

ABSTRACT

TITLE: Close-Coupled Two-Stage Catalytic Liquefaction - Continuous Bench-Scale and Support Studies

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OBJECTIVE: To achieve higher distillate yields and better quality products at lower capital and production costs in comparison to existing technologies. Specifically to:

1. Improve further our understanding of the complex reactions in coal liquefaction that may lead to process improvements.
2. Increase effectiveness and lower costs of catalysts.
3. Improve hydrogen management and costs.
4. Identify coals that have the greatest potential for liquefaction at mild conditions.
5. Develop scale-up data in a Mini-PDU.

ACCOMPLISHMENTS AND CONCLUSIONS:

The CTSL™, Catalytic Two-Stage Liquefaction Process, has been under DOE sponsored development since 1983 with most of the early studies being conducted on Illinois No. 6 bituminous coal. Present studies in a three year contract (1988-91) have been with sub-bituminous and bituminous coals and include variations on Two-Stage Catalytic Processing.

**ACCOMPLISHMENTS AND
CONCLUSIONS (CONTD):**

In Bench-Scale experiments from October 1990 to date, studies were carried out on On-Line Hydrotreating, Filtration for Solid Separation, Rejuvenation of Catalyst, Effect of CO₂ Addition and the Evaluation of Predispersed FeCOH on Illinois No. 6 Coal.

On-Line hydrotreating was found to be very effective in reducing nitrogen and sulfur in light distillate fractions. Further studies to evaluate long term catalyst life are recommended.

On the basis of small scale filtration tests by the British Coal Corporation, filtration will be scaled-up to PDU evaluation.

Rejuvenation of spent NiMo catalyst was successfully demonstrated while processing sub-bituminous coal. Removal of metals and carbon nearly restores original activity.

The addition of high concentrations of CO₂ significantly enhanced coal conversion, but resulted in a shift to more methane, CO and water.

The successful application of a dispersed iron-oxide hydroxide catalyst in two-stage processing has provided a basis for further experimentation using incipient wetness and ion exchange dispersion techniques.

Methods to improve the quality and economics of two-stage products have been demonstrated. Scale-up of the CTSL extinction recycle process is planned for late 1991, and further studies of dispersed and supported catalysts have been proposed.

INTRODUCTION

The two-stage direct liquefaction work described herein covers the period from October 1990 to September 1991, the final year of the three year DOE contract that commenced in October 1988. DOE has sponsored the development of Catalytic Two-Stage Liquefaction CTSL™ since 1983 with the major purpose being to achieve higher distillate yields and better quality product while lowering production and capital costs. Specifically, studies were directed to obtaining a better understanding of the process, to better hydrogen management, to more effective catalysts, to PDU scale-up to finding better coals for liquefaction, and to improving process economics.

Studies completed in this period are On-Line Hydrotreating, Solid Separation-Filtration, Catalyst Rejuvenation, Effect of CO₂ and the Evaluation of an FeOOH catalyst.

PROCESS DESCRIPTION

The CTSL Process consists of two ebullated-bed reactors close coupled in series with the first reactor operating at a lower temperature than the second. Thus the lower temperature first-stage favors catalytic hydrogenation through the maintenance of donor solvent quality. Further conversion and heteroatom removal occurs in the second stage at a higher thermal severity selected to minimize dehydrogenation of first-stage products. Figure 1 depicts the process without defining a method of solid separation. In a heavy oil extinction operation, all the heavy oil must be separated from the unconverted coal and ash (solids) and used as the recycle and slurring oil. Catalyst activity, process severity and recycle cut point are selected to maintain the extinction balance. The equipment used for the bench-scale studies consists of two close-coupled 2000 cc ebullated-beds with vapor/liquid separation, continuous atmospheric distillation, filtration and a 1000 cc on-line hydrotreater. Operations are continuous excluding coal preparation, solid separation and heavy recycle oil preparation. A single batch of supported catalyst is used for a run; therefore, each experiment must account for deactivation in the interpretation of results. At a minimal capacity of 50 lbs/day this unit clearly defines process chemistry and scales directly to larger size units.

The microautoclave equipment used is a standard, vertically shaken 20 cc tubing bomb reactor that is fitted with a catalyst basket for supported catalyst experiments. Gas bags are incorporated to identify and obtain gas yields. TGA is used to quantify resid yields.

