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TWO-STAGE, CLOSE COUPLED CATALYTIC LIQUEFACTION OF COAL

TENTH QUARTERLY REPORT FOR THE PERIOD

1 JANUARY 1991 - 31 MARCH 1991

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WORK PERFORMED UNDER CONTRACT

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100 OVERLOOK CENTER, SUITE 400

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ABSTRACT

This quarterly report covers activities of the Two-Stage, Close-Coupled Catalytic Liquefaction of Coal program during the period January 1, - March 31, 1991, at Hydrocarbon Research, Inc., in Lawrenceville and Princeton, New Jersey. This DOE contract period is from October 1, 1988 to December 31, 1991.

The overall purpose of the program is to achieve higher yields of better quality transportation and turbine fuels and to lower the capital and production costs in order to make the products from direct coal liquefaction competitive with other fossil fuel products.

The quarterly report covers work on Microautoclave Testing, Bench-Scale Illinois No. 6 and New Mexico coals experimentation, Technology Assessment, Modelling and scheduling.

SUMMARY

The first calendar quarter of 1991 was a productive period with two bench-scale studies, microautoclave support studies, mini-PDU preparations, and process modelling.

Several catalyst presulfiding agents and CO_2 effects upon liquefaction were evaluated in microautoclave scale tests. Dimethyl disulfide will be used for the PDU scale-up based on the results of these tests and prior data. Carbon dioxide appears to enhance coal conversion; however, gas and water yields are increased indicating possible water gas shift-hydrocarbon synthesis reactions.

In the bench-scale studies, the rejuvenation of spent catalyst with acid and carbon burn-off produced catalytic activity akin to fresh catalyst in a 12 day evaluation.

A 14 day study of the addition of high concentrations of CO_2 to a sub-bituminous coal liquefaction system demonstrated the occurrence of water gas shift hydrocarbon synthesis reactions and conversely higher coal conversions and distillate yields with high hydrogen consumptions.

Preparations for a PDU Demonstration Run on Black Thunder Mine coal are underway. The British Coal Filtration Process will be used for solid separation.

The results of microautoclave scale tests on Illinois, Ohio and Black Thunder Mine coals were reviewed and statistically analyzed to provide a sound basis for kinetic interpretation.

INTRODUCTION

The studies conducted in this, the tenth quarterly report of Contract No. DE-AC22-88PC88818, are reported by task and in sequence.

Task 1 is the Management Plan and is complete. Task 2 is for Laboratory Studies and includes microautoclave and microreactor work. Task 3 is for Bench-Scale studies and in this report covers results of Runs CC-12, and 13. Task 4 is for Mini PDU Scale-up. Task 5 is the Technical Assessment, including Modelling, Design and Economics. Task 6 is Administration.

The contract period was from October 1, 1988, to September 30, 1991, and is being extended to December 31, 1991.

TASK 2 - LABORATORY STUDIES

EVALUATION OF CATALYST SULFIDE MAINTENANCE AGENTS

A series of microautoclave tests were carried out evaluating candidate agents for maintaining the sulfide state of the catalyst in the PDU, specifically, TNPS (di-Tertiary Nonyl Polysulfide), DMDS (Dimethyl Disulfide), and elemental Sulfur.

A total of 16 tests were done at 825°F, 2000 psig hydrogen pressure, using Presulfided Shell S-317 catalyst, and a coal liquefaction distillate as carrier, with 1 weight of carrier per weight of catalyst. The sulfide maintenance agent was equivalent to 0.05 and 0.10 grams per gram of catalyst, at test times of 15 and 45 minutes. The following conclusion were drawn:

Sulfiding Effectiveness - Product catalysts from each test had a higher sulfur content than in the presulfided catalyst charged (which contained 6.54% sulfur, equivalent to 90% sulfiding to MoS_2 and NiS) by a factor of up to 1.2. The highest level of sulfur was obtained in the longer tests with the higher proportion of sulfiding agent with each agent. Although the very highest degree of sulfur addition was obtained in a DMDS test, all three agents had essentially same performance in this respect.

Utilization of the Agents - Some unconverted sulfur remained with solvent phase after the tests with the sulfiding agents. With TNPS this proportion was 13-16% of the sulfur in the agent, essentially the same level for all of the tests. With DMDS this proportion was 6-10% of the sulfur in the agent, unrelated to the test time, but perhaps at the lower proportion with the lower concentration of the agent. With elemental sulfur this proportion was 9-14% of the sulfur in the agent, with no relation to concentration of the agent, but perhaps lower for the long residence time tests.

Light Gas Yields - Light Gas yields with the TNPS and elemental sulfur agents were marginally higher than was obtained in background tests without any agent, e.g. in 45 minutes tests, methane yields were 0.5-0.7% of solvent when using the agents compared to 0.5% with no agent, and approximately 0.4-0.5 as great in all of the 15 minute tests. However, appreciably more methane was formed in the DMDS tests, with the increment of methane formation averaging 87% of the theoretical formation of methane from the decomposition of the DMDS, very close to apparent reaction, 92%, of the agent based on the retained sulfur contents.

Light Liquid Formation - GC simulated distillation of the product liquid from a test with TNPS showed a very considerable enhancement of peaks in nominal 225-250°F boiling range, particularly three peaks, corresponding to the expected range for C_9 isomers. The total of the enhanced peaks corresponded to 76% of the quantity to be expected if the TNPS were all converted to C_9 isomers, which is slightly below the degree of reaction of the TNPS, 85%, indicated by the sulfur retention in the solvent.

It is concluded that all three agents would be effective in maintaining sulfide levels, but would leave a small residue of unused material. DMDS would cause additional methane yield, about 0.5 times the amount of sulfur added. TNPS would produce additional naphtha boiling range product, about 1.7 times the amount of sulfur added.

IMPACT OF CO_2 UPON LIQUEFACTION

Two microautoclave tests were done using 10% CO_2 in hydrogen as the vapor phase environment rather than 100% hydrogen used in most tests. The tests were done with the HRI 5713 Shipment of Black Thunder coal, at 800°F and 2000 psig, for 30 minutes, with HRI 5198 Coal liquefaction distillate as solvent and 1 gram of Presulfided Shell S-317 Catalyst per gram of coal. The following results were obtained, compared to the recent test with 100% hydrogen atmosphere:

CO_2 in Vapor, V%	0.0	0.0	10.8	10.8
Solvent/Coal, Gms/Gm	4.0	4.0*	2.0	1.0
Coal Conversion, W%	85.1	86.6	90.9	89.9
Resid. Yield, W% of Conv. Coal	31.9	22.3	21.7	21.6
H_2O Recovery, W% of Conv. Coal			26	35

* Coal sample contained 6.4% water.

These results indicate no deleterious impact of the CO_2 upon conversion, or formation of residual oil, and a possible improvement in performance in these respects. The apparent water formation was considerably higher than can be ascribed to the derivation from coal alone. CO formation in the second test corresponded to only 1% of the coal reacted, which would discount the possibility of the water gas shift reaction of H_2 and CO_2, alone, accounting for the additional water formation. However, the light gas formation for this test, 5.4 W% of coal, was 2-3 times the amount expected on the basis of other tests, with no CO_2, indicating the possibility of water gas shift-hydrocarbon synthesis reaction sequence.

TASK 3 - BENCH SCALE STUDIES

RUN CC-12 (227-70) CATALYST REJUVENATION

Objectives

The objectives for this run was to evaluate a rejuvenated catalyst (acid wash and carbon removal) that had been recovered after earlier CTSL bench unit operations on Black Thunder Mine (Wyoming) coal.

The rejuvenated catalyst had residual oil conversion activity, hydrogenation and denitrogenation activity essentially that of fresh catalyst and markedly greater than that of catalyst aged in CTSL operations. There were slightly lower yields of distillate product with the rejuvenated catalyst because of lower coal conversion and higher carbon oxides yields, factors which might not be associated with the catalyst performance. The rejuvenated catalyst was of much lower physical strength, and very much shortened particle length, than fresh catalyst, and a more durable initial catalyst might be more appropriate if rejuvenated catalysts are to be used commercially.

Scope of Work

The recovered Shell S-317 catalyst from earlier CTSL runs was acid washed and then regenerated using diluted air. The rejuvenated catalyst was then evaluated in Run CC-12 at a single set of operating conditions to evaluate the deactivation of the rejuvenated catalyst with a comparison with the results of operations with Fresh Shell S-317 catalyst.

Coal

Black Thunder Mine (Wyoming) sub-bituminous coal (HRI 5713) was used as the feed stock. The coal analyses of the feed are given in *Table 1* along with earlier analyses of this coal.

Catalyst

The catalyst rejuvenated for use in Run CC-12 had been recovered after Runs CC-4 and CC-7, both of which had been operated with Black Thunder Mine coal and had re-used catalysts recovered after Runs CC-1, CC-2 and CC-5. In these previous operations, the blended catalyst for rejuvenation had processed 1120 lbs coal/lb fresh catalyst. *Table 2* includes the analysis of the recovered catalyst to rejuvenation, as well as the acid-washed catalyst and the final rejuvenated catalyst used in Run CC-12.

The acid washing phase of the rejuvenation procedure was an agitated batch operation for 30 minutes at 150°F using 5 weights of 3.5 W% sulfuric acid solution per weight of catalyst. The regeneration of the acid washed catalyst was carried out in two fixed beds in series for the first for 4 hours at 750°F, with gas containing 2.5% oxygen, then increasing the temperature to 800°F for four hours, and then progressively increasing the oxygen content to 5%, 7.5%, and 21% over a six hour period. The oxygen fed with the most dilute gas corresponded to about 100% excess above the amount required for the combustion of the available carbon.

The metals accountability of this sequence of operations is summarized by *Table 3.* Of the contaminants, over 95% of the calcium, 95% of the sodium and 60% of the iron was removed in the acid washing step. There were some losses the promoting metals, about 20% of the molybdenum, and 60% of the nickel was removed by the acid-washing. Apparently some of the catalyst support dissolved as well, with aluminum found in the acid washing liquor corresponding to about 5% of the Al_2O_3 content of original recovered catalyst.

The rejuvenated catalyst had a crush strength considerably lower than that of fresh catalyst, 1.23 lb/mm against 1.94 lb/mm. Also, the rejuvenated extrudates were only half as long, on the average, than fresh extrudates, 1.9 mm against 4.2 mm, although the extrudate diameters were essentially the same. There were a very large number of very short particles, less than 1 m, in rejuvenated catalyst. This factor caused several false starts for Run CC-12, even before coal feed was started, when the smaller particles became enmeshed in the catalyst support. Successful operation was achieved after the shorter particles were removed by screening. While the recovery of catalyst from the first stage reactor after Run CC-12, 89 V%, was in the range of values of recovery after operations with fresh catalyst, the recovery of catalyst from the second stage after Run CC-12 was relatively low, 63%, perhaps a consequence of the low crush strength.

Run Plan

The run plan is given in *Table 4.* The run duration was 12 days. The liquefaction conditions were kept constant during this period. The coal space velocity was 45 lb dry coal/hour/ft3 of catalyst (per stage). The first stage liquefaction temperature was 750°F and the second stage temperature was 800°F. The operating conditions were the same as those used in the first operations of Run CC-1. The net liquid products were: 1) separator overhead (SOH) the condensate after cooling to ambient temperature the vapor from the 610°F hot separator at the outlet of the second stage; 2) atmospheric overhead (ASOH) from distillation at 525°F of the slurry from the hot separator; 3) and pressure filter liquid (PFL), in excess of the recycle to slurry the feed coal, obtained by batch filtration of the slurry from the atmospheric still. The solids from the filtration (PFS) were also a net product of the operation. The in-line hydrotreater for the hot separator vapors was not in service for this run.

H_2S, corresponding to 2 W% of the coal, was fed continuously during the run to provide a sulfiding atmosphere.

Performance and Results

The liquefaction performance of Run CC-12 is summarized in *Table 5*, which gives the detailed product distribution. *Figures* 1, 2, and 3 summarize the day-to-day coal conversions, yield of total C_4-975°F distillate product, and yield of 975°F$^+$ residual oil, respectively, and include a comparison with the results of Run CC-1 with fresh catalyst using the same operating conditions.

Coal conversion in Run CC-12 averaged 84.7% of maf coal when the unit had equilibrated after the start-up interval. There was an uncertain downward tend in conversion, of about 1%, as the run progressed. This conversion, for a relatively low-severity operation, was about 1.5% lower than had been obtained with fresh catalyst during Run CC-1. To assign these differences in catalyst performance is uncertain, since in other operations coal conversion, while improved by the presence of catalyst, has shown virtually no change as the catalyst deactivated as indicated by other performance parameters, viz. residual oil formation, hydrogenation, and denitrogenation, and rejuvenated catalyst in Run CC-12 was clearly of high activity in these regards, see below. It is possible these differences are due to differences in the coal shipments, with the CC-12 feed containing about 0.5% more ash, and 0.4% less hydrogen than in the CC-1 feed, see *Table 1*.

The yield of C_4-975°F distillate product In Run CC-12 averaged 59.0% of maf coal, with a downward trend of about 2% over the course of the run, *Figure 2*. The trend is about the same as obtained in runs with fresh catalyst. However, this yield in Run CC-12 was about 3% lower than obtained with fresh catalyst in Run CC-1. This difference is discussed more fully below in a comparison with the Run CC-1 results.

The yield of $975°F^+$ residual oil averaged 2.8 W% of dry coal during Run CC-12, with a definite upward trend of about 2% over the course of the run, *Figure 3*. The residual oil yield in Run CC-12 was virtually the same as had been obtained with fresh catalyst in Run CC-1 at the same operating conditions, and the trend with increasing catalyst age in Run CC-12 was close to that obtained with fresh catalyst.

