THE DIRECT LIQUEFACTION PROOF OF CONCEPT PROGRAM

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ABSTRACT

The goal of the Proof of Concept (POC) Program is to develop Direct Coal Liquefaction and associated transitional technologies towards commercial readiness for economically producing premium liquid fuels from coal in an environmentally acceptable manner. The program focuses on developing the two-stage liquefaction (TSL) process by utilizing geographically strategic feedstocks, commercially feasible catalysts, new prototype equipment, and testing co-processing or alternate feedstocks and improved process configurations.

Other high priority objectives include dispersed catalyst studies, demonstrating low rank coal liquefaction without solids deposition, improving distillate yields on a unit reactor volume basis, demonstrating ebullated bed operations while obtaining scale-up data, demonstrating optimum catalyst consumption using new concepts (e.g. regeneration, cascading), producing premium products through on-line hydrotreating, demonstrating improved hydrogen utilization for low rank coals using novel heteroatom removal methods, defining and demonstrating two-stage product properties for upgrading; demonstrating efficient and economic solid separation methods, examining the merits of integrated coal cleaning, demonstrating co-processing, studying interactions between the preheater and first and second-stage reactors, improving process operability by testing and incorporating advanced equipment and instrumentation, and demonstrating operation with alternate coal feedstocks.

During the past two years two major PDU Proof of Concept runs were completed. POC-1 with Illinois No. 6 coal and POC-2 with Black Thunder sub-bituminous coal. Results from these operations are continuing under review and the products are being further refined and upgraded. This paper will update the results from these operations and discuss future plans for the POC program.

The Direct Liquefaction Proof-of-Concept Program
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INTRODUCTION

Coal is the most abundant fossil fuel resource of the United States. The technology for its conversion to liquid transportation fuels such as gasoline, kerosine, and diesel is being continually improved at Hydrocarbon Technologies, Inc. (HTI). The state-of-art direct coal liquefaction process has brought down the crude equivalent price of coal liquids to about $30.00 a barrel from over $70 a barrel by the technologies existing in the early 70s. The most widely researched technology today is the Catalytic Two Stage Liquefaction Process (CTSL$^+$), invented by Hydrocarbon Research, Inc. during the late 80s. The Catalytic Two Stage Liquefaction Process is an advanced direct coal liquefaction process that utilizes a low temperature first stage to foster hydrogenation in the presence of a nickel molybdenum ebullated bed catalyst and a higher temperature second stage to increase conversion and heteroatom removal. A preferred mode of operation developed at the Bench Scale is with extinction recycle of the 700°F$^+$ fraction to produce a premium quality light distillate product. The CTSL™ technology is also environmentally benign. Most of the R & D work on CTSL was funded by the U.S. Department of Energy during the last decade. The U.S. DOE also co-sponsored a demonstration program at the Proof-of-Concept (POC) scale for the CTSL™ Technology during the last three years at Hydrocarbon Technologies, Inc. As a result of this, extensive modifications were made to HTI's 4.0 TPD Process Development Unit incorporating equipment from Wilsonville Advanced Coal Liquefaction Facility and upgrades in the period from December 1992 into October 1993. This created a unique POC unit consisting of two ebullated bed reactors plus an on-line hydrotreater and three modes of solid separation: vacuum distillation, ROSE-SR℠, a pressure filtration. Two long duration process demonstration runs were accomplished during 1993 and 1994. POC Run 1 evaluated the liquefaction behavior of a bituminous coal from Illinois No. 6 seam, Crown II mine. POC Run 2 demonstrated the performance using a sub-bituminous coal from Wyoming Black Thunder mine, followed by several days of co-liquefaction operations of coal with plastics and waste tire rubber.

PROGRAM OBJECTIVES

The overall objective of the Proof of Concept (POC) Program is to develop Direct Coal Liquefaction and associated transitional technologies towards commercial readiness for economically producing premium liquid fuels from coal in an environmentally acceptable manner. The program focuses on developing the two-stage liquefaction (TSL) process by utilizing geographically strategic feedstocks, commercially feasible catalysts, new prototype equipment, and testing co-processing or alternate feedstocks and improved process configurations. Other high priority objectives include:

- dispersed catalyst studies, demonstrating low rank coal liquefaction without solids deposition, improving distillate yields on a unit reactor volume basis, and demonstrating ebullated bed operations while obtaining scale-up date.
- demonstrate optimum catalyst consumption using new concepts (e.g. regeneration, cascading), produce premium products through on-line hydrotreating, demonstrate improved hydrogen utilization for low rank coals using novel heteroatom removal methods.
- define and demonstrate two-stage product properties for upgrading, demonstrate efficient and economic solid separation methods, examine the merits of integrated coal cleaning.
- demonstrate co-processing, study interactions between the preheater and first and second-stage reactors, improve process operability by testing and incorporating advanced equipment and instrumentation, and to demonstrate operation with alternate coal feedstocks.