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

SIMPLIFIED FLOW PLAN

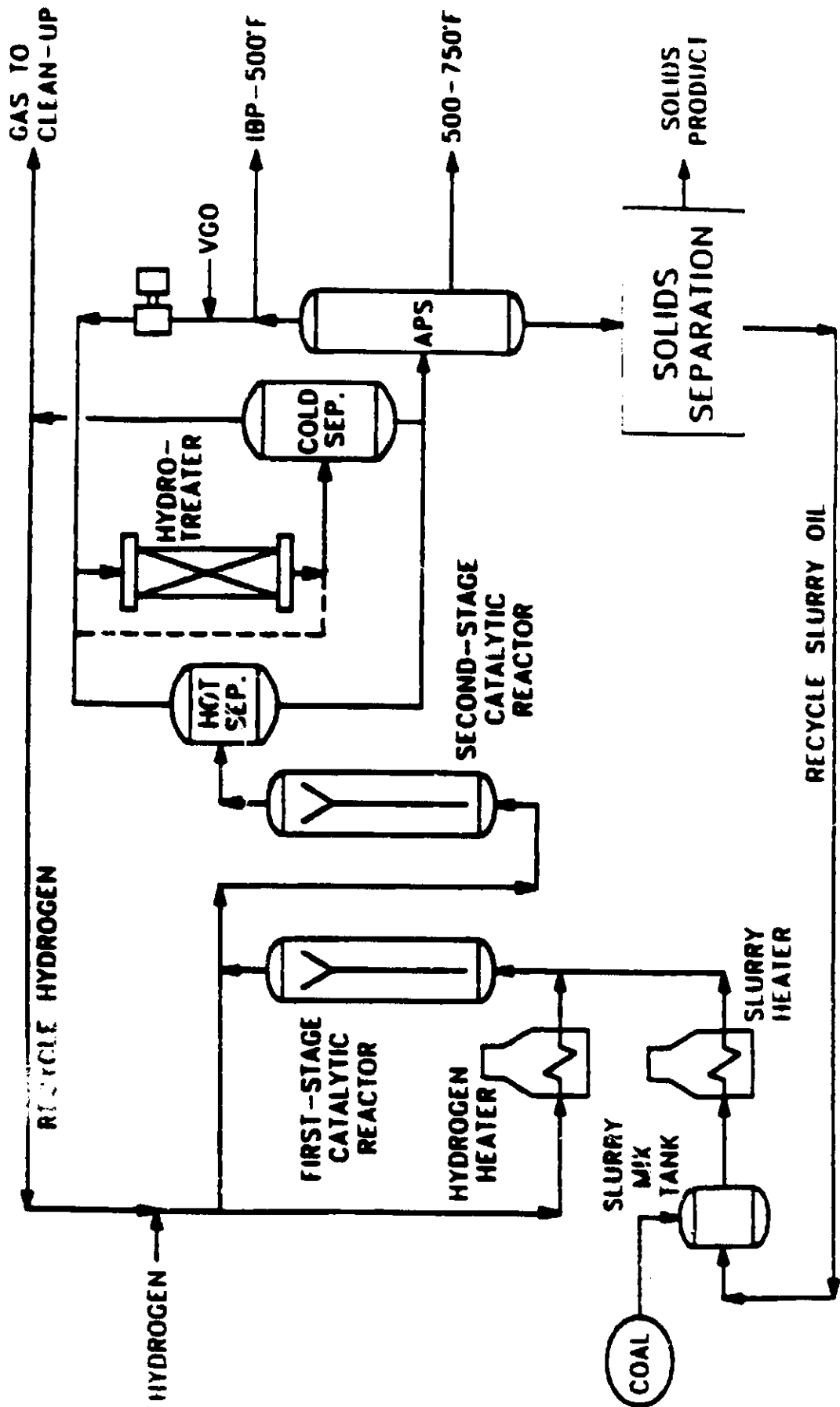


FIGURE 1

CC-10 ON-LINE HYDROTREATING

On-Line Hydrotreating, using the high hydrogen partial pressure and excess hydrogen exiting the reactor, provides an attractive option for improving product quality. This 16 day study used a low sulfur New Mexico McKinley Mine sub-bituminous coal containing over 1 W% nitrogen. Table 1 shows an analysis of this coal. A Shell 424 trilobe NiMo catalyst was used in the hydrotreater.

The run was designed to study upgrading of the entire distillate product slate in three fractions; 550°F minus, 625°F minus and 975°F minus. A summary of operating conditions and performance is shown in Table 2; note that the hydrotreater was on stream and off in alternate periods with 11 W% VSOH added into the hydrotreater feed stream in period 16. The resid conversion and distillate yields are reflective of the high space velocity (68 lbs/hr/ft³ catalyst) of the operation.

Product quality is measurably improved by on-line hydrotreating. As seen in Table 3 nitrogen and sulfur contents are reduced to the 10 ppm level and hydrogen addition is significant. The product characterization results shown in Table 4 indicate that substantial aromatics saturation has occurred. Thus for example, the 390-650°F fraction would yield a higher cetane number and a cleaner burning diesel fuel.