Comparison with Fresh Catalyst Performance

Table 6 compares the product distribution during Run CC-12 with those with fresh catalyst during Run CC-1. This table includes data from the later portions of Run CC-1, which were a higher severity operation with 25°F higher second stage temperature with a portion of the solvent recycle being atmospheric still bottoms slurry which included some unconverted coal. *Table 7* gives hydrogen contents, nitrogen contents, sulfur contents, and solvent fractionation results for the products of the two runs.

Product Distribution

Referring to *Table 6*, in addition to the differences in coal conversion (1.8% lower in Run CC-12), C_4-975°F distillates yields (3.2% lower), and residual oil yields (within 0.1%) noted above the principal difference in the yields of the two runs was 1.4 W% higher carbon oxides yield in Run CC-12, and 0.8 W% higher C_1-C_3 gas yield. If the yields of the two runs were normalized to a common yield of carbon oxides and water then the yield of C_4-975°F distillate would then be about 1.5 W% different for the two runs, the difference in coal conversions.

The trend in residual oil yield in Run CC-12, for the six day interval between the sixth and twelfth day, corresponded to that of nine day interval between the tenth and nineteenth day of Run CC-1. *Figure 4* summarizes another aspect of the catalyst performance with respect residual oil kinetics of the two catalysts, plotting the concentration of residual oil in product slurry from the system against time of operations (catalyst age). In this figure, the trends with time are virtually identical during the two runs. Actually, in the first operations of the two runs, at common operating conditions, in terms of the residual concentration required for the observed kinetic performance there was a lower concentration during Run CC-12 than in Run CC-1. This difference indicates better kinetic performance of the rejuvenated catalyst than for the fresh catalyst.

Product Properties

Hydrogen contents, in the *Table 7* analyses of the products, for the first operations of two runs, were in same range +/- 0.5%. In the final operations of Run CC-12 the hydrogen contents average 0.2% higher than during the first operations of that run, perhaps not a statistically significant difference, but a considerable contrast to the results with the fresh catalyst where hydrogen contents decreased by up to 0.8% between the tenth and nineteenth days. The hydrogen contents of the first operations of Run CC-12 averaged 0.6% higher than those of the final operations of Run CC-1. The hydrogen contents may have begun to be equilibrium limited at the higher operating temperatures of Run CC-1.

Nitrogen contents in the first operations of Run CC-12 were one-fourth to one-third of those in the final operations of Run CC-1, and generally lower than had been obtained in the first operations of Run CC-1. The nitrogen analyses during Run CC-12 did not demonstrate the stability exhibited by the hydrogen analyses, although the rate of deactivation in this respect may also have been more moderate than shown in Run CC-1.

Sulfur contents for the products for both runs were in the minimum range that could be determine accurately with the analyzer that was in use.

The cyclohexane insolubles content of the 975°F$^+$ products throughout Run CC-12 remained at the very low levels that were obtained in first operations of both runs. This stability was in contrast to the pattern of Run CC-1 where there was a 6-7 fold increase in this content between the sixth and nineteenth days.

These analyses show that the rejuvenation effort returned the catalyst kinetic performance to equivalent to that of fresh catalyst. The greater stability of the Run CC-12 results may have been partly due to inclusion of 2% H_2S with the feed to maintain sulfiding levels (which was not done during Run CC-1). However, in Run CC-11, using fresh catalyst with continuous H_2S addition and Biack Thunder Coal, hydrogen contents declined progressively through the run and averaged 0.3 W% lower in the thirteenth day than in the fifth day, in contrast to the stable or increasing hydrogen contents in Run CC-12.

TABLE 1

ANALYSES OF FEED COAL FOR RUN CC-12

Coal	Black Thunder Mine (Wyoming)	
HRI No.	5713	5630
Feed for Run	CC-12	CC-1
Moisture (As Fed)	5.23	8.92
W% Dry Basis		
Carbon	68.20	67.70
Hydrogen	4.19	4.54
Sulfur	0.54	0.48
Nitrogen	0.87	1.05
Ash	(7.72)	(7.15)
Sulfur in Ash	(5.62)	(6.35)
Ash (SO_3-free)	6.73	6.01
Oxygen (by difference)	19.47	20.18
Ash Analysis (Ignited, W% Ash) (W% Ignited)		
Silica, SiO_2	36.16	
Alumina, Al_2O_3	17.54	
Titania, TiO_2	1.27	
Ferric Oxide, Fe_2O_3	5.01	
Lime, CaO	19.69	
Magnesia, MgO	3.99	
Potassium Oxide, K_2O	0.43	
Sodium Oxide, NaO	0.39	
Sulfur Trioxide, SO_3	12.93	
Phosphorous Pentoxide, P205	0.89	
Strontium Oxide, SrO	0.95	
Barium Oxide, BaO	0.64	
Manganese Oxide, Mn304	0.11	
Undetermined	0.00	
Microautoclave Results*		
Thermal Coal Conversion	80.3	76.6
Thermal 975°F$^+$ Conversion	45.4	44.3
Catalytic Coal Conversion	89.8	87.9
Catalytic 975°F$^+$ Conversion	66.4	72.9

* 800°F, 30 minutes, 2000 psig H_2
4/1(1) Solvent/Coal/(Shell S-317 Catalyst)
Solvent - Wilsonville Coal Liquefaction Distillate

TABLE 2

Preparation of Rejuvenated Catalyst for Run CC-12

Analyses of Catalysts

Catalyst	Fresh S-317	Recovered CC-4, CC-7	Acid Washed	Rejuvenated to CC-12
Chemical Analysis, W%				
Molybdenum	11.4	7.8	7.1	9.8
Nickel	2.2	1.69	0.86	1.34
Carbon		17.27	18.71	0.73
Hydrogen		0.66	0.79	0.70
Nitrogen		0.10	0.19	0.00
Sulfur		4.95	5.56	1.10
Iron		0.48	0.22	0.40
Calcium		0.57	0.02	0.05
Titanium		0.04		
Ignition Weight Loss, W%		22.3		6.86
Physical Properties				
Bulk Density, Gms/cc	0.588			0.649
Particle Density, Gms/cc	0.941	1.398	1.310	0.961
Pore Volume				
cc/gram	0.697	0.249	0.290	0.592
cc/cc particle	0.656	0.348	0.380	0.569
Surface Area				
Sq. M./gram	267	122	129	197
Sq. M./cc particle	251	171	169	189
Crush Strength, Lb/mm	1.94	1.78	1.48	1.23
Dimensions				
Average Dia., mm Length	1.0			0.99
Average, mm	4.2			1.9
N% < 1 mm	0			22

TABLE 3

Preparation of Rejuvenated Catalyst for Run CC-12

Metals Balance - Acid Washing and Regeneration

							Regeneration		
Stream	Acid Wash Charge	Acid Wash Catalyst	Removed	Acid Washing Liquor	Acid Washing Fines	Recovered	Charged	Recovered	Change
Analysis, W%									
Molybdenum	7.78	7.13		0.013	5.7		7.13	9.82	
Nickel	1.69	0.86		0.039	0.37		0.86	1.34	
Sodium	0.89	0.03		0.012	0.05		0.03	0.05	
Calcium	0.57	0.02		0.024	0.16		0.02	0.05	
Iron	0.48	0.22		0.032	0.91		0.22	0.4	
Carbon	17.05	18.71			42.42		18.71	0.73	
Aluminum				0.298					
Silicon				0.0045					
Solids (Ashed)				0.98	37.37			93.14	
Weights, Grams									
Total	1,951	1,687	264	12,883	1.9		1,644	1,224	-420
Molybdenum	151.8	120.3	31.5	1.7	0.108	1.8	117.2	120.2	3.0
Nickel	33.0	14.5	18.5	5.0	0.007	5.0	14.1	16.4	2.3
Sodium	17.4	0.5	16.9	1.5	0.001	1.5	0.5	0.6	0.1
Calcium	11.1	0.3	10.8	3.1	0.003	3.1	0.3	0.6	0.3
Iron	9.4	3.7	5.7	4.1	0.017	4.1	3.6	4.9	1.3
Carbon	332.6	315.6	17.0		0.806		307.6	8.9	-298.7
Aluminum				38.4		38.4			
Silicon				0.6		0.6			
Solids (Ashed)				126		126			

TABLE 4

RUN CC-12 - RUN PLAN

Catalyst: Rejuvenated Shell S-317

Period (Days)	1 A to 13A
Nominal Conditions	
Unit Pressure	2,500
Coal Feed, lb/hr/ft^3 (Catalyst)	45
Filter Liquid Recycled, W% Dry Coal	116
Hydrogen Sulfide Feed, W% Dry Coal	2
Atmospheric Still Reboiler Temp., °F	525
Reactor Temperature, °F	
First Stage	750
Second Stage	800

TABLE 5

Liquefaction Performance Run CC-12

Black Thunder Mine Coal - Rejuvenated Catalyst

Period (Days)	**5-6**	**8-9**	**11-12**
Added Catalyst Age, Lb Coal/Lb Catalyst (Stage)	127	207	288
Coal Feed Rate Lb/hr/ft^3 Catalyst (Stage)	45.2	45.8	45.4
Temperatures, °F			
First Stage	750	750	750
Second Stage	800	800	800
Hot Separator	609	609	609
Atmospheric Still	531	536	536
Pressure, psig	2,509	2,513	2,510
Recycle, Lb/Lb Coal			
Filtered Liquid	1.16	1.16	1.16
Atmospheric Bottoms Slurry	0.00	0.00	0.00
Normalized Yields (% Coal)			
C_1-C_3	6.79	6.71	6.53
C_4-390°F	17.87	16.78	15.62
390-650°F	23.51	23.82	23.78
650-850°F	12.14	11.55	12.36
850-975°F	2.27	2.46	2.71
975°F$^+$ Liquid	2.19	2.94	3.74
Unconverted Coal	13.88	14.94	14.38
Ash (SO_3 free)	6.97	6.68	6.39
$CO + CO_2$	1.88	1.94	1.66
NH_3	0.85	0.75	0.78
H_2S	0.26	0.26	0.26
H_2O	18.57	18.44	18.94
Total (100 + H_2) Consumption	107.21	107.23	107.21
Process Performance (W% MAF)			
Coal Conversion	85.0	83.8	84.6
Coal Plus Resid Conversion	82.7	80.6	80.6
C_4-975°F Yield	60.0	58.4	58.2
Desulfurization	44.6	46.5	44.5
Denitrogenation	80.0	70.9	73.8

TABLE 6

Liquefaction Performance Run CC-12 and Run CC-1

Rejuvenated and Fresh Shell S-317 Catalyst

Run	**CC-12**		**CC-1**		
Catalyst	**Rejuvenated**		**Fresh**		
Period (Days)	**5-6**	**11-12**	**5-6**	**9-10**	**19**
Added Catalyst Age, Lb Coal/Lb Catalyst (Stage)	127	288	140	256	541
Coal Feed Rate Lb/hr/ft^3 Catalyst (Stage)	45.2	45.4	44.6	45.4	45.4
Temperatures, °F					
First Stage	750	750	750	750	750
Second Stage	800	800	800	824	824
Hot Separator	609	609	640	622	611
Atmospheric Still	531	536	524	295	294
Pressure, psig	2,509	2,510	2,502	2,498	2,503
Recycle, Lb/Lb Coal					
Filtered Liquid	1.16	1.16	1.23	0.84	0.84
Atmospheric Bottoms Slurry	0.00	0.00	0.00	0.38	0.38
Yields, W% of Dry Coal)					
C_1-C_3	6.79	6.53	7.59	8.19	8.88
C_4-390°F	17.87	15.62	17.59	20.14	19.90
390-650°F	23.51	23.78	27.92	29.18	27.30
650-850°F	12.14	12.36	11.82	12.12	10.57
850-975°F	2.27	2.71	2.06	2.06	1.97
975°F$^+$ Liquid	2.19	3.74	2.12	2.56	4.15
Unconverted Coal	13.88	14.38	12.42	8.12	7.71
Ash (SO_3 free)	6.97	6.39	6.01	6.01	6.01
CO + CO_2	1.88	1.66	0.48	0.34	0.82
NH_3	0.85	0.78	0.92	0.97	0.97
H_2S	0.26	0.26	0.36	0.36	0.36
H_2O	18.57	18.94	18.26	17.66	18.9
Total (100 + H_2) Consumption	107.21	107.21	107.55	107.74	107.56
Process Performance (W% MAF)					
Coal Conversion	85.0	84.6	86.8	91.2	91.8
Coal Plus Resid Conversion	82.7	80.6	84.6	88.6	87.4
C_4-975°F Yield	60.0	58.2	63.2	67.4	63.6
Desulfurization	44.6	44.5	70.0	71.2	71.3
Denitrogenation	80.0	73.8	72.2	75.7	75.7

TABLE 7

CTSL Operations - Rejuvenated and Fresh Catalysts

Run	CC-12			CC-1		
Catalyst	Rejuvenated			Fresh		
Days of Operation	6	9	12	6	10	19
Temperatures, °F						
First Stage	750	750	750	750	750	750
Second Stage	800	800	800	800	824	824
Hydrogen Contents, W%						
Separator Overhead	12.91	12.84	12.86	12.46	12.31	12.34
Atmospheric Overhead	12.57	12.35	12.47	12.28	12.89	13.06
Filtered Liquid						
IBP-650°F	11.43	11.39	11.35	11.58	11.10	10.97
650-850°F	10.52	10.90	10.94	10.94	10.34	9.85
850-975°F	9.40	9.82	9.91	9.08	8.94	8.29
975°F$^+$	7.92	8.62	8.59	8.45	7.30	6.50
Nitrogen Contents, W%						
Filtered Liquid						
IBP-650°F	0.05	0.06	0.06	0.18	0.13	0.22
650-850°F	0.03	0.20	0.16	0.12	0.11	0.26
850-975°F	0.11	0.28	0.18	0.26	0.30	0.50
975°F$^+$	0.25	0.32	0.28	0.39	0.51	0.74
Sulfur Contents, W%						
Filtered Liquid						
IBP-650°F	0.00	0.01	0.00	0.01	0.00	0.00
650-850°F	0.00	0.01	0.01	0.01	0.01	0.00
850-975°F	0.00	0.00	0.00	0.02	0.00	0.01
975°F$^+$	0.06	0.07	0.00	0.00	0.01	0.01
975°F+						
Cyclohexane Insoluble, W%	1.83	3.83	2.09	4.35	13.87	32.55
Toluene Insoluble, W%	0.14	0.04	0.92	0.10	0.70	6.15