PROCESSING CONFIGURATION

The Proof of Concept Facility consists of several distinct process units, a Coal Handling System, Two Ebullated-Bed Reactors in series, an On-Line Hydrotreater, Separation and Pressure Let-Down System, Scrubbing and Oil-Water Separation, Flash Vessels and Atmospheric and Vacuum Distillation Equipment a ROSE-SR℠ and U.S. Filter Solid Liquid Separation Systems and Produce Storage. The heart of POC reaction section is two ebullated bed reactors employing an extrudate hydroprocessing catalyst. Ebullated bed reactors offer several advantages as a well back-mixed reactor, it provides a uniform temperature and a control of exothermic heat of reactions. It also provides a facility for on-line catalyst replacement. The POC Process Development Unit (PDU) processes about 3 tons a day of coal producing about 15 barrels per day of clean distillate liquid product and can operate with or without solids containing recycle solvent. The ROSE-SR℠ unit and On-Line Hydrotreater were added along with other improvements to the equipment and control systems prior to the CTSL™ Process Scale-Up with Illinois #6 Bituminous Coal. *Figure 1* shows a schematic of the process.

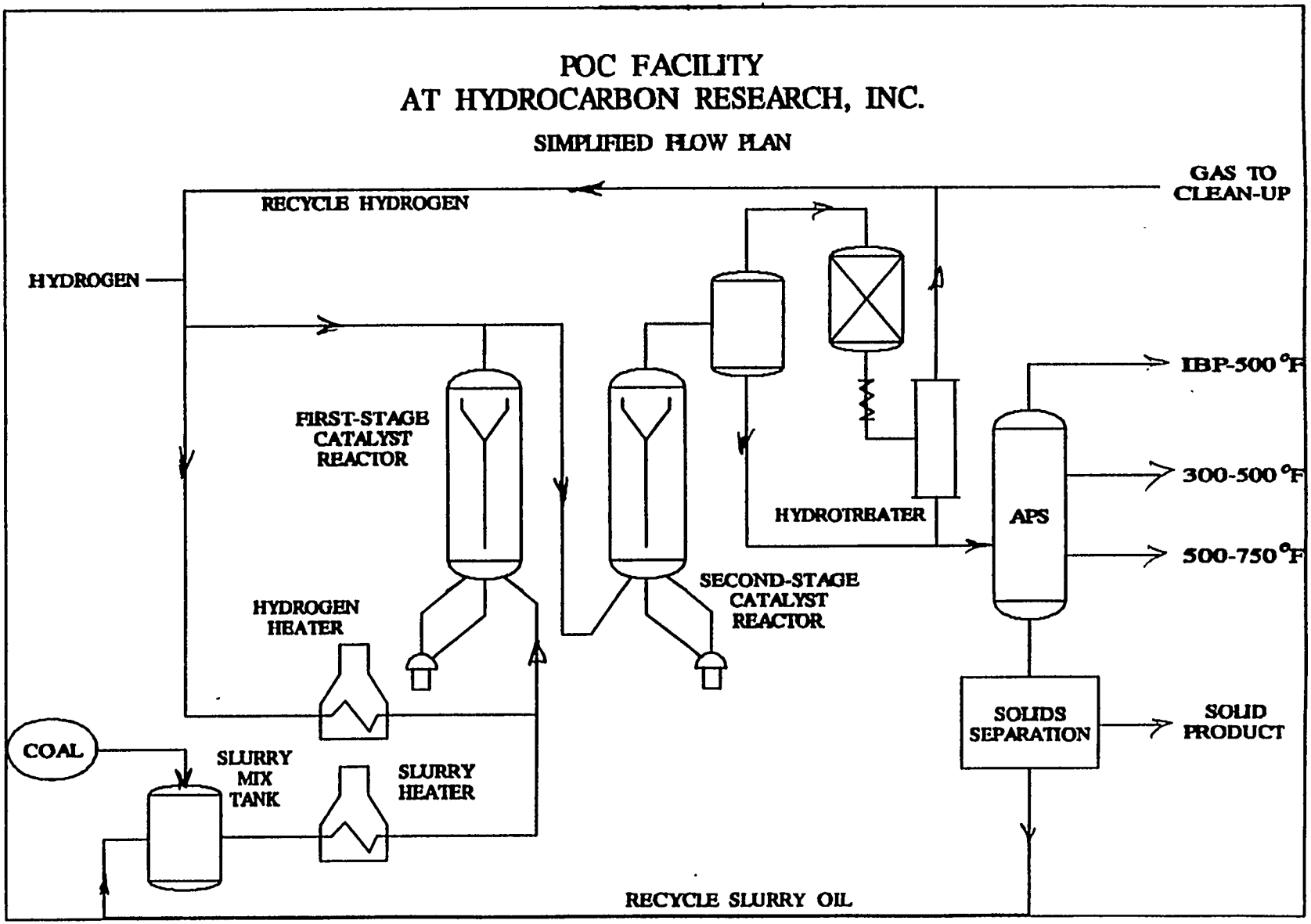
POC FACILITY
AT HYDROCARBON RESEARCH, INC.
SIMPLIFIED FLOW PLAN
GAS TO CLEAN-UP
RECYCLE HYDROGEN
HYDROGEN
FIRST-STAGE CATALYST REACTOR
HYDROTREATER
APS
IBP-500 °F
300-500 °F
500-750 °F
SECOND-STAGE CATALYST REACTOR
HYDROGEN HEATER
SOLIDS SEPARATION
SOLID PRODUCT
COAL
SLURRY MIX TANK
SLURRY HEATER
RECYCLE SLURRY OIL