TABLE 1**ANALYSES OF FEED COALS**

Coal	New Mexico (Mckinley Mine) 5709	Wyoming Black Thunder 5828
HRI No.		
<u>W% Dry Basis</u>		
Carbon	66.87	68.01
Hydrogen	4.60	4.10
Nitrogen	1.12	0.93
Sulfur	0.60	0.55
Ash	11.51	6.50
Oxygen (by difference)	15.3	19.91
<u>Ash Analysis (Ignited, W% Ash)</u>		
SiO ₂	59.00	36.4
Al ₂ O ₃	24.41	15.7
TiO ₂	1.14	1.2
Fe ₂ O ₃	5.07	6.6
CaO	3.77	19.8
MgO	1.04	4.0
K ₂ O	1.02	0.4
Na ₂ O	1.82	0.8
SO ₃	1.30	12.4
P ₂ O ₅	0.31	0.8
Undetermined	0.12	0.5

TABLE 2**CC-10****LIQUEFACTION PERFORMANCE**

CONDITION	1	2	3	4	5¹
Periods	4-7	9	11-12	14	16
Catalyst Age (Per Stage) (Lb Coal/Lb Catalyst)	230	301	489	598	683
<u>Temperatures, °F²</u>					
Hot Separator	550	550	625	625	625
Hydrotreater	650	-	650	-	675
Hydrotreater Space Velocity (lb product/lb cat/hr)	0.46	-	0.55	-	1.04
<u>Normalized Yields, W% MAF Coal</u>					
C₁-C₃	7.1	7.0	7.8	6.5	7.5
C₄-390°F	17.6	14.4	16.8	14.8	16.0
390-650°F	30.6	29.8	29.2	27.4	27.4
650-975°F	18.0	19.5	11.8	21.9	18.9
975°F	4.1	5.0	5.9	6.8	6.5
Gases	2.4	3.0	2.8	2.6	2.8
Water	14.2	14.8	16.4	12.0	13.6
<u>Process Performance, W% MAF</u>					
Hydrogen Consumption	7.8	7.3	7.8	7.1	7.2
Coal Conversion	86.3	85.7	83.0	85.2	85.7
Resid Conversion	82.2	80.7	77.1	78.3	79.2
HDS	75.7	75.0	70.1	69.1	71.0
HDN	77.9	70.4	72.6	67.2	74.7
C₄-975°F Yield	66.2	63.7	57.8	64.1	62.4

¹11% VSOH added in Condition 5.²Reactor Temperatures 760/815°F

TABLE 3**QUALITY OF SEPARATOR OVERHEAD**

CONDITION Period	1 7	2 9	3 12	4 14	5 16
*API Gravity	39.9	36.2	36.7	34.3	29.1
Carbon, W%	86.33	86.58	86.36	86.87	87.29
Hydrogen, W%	13.71	13.33	13.64	12.63	12.48
Nitrogen, ppm	9	1,280	89	1,600	72
Sulfur, ppm	14	230	6	240	2
VABP, °F	401	421	442	1449	525
H/C Ratio	1.91	1.85	1.88	1.74	1.72
Watson K	11.25	11.25	11.12	11.02	10.91

TABLE 4**CHARACTERIZATION OF HYDROTREATED
DISTILLATE FRACTIONS**

TPB Cut	<u>180-390°F</u>	<u>390-500°F</u>
Paraffins	19.00 --	18.70 --
Olefins	0.80 --	1.00 --
Monocycloparaffins	56.83 (51.7)	28.09 (28.4)
Dicycloparaffins	12.20 (15.2)	20.97 (17.5)
Alkylbenzenes	8.96 (9.3)	9.56 (10.9)
Indanes/Tetralins	1.69 (2.5)	18.89 (21.4)
Naphthalenes	0.52 (.63)	2.79 (4.3)

	<u>500-650°F</u>
Paraffins	13.47
Monocycloparaffins	2.59 (7.4)
Dicycloparaffins	22.59 (13.7)
Tricycloparaffins	14.53 (7.4)
Alkylbenzenes	9.06 (12.0)
Indanes/Tetralins	11.35 (14.0)
Indenes	11.00 (13.7)
Naphthalenes	8.46 (12.1)
Acenaphthenes	4.12 (6.3)
Acenaphthalenes	1.63
Tricyclic Aromatics	1.20

() = Untreated

CC-11 SOLID SEPARATION - FILTRATION

Arrangements were made with the British Coal Corporation to examine the separation of CTSL bottoms using their proprietary filtration process.

Twenty kilograms of atmospheric bottoms were collected in a 13 day operation on Wyoming Black Thunder coal at 68 lbs/hr/ft³ catalyst space velocity. A large capacity feed tank and process derived start-up oil were used to provide inventory for collection.

The filtration evaluation by BCB gave acceptable rates for scale-up of this process for the 3 ton/day PDU level. Techniques have been developed by BCB that permit the use of larger mesh screens that nearly eliminate screen blinding and recover over 90% of the oil from the cake.

CC-12 EVALUATION OF REJUVENATED CATALYST

Following earlier tests in the program on supported iron promoted and on dispersed iron catalysts, a study was conducted on "rejuvenated" supported, nickel molybdenum catalysts. Rejuvenation, an HRI patented process, consists of an acid treatment to remove metals followed by carbon burn-off. A spent catalyst from earlier runs was rejuvenated in a batch operation, charged to the reactors and tested while feeding Wyoming Black Thunder coal at baseline conditions in a 12 day operation. This was the first bench test of a rejuvenated NiMo catalyst.