FIGURE 1

COAL CONVERSION

Cat. – Rejuvenated (CC–12), Fresh (CC–1)

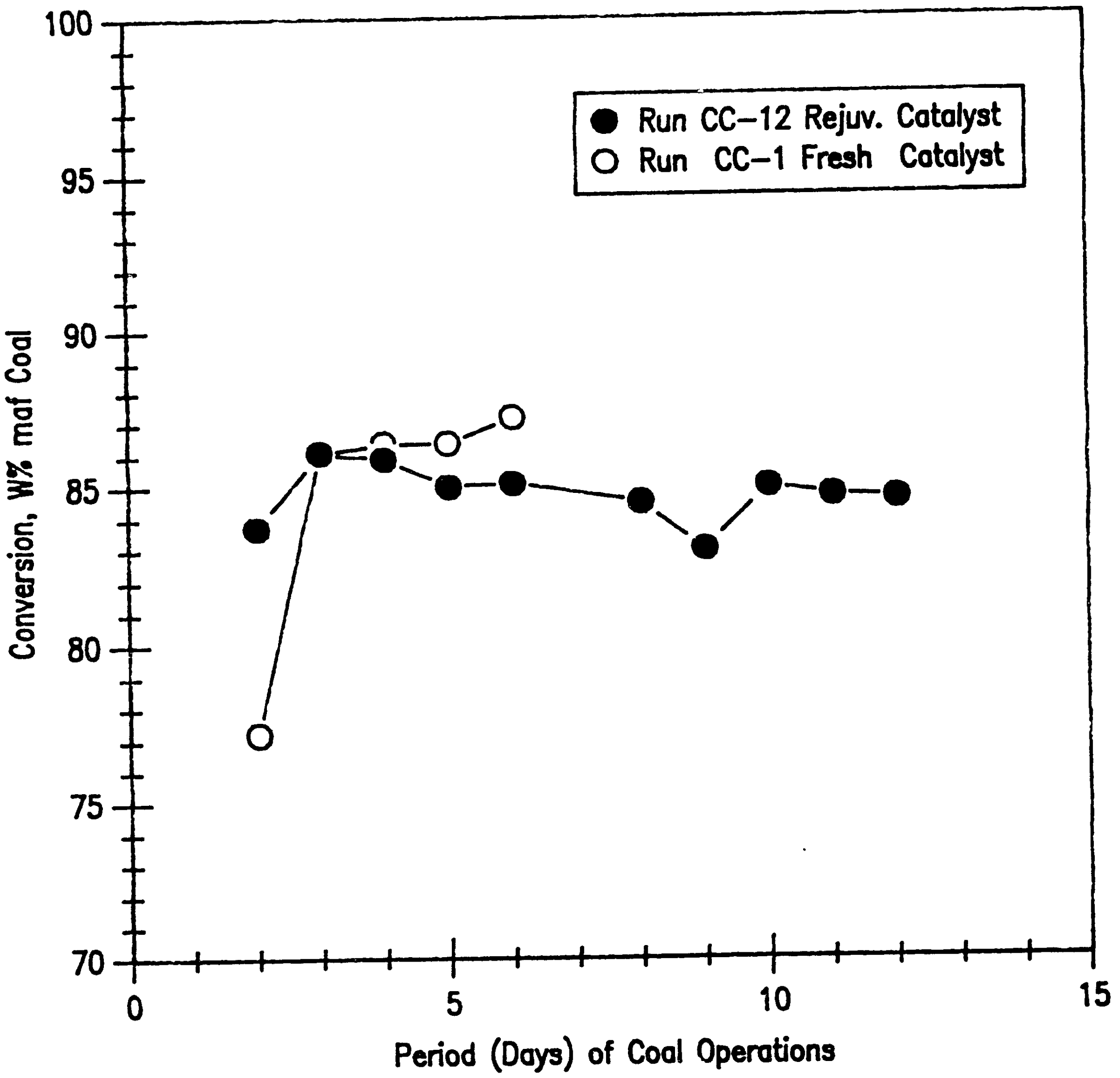
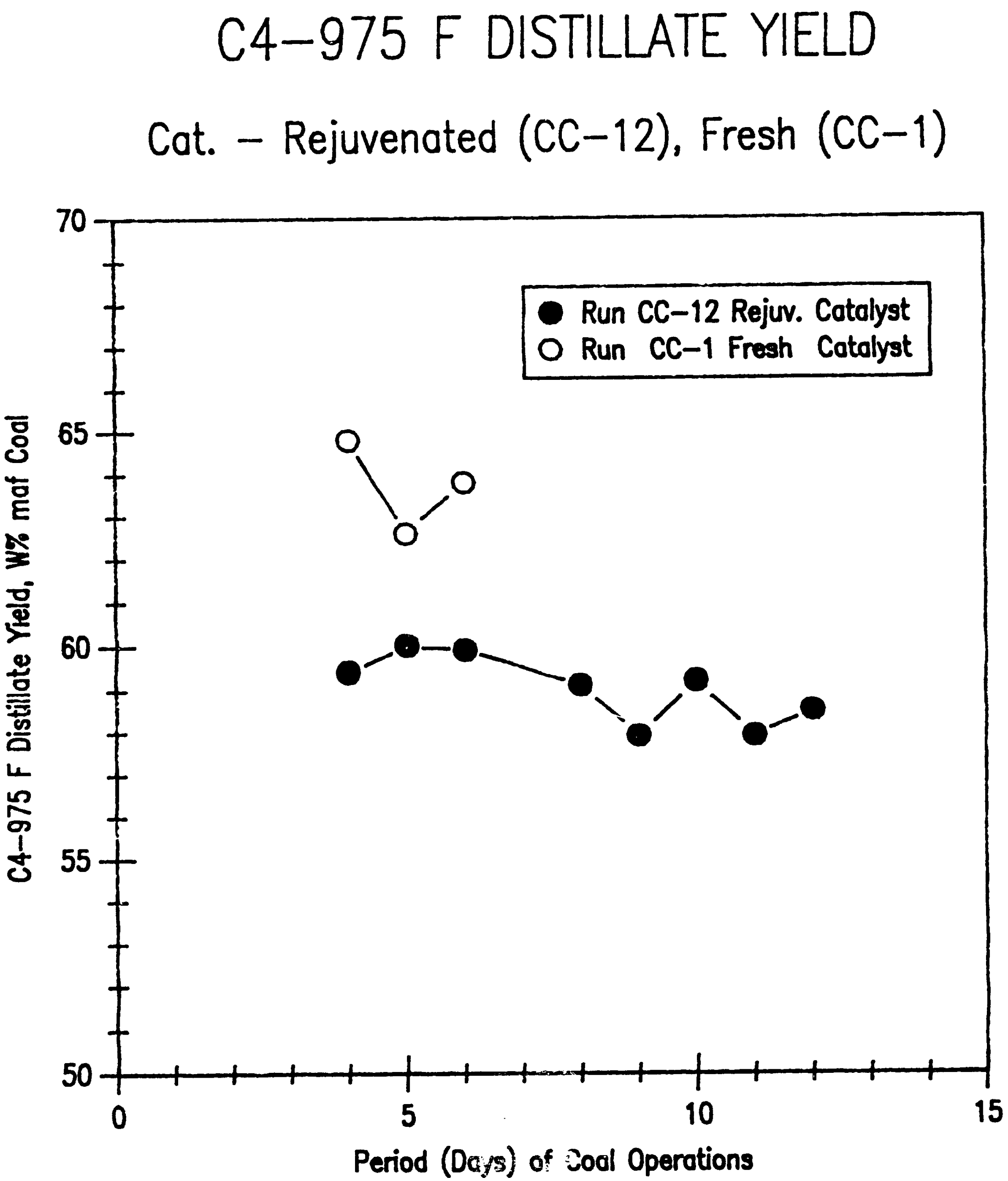


FIGURE 2



C4–975 F DISTILLATE YIELD

Cat. – Rejuvenated (CC–12), Fresh (CC–1)

FIGURE 3

975 F+ RESIDUUM YIELD

Cat. – Rejuvenated (CC–12), Fresh (CC–1)

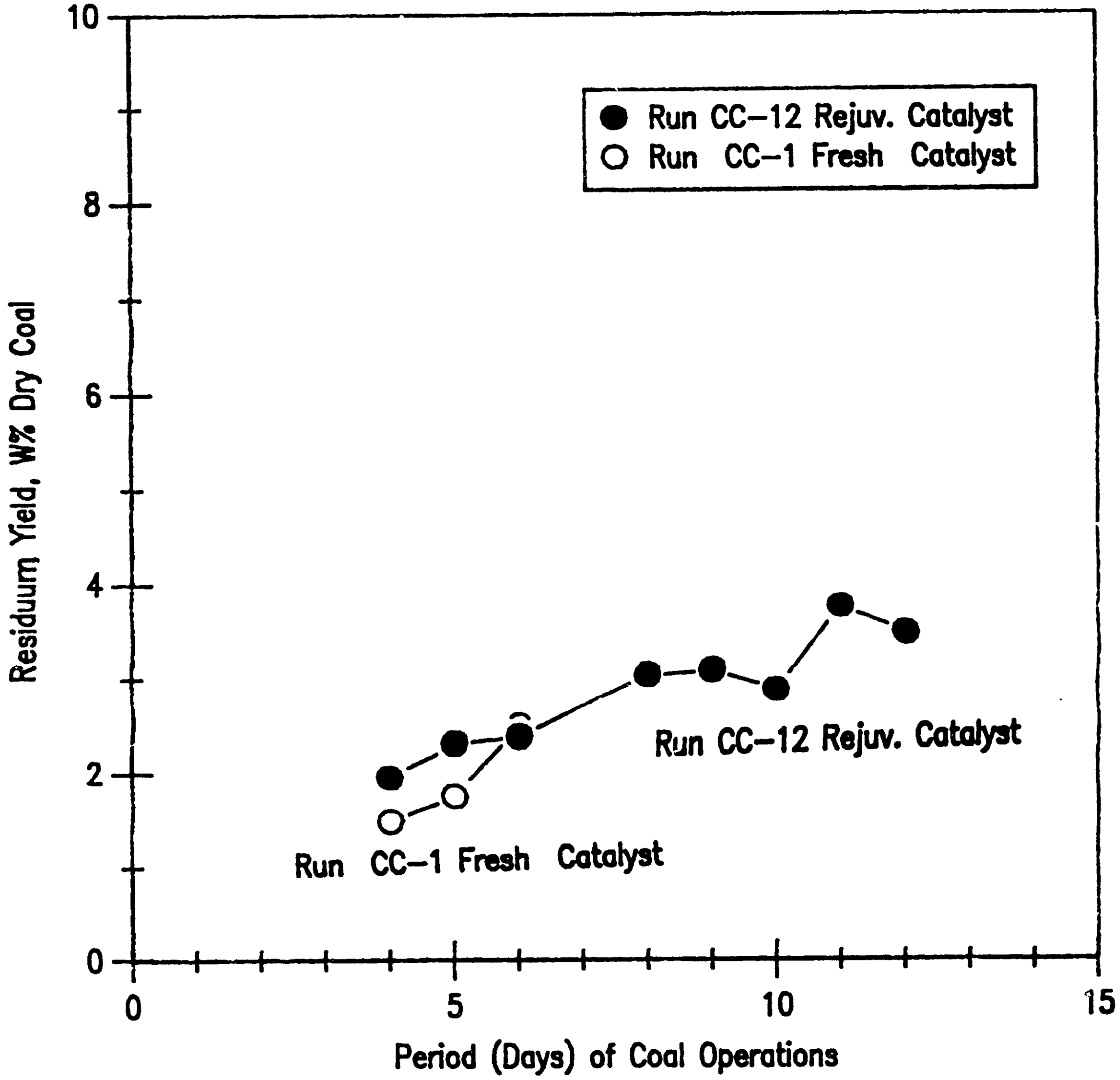
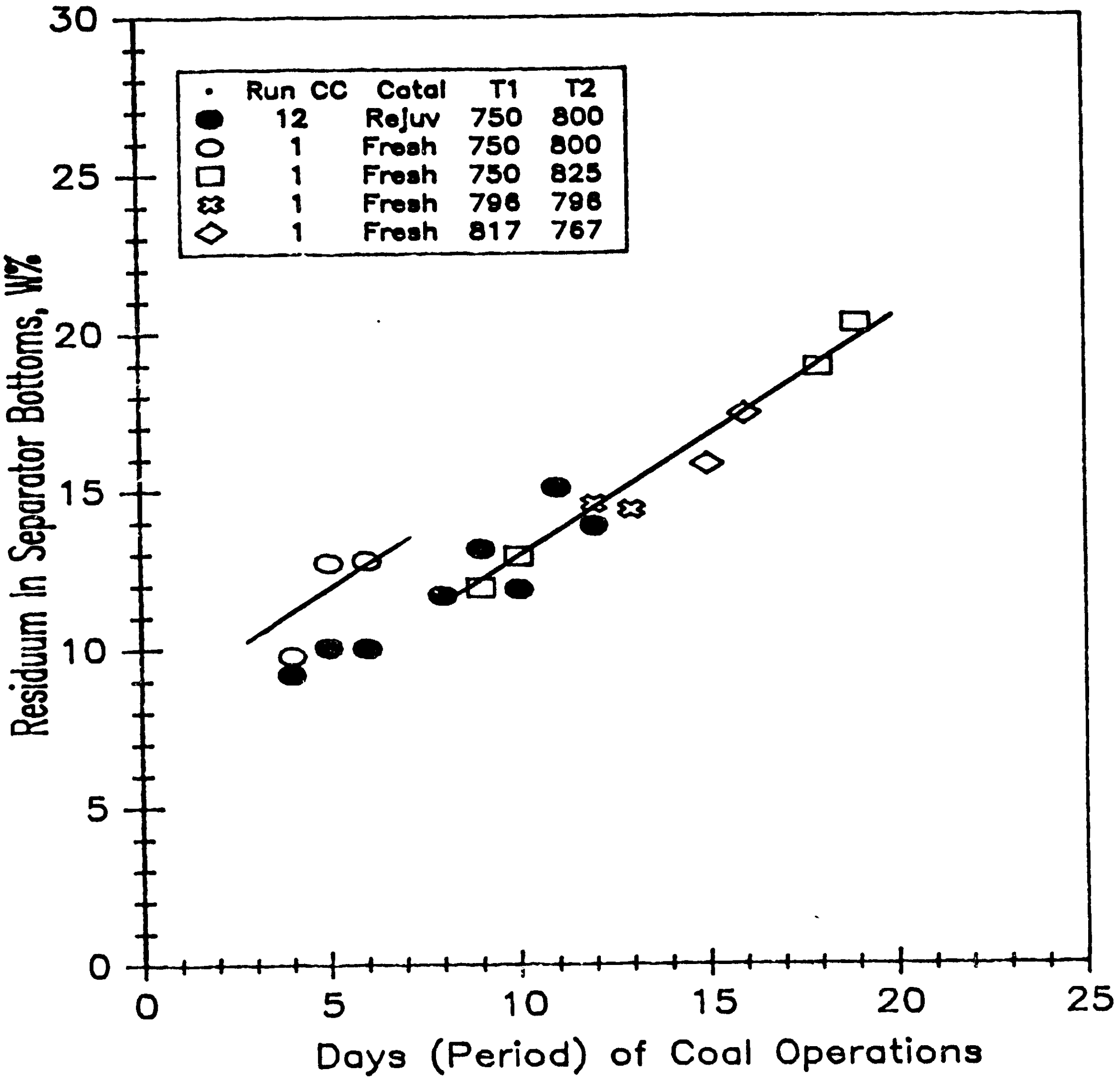


