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QUARTERLY REPORT
ADVANCED DIRECT COAL LIQUEFACTION CONCEPTS

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SUMMARY

Construction and commissioning of the bench unit for operation of the first stage of the process was completed. Solubilization of Black Thunder coal using carbon monoxide and steam was successfully demonstrated in the counterflow reactor system. The results were comparable with those obtained in the autoclave with the exception that coal solubilization at the same nominal residence times was slightly lower. The bench unit has now been modified for two stage operation.

The Wilsonville process derived solvent for Black Thunder coal (V-1074) was found to be essentially as stable as the previous solvent used in the autoclave runs (V-178 + 320) at reactor conditions. This solvent (V-1074) is, therefore, being used in the bench unit tests.

Carbon monoxide may be replaced by synthesis gas for the coal solubilization step in the process. However, in autoclave tests, coal conversion was found to be dependent on the amount of carbon monoxide present in the synthesis gas. Coal conversions ranged from 88% for pure carbon monoxide to 67% for a 25:75 carbon monoxide/hydrogen mixture at equivalent conditions.

Two stage liquefaction tests were completed in the autoclave using a disposable catalyst (FeS) and hydrogen in the second stage. Increased coal conversion, higher gas and oil and lower asphaltene and preasphaltene yields were observed as expected. However, no hydrogen consumption was observed in the second stage. Other conditions, in particular, alternate catalyst systems will be explored.

INTRODUCTION

The previous quarterly report covered the activities and results obtained for this project up to March 31, 1993. The following is a summary of the progress that had been achieved by that date.

1. The feedstocks required for the execution of the project had been acquired and characterized with the exception of an Illinois #6 derived oil.

2. Agglomeration tests on both Black Thunder and Illinois #6 coal had been completed. The level of ash reduction in each case was minimal at the best conditions. Therefore, for this process, and with these coals, the additional cost of agglomeration would not appear to be justified.

3. The autoclave program designed to establish the conditions to be used in the first stage of the bench unit for Black Thunder coal had been essentially completed.

4. The construction of the bench unit was nearing completion, with anticipated final commissioning and start up scheduled for the week of April 26, 1993.

During this quarter, therefore, the efforts have been concentrated in the following areas:

1. Confirming the stability of the Black Thunder derived oil V-1074 to be used in the bench unit runs.

2. Completing autoclave tests using various mixtures of carbon monoxide and hydrogen to determine the effect of synthesis gas composition on first stage process performance.

3. Examining two stage operation in the autoclave to assess second stage operation

and product yields and quality.

4. Commissioning the bench unit, completing operations on the first stage of the process, and preparing the unit for two stage operation.

Details of these major activities, and the results obtained are described in the subsequent sections.

EXPERIMENTAL PROGRAM

Task 2 Feedstocks

The feedstocks used in this quarter had been previously procured and characterized. These include:

Black Thunder coal	-	low ash subbituminous coal from Wyoming.
Coal Derived Solvent, V1074	-	a blend of 4 barrels of Wilsonville product ex Run 263, boiling range 256 to over 525°C, 12.1% asphaltenes.

A catalyst, ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$ was obtained from Aldrich.

Task 3 Experimental Work

3.1 Ash Removal- Selective Oil Agglomeration

There was no activity in this area this quarter.

3.2 Autoclave Program

3.2.1 One Stage

The experimental procedure has been described in the previous quarterly reports. Briefly, the following was charged to the 1 litre autoclave, coal:80g, solvent:120g, catalyst (K_2CO_3):4g, water:13 - 27g and carbon monoxide:400-800 psi. The unit was raised to temperature at 4.3°C/minute, held at reaction temperature, then cooled rapidly via an internal cooling coil. Product gas was discharged at 130 - 140°C, and collected. Nitrogen was used to flush out the remaining gas. Both product and flushed gases were

characterized by gas chromatography.