The rejuvenation process did lower the catalyst crush strength by over 30% but recovered 87% of the pore volume and 75% of the surface area. The rejuvenated, supported nickel moly catalyst performed flawlessly for a planned 12 day operation generating consistent yields with minimal residual oil conversion deactivation, and, surprisingly, hydrogenation improved as the run progressed. For comparable periods the resid conversion averaged 83.6 W% MAF coal versus 84.6% for fresh catalyst at similar ages; most of the difference can be attributed to a lower coal conversion for the current lot of coal. Figure 2 shows the minimal change in 975°F resid formation during the test. The stability of residuum hydrogenation with time is depicted in Figure 3.

975 F+ RESIDUUM YIELD REJUVENATED & FRESH CATALYST COMPARISON

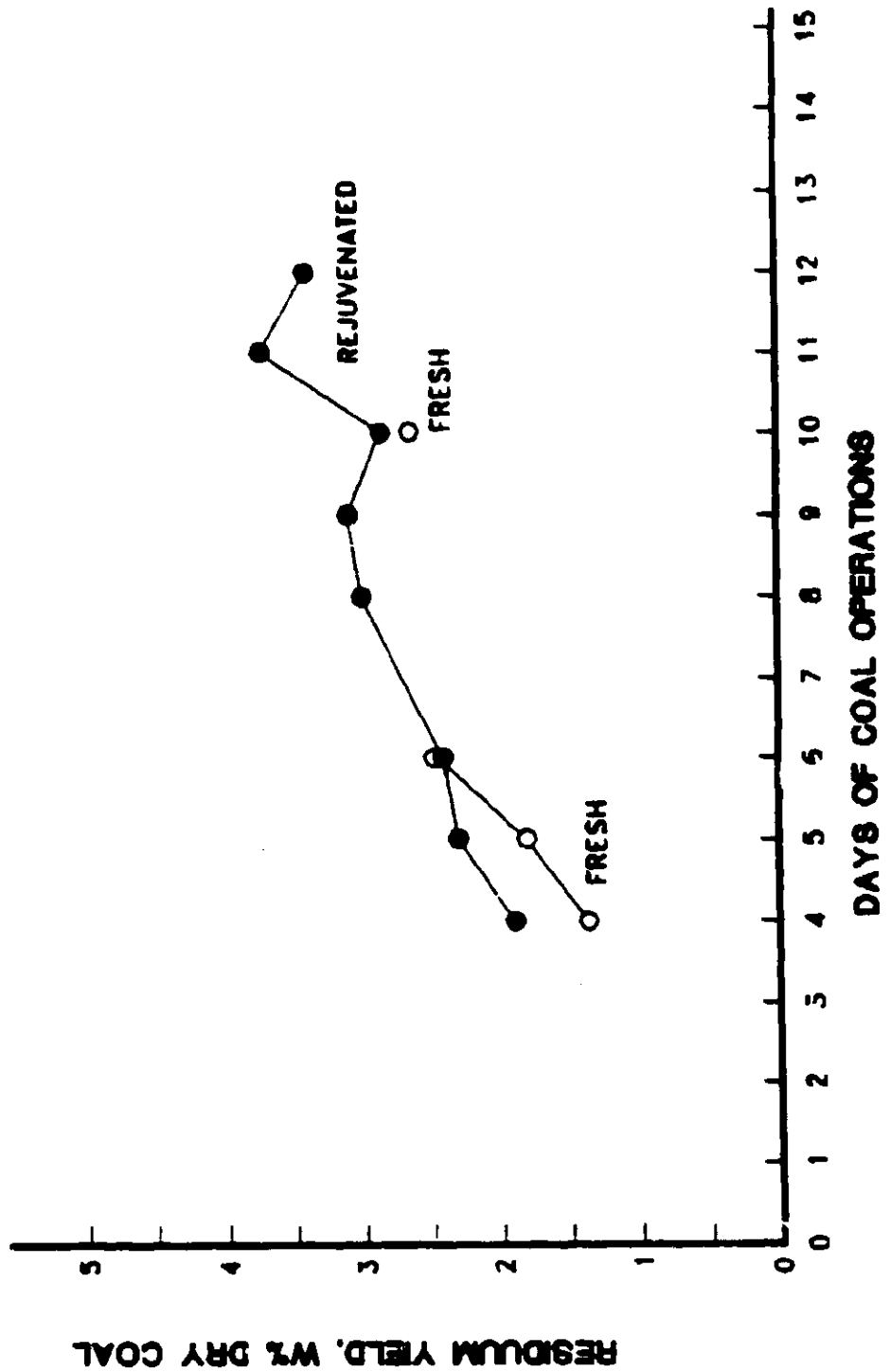


FIGURE 2

H/C RATIO OF RESIDUUM REJUVENATED & FRESH CATALYST COMPARISON

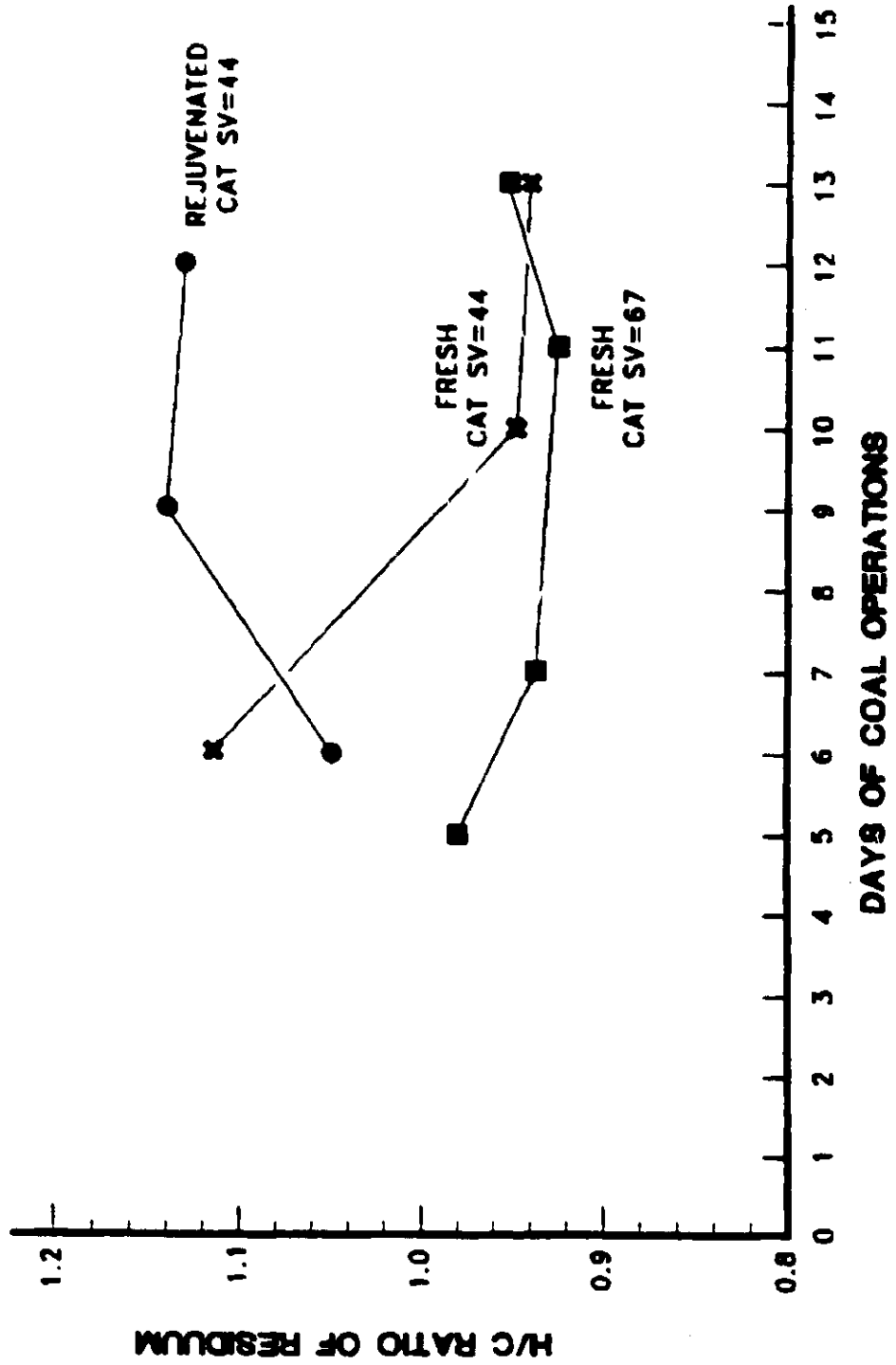


FIGURE 3

CC-13 CO₂ COAL SLURRY EVALUATION

The objectives of this run were to evaluate a feed slurring agent that would vaporize in the reactor to afford less dilution to promote more complete reaction of the coal and heavy liquid products and also reduce recycle requirements.

The initial intention was to use CO₂ as the feed coal slurring agent directly, by means of a pressurized, refrigerated slurry preparation system. However, the attempts to prepare a pumpable CO₂/coal slurry resulted in high vaporization and vapor-binding of the slurry feed pump. The run plan was then changed to feed CO₂ in addition to a feed slurry incorporating a normally liquid material, recycled filtered liquid or light gas oil make-up (which in process application could be recycled from the distillation of the reactor products).

The run conditions and performance of this 14 day operation on Wyoming Black Thunder coal are shown in attached Table 5. Note the high gas make, shift to lighter distillates, high hydrogen consumption and high coal conversion and yields. This is the highest coal conversion obtained in CTSL operations with Black Thunder coal indicating some interaction of the coal with CO₂ and also the concentration effect with the light solvent.

A comprehensive analysis of the gases produced indicates that 58% of the CO₂ reacts to form CO, CH₄, and H₂O, yields of C₂, C₃, and C₄ gases were lower with CO₂ addition.

Thus, this study indicates that CO₂ does shift to methane and water at CTSL reaction conditions while improving coal conversion and light distillate production.

TABLE 5**Liquefaction Performance Run CC-13****Black Thunder Mine Coal - CO₂ and Light Solvent Slurry Addition**

CONDITION	1	2	3	4	5	CC-1
Periods (Days)	5	7	9	11	14	9
Catalyst Age, Lb Dry Coal/Lb Catalyst (Stage)	143	201	259	318	401	256
CO ₂ Addition, Lb/Lb Dry Coal	0.0	0.10	0.245	0.255	0.556	--
Oil Addition (HRI-5663), Lb/Lb Dry Coal	0.0	0.0	0.0	1.18	0.0	--
Filtered Liquid Recycle, Lb/Lb Dry Coal	1.18	1.20	1.18	0.00	1.04	1.1
<u>Normalized Yields (W% of Dry Coal)</u>						
C ₁ -C ₃	11.49	(12.81)	12.76	10.96	16.97	8.2
C ₄ -390°F	22.27		21.30	11.69	17.62	20.1
390-650°F	25.51		33.68	22.73	33.94	29.2
650-850°F	7.83		6.36	11.85	7.53	12.1
850-975°F	1.16		1.07	5.66	0.53	2.1
975°F Liquid	1.29		1.15	5.89	0.86	2.6
Unconverted Coal	8.63		7.03	5.64	6.53	8.1
Ash (SO ₂ -free)	6.50		6.50	6.50	6.50	6.0
Water	21.31	(21.91)	37.66	37.44	39.32	17.7
CO	0.48	(1.30)	0.97	3.62	7.31	0.1
CO ₂	0.72	(0.36)	-18.34	-13.71	-26.25	0.2
NH ₃	1.02		0.96	0.92	0.95	1.0
H ₂ S	0.37		0.39	0.44	0.44	0.4
Total (100 + H₂ Consumption)	108.59		111.51	109.62	112.26	107.8
<u>Process Performance (W% MAF)</u>						
Coal Conversion	90.8	91.2	92.5	94.0	93.0	91.8
975°F Conversion	89.4		91.2	87.7	92.1	87.4
C ₄ -975°F Distillate Yield	60.7		66.8	55.5	63.8	63.6
Desulfurization	63.5		67.3	75.7	75.4	71.2
Denitrogenation	90.7		84.9	81.0	84.3	75.7

NOTES:

1. Period 7 yields are collected yields, other yields are normalized yields.
2. Space Velocity - 45 lbs/hr/ft³ catalyst.
3. Reactor temperatures and pressure, 750/825°F, 2500 psig

CC-14 EVALUATION OF FeOOH DISPERSED CATALYST

An iron-oxide hydroxide treated Illinois #6 coal prepared at PETC In-House R&D by an incipient wetness procedure was evaluated versus untreated coal and with molybdenum dispersed as Ammonium Tetrathio Molybdate in a three-stage process configuration. The first stage being a low temperature (525°F) activation stage followed by a high temperature (800°F) back-mixed stage and a third ebullated-bed stage with NiMo catalyst at 780°F.

The catalyzed and untreated coal analyses are shown in Table 6 and the operating conditions and performance in Table 7. Figures 4 and 5 show the comparative distillate yields and performance of the FeOOH at two reactor severity levels. The iron-based chemically dispersed catalyst performed very well with distillate yields C_4 -975°F of over 75 W% of MAF coal with the first stage at 800°F and the second ebullated-bed stage at 775°F. Increasing the thermal severity to 825°F lowered the distillate yield and increased hydrogen consumption by producing more C_1 - C_3 gases. Molybdenum based dispersed catalyst appears to yield better or equivalent performance with respect to residuum conversion and product quality; however, the relative performance may be over shadowed by deactivation of the supported catalyst in the ebullated-bed reactor.

Further optimization of the FeOOH catalyst formulation and operating conditions are warranted based on the results of this study. The yields in condition 1 approach the maximum obtained at HRI with two ebullated-bed reactor stages. See Table 8 for a comparison, although the coal shipments, time periods and cleaning techniques differ, the overall performance is similar.

TABLE 6**CONTINUOUS BENCH-SCALE
EVALUATION OF DISPERSED FeOOH AND
AMMONIUM TETRATHIO-MOLYBDATE**

Condition	1	2	3	4	5
Additive	FeOOH	FeOOH	ATTM	None	FeOOH
Amount	2,800 ppm	2,800 ppm	1,500 ppm	-	2,800 ppm
<u>Reaction Temp., °F</u>					
Pretreater	525	527	523	528	527
First Stage	799	825	822	822	825
Second Stage	775	775	775	774	774
<u>Yields, W% MAF Coal</u>					
C ₁ -C ₂	8.6	12.3	11.5	12.0	12.5
C ₃ -390°F	20.7	26.5	24.0	21.7	23.3
390-650°F	34.9	32.3	33.1	31.9	30.6
650-975°F	19.5	10.2	14.7	13.6	11.8
975°F	5.7	3.6	4.6	7.3	7.4
<u>Performance, W% MAF Coal</u>					
C ₃ -975°F	75.1	69.0	71.8	67.2	65.7
975°F Conversion	88.0	80.4	89.5	86.4	87.5
Hydrogen Consump. W%	7.5	8.2	8.1	7.4	7.8
Coal Conversion	94.0	94.6	94.5	94.2	95.0