FIGURE 4

RESIDUUM CONCENTRATION IN PRODUCT SLURRY

CTSL — Rejuvenated and Fresh Catalyst



RUN CC-13 (227-71) CO_2 AND LIGHT DISTILLATE SLURRYING

Objectives

The objectives of this run were to evaluate CO_2 or a vaporizable distillate as feed slurrying agents for coal to the CTSL operation.

Scope of Work

A feed slurrying agent that would vaporize in the reactor would afford less dilution, than with the usual slurrying agents, of the resulting slurry phase and promote more complete reaction of the coal and heavy primary liquid products to lighter liquids. CO_2 has been demonstrated as a feasible slurrying agent for pipeline transport of coal and might be applied for this use in CTSL liquefaction. However, on the small scale of Bench Unit operations it was not possible to maintain CO_2/slurry feed to the unit, and the test program was modified to study the impact of CO_2 feed to the process while using the conventional CTSL practice of slurrying the coal with recycled filtered liquid. Also, there was an attempted operation using a light gas oil as slurrying agent in place of the filtered liquid, which was maintained for 40 hours before problems developed in maintaining feed slurry flow.

Coal and Light Slurry Oil

The coal feed for Run 227-71 was a recent shipment of Black Thunder Mine coal, HRI 5828. The coal analyses are given in *Table 8*. The light slurry oil used in a portion of the run, HRI 5663, was a coal derived distillate obtained from the Wilsonville Coal Liquefaction facility. Its analyses are given in *Table 9*.

Catalyst

Shell S-317 NiMo catalyst was used in both stages in 1/32 inch extrudate form. The catalyst was sulfided during the start-up by doping the start-up oil with TNPS (di-tertiary nonyl polysulfide). During coal operations H_2S, corresponding to 2 W% of the coal, was continuously added to maintain the sulfide level of the catalyst.

Run Plan

The initial intention was to use CO_2 as the feed coal slurrying agent directly, by means of a pressurized, refrigerated slurry preparation system. However, the attempts to prepare a pumpable CO_2/coal slurry on the Bench Unit scale of operations were unsuccessful, principally because high vaporization and vapor-binding of the slurry feed pump. The run plan was then changed to feed CO_2 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 recycle from the distillation of the reactor products).

The final run plan is given in *Table 10*. The run duration was 14 days. After an initial operation of five days, in a normal CTSL configuration with filtered liquid slurrying oil recycle and without CO_2 addition, addition of CO_2 was started first at a rate of 0.1 lbs/lb coal, then increasing to 0.25 lbs/lb coal. Then, on the tenth day, filtered liquid recycle was stopped and replaced by an equal amount of light gas oil make-up. The operation with light gas oil make-up was maintained for 40 hours to the end of the eleventh day, when the feed slurry flow failed because of difficulties in keeping the coal in suspension in the light oil. The twelfth day was spent in stabilizing the unit for the final operation with the filtered liquid recycle resumed and the CO_2 addition increased of 0.6 lbs/lb coal to the scheduled end of operations after 14 days.

Performance and Results

The liquefaction performance during Run CC-13 is summarized in *Table 11*, which gives the detailed product distribution. *Figure 5* summarizes the day-to-day coal conversion. *Figures 6* and *7* graphically compare for the four principal operating periods of the run the yield of C_4-975°F distillate product and the yield of 975°F$^+$ residual oil, respectively.

Coal Conversion

Coal conversion in Run CC-13 ranged from 90.0 to 94.0 W%, see *Figure 5*. The lowest coal conversion was in the first operation of the run, with no CO_2 addition. The highest coal conversion was in the operation using light gas oil make-up, and is the highest coal conversion obtained in any CTSL operation with Black Thunder Coal in the current program. The following tabulation summarizes the average coal conversions for the various operations of the run.

CO_2 Lb/Lb Coal	PFL Recycle Lb/Lb Coal	LGO Make-Up Lb/Lb Coal	Coal Conversion W% of MAF Coal
0.00	1.18	0.00	90.4
0.08	1.20	0.00	91.4
0.25	1.18	0.00	92.5
0.25	0.00	1.18	94.0
0.56	1.04	0.00	93.0

The very high conversion in the operation with light gas oil make-up conforms to the conception of promoting the coal conversion reaction because of less dilution of slurry phase reactants. As an index of this factor, the concentration of mineral matter (ash) in the product slurry from the hot separator (which is an indicator of slurry phase concentrations in the reactors) was about 1.15 times as great with light gas oil make-up as in the previous operation with filtered liquid recycle, while unreacted coal concentration was virtually unchanged. The increase in coal conversions because of the CO_2 additions did not have a similar relation to apparent changes in slurry phase compositions. Apparently, the CO_2 either had an interaction with the unreacted coal, or improved the liquid/coal contact to promote higher coal conversions.

Actually, the reduction of in the amount of product slurry (in effect the impact upon heavy reactant dilution) was not as great as might be obtained with a more volatile slurrying agent. The increase in hot separator vapor phase condensate by using the light gas oil slurrying agent was about 30% of the amount of the light gas oil feed. In effect, about 70% of the light gas oil wound up in the slurry phase. Presumably, a still lighter slurrying agent would promote higher coal conversion, although the problems of handling the light oil/coal would be compounded.

C_4-975°F distillate yield was 60.7 W% of MAF coal in the conventional reference operations at the beginning of the run, 3-6 W% higher in the operations with CO_2, and 5 W% lower in the operations with the light gas oil slurrying agent, see *Figure 6*. The nominal impact of CO_2 addition was greater than the associated 2% increase in coal conversion, indicating a possible ancillary contribution to the change in C_4-975°F distillate yield. Since there was only a small impact of CO_2 addition upon residual oil yield, see below, this leaves the possibility of some hydrocarbon synthesis (Fischer-Tropsch) reaction to produce liquids. While there was almost certainly additional methane formation with the CO_2 addition, see below, there was apparently very little change in C_2 and C_3 hydrocarbon formation so that the synthesis of still heavier hydrocarbons seems unlikely. The difference in incremental liquid yield and incremental coal conversion more probably reflects material balance difficulties which were occasioned by the somewhat erratic rate of CO_2 addition during these operations.

The 5 W% lower C_4-975°F distillate yield while using the light gas oil makeup, despite a 3% increase in coal conversion, was caused largely by the 5 W% higher residual oil yield for that operation. This change was not because of any kinetic impact of the light gas oil, but rather because there was no residual oil recycle, and an appreciable amount of net slurry product was generated, approximately one pound per pound of coal fed. The ultimate application of light slurry recycle will have to incorporate a portion of residual oil recycle to limit the formation of residual oil, i.e. a lower concentration of the resid reactant gives a lower rate of production of distillate product, even if the rate constant remains the same.

975°F$^+$ Residual oil yield was 1.3 W% of MAF coal in the conventional reference operations at the beginning of the run, about this level or slightly lower in the operation with CO_2 addition, and 5 W% higher in the operation using the light gas oil slurrying agent, see *Figure 7*. *Figure 8* reflects the apparent kinetics of second residual oil conversion reactions, by comparing the residual oil concentrations in the product (hot separator) slurry for the various operations of Run CC-13, and comparable operations of CC-1, in which no CO_2 was added. In general, the residual oil concentrations for the operations with CO2 addition lie below what would be expected for a comparable operation with no CO_2 addition. However, the differences are small in the first part of Run CC-13, and the larger difference at the end may largely be due failure to reach an equilibrated condition after the upset at the end of the eleventh day and stabilizing the unit in the twelfth day.

Figure 8 shows, for the operation with the light gas oil slurry agent, a very much lower residual oil concentration, by a factor of 2, in the product slurry than in the contemporary operations of the run. This nominally indicates enhanced residual oil kinetics in this mode, although more detailed flash calculations at the actual reactor conditions (at 825°F against the separator temperature of 600°F) will have to be made to see if the difference in compositions is as great at the reactor conditions.

CO_2 Reactions

It is to be noted in *Table 11*, that there are apparent negative yields of CO_2 for all of the operations with CO_2 addition, and higher yields of C_1-C_3 gases, CO, and water than were obtained in the reference operation at the beginning of the run with no CO_2 addition. *Figure 9* relates the amount of CO_2 in the outlet gases to the amount of CO_2 added to the operation. *Figures 10*, *11*, and *12* give a similar relation for the net yields of H_2O, CO, and CH_4, respectively. Each of these figures contain the least squares relations for the factors correlated, all of which were highly significant, statistically, with confidence levels above 99%.

The correlated values for the proportion of CO_2 addition that reacts, and the amounts of additional products were the following:

	Lbs/Lb CO_2 Added
CO_2 Reacted	0.583
Incremental H_20 Formed	0.427
Incremental CO Formed	0.105
Incremental CH_4 Formed	0.143
C in CO_2 Reacted	0.159
O in CO_2 Reacted	0.424
C in CO and CH_4 Formed	0.152
O in CO and H_2O Formed	0.439
H in CH_4 and H_2O Formed	0.083

These correlations indicate that 58.3% of the CO_2 was reacted. The elemental balances indicate that CO, CH_4, and H_2O were the only products that were formed from the CO_2.

Considering the other light gas products that might have been formed, the following tabulation compares their average collected yields for the operations with and without CO_2 addition:

	Yields, W% of Dry Coal		
	No CO_2	**CO_2 Added**	**Confidence Level, %**
C_2 Hydrocarbons	2.61	2.11	83.7
C_3 Hydrocarbons	3.23	3.06	39.1
C_4 Hydrocarbons	2.44	2.26	57.1
Total	**8.28**	**7.43**	**76.5**

The confidence levels noted here are a comparison of the averages with and without CO_2 addition. Although in each case the average of the yields with CO_2 addition was lower than that without CO_2 addition, the scatter of the data was such as to result in relatively low statistical confidence levels. The sum of the C_2, C_3, and C_4 yields did have a marginally significant correlation against the amount of CO_2 fed, 92.3% confidence level, as summarized by *Figure 13*. The correlation indicates 1.8 W% of dry coal lower yield of these components when the CO_2 addition was 0.6 lbs/lb dry coal. This relation suggests that CO_2 inhibits the formation of light gases during the liquefaction/conversion of the coal, ostensibly by a chain quenching effect, although the experimental support of such a hypothesis is weak.

Product Properties

Table 12 summarizes the hydrogen, nitrogen, and sulfur analyses of the liquid products from Run CC-13. The hydrogen contents of the products for the final operation of the run, while feeding 0.55 lbs CO_2/lb coal, were 0.18% to 1.23% lower than those of the products in the conventional operation at the beginning of the run, with the difference being the greatest for the heavy liquid product fractions. In Run CC-11 the decrease in hydrogen contents over a comparable interval of the run was 0.09% to 0.44%, so that Run CC-13 operation with CO_2 addition displayed a lower hydrogenation effectiveness. This difference might be due to some degree to dilution of the hydrogen because of the added CO_2 and its products, but the hydrogen partial pressure was only about 100 psi lower in the final operation of Run CC-13 than in the initial operation, because the system pressure had been raised to 2800 psi, from 2500 psi, for the final operation.

The change in nitrogen contents of the products in course of Run CC-13 were approximately the same as during Run CC-12.

Cyclohexane insolubles content of the 975°F^+ product for the final operations of Run CC-13 were over twice the amount for the final operations of Run CC-11.