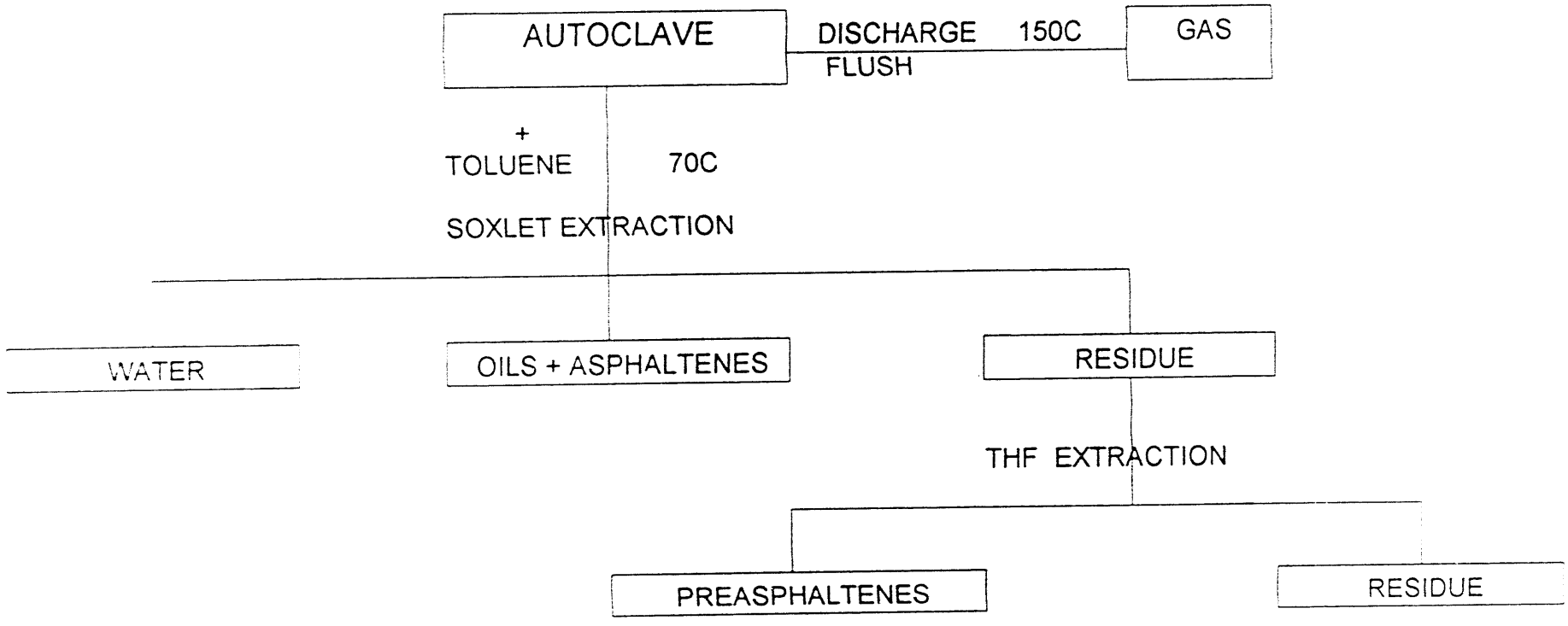
The work-up procedure was revised in order to allow a better understanding of the process chemistry. The revised work-up procedure used a solvent extraction procedure to define oil yields. This procedure was utilized in all runs following DOE-32.

The work-up procedure is shown in Figure 1. Following discharge of the gas and the previously established flushing step, the autoclave was cooled to about 70°C. The liquid products in the autoclave were mixed with 50 mL of toluene and then transferred quantitatively (without loss) to a filter paper. The filter paper and contents were loaded into an extraction thimble which was placed into a Dean-Stark apparatus. The filtrate was used as the extraction medium and to recover the water from the products (previously this had been lost during the THF extraction). When the extraction was complete (~24 hours), the solution was removed and the solvent evaporated to recover the oils (+ asphaltenes). The solids were further extracted with THF to recover the preasphaltenes. The residue was then dried to constant mass as before. A portion of the oils was analyzed for asphaltenes by pentane precipitation.

3.2.2 Two Stage

The procedure followed that of the one stage mode of operation, except that both catalysts (K_2CO_3:4g + FeS:4g) were charged initially. When the first stage was complete the temperature of the contents was lowered to about 300°C and the gas was discharged. The autoclave was flushed with nitrogen (75 L), then recharged with sufficient hydrogen pressure to permit the operating pressure to be 2500-3000 psi at temperature. Heating was restarted and the temperature raised to the new set value and held for the required period. The procedure for let down and work-up then paralleled that of the one stage mode.