Figure 1

INSPECTION OF FEED COALS

Illinois No. 6 Crown II mine coal is a high volatile bituminous coal with high mineral matter and sulfur contents, while Wyoming Black Thunder mine is a lower rank coal with high oxygen and low sulfur contents. The analysis of these two coal feedstocks is shown in *Table 1.*

Table 1. Analysis of Feed Coals in POC Program

Coal	Illinois No. 6 Crown II Mine	Wyoming Black Thunder Mine
Moisture (as-received), w%	15.2	28.2
Ash (dry basis), w%	9.5	6.7
Elemental Analysis, w% Dry		
Carbon	70.3	70.2
Hydrogen	5.2	5.1
Nitrogen	1.5	1.0
Sulfur	4.0	0.3
Oxygen (by difference)	5.5	16.7
H/C Ratio	0.89	0.88

RESULTS AND ACCOMPLISHMENTS

POC-Run1

The main objective of POC-1 was to scale-up the CTSL™ process with Illinois No. 6 coal in the extinction recycle mode to produce an all distillate slate of products. This was the culmination of a ten year effort devoted to the development and scale-up of the two stage low - high temperature sequencing ebullated bed process. Alternate goals were to confirm new equipment operability, to collect data in the CTSL™ mode for comparison with the existing data base, to collect 2500 gallons of distillate for downstream refining studies and to evaluate the ROSE-SR and U.S. Filter systems. Following is a list of the several run conditions and variables studied. *Table 2* shows the actual conditions and set points. Hydrotreater was bypassed during most of the operation.

TABLE 2. POC-01 Operating Summary
Illinois No. 6 Crown II Mine Coal
Akzo AO-60 1/16" Extrudate Catalysts

Condition Period No.	1 13-19	2 20-26	3 27-32	3B 41-44A	4 A/B 47-50	4C 54-57	5 58
Recycle Mode	Ashy	<-----	Solid	Free	-------	-->	
Space Velocity [Kg mf coal/h/m^3 reactor]	304	320	464	464	432	464	448
Solvent/Coal Ratio	1.2	1.25	1.26	1.39	1.4	1.0	1.1
First Stage							
Temp deg C	409	408	413	410	413	413	413
Cat. Repl. Rate [kg/ton mf coal]	0.3	0.8	0.8	0.8	0	0	0
Second Stage							
Temp deg C	426	432	435	432	433	438	440
Cat. Repl. Rate [Kg/ton mf coal]	0.5	1.5	1.5	1.5	1.5	0	0