TABLE 8

Analyses of Feed Coal for Run CC-13

Coal	Black Thunder Mine (Wyoming)	
HRI No.	**5828**	**5630**
Feed for Run	CC-13	CC-1
Moisture (As Fed)	4.83	8.92
W%, Dry Basis		
Carbon	68.01	67.70
Hydrogen	4.10	4.54
Nitrogen	0.93	1.05
Ash	(7.64)	(7.15)
Sulfur in Ash	(5.97)	(6.35)
Ash (SO_3-free)	6.50	6.01
Oxygen (by difference)	19.91	20.18
Ash Analysis (Ignited, W% Ash)		
Silica, SiO_2	36.42	34.61
Alumina, Al_2O_3	15.67	16.98
Titania, TiO_2	1.22	1.30
Ferric Oxide, Fe_2O_3	6.64	6.94
Lime, CaO	19.83	21.74
Magnesia, MgO	3.98	4.40
Potassium Oxide, K_2O	0.39	0.35
Sodium Oxide, NaO	0.76	0.97
Sulfur Trioxide, SO_3	12.36	10.74
Phosphorous Pentoxide, P_2O_5	0.77	1.01
Strontium Oxide, SrO	0.83	0.29
Barium Oxide, BaO	0.46	0.37
Manganese Oxide, Mn_3O_4	0.15	0.00
Undetermined	0.52	0.30
Microautoclave Results**		
Thermal Coal Conversion	80.3	
Thermal 975°F$^+$ Conversion	45.4	
Catalytic Coal Conversion	89.8	84.2
Catalytic 975°F$^+$ Conversion	66.4	63.9

** 800°F, 30 minutes, 2000 psig H_2,
4/1/(1) Solvent/Coal/(Shell S-317 Catalyst)
Solvent - Wilsonville Coal Liquefaction Distillate

TABLE 9

Inspection Light Solvent Slurry Oil for Run CC-13

Designation	HRI 5663
Gravity, °API	26.0
Distillation Temp., °F	
IBP	148
10 V%	250
20 V%	323
30 V%	390
40 V%	474
50 V%	520
60 V%	543
70 V%	580
80 V%	615
90 V%	660
E.P.	748
Recovery, V%	100
Residue, W%	0.0
W% @ 650°F	79.9
Carbon, W%	87.71
Hydrogen, W%	12.09
Nitrogen, W%	0.16
Sulfur, W%	0.02

TABLE 10

Run CC-13 (227-71) - Operational Summary

Catalyst - Fresh Shell S-317

Condition	1	2	3	4	5
Period (Days)	1-5	6-7	8-9	10-11	12-14
Nominal Conditions					
Unit Pressure, psig	2500				
Coal Feed, Lb/Hr/Ft^3 (Catalyst)	45				
Filtered Liquid Recycle, Lb/Lb/Dry Coal	1.2	1.2	1.2	0.05	1.2
Hydrogen Sulfide Feed, W% of Dry Coal	2				
Atmospheric Still Reboiler Temp., °F					
Reactor Temperatures, °F					
First Stage	750				
Second Stage	825				
CO_2 Addition, Lb/Lb Dry Coal	0.0	0.1	0.25	0.25	0.6
Light Gas Oil Addition, Lb/Lb Dry Coal	0.0	0.0	0.0	1.1	0.0

TABLE 11

Liquefaction Performance Run CC-13

Black Thunder Mine Coal - CO$_2$ Addition and Light Solvent Slurry

CONDITION	**1**	**2**	**3**	**4**	**5**
Periods (Days)	**5**	**7**	**9**	**11**	**14**
Catalyst Age, Lb Dry Coal/Lb Catalyst) (Stage)	143	201	259	318	401
Coal Feed Rate, Lb/Hr/Ft^3 Catalyst (Stage)	44.2	44.7	44.9	44.9	43.3
CO$_2$ Addition, Lb/Lb Dry Coal	0.0	0.74	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
Temperatures, °F					
First Stage	752	750	752	752	751
Second Stage	829	827	828	828	829
Hot Separator	607	608	599	602	594
Atmospheric Still	534	537	--	525	524
Pressure, psig	2,502	2,596	2,595	2,652	2,806
Normalized Yields (W% of Dry Coal)					
C$_1$-C$_3$	11.49	(12.81)	12.76	10.96	16.97
C$_4$-390°F	22.27		21.30	11.69	17.62
390-650°F	25.51		33.68	22.73	33.94
650-850°F	7.83		6.36	11.85	7.53
850-975°F	1.16		1.07	5.66	0.53
975°F$^+$ Liquid	1.29		1.15	5.89	0.86
Unconverted Coal	8.63		7.03	5.64	6.53
Ash (SO$_3$-free)	6.50		6.50	6.50	6.50
Water	21.31	(21.91)	37.66	37.44	39.32
CO	0.48	(1.30)	0.97	3.62	7.31
CO$_2$	0.72	(0.36)	-18.34	-13.71	-26.25
NH$_3$	1.02		0.96	0.92	0.95
H$_2$S	0.37		0.39	0.44	0.44
Total (100 + H$_2$ Consumption)	108.59		111.51	109.62	112.26
Process Performance (W% MAF)					
Coal Conversion	90.8	91.2	92.5	94.0	93.0
975°F$^+$ Conversion	89.4		91.2	87.7	92.1
C$_4$-975°F Distillate Yield	60.7		66.8	55.5	63.8
Desulfurization	63.5		67.3	75.7	75.4
Denitrogenation	90.7		84.9	81.0	84.3

Period 7 yields are collected yields, other yields are normalized yields.

TABLE 12

Analyses of Products - Run CC-13

CTSL Operations - CO_2 and Light Distillate Feed

Days of Operation	5	9	11	14
CO_2 Feed, Lbs/Lb Dry Coal	0.00	0.245	0.255	0.556
Light Gas Oil Feed, Lbs/Lb Dry Coal	0.00	0.00	1.18	0.00
Filtered Liq. Recycle, Lbs/Lb Dry Coal	1.18	1.18	0.00	1.04
Hydrogen Contents, W%				
Separator Overhead	12.73	12.50	12.96	12.06
Atmospheric Overhead	12.27	12.12	12.04	11.90
Filtered Liquid				
IBP-650°F	11.31	11.02	11.02	10.90
650-850°F	10.07	9.81	10.13	9.89
850-975°F	8.50	7.98	8.26	7.73
975°F$^+$	6.96	6.38	6.26	5.73
Nitrogen Contents, W%				
Separator Overhead	0.04	0.12	0.11	0.14
Atmospheric Overhead	0.07	0.15	0.14	0.22
Filtered Liquid				
IBP-650°F	0.08	0.14	0.13	0.15
650-850°F	0.05	0.11	0.28	0.19
850-975°F	0.23	0.34	0.47	0.42
975°F$^+$	0.50	0.62	0.66	0.68
Sulfur Contents, W%				
Separator Overhead	0.00	0.02	0.02	0.03
Atmospheric Overhead	0.01	0.03	0.00	0.00
Filtered Liquid				
IBP-650°F	0.01	0.01	0.03	0.03
650-850°F	0.03	0.02	0.04	0.03
850-975°F	0.02	0.01	0.02	0.04
975°F$^+$	0.03	0.05	0.06	0.04
975°F+				
Cyclohexane Insoluble, W%	18.1	27.5	41.3	35.3
Toluene Insoluble, W%	1.1	1.0	3.1	6.2

FIGURE 5

COAL CONVERSION RUN CC–13

CTSL – With CO2 and Light Distillate

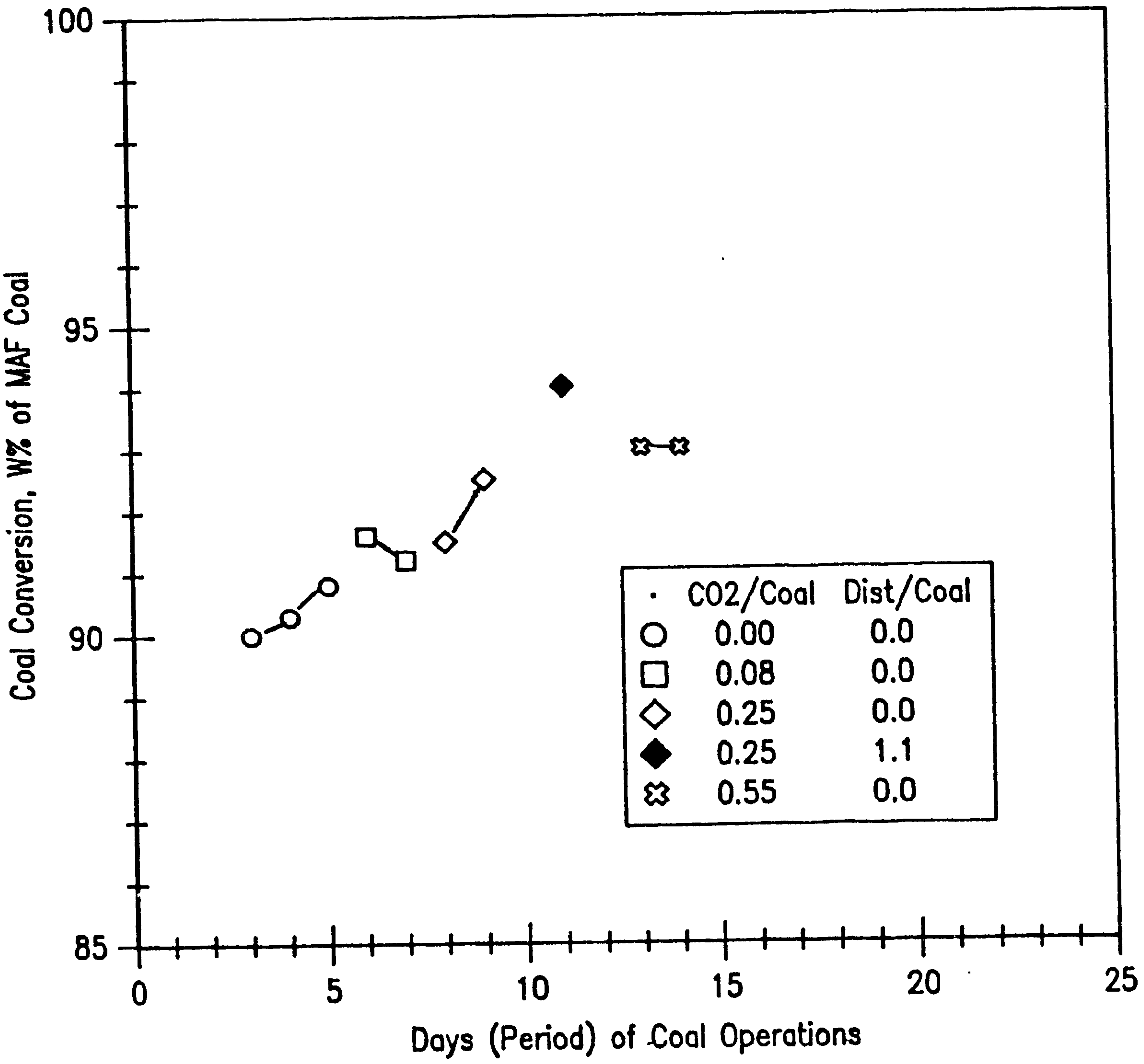
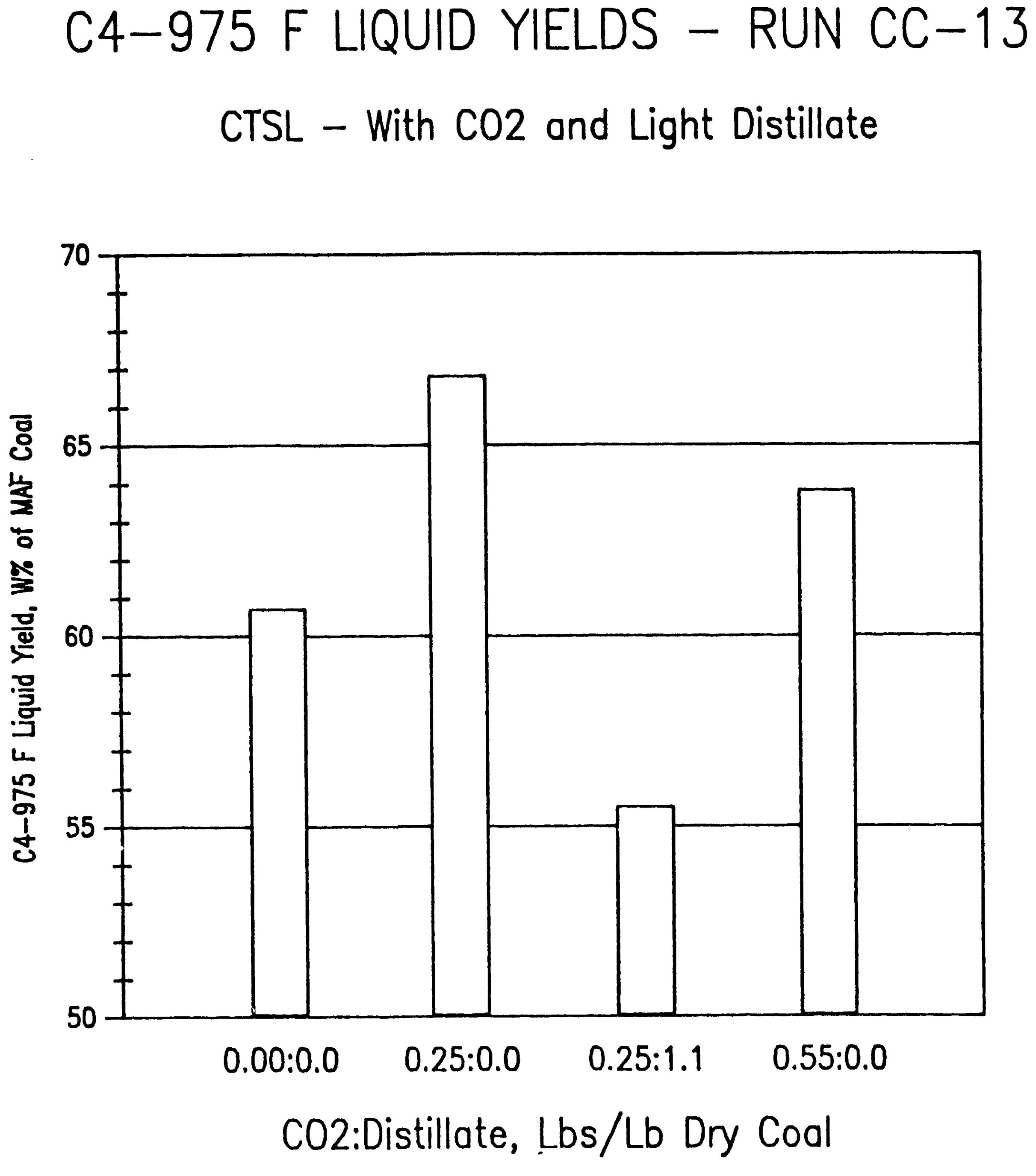


FIGURE 6



C4-975 F LIQUID YIELDS - RUN CC-13
CTSL - With CO2 and Light Distillate
C4-975 F Liquid Yield, W% of MAF Coal
70
65
60
55
50
0.00:0.0
0.25:0.0
0.25:1.1
0.55:0.0
CO2:Distillate, Lbs/Lb Dry Coal

FIGURE 7

Residual Oil Yields – Run CC-13

CTSL – With CO2 and Light Distillate

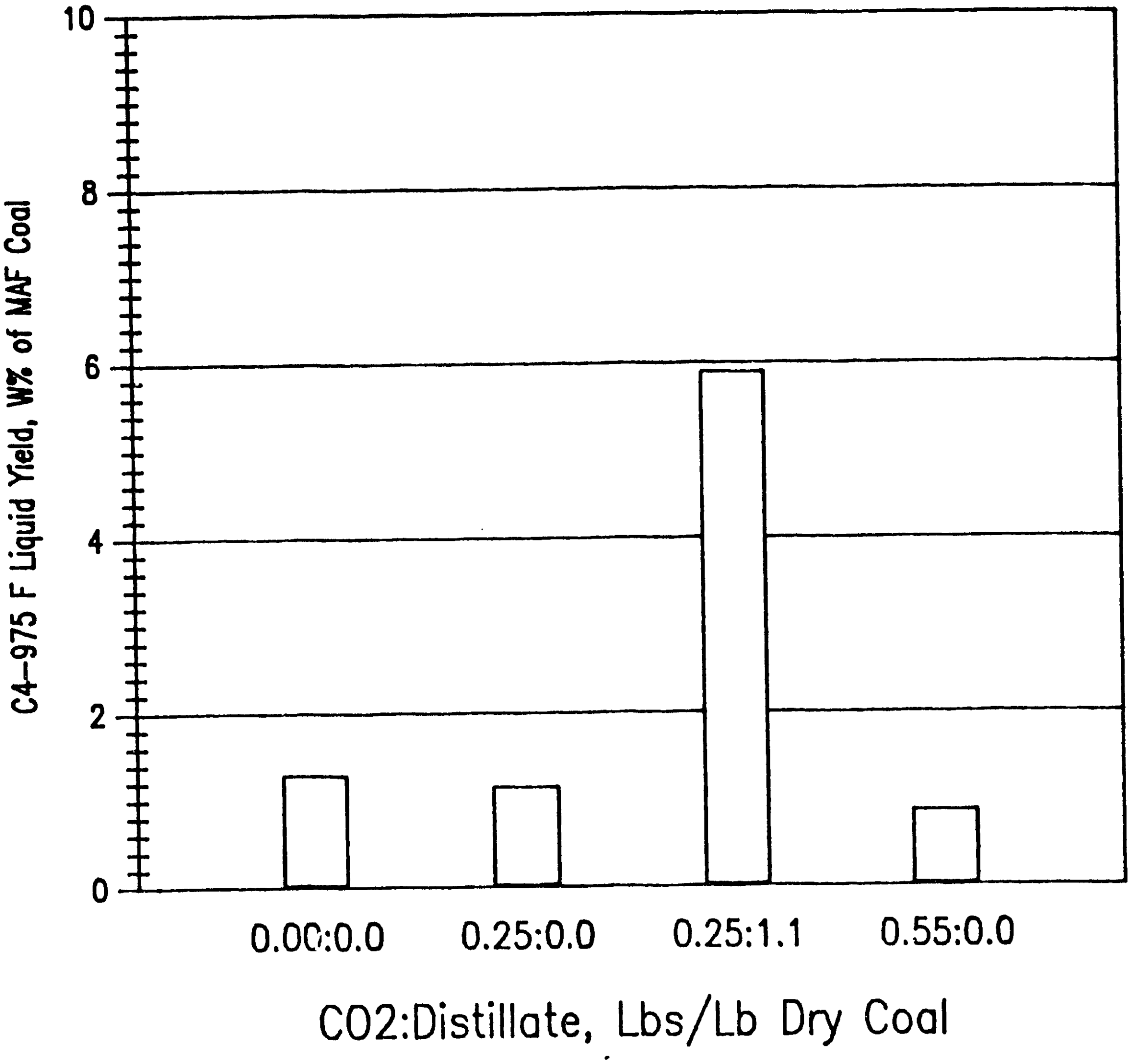
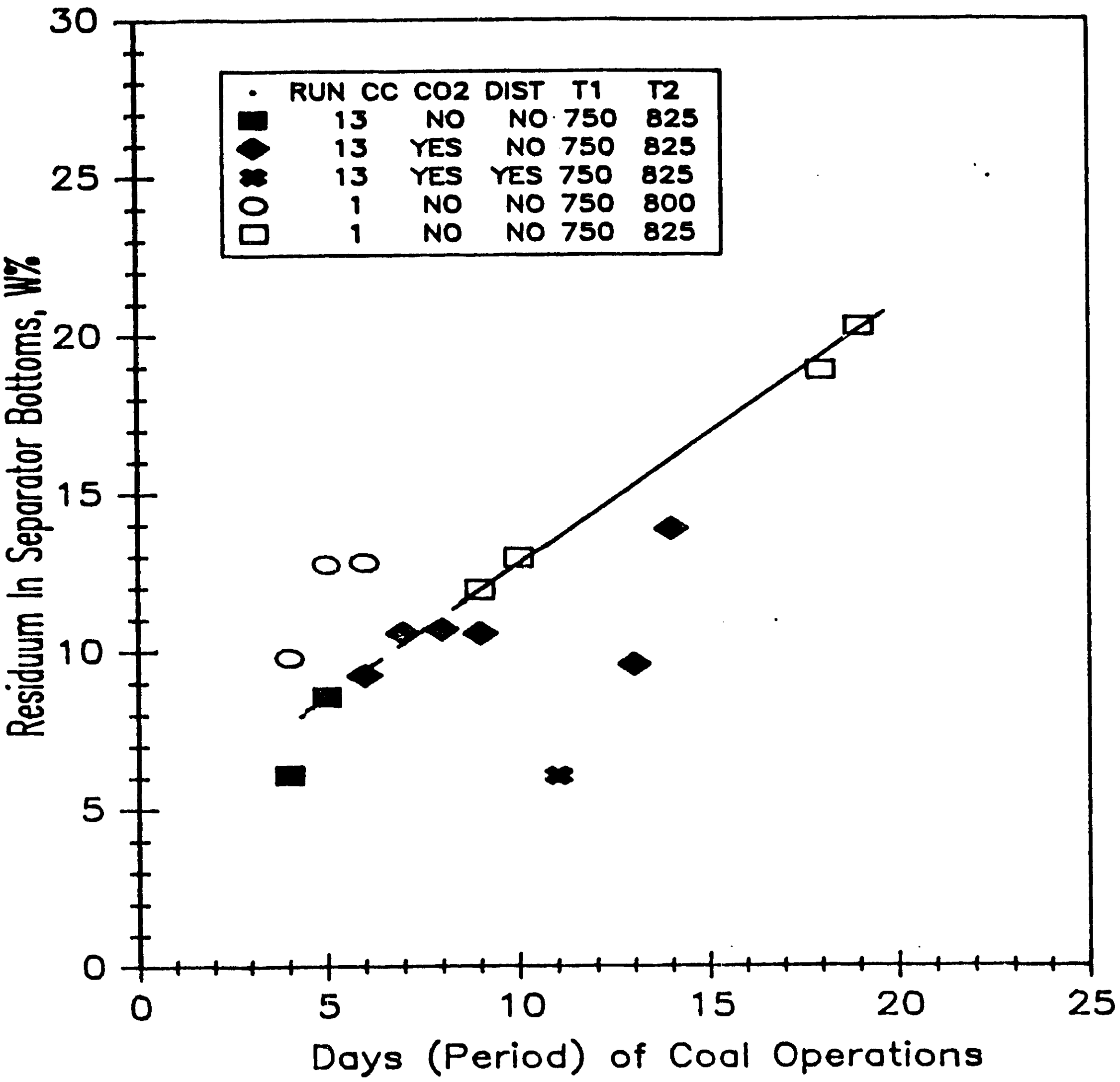


FIGURE 8



RESIDUUM CONCENTRATION IN PRODUCT SLURRY

CTSL – With CO2 and Light Distillate

FIGURE 9

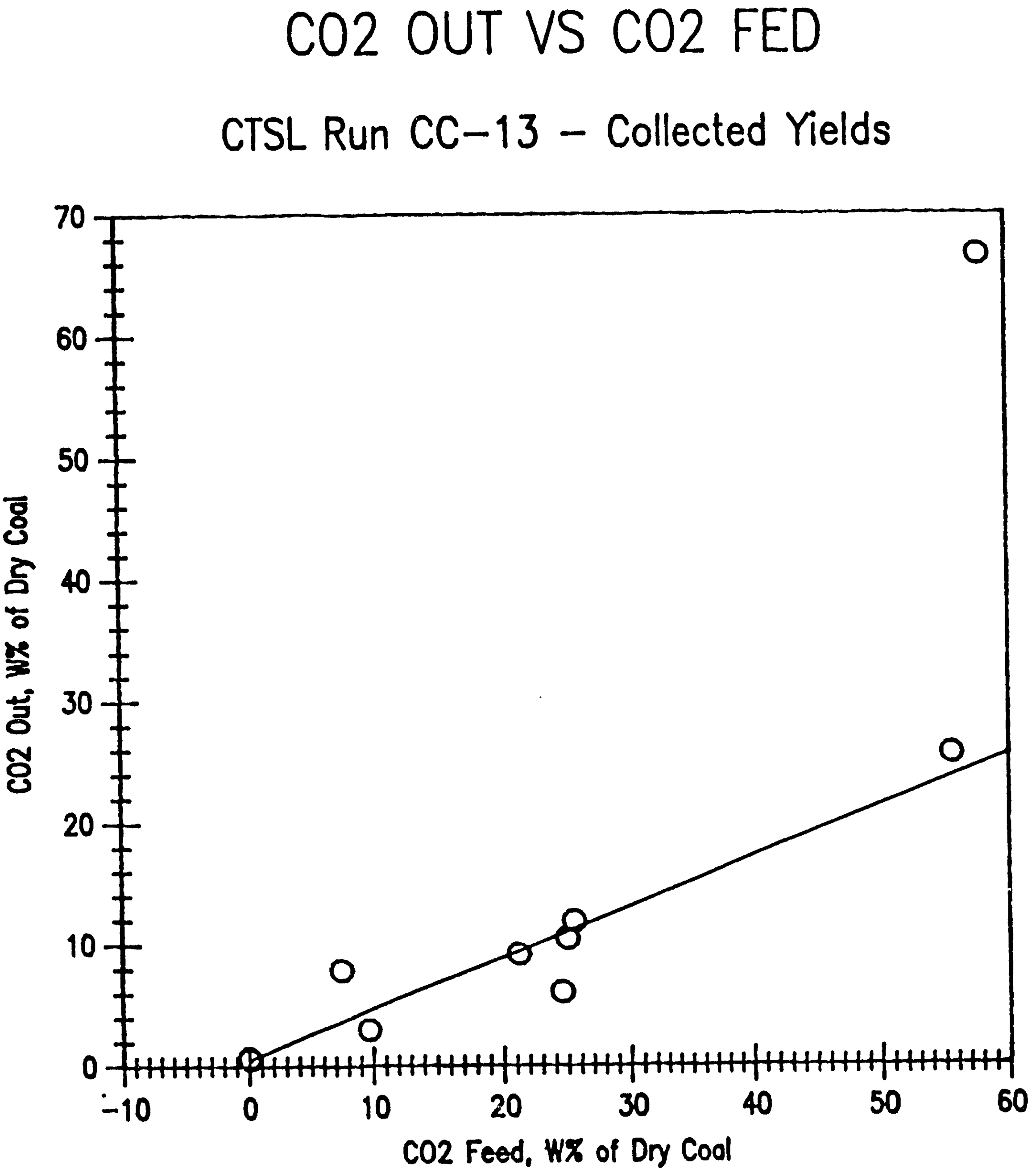

CO2 OUT VS CO2 FED
CTSL Run CC-13 - Collected Yields
CO2 Out, W% of Dry Coal
0
10
20
30
40
50
60
70
-10
0
10
20
30
40
50
60
CO2 Feed, W% of Dry Coal

FIGURE 10

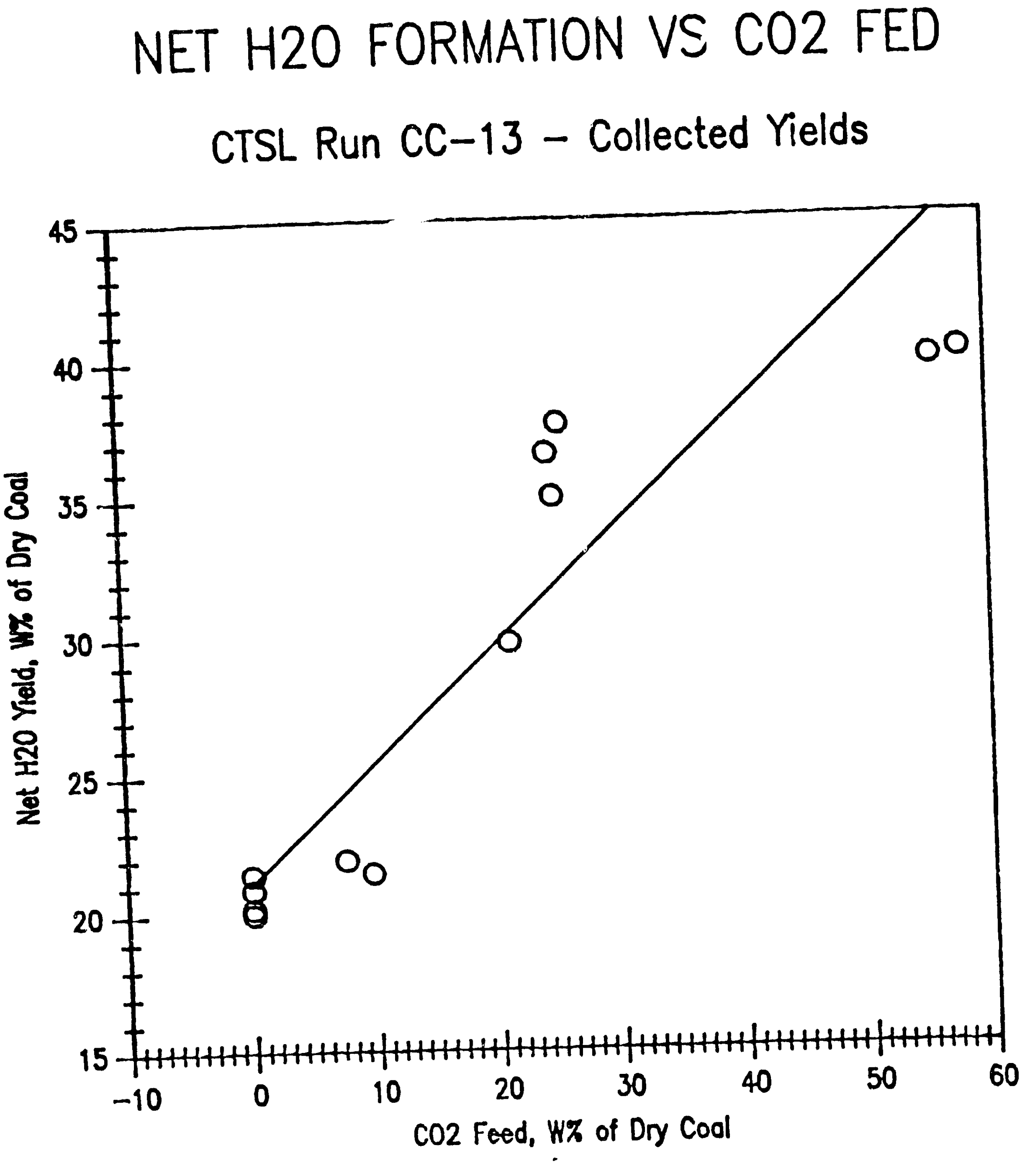

NET H2O FORMATION VS CO2 FED
CTSL Run CC-13 - Collected Yields
Net H2O Yield, W% of Dry Coal
45
40
35
30
25
20
15
-10
0
10
20
30
40
50
60
CO2 Feed, W% of Dry Coal

FIGURE 11

CH4 YIELD VS CO2 FED

CTSL Run CC-13 - Collected Yields

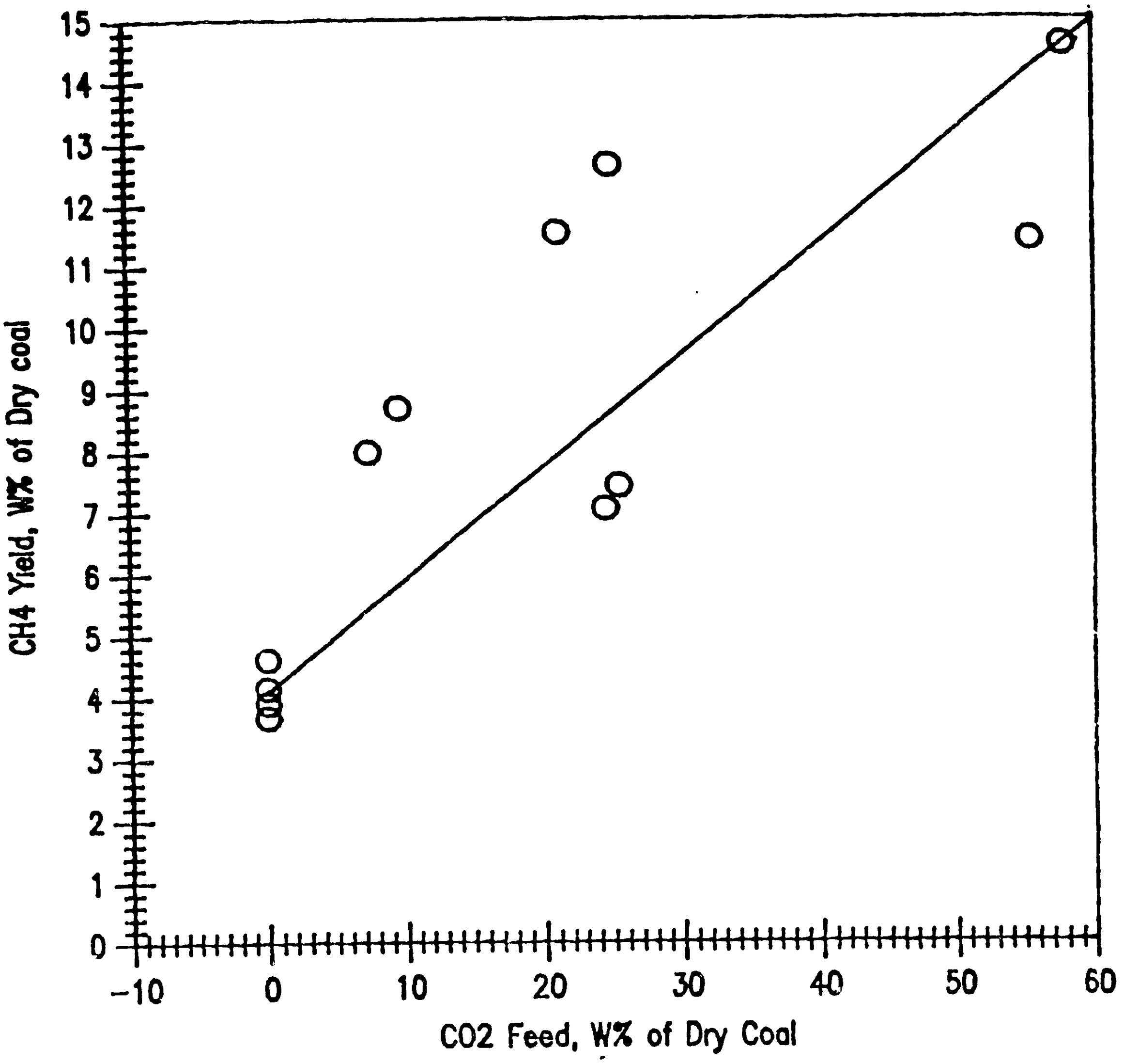
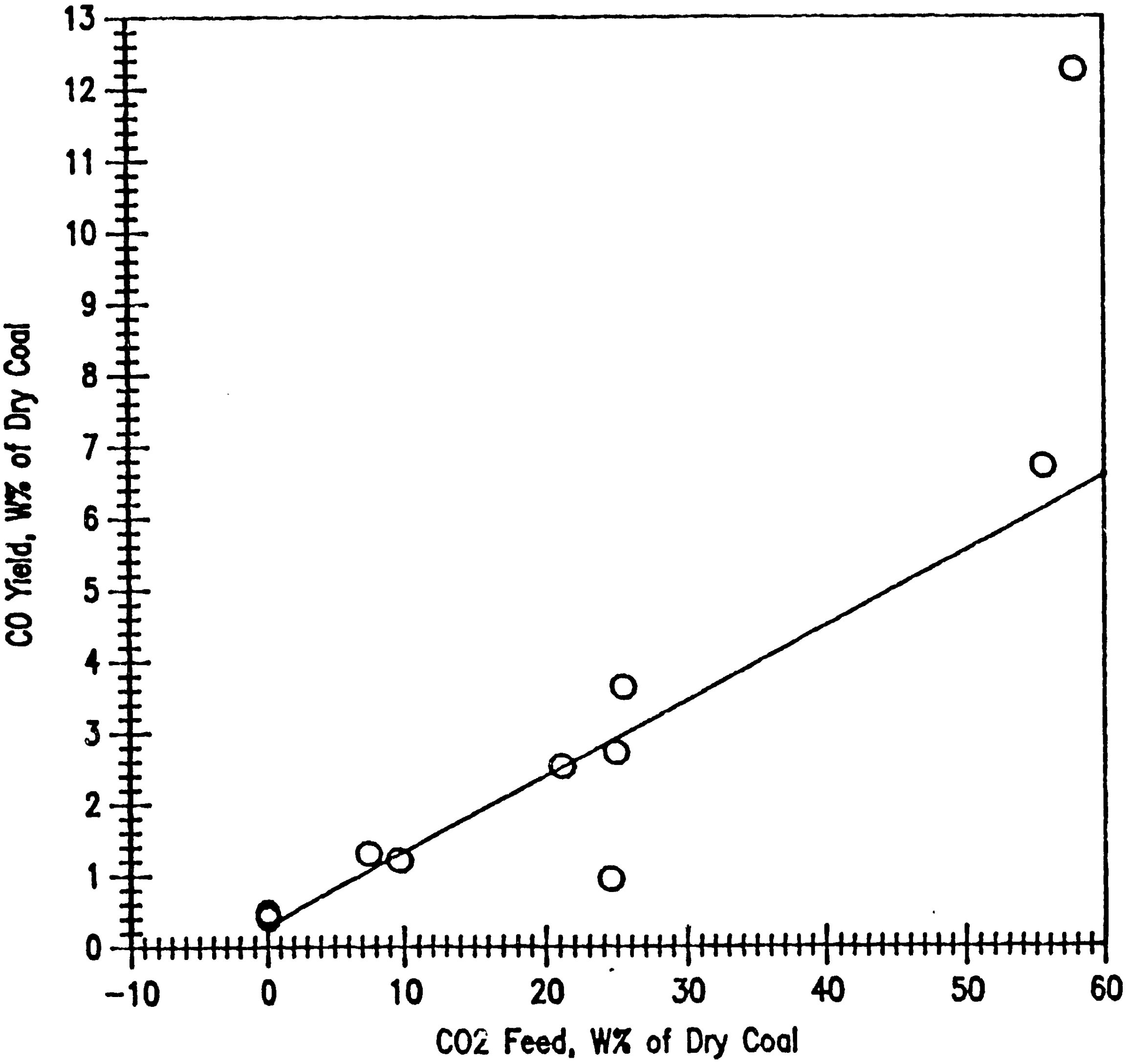


FIGURE 12



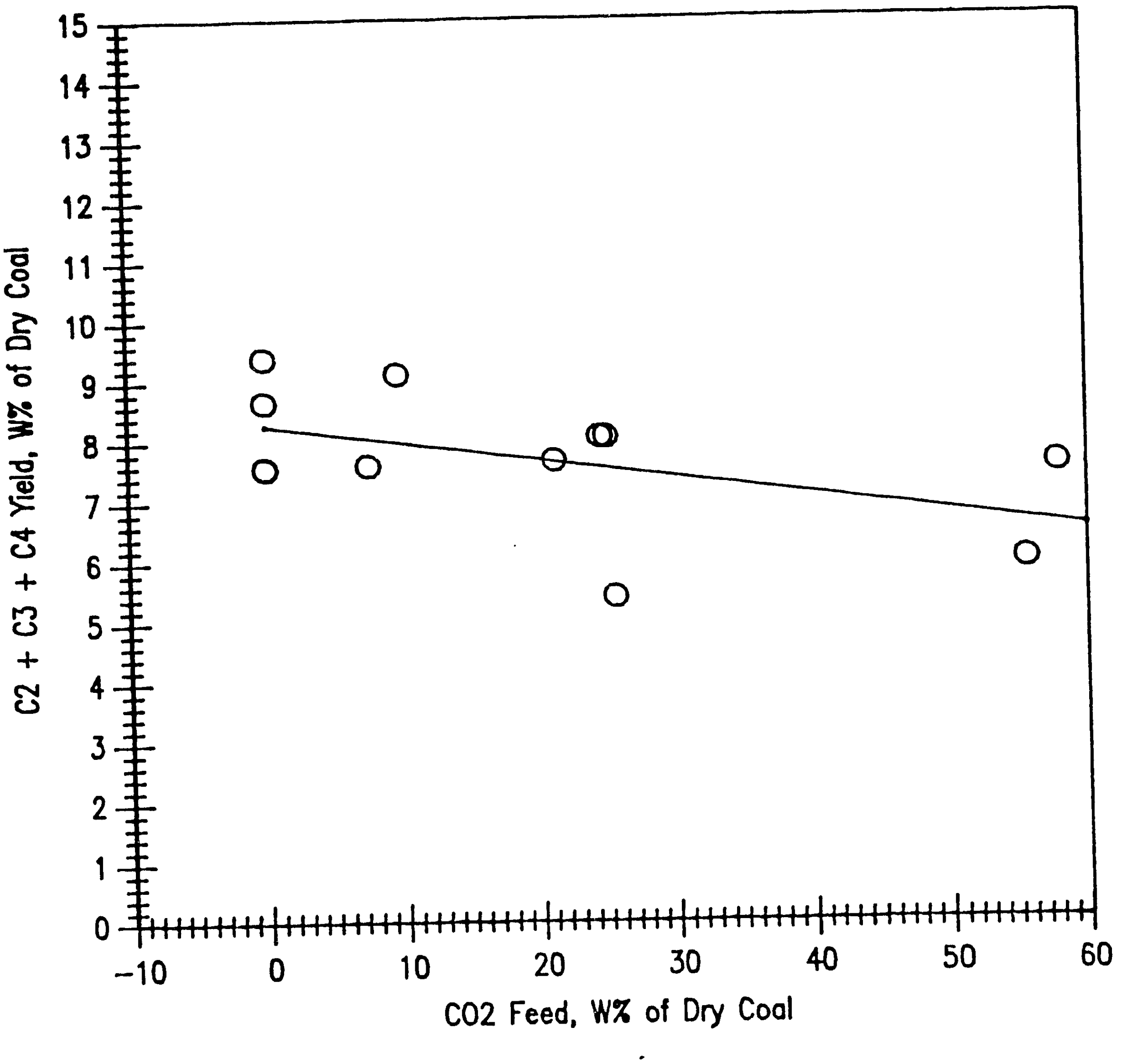
CO YIELD VS CO2 FED

CTSL Run CC-13 - Collected Yields

FIGURE 13

C2–C4 GAS YIELD VS CO2 FED

CTSL Run CC–13 – Collected Yields



TASK 4 - MINI-PDU SCALE-UP

Preparations

Plans are being formulated to test the Black Thunder feed coal prepared at Empire Coke in Alabama where the coal for the Wilsonville, Alabama operation is prepared. Start-up solvent will be obtained from the Wilsonville plant.

Orders have been placed for Shell 317 catalyst in both 1/32 and 1/16" diameters.

The British Coal Corporation Filtration Process utilizing a U.S. vertical leaf pressure filter will be installed for liquid-solid separation.

TASK 5 - TECHNICAL ASSESSMENT

MODELLING

Residuum Yields in Microautoclave Tests of Coals

The results of coal evaluation tests during the current program of various coals have been reviewed comparing the residual oil yields of the catalytic and thermal (non-catalytic) tests. The conditions for these tests have been 2,000 psig H_2 pressure, 30 minutes residence time, 800°F, 4 grams of coal liquefaction derived distillate oil per gram of coal, and 1 gram presulfided S-317 catalyst per gram of coal. This analysis indicated apparently significant differences in residual oil yield for various coals, and in the catalytic and thermal yields, as summarized in the following table:

	Resid. Yld, W% of Conv. Coal-		
	Thermal Test	**Catalyst Test**	**Ratio**
Illinois No. 6	46.4	32.1	0.69
Black Thunder			
Untreated	37.1	23.2	0.63
Thermally Treated	50.2	25.4	0.51
Other Sub-Bitumin	38.1	20.0	0.52

These results are the averages of 37 pairs of the thermal and catalytic tests, 12 with the Black Thunder Coal, 14 with the Illinois Coal (cleaned and uncleaned), and 11 with six other Sub-bituminous coals.

Statistically, the higher residual oil yields with Illinois No. 6 coal than Black Thunder coal has a confidence level of 99.0%. The higher residual oil yield for thermally treated (at 400-600°F) Black Thunder coal compared to the untreated coal has a statistical confidence level of 99.5%, but the difference in catalytic results is not significantly different. Nominally, the thermal treatment does increase the potential for residual oil yield, but this is readily overcome in the catalytic operation. The relative residual oil yields of catalytic and thermal operation differ from coal to coal on the average, but the variability of the data (the standard error of the yields was 5.6%) indicates only a 40% confidence level in the significance of such apparent differences.

A similar comparison was made of the results for Illinois No. 6 and Ohio 5/6 coals in tests made during the previous program. Here, the test program included tests at 750°F and 825°F in addition to the tests at 800°F, so that the correlation against severity could be developed. Figure 1 compares the thermal and catalytic results for the two coals, by plotting the residual oil yield (logarithmic scale) and against nominal thermal severity, STTU (test time adjusted to equivalent time at 840°F, using an Arrhenius activation energy of 89,500 Btu/lb mole).

In Figure 14, the residual oil yields in the tests with the Ohio Coal was generally higher than those with the Illinois Coal at comparable condition. The trends of residual oil yields in the thermal tests against severity correspond reasonably closely to a linear trend of the logarithm of the residual oil formation against severity (STTU) indicating the activation energy used in the calculation of STTU is appropriate.

Further interpretation was attempted with a very simple kinetic model, which assumed that the conversion reaction of the coal is very rapid and produces a fixed proportion of the residual oil subject to secondary reaction. This primary quantity of residual oil then undergoes secondary reaction following simple, single species, first order kinetics. With this model, extrapolation of the thermal tests results to a 0.0 value of STTU indicates the amount of primary residual oil formation, with a value of about 72% of converted coal for the Ohio Coal, and of about 62% for the Illinois coal. The lower yields of residual oil in the catalytic tests indicate additional reaction rate because of the catalyst tests, and permit calculation of apparent relative reaction rate constants for the thermal and catalytic tests.

The following apparent first order rate constants (1/hours) for the various tests were then calculated:

	Ohio Coal		**Illinois Coal**	
	Thermal	**Catalytic**	**Thermal**	**Catalytic**
Temp., °F (STTU)				
750 (2.3)	0.060	1.012	0.070	0.926
800 (10.0)	0.860*	1.341	0.340	1.444
825 (20.0)	0.538	1.976	0.618	1.752

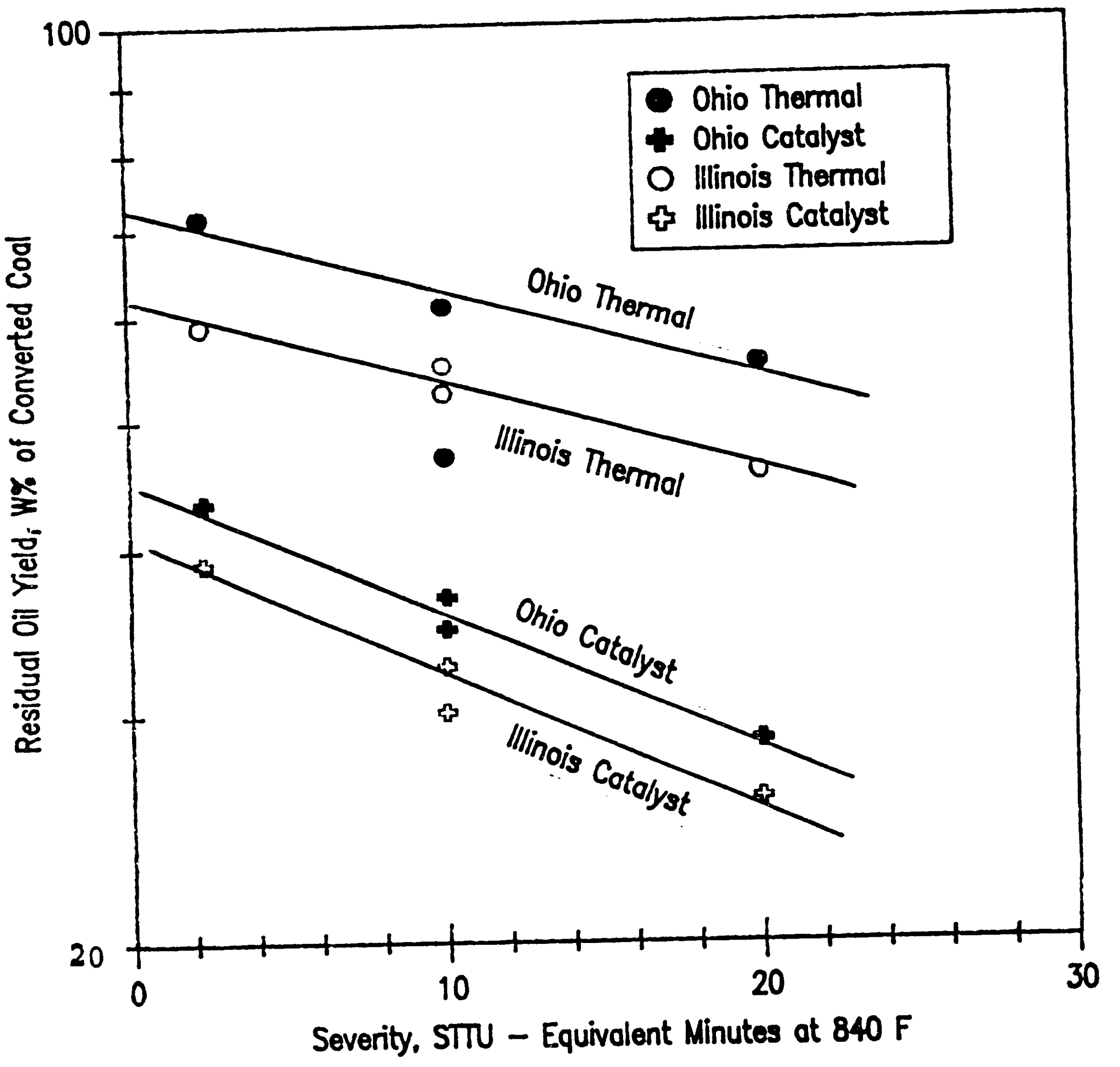
* Disregarded

Taking the increment between the catalytic result and the thermal result as the contribution of the catalyst itself indicates a value of 1.13-1.44 hr^{-1} at 825°F, with an activation energy of about 12,000-17,000 Btu/lb mole for the catalytic rate constant.

FIGURE 14

RESIDUUM YIELD – OHIO AND ILLINOIS COALS

Microauto. – 30 Min. – 1 gm Cat/gm Coal



TASK 6 - ADMINISTRATION

In the balance of the current contract the PDU scale-up demonstration run remains. Topical reports for the Bench-Scale and Laboratory-Scale Studies are being prepared.

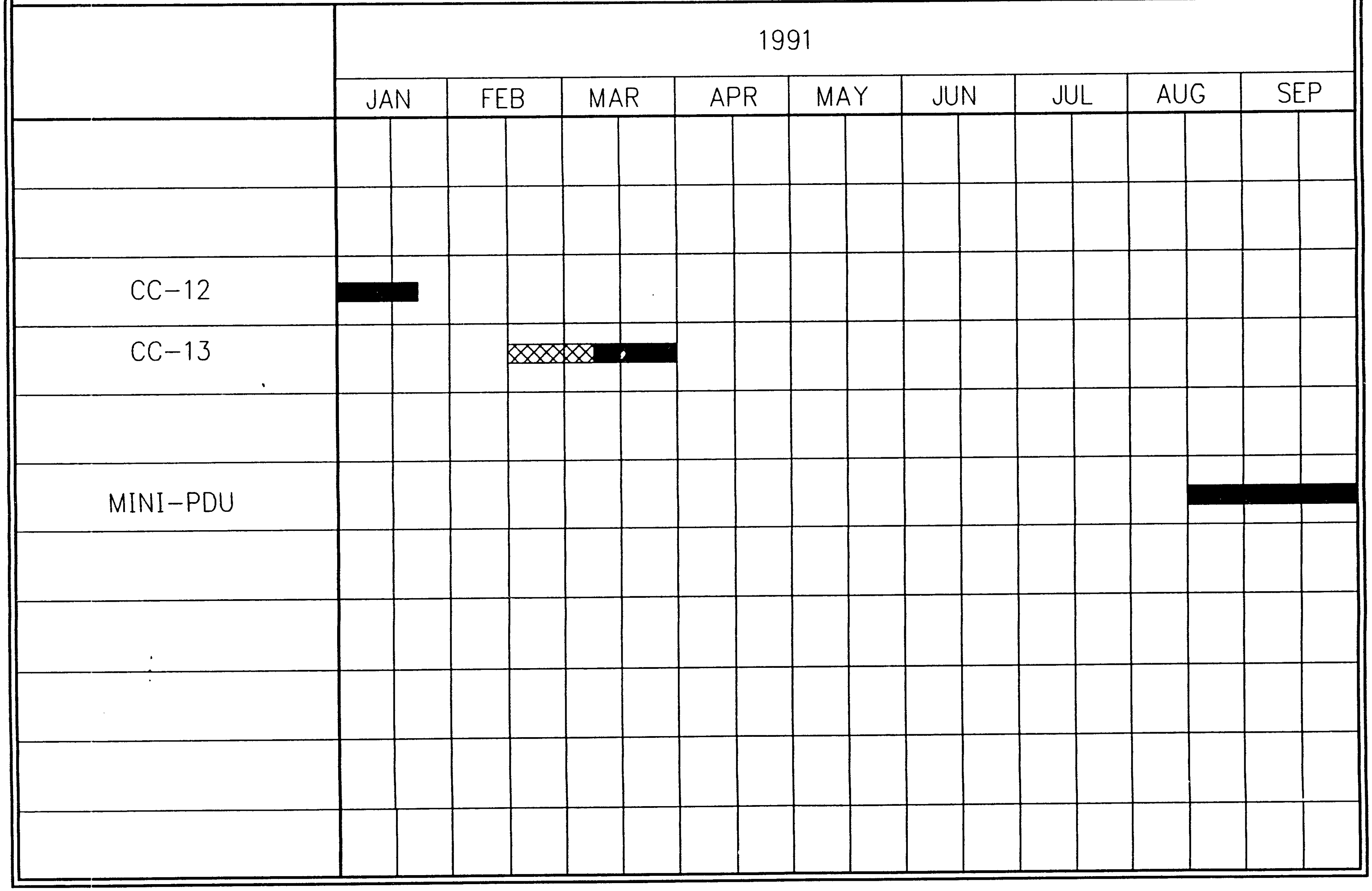
A paper entitled "CTSL™ Catalytic Two-Stage Liquefaction Coupled with Coal Cleaning" was prepared for presentation at the 201st National ACS Meeting in Atlanta Georgia on April 14-19, 1991.

The attached schedule shows the run activities for the remainder of the contract.

HRI, INC.
PRINCETON, N.J.

REVISED CC-CTSL SCHEDULE

DATE: 3/31/91



END

DATE
FILMED
02/13/92

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