FIGURE 1: PRODUCT WORK-UP SCHEME



ASPHALTENES BY PENTANE PRECIPITAITON

3.2.3 Results and Discussion

The program concentrated on three themes during this quarter:

- solvent stability and assessment
- Syngas compositional effects
- 2 stage tests

The stability of the V-1074BL solvent was established, and results were compared to data generated with the V-178 + 320 (Table 1) solvent. The procedure followed that for the coal liquefaction tests, but no coal was added, and the quantity of solvent was raised accordingly to 200 g. At first stage conditions, 410°C/800 psi/30 minutes, 4g K_2CO_3, the V-1074BL showed little change in composition (DOE-32). Less than 1% was converted to gas and the asphaltenes were unchanged. CO conversion was 57% compared with 58% in the V-178 run. At the more severe conditions experienced in a two stage test (DOE-33), 430°C /1100 psi H_2/60 minutes, 4g FeS, there was a small amount of breakdown of the solvent since 2.4% gas was produced. Again there was no change in the asphaltene content.

One tie-point test (DOE-28) had been performed in the last quarter. This indicated that coal conversion in the V-1074BL solvent may exceed the V-178 +320 material. Additional tests were performed to confirm this observation. At both the most severe (DOE-35), and the least severe (DOE-38) conditions, the results for coal conversion, CO conversion, gas production and hydrogen consumption virtually duplicated those achieved with V-178 + 320. The median value for coal conversion at the centre point, 390°C/600 psi/30 minutes, was slightly improved with the V-1074BL (88% vs 83%), but other measured parameters i.e. CO conversion (80 ± 1% vs 79 ± 1), gas production (1.4 ± 0.1% vs 1.4 ± 0.2) and hydrogen consumption (1.6 ± 0.2g/100g vs 1.8 ± 0.2) showed that process performance of the solvents was very similar. [Solvent quality was assessed by Dick Winschel, of Consol, by a micro autoclave procedure. He reported verbally that the solvents had poor

TABLE 1 AUTOCLAVE PROGRAM : SOLVENT ASSESSMENT

RUN #	RUN CONDITIONS			CO CONV	COAL CONV	GAS YIELD	H2 CONS	MASS BAL.	NOTES
	TEMP.	PRESS.	TIME	%	%	g/100g	g/100g	wt %	
	oC	psi	minutes						

A. SOLVENT STABILITY TESTS: V-1074BL

DOE - 32	410	800	30	57	---	0.8	---	101.4	1st stage
DOE - 33	430	1100	60	----	---	2.4	---	100.2	2nd stage

B. SOLVENT ASSESSMENT: V-1074BL

DOE - 35	410	800	30	83	88	2.8	2.1	99.0	Repeat run# 5
DOE - 28	390	600	30	78	88	1.4	1.4	98.3	Repeat run# 6
DOE - 34	390	600	30	81	77	1.3	1.7	95.9	Repeat run# 6
DOE - 37	390	600	30	80	88	1.4	1.6	97.0	Repeat run# 6
DOE - 36	370	400	30	70	61	0.8	1.2	103.5	Repeat run#15
DOE - 38	390	600	0	75	67	1.0	2.0	94.6	aborted

C. SOLVENT ASSESSMENT: V-178+320 (Reported in previous Quarter)

DOE - 5	410	800	30	83	89	2.8	2.1	---	CO2 lost, poor MB
DOE - 6	390	600	30	79	83	1.3	1.6	---	CO2 lost, poor MB
DOE - 15	370	400	0	71	63	0.8	1.2	93.8	
DOE - 18	360	600	0	29	40	0.1	1.2	96.3	

The amount of water was adjusted to initial CO pressure: 13g at 400psi, 20g at 600psi and 27g at 800psi

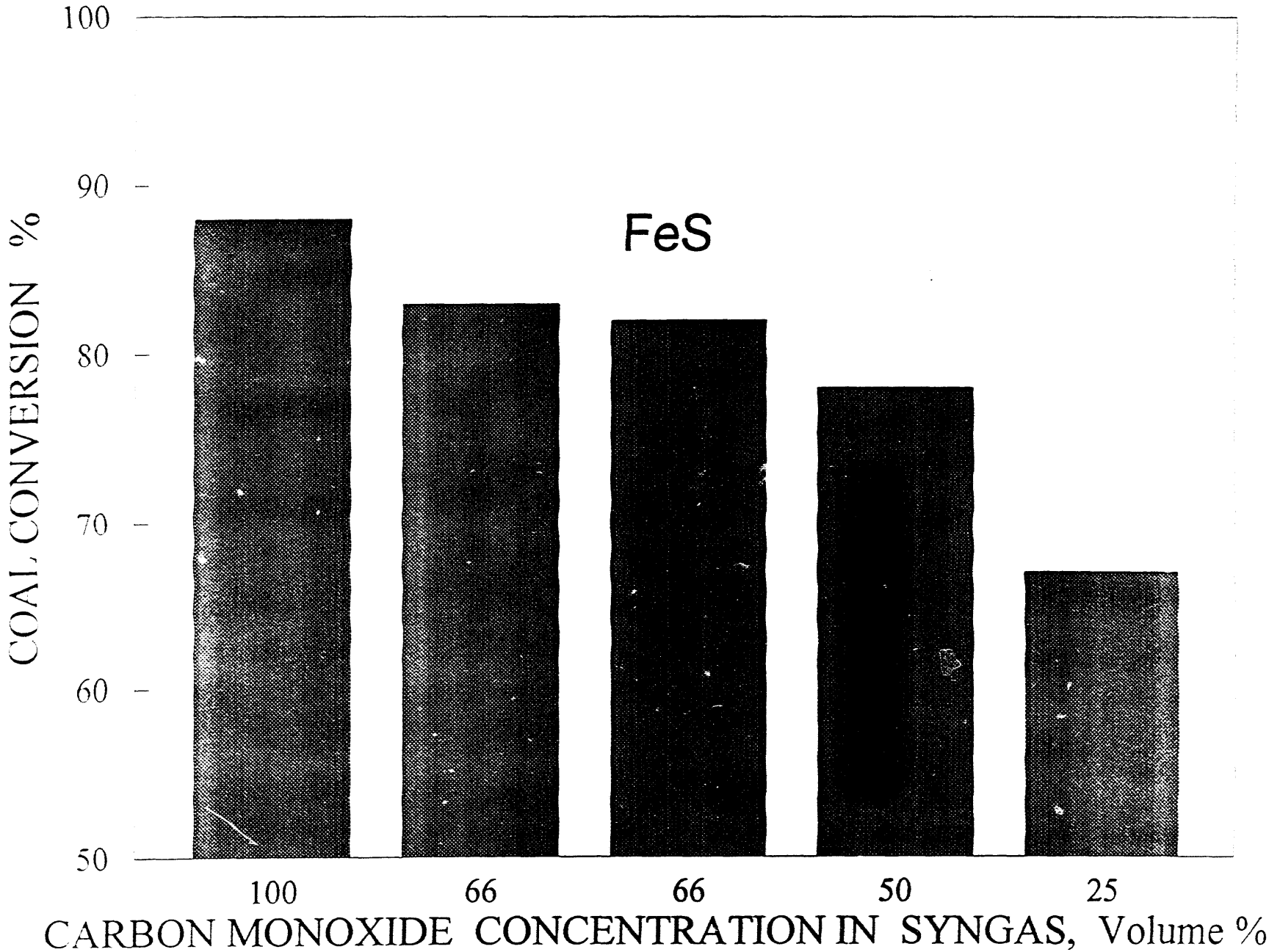
to moderate donor capability typical of paraffinic coal derived liquids from subbituminous coals.] The results confirm that the V-1074BL is capable of solubilizing the majority of the coal at first stage processing conditions.

The replacement of carbon monoxide by a syngas has practical implications, since syngas mixtures may be available from natural gas, from gasification of coal, or from gasification of bottoms products from coal liquefaction. Initial tests (DOE-29, 30, 31) used V-178 + 320 solvent, since there was a database (these tests were to coincide with start-up of the bench unit program). Results are listed in Table 2. At 25% CO/75% H_2, coal conversion declined by about 10% compared to pure CO. This is attributable to the decrease in available CO, since only 0.55 moles were converted vs 1.64 moles in pure CO.

The hydrogen was replaced by nitrogen in DOE-30. CO conversion increased since the equilibrium was shifted to the product side in the absence of initial hydrogen and by utilization during liquefaction. Despite this better CO usage coal conversion was only 68% or 15% below pure CO. The last test in this series was with pure nitrogen to define the lower limit of coal conversion in the absence of CO or hydrogen. The need for the CO or H_2 was apparent, since only 50% coal conversion was obtained. This represented the coal solubilization that could be attributed to the solvent.

A more systematic sequence of tests was completed with V-1074BL (Table 2) where CO concentration in the syngas ranged from 25 to 100%. FeS (4g) was added in one run (DOE-44) to see if this second stage catalyst would have any effect on first stage performance. Coal conversion again declined sequentially as the CO concentration was lowered. The results did show that substantial coal conversion (close to 80%) could be maintained even when a 50:50 CO/H_2 syngas was the reducing atmosphere (Figure 2). Coal conversion was unaffected by the presence of FeS, as were other measures of process performance.

FIGURE 2: AUTOCLAVE PROGRAM - INFLUENCE OF SYNGAS ON COAL CONVERSION



The utilization of carbon monoxide is presented in Table 2 as moles converted per 100g coal. This data gives a linear response when plotted against coal conversion (Figure 3). Hydrogen consumption also gave a linear response, but at a numerical lower value. The efficiency of hydrogen utilization was determined, i.e. efficiency = moles H_2 consumed/moles CO converted. An average 51 ± 7% of the hydrogen, derived from the shift reaction, was consumed during coal solubilization. The efficiency at a syngas composition of (25:75 CO/H_2) was the lowest of the group at 40%, but this was not statistically different from the mean. The graph suggests that in pure hydrogen the coal conversion should be 61% at the mid-point operation conditions. This is an improvement over the nitrogen only test (with V-178 + 320), so there may be a contribution from the hydrogen in the syngas, although smaller than that of the carbon monoxide.

Four 2-stage tests were completed during the period (Table 3). In all cases the first stage conditions were held constant at 390°C/600 psi/30 minutes. CO conversion and gas production were constant and duplicated those for the centre point tests. The hydrogen consumption was a little more scattered but the median value was typical of earlier tests.

On DOE-39 the initial pressure at 300°C was below that required to reach 2500 psi. The test was finished and worked up as normal. Coal conversion was higher than for any single stage test. Since the temperature was 430°C in the second stage an increase in the gas make was observed due to thermal cracking of the solubilized coal. Also, there was a small positive change in the hydrogen content for the same reason. At the higher pressure, Run DOE-40 and 45, the gas and hydrogen production were similar to the lower pressure run. In both cases the coal conversion improved further to 94 - 95%.

The final Run DOE-46 operated at a higher second stage temperature, 445°C. There was no improvement in coal conversion. The only significant change was a further increase in gas yield to 10.0%, for a combined 11.3% for both stages. Autoclave tests often give a higher level of gas production than continuous flow through tests. However, it appears that with the FeS catalyst gas production is apparently not suppressed.

TABLE 2 AUTOCLAVE PROGRAM : SYNGAS COMPOSITION

RUN #	SYNGAS COMPOSITION			CO CONV	COAL CONV	GAS YIELD	H2 CONS	CO:COAL	MASS BAL.
	%N2	%CO	%H2	%	%	g/100g	g/100g	moles/100g	wt %
A. SOLVENT: V178 +320									
DOE - 6		100	0	79	83	1.3	1.6	1.63	---
DOE - 29		25	75	83	74	1.7	0.2	0.56	97.9
DOE - 30	75	25	0	90	68	1.6	1.0	0.66	94.6
DOE - 31	100	0	0	---	50	1.6	0	---	95.4
B. SOLVENT: V1074BL									
DOE - 37		100	0	80	88	1.4	1.6	1.64	97.0
DOE - 41		66	33	83	83	2.0	1.2	1.09	99.5
DOE - 42		25	75	85	67	1.7	0.3	0.43	95.8
DOE - 43		50	50	84	78	1.5	0.9	0.82	94.5
DOE - 44	*	66	33	85	82	1.5	1.2	1.06	---

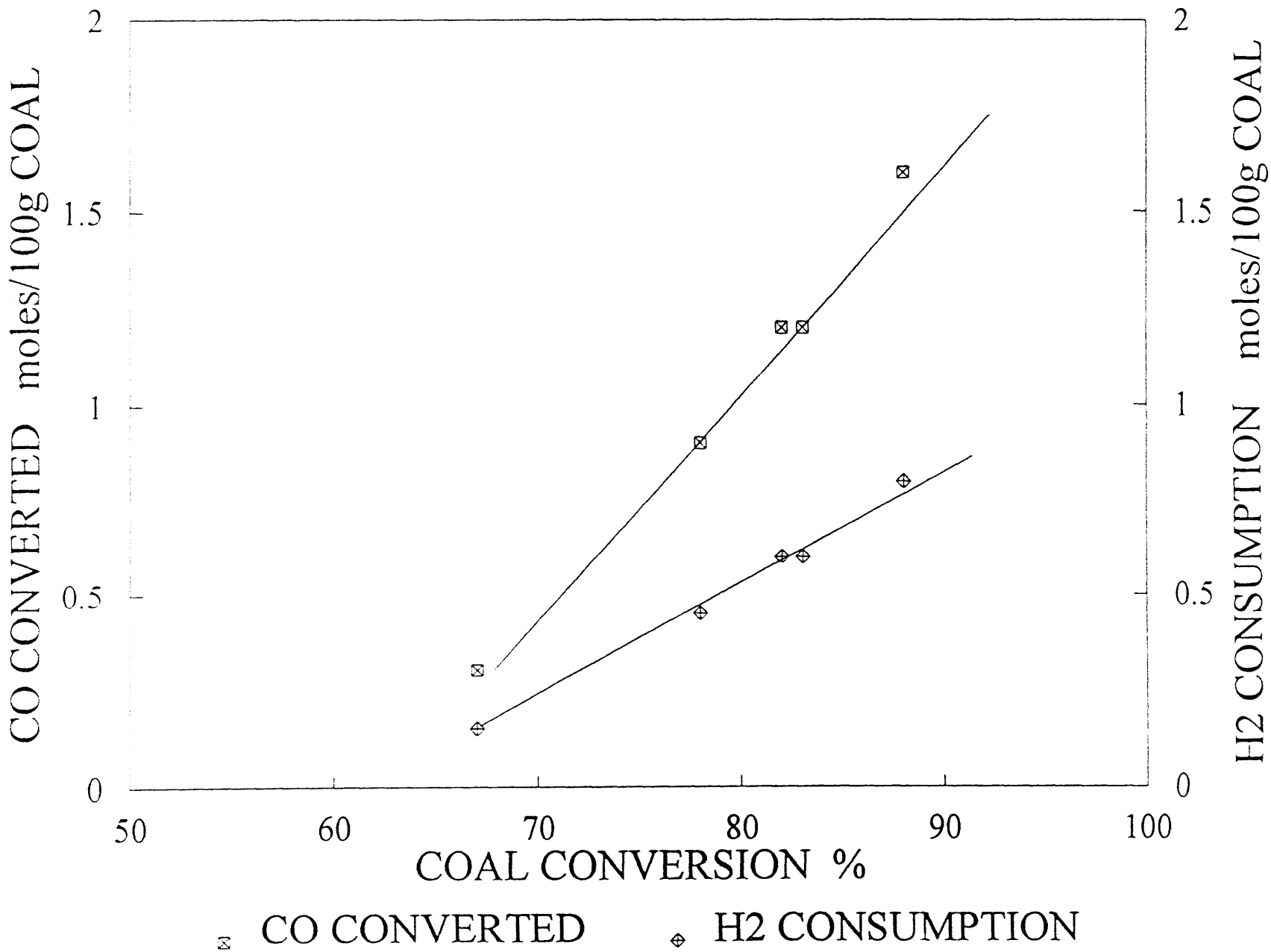
CONDITIONS : TEMPERATURE 390oC
PRESSURE 600psi
TIME 30 minutes

* 4g FeS added

TABLE 3 AUTOCLAVE PROGRAM : TWO STAGE TESTS

RUN #	RUN CONDITIONS			CO CONV	COAL CONV	GAS YIELD	H2 CONS	MASS BAL.	NOTES
	TEMP.	PRESS.	TIME	%	%	g/100g	g/100g	wt %	
	oC	psi	minutes						
DOE - 39									
1st STAGE	390	600	30	81		1.7	0.9		CO/H2O
2nd STAGE	430	1900	60		91	5.5	-0.3	95.1	H2 + FeS
DOE - 40									
1st STAGE	390	600	30	81		1.8	1.2		CO/H2O
2nd STAGE	430	2950	60		94	5.8	-0.3	98.9	H2 + FeS
DOE - 45									
1st STAGE	390	600	30	79		1.5	1.3		CO/H2O
2nd STAGE	430	2750	30		95	6.8	-0.4	102.4	H2 + FeS
DOE - 46									
1st STAGE	390	600	30	79		1.3	1.6		CO/H2O
2nd STAGE	445	2750	30		94	10.0	-0.1	97.9	H2 + FeS

FIGURE 3: AUTOCLAVE PROGRAM - COAL CONