, °C Pretreater/K-1/K-2 HTU	300/440/450 350-380	300/440/450 350-380	300/440/450 350-380	300/440/450 350-380	300/440/450 350-380
Space Velocity (Nominal) kg MF coal/h/m ³ , each reactor	670	561	561	400	481
Cat Addition Rates, ppm MF Coal Molyvan A (as Mo) Fe-based (as Fe) H ₂ S	100 10000 30000	100 10000 30000	70 7000 30000	70 7000 30000	70 7000 30000

- OA = low-pH oil agglomeration product.; DW-HT = VSOH will be dewaxed using acetone at ca. -5 °C, then hydrotreated.
- Other recycle conditions were: recycle to MF coal ratios of 1.60, including buffers, (1.52, excluding buffers), except as noted for Condition 5; and target of 75% solids in toluene-washed PFC.
- For this condition, the recycle to MF coal ratio is reduced by yield of wax.
- "Y" is same recycle ash/MF coal ratio as in the baseline Condition 1.
- The Continuous Atmospheric Still (CAS) 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

	Agglom. Oil (As- Det'd Basis)	Black Thunder Mine Coal		Whole Agglom. Run C1-C10 Average	Oil-Free Agglom. Run C1-C10 Average	Whole Agglom. Run C2-C9 Composite
		Drum Sample	Lab Sample			
Moisture, wt % As-Det. Ash, wt % MF, Incl. SO ₃ SO ₃ , wt % of Ash HHV, Btu/lb (MF)	17954	9.91 6.23 11.78 12069	9.70 6.26 16.42 11967	7.54 ±1.22 2.83 ±0.12 9.65 ±1.19 13644 ±89		6.91 2.77 9.32 13559
<u>Ultimate, wt % MF, SO₃-Free Ash Basis</u> Carbon Hydrogen Nitrogen Sulfur Oxygen (by Diff.) Ash, SO ₃ -Free	89.74 8.81 0.59 0.03 0.84	71.08 4.69 0.92 0.50 17.32 5.50	70.72 4.74 1.00 0.49 17.82 5.23	75.84 ±0.34 6.13 ±0.10 0.86 ±0.01 0.73 ±0.03 13.88 ±0.43 2.56 ±0.11	71.21 ±0.45 5.23 ±0.14 0.96 ±0.01 0.97 ±0.04 18.33 ±0.59 3.30 ±0.14	75.00 6.07 0.85 0.74 14.83 2.51
<u>Major Ash Elements, Oxide wt % of SO₃- Free Ash</u> Na ₂ O K ₂ O CaO MgO Fe ₂ O ₃ TiO ₂ P ₂ O ₅ SiO ₂ Al ₂ O ₃ Total			1.75 0.51 25.78 5.40 6.66 1.45 1.36 37.34 19.14 99.40	0.41 ±0.04 0.53 ±0.04 8.99 ±0.50 1.45 ±0.12 8.87 ±0.60 2.51 ±0.08 2.13 ±0.14 47.84 ±1.11 26.93 ±0.50 99.65 ±1.06		0.40 0.53 8.53 1.41 9.61 2.57 2.02 46.06 26.22 97.34

(a) By Calculation from Whole Agglomerates

TABLE 3. PRELIMINARY YIELD AND PROCESS PERFORMANCE DATA FROM HTI RUN ALC-1 (227-94), RESULTS AS OF 6/12/96

Date Condition/Period Coal Type or Agglom. Product No. C_	4/24/96 1/6 Raw	5/1/96 2/13 C6/C7	5/5/96 3/17 C8/C9	5/8/96 4/20 C1/C10	5/13/96 5/25 Raw
<u>Net Normalized Yields, wt % MAF Coal</u> C ₁ -C ₃ in Gases C ₄ -C ₇ in Gases IBP-177 °C (IBP-350 °F) 177-260 °C (350-500 °F) 260-343 °C (500-650 °F) 343-454 °C (650-850 °F) 454-524 °C (850-975 °F) 524 °C* (975 °F*) Unconverted Coal Water Yield by Material Balance COx NH ₃ H ₂ S Unnormalized Wax Product	10.10 4.96 13.04 11.32 23.44 14.76 1.26 4.43 5.04 13.66 5.93 0.64 -1.13	12.51 5.19 13.27 7.33 19.76 8.86 1.50 15.42 2.31 17.90 2.79 0.28 -0.28	11.47 5.06 13.93 7.75 23.60 12.87 -2.52 10.38 2.42 17.20 4.44 0.36 0.03	13.00 6.48 15.96 9.70 23.88 13.24 -3.75 4.56 2.51 17.01 4.27 0.65 -0.09	10.07 4.17 12.01 13.43 29.96 2.13 -1.17 7.22 5.28 13.40 6.59 1.04 -1.13 4.70
<u>Process Performance, wt % MAF Coal</u> Hydrogen Consumption Coal Conversion (SO ₃ free) 524 °C* Conversion C ₄ -524 °C Distillate 524 °C* Resid Yield, MAF	7.45 94.96 90.53 68.78 4.43	6.85 97.69 82.27 55.92 15.42	7.00 97.58 87.20 60.70 10.38	7.43 97.49 92.93 65.52 4.56	7.69 94.72 87.49 65.22 7.22