During the run POC-01, Illinois No. 6 coal was successfully converted to light distillate liquids with low heteroatom (N, S, and O) contents. Throughout the entire 57 day operation, coal conversion (based on quinoline solubility) was high, in the range of 94.7 to 95.4 w% of moisture-ash free (maf) coal. Removal of organic sulfur and nitrogen was also high *(Table 7)*. A major portion of the converted coal was in the form of distillate liquids. The C^4-524°C distillate yield was in the range of 72.8 to 75.1 w% maf coal. When the process severity was reduced by increasing the space velocity from about 320 to 460 Kg/h/m^3 reactor, the distillate yields dropped down to about 70% and further to below 60% when on-line periodic catalyst replacement was terminated. The overall process performance from POC-01 is summarized in *Table 3.* The typical distribution of light distillates and their properties are shown in *Table 6a.* As shown in this Table, a typical total distillate product from POC-01 is characterized by its low nitrogen and sulfur contents, and high hydrogen contents and API gravity.

POC-Run 2

The main objective of POC-2 was to scale-up the CTSL extinction recycle process on sub-bituminous coal including on-line hydrotreating of the IBP-343°C distillate. Of major concern was whether or not calcium-carbon deposits would occur as has been evident in other low rank coal processes. *Table 3* shows the operating plan and conditions. An additional objective of major importance was the addition of nine days of operation to study the co-liquefaction of plastics with coal and waste tire rubber and coal. This was a scale-up from microautoclave and one liter reactors to a 3 ton/day unit.

TABLE 3. POC-01 PROCESS PERFORMANCE
Coal: Illinois No. 6 Crown II Mine (10.4 w% Dry Ash)
Catalyst: Akzo AO-60 1/16" NiMo Extrudates in both Reactors

Process Conditions Period/s	1 18-20	2 24-26	3B 42-43	4B	4C
Recycle Type	Ashy	<-----	Ash-free	------	--->
Process Performance					
Chemical H^+ Consumption, W% MAF	7.1	7.1	6.1	5.9	5.3
Coal Conversion, W% MAF	95.6	95.0	94.7	95.1	95.4
524 C+ Conversion, W% MAF	86.6	86.6	83.0	78.0	76.0
Desulfurization (Organic), W%	98.0	97.7	96.0	94.4	94.0
Denitrogenation, W%	86.0	82.5	78.2	75.9	78.0
C^4-524°C Distillates, W% MAF	72.8	74.2	70.64	63.2	58.8
Deasher Performance					
Deasher	<--	------	ROSE-SR	----	-->
Energy Rejection, %	25.2	16.5	12.8	22.5	33.0
Deasher Coal Conversion, W% MAF	95.7	95.1	95.2	95.2	94.9

TABLE 4. POC-02 Catalytic Two-Stage Liquefaction of Wyoming Black Thunder Coal

Condition No.	1	2	3	4
Period No.	1-15	16-22	23-33	34-36
Feed Composition Ratio	Coal 1.2/1	Coal 1.2/1	Coal 1.2-1.5/1	Coal 1.2/1
Temperatures K-1/K-2, °C K-3 Hydrotreating, °C	 400/435 370	 413/443 372	 432/446 382	 432/446 382
Space Velocity, $Kg/hr/m^3$	320	320-480	640	640
Catalyst Replacement, kg/ton maf Coal K-1 K-2	 0.5 1.0	 0.5 1.0	 0.8 1.3	 0.8 1.3
Recycle Mode	Ashy	Ashy	Ashy	Ashy
Other				Molyvan 150 ppm

As mentioned earlier, Wyoming Sub-bituminous Black Thunder mine coal was processed during POC-02 during the first 36 days of operations, with an in-line hydrotreater. The operating conditions are summarized in *Table 4.* POC-2 was a very successful scale-up of the CTSL processing of sub-bituminous coal producing high yields of clean hydrotreated distillate at space velocities as projected by Bench-Scale Testing. The typical process performance for POC-02 operations is summarized in *Table 5.*

TABLE 5. POC-02 PERFORMANCE

Condition	1	2	4A	4B
Hydrogen Consumption	8.6	8.3	6.9	8.1
Coal Conversion	90	92.6	91.8	93.5
Resid Conversion	86	84	84	82
C^4 - 343°C Net Distillate	58	54	56	49
C^4 - 524°C Distillate	66	62	56.6	57.5
Deasher Performance				
Organic Rejection, %	24.3	22.0	12.7	13.8
Deasher Rejection, %	23.1	21.0	12.0	13.6

