CTSL™ CATALYTIC TWO-STAGE LIQUEFACTION COUPLED WITH COAL CLEANING

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Introduction

The overall objective of the CTSL process, which has been under DOE sponsored Bench-Scale development since 1983, is to achieve higher distillate yields, better quality products and to lower production and capital costs in relation to existing direct coal liquefaction technologies.

CTSL is a two-stage direct liquefaction process using close-coupled ebullated-bed reactors with the first stage operating at milder temperatures than the second stage (see Figure 1). Cobalt or nickel molybdenum on alumina catalysts are used to produce an all distillate slate of products with low sulfur and nitrogen contents. The lower temperature first stage promotes hydrogenation of the coal derived oils and of the recycled solvent prior to hydrocracking and additional heteroatom removal in the second stage.

Efforts have been underway to improve economics of the process by improving yields while reducing erosion and solids separation requirements through cleaning and beneficiation of the coal prior to liquefaction. Various techniques have been examined and tested in HRI's Bench-Scale unit. The Bench-Scale unit consists of a two-stage continuous ebullated-bed reactor system with on-line fractionation and optional on-line fixed-bed hydrotreating. At a nominal capacity of 50 pounds of coal per day, this size unit clearly defines process chemistry of a CSTR system with operations in a batch mode with respect to catalysts. Scale-up is on a 1/1 basis to the next larger PDU operations size on a selected equilibrium catalyst activity basis.

HRI has examined various modes of beneficiation//cleaning and evaluated them in both single and two-stage processing. Some of the techniques evaluated were: Heavy Media Cleaning, Electrostatic Precipitation, Oil Agglomeration of Pulverized Coal, Oil Agglomeration of Micronized Coal and Chemical Leaching.

Program

Present direct coal liquefaction studies at HRI are sponsored by DOE under a three year contract from 1988 to fiscal 1992. The baseline coal for cleaned and beneficiated coal studies has been Illinois #6 Burning Star coal with a typical analysis as shown in Table 1. The evaluations of heavy media and electrostatically cleaned coals occurred in a preceding contract in 1986, the oil agglomeration tests were recently completed in 1990.

Objective

The specific objectives of these studies were to quantify the reactivity differences resulting from beneficiation and to determine the processing advantages resulting in solid separation and product handling.

Studies

Five samples of Illinois #6 Burning Star Mine coal cleaned by different techniques were evaluated in continuous two-stage ebullated-bed bench-scale operations to examine their liquefaction behavior. The five cleaning techniques were: heavy media density separation, electrostatic precipitation, chemical leaching and oil agglomeration of pulverized and micronized coal. Operations and results of the cleaned coals were compared directly with a sample of conventionally cleaned (washed) coal from the mine and run at near identical conditions.

The coal samples were prepared at other laboratories briefly as follows: Heavy Media cleaned coal was cleaned at the Bituminous Coal Research facility in Monroeville, PA using magnetite as the dense phase with a total recovery of about 67 W% of the feed coal. Coal cleaned and beneficiated by electrostatic precipitation was prepared in a proprietary process by AED, Advanced Energy Dynamics of Natick, Mass. using a vertical belt separator feeding -70 mesh dried coal supplied by HRI. Recovery was 47% with a possible of 85% using a finer grind and rotary apparatus. The coal prepared by the "Ash Lite", Resource Engineering, Inc. leaching method also used -70 mesh coal from HRI and was prepared in Waltham, Mass. with a reported carbon yield of over 90% and an ash reduction to 3.6%. A major change was noted with an increase in the chlorine content of the coal from 0.06 W% to 1.8 W% after cleaning.

A coal sample was prepared at Homer City, PA by Bechtel under contract to DOE using spherical agglomeration with heptane and asphalt while feeding coal pulverized to less than 50 mesh. The coal was supplied with a hard asphalt content of 1.9 W% and 6.8 W% moisture and fed to the bench unit as received.

A fifth cleaned and beneficiated coal was prepared in Syracuse, NY by the proprietary "OTISCA" coal process and supplied as a 35% slurry in water. This coal is also cleaned using light solvents and a fine micronized coal of 5 micron median diameter. This was the only coal sample that required special handling to remove the water to low levels prior to liquefaction.

Maceral analysis were obtained on each of the coals in addition to ash and sulfur and other heteroatoms to determine the degree of beneficiation and effects on liquefaction and reactivity of the coals in a catalytic ebullated-bed system. A 1/32" extrudate catalyst of alumina promoted with nickel molybdate was used in all the sample evaluations and start-up oil was a Wilsonville derived heavy distillate from Illinois Coal. The operating conditions were 2500-2800 psig system pressure, reaction temperatures of 750/800°F, space velocity of 45 lbs/hr/ft^3 of settled catalyst and oil/coal ratio of 1.1/1 except for the OTISCA coal at about 2 to 1.

Results and Discussion

The coal prepared by REI using the "Ash Lite" process showed lower reactivity than other samples when screened on a microautoclave scale and failed due to a high pressure drop after operating 13 hours in the continuous bench-scale apparatus. As a result, only minimal data was obtained on this sample.