FIGURE 4

DISPERSED CATALYST RUN (CC-14) DISTILLATE YIELD

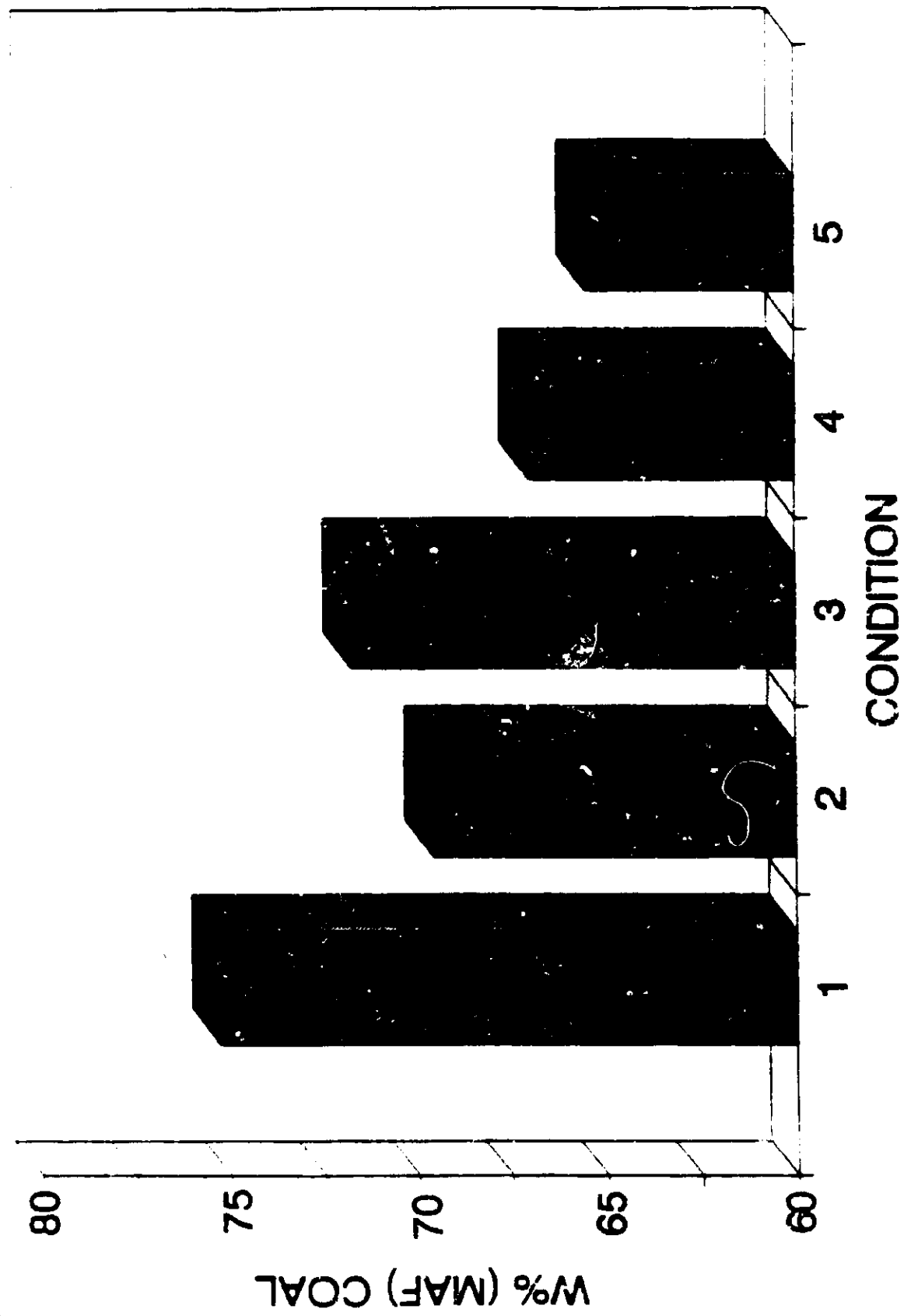


FIGURE 5

DISPERSED CATALYST RUN (CC-14) PRODUCTS YIELD WITH FE CATALYST

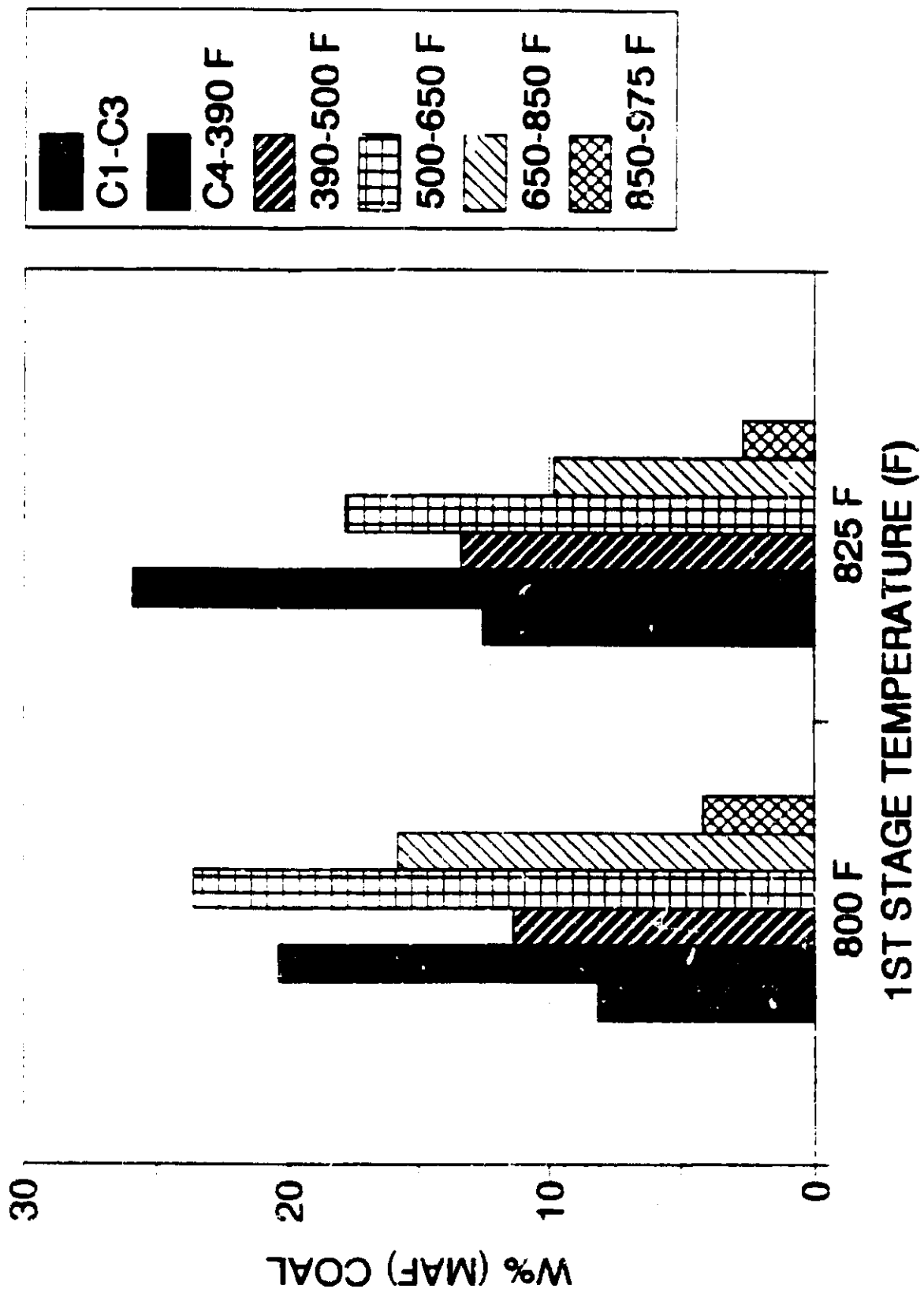


TABLE 7**A COMPARISON ILLINOIS #6 COAL PROCESSING WITH FeOOH CATALYST AND SUPPORTED CATALYSTS¹**

Catalyst	FeOOH	NiMo
Process	Pretreat Stage First Stage Back- Mixed Second Stage- Ebullated	Ebullated-Bed Two Stages
Catalyst Age, lbs coal/lb cat. Stage 2	145	233
<u>Reaction Temperature, °F</u>		
Pretreater (First Stage)	525	--
Second Stage	600	750
Third Stage	775	800
<u>Performance, W% MAF Coal</u>		
C ₄ -975°F	75.1	76.2
975°F Conversion	88.0	90.2
Hydrogen Consumption, W%	7.5	7.4
Coal Conversion	94.0	95.4

¹Different Shipments of Illinois #6 Coal.

LABORATORY SCALE/TECHNICAL ASSESSMENT

Other studies were conducted during this period including microautoclave and microreactor studies with rejuvenated catalysts, sulfiding additives, CO₂ and various solvents. Process modelling efforts through interpretation of bench and small-scale results continued as did economic screening and cost analysis of the CTSL processing of low rank coals. An overview of the production costs of Wyoming coals is shown in Table 8. The economics are based on large reactors, present on-site raw material costs and a Gulf Coast location for labor rates. Capital costs, depending on methods of financing, would at least be equal to the production costs.

SUMMARY

The studies conducted have demonstrated pathways to significant reductions in product cost through:

- improved product quality and efficiency of on-line hydrotreating
- economic methods of solid separation
- the reduction of catalyst costs by rejuvenation and low cost dispersed catalysts
- a better understanding of the process of catalytic two-stage direct liquefaction.

PLANS

Remaining work under this contract, extended to December 31, 1991, consists of a PDU Run to demonstrate the CTSI extinction recycle process while feeding low rank Wyoming coal and to scale-up the BCB filtration process for recycle oil recovery and solid separation.

Acknowledgements

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