As shown in Table above, the high oxygen-containing lower rank sub-bituminous coal exhibited a lower degree of conversion, 90 to 93.5 w% maf coal, and yields higher amounts of light hydrocarbon gases and water. The light premium distillate yield was 66% maf at coal space velocity of 320, and reduced to about 57% maf at a higher space velocity of 640 kg/h/m^3 reactor. The typical overall process performance for POC-02 operations is summarized in *Table 7.* The quality of distillates obtained from POC-02 was excellent as a result of an in-line hydrotreater. As summarized in *Table 6b,* for a typical POC-02 Condition, high proportion of the distillate was lighter than 343°C and had less than 40 ppm nitrogen, 10 ppm sulfur, and high H/C atomic ratios.

TABLE 6a. QUALITY OF THE PREMIUM DISTILLATE PRODUCTS FROM POC-01 OPERATIONS

Boiling Fraction	Distribution, W%	API Gravity	S, ppm	N, ppm	H/C Atomic Ratio
IBP-177°C	25.5	51.4	4.1	88	1.97
177-288°C	43.7	27.7	77	146	1.71
288-343°C	25.6	20.6	94	187	1.63
343°C+	5.2	16.3	652	263	1.54
Whole Product	100.0	33.4	153	240	1.75

TABLE 6b. QUALITY OF THE PREMIUM DISTILLATE PRODUCTS FROM POC-02 OPERATIONS

Boiling Fraction	Distribution, W%	API Gravity	S, ppm	N, ppm	H/C Atomic Ratio
IBP-177°C	32.8	56.4	1	5	1.94
177-288°C	51.3	32.1	1	30	1.71
288-343°C	13.9	24.6	9	38	1.61
343°C$^+$	2.0	19.1	40	81	1.56
Whole Product	100.0	36.2	5	21	1.78

TABLE 7. OVERALL SUMMARY OF CTSL™ PROCESSING AT PROOF-OF-CONCEPT SCALE

COAL TYPE	ILLINOIS NO. 6 (BITUMINOUS COAL)	BLACK THUNDER MINE (SUB-BITUMINOUS COAL)
PDU OPERATION	POC-01	POC-02
SOLIDS-SEPARATION	ROSE-SR™	ROSE-SR™
RECYCLE TYPE	Ash-free	Ashy
SPACE VELOCITY Kg/hr/m^3(Stage)	310	460
Reactor K-1 Temperature, °C	407	413
Reactor K-2 Temperature, °C	432	445
Backpressure, MPa	6.8	6.8
Process Performance		
Overall Material Balance, W%	98.1	100.3
Coal Conversion, W% maf	95.0	92.6
524°C$^+$ Resid Conversion, w% maf	86.6	84.0
C4-524°C Distillate Yield, w% maf	74.2	62.0
C4-524°C, Barrels/Ton maf coal	5.0	4.1
Hydrodesulfurization, %	97.7	96.5
Hydrodenitrogenation, %	82.5	95.5
Hydrogen Consumption, w% maf	7.1	8.3
C4-343,°C Distillate Quality		
API Gravity	33.4	35.8
Nitrogen, ppm	153	40
Sulfur, ppm	240	5
H/C Atomic Ratio	1.75	1.80
Deasher Performance		
Organic Rejection, w% maf	15.2	22.0
Energy Rejection, w% maf	16.5	21.0

POC-2 Plastics and Rubber Co-Processing with Coal

In the closing condition of Run POC-2, pulverized waste tires and mixed plastics were processed with coal at 3 tons/day to produce products, to study scale-up and to highlight process problems. Operations were sustained for several days with 25% tire rubber - 75% coal and 30% plastic and 70% coal. The component ratio of the plastics was 50% High Density Polyethylene, 35% polystyrene and 15% polyethylene terephtalate. A total of 15 tons of plastics, coal and used tires and coal were converted to light (180-650°F) distillate of less than 10 ppm sulfur and 25 ppm nitrogen and cetane index over 40 thus demonstrating the feasibility of processing wastes with coal and defining areas requiring further R&D.

PLANS

The POC program is being modified to include a series of 9 continuous Bench Scale Runs examining variant co-liquefaction schemes and optional POC Runs for scale-up and demonstration. The POC schedule shows nine Bench-Scale runs occurring from July, 1995 through June, 1997 with two POC-PDU runs in fiscal 1998, December through May.