Each of the other coals operated smoothly showing enhanced reactivity when compared with untreated, mine washed coal. In the OTISCA coal/water slurry tests coals were compared on the same micronized size and water concentration basis.

The proximate and petrographic analysis of the coal samples are presented in Table 2. In each cleaning technique, the coals are beneficiated by a reduction in the inerts and fusinite. A summary of normalized yields and performance data are presented in Table 3. Comparisons are made with mine washed coal and with unagglomerated micronized coal.

Coal Conversion - The coal conversion follows the decrease in inertinite and ash contents showing higher conversion ranging from 89 to 96 W%. The lower coal conversions for the micronized coal studies may be attributed to the use of 10% lower slurry coal concentration and subsequent lower residence time.

Resid Conversion - Residual oil or 975°F⁺ conversion (basis = 100-unconverted coal and residual oil) is considerably improved as the ash content is reduced, ranging from 82 to 92% for the lowest ash coal.

Distillate Yields - Distillate yields follow a similar pattern, ranging from 66 to 69% for the uncleaned coals to 71 to 76 W% MAF for the cleaned and beneficiated coals. A bar chart comparison is shown in Figure 2 with the spherical oil agglomerated cleaned coal showing the highest yield at 76.2 W% of MAF coal. The electrostatically cleaned coal falls outside the pattern; this may be the result of some oxidation as shown by high sulfate sulfurs.

Product Quality - The quality of the oils produced was generally enhanced by cleaning, showing higher hydrogen contents and lower heteroatom levels. Table 4 illustrates the improved quality of the 500-650°F product as obtained with coal cleaned by spherical agglomeration.

Conclusions

- Coal cleaning and beneficiation (reduction of inert organic matter) by methods studied herein produces higher coal conversion and distillate yields in ebullated bed reaction systems.
- The improved productivity is accompanied by lower solid removal requirements and a probable lower erosion rate in let-down valves and lines.
- The highest yields were obtained with the heavy media cleaned and spherical oil agglomeration products.
- Residual oil conversion appears to correspond directly with ash content (see Figure 3) which may be the result of reducing catalyst poisons.

Economic studies are currently underway to determine the product cost benefit of using cleaned coal techniques. The two methods currently under consideration based on the results of this study are heavy media and spherical oil agglomeration cleaning.

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TABLE 1

FEED COAL ANALYSES

ILLINOIS NO. 6 BURNING STAR MINE

Feed Designation	(Run-of-Mine)	(Agglomerated)
Ultimate Analysis (W%, Dry Basis)		
Carbon	65.12	74.75
Hydrogen	4.57	5.23
Sulfur	3.80	2.90
Nitrogen	1.33	1.53
Ash	15.21	4.62
Oxygen (by difference)	9.97	10.97
Sulfur Forms (W%, Dry Basis)		
Sulfate	0.12	0.05
Pyrite	1.84	0.59
Organic	1.74	2.23
Mineral Analysis of Ash (W%, Ignited		
Silica, SiO_2	49.50	38.40
Alumina, Al_2O_3	19.62	18.00
Titania, TiO_2	0.90	0.99
Ferric Oxide, Fe_2O_3	20.52	28.02
Lime, CaO	4.08	4.96
Magnesia, MgO	1.04	1.10
Potassium Oxide, K_2O	1.76	1.70
Sodium Oxide, Na_2O	0.85	1.30
Sulfur Trioxide, SO_3	1.09	4.11
Phosphorous Pentoxide, P_2O_5	0.31	0.31
Undetermined	0.33	1.11

TABLE 2

CLEANED, BENEFICIATED COAL ANALYSIS

Ultimate, W% Dry	Mine Washed	Heavy Media Cleaned	Electrostatic Cleaned	Chemical Cleaning	Oil Agglom. Pulverized	Oil Agglom. Micronized	Micronized Unagglom.
Carbon	70.4	73.9	74.3	74.0	74.8	75.9	69.3
Hydrogen	4.5	4.9	4.7	4.8	5.2	5.2	4.5
Nitrogen	1.4	1.5	1.5	1.9	1.5	1.5	1.3
Sulfur	3.6	2.8	3.1	3.2	2.9	2.7	3.5
Ash	10.6	5.8	4.9	3.6	4.6	3.5	10.6
Oxygen (Diff.)	9.5	12.1	11.4	10.8	11.0	11.3	10.7
Sulfur Forms, W% Dry							
Sulfate	0.12	0.25	0.30	0.01	0.05	0.07	0.11
Pyrite	1.8	0.5	0.7	1.1	0.6	0.6	1.3
Organic	1.7	2.1	2.0	2.3	2.2	2.1	2.0
Petrographic, V%							
Total Reactives	88.2	91.5	92.6	90.1	91.9	84.5[(1)]	81.1[(1)]
Total Inerts	11.8	8.5	7.4	9.9	8.1	15.5	19.9
Fusinite	1.9	0.3	0.5	0.8	3.3	NA	NA

(1) Performed at a different laboratory

TABLE 3

YIELDS AND PERFORMANCE OF CLEANED COALS

	Mine Washed	Heavy Media Cleaned	Electrostatic Cleaned	Oil Agglom. Pulverized	Oil Agglom. Micronized	Micronized Unagglom.
<u>Yields, W% MAF</u>						
C_1-C_3	5.9	6.2	6.7	7.3	8.3	5.6
C_4-390°F	17.1	19.0	18.9	22.3	21.6	18.1
390-650°F	32.9	35.7	32.4	33.1	39.6	29.0
650-975°F	19.2	18.6	20.1	17.3	11.9	19.2
975°F$^+$	8.3	8.3	9.5	4.9	1.4	7.5
Performance, <u>W% MAF</u>						
Coal Conversion	93.0	96	96.2	95.4	93.3	89.3
975°F$^+$ Conv.	84.7	87.8	86.6	90.2	91.9	82
C_4-975°F$^+$ Yield	69.2	73.3	71.4	76.2	73.1	66.3
Hydrogen Consumption	7.1	7.5	7.3	7.0	7.9	6.7

TABLE 4

DETAILED COMPARISON OF SPHERICAL AGGLOMERATED COAL

Coal Feed	Agglomerated		R-O-M
Ash in Coal Feed, W%	4.62	4.62	15.21
NiMo Catalyst Age. Lb Coal/Lb Cat.	106	233	319
<u>Yields, W% MAF Coal</u>			
C_1-C_3 Hydrocarbon Gases	7.9	7.6	8.9
C_4-975°F Liquids	75.0	76.2	68.8
975°F$^+$ Residual Oil	2.0	5.1	7.1
H_20, NH_3, H_2S, CO_x	17.1	13.8	16.4
Hydrogen Consumption	7.7	7.4	7.4
Coal Conversion	94.5	95.4	93.7
Product (Recycle) Resid. Conc., W%	16.6	26.7	31.0
<u>Properties, 500-650°F Product</u>			
Hydrogen, W%	11.57	11.39	11.08
Nitrogen, W%	0.11	0.10	0.13
Sulfur, W%	<0.01	<0.01	<0.02

HRI EBULLATING-BED
CATALYTIC TWO-STAGE COAL LIQUEFACTION (CTSL) PROCESS
SIMPLIFIED FLOW PLAN

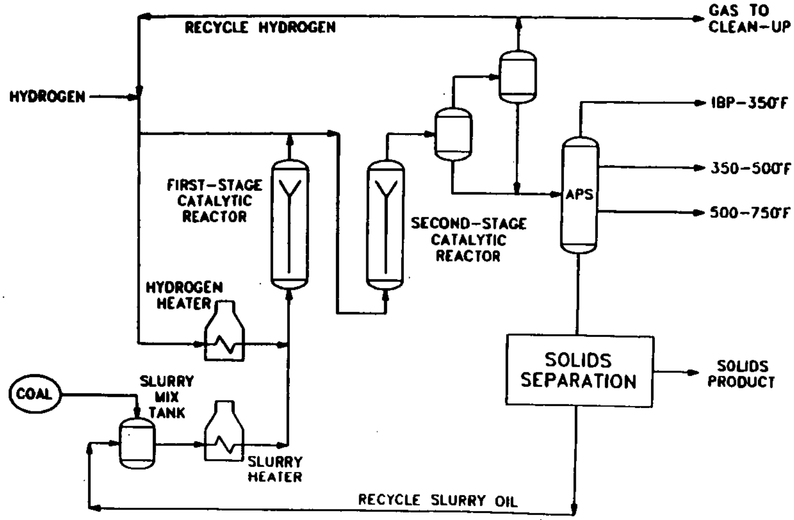

FIGURE 1

FIGURE 2
CLEANING METHOD EFFECT
ON DISTILLATE YIELDS

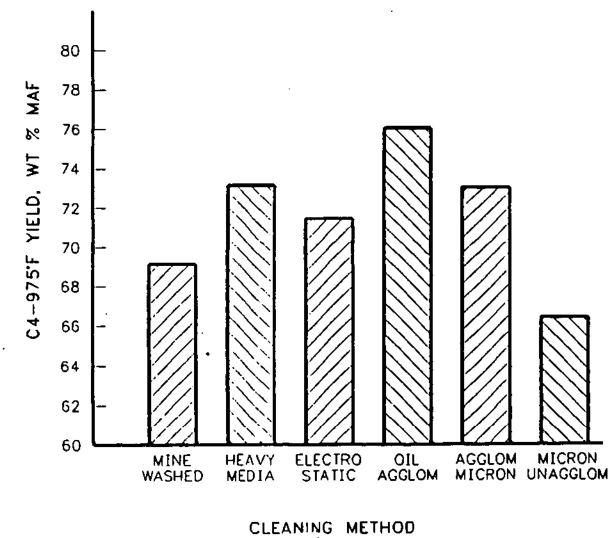

FIGURE 3

ASH EFFECT ON RESIDUAL OIL CONVERSIONS IN EBULLATED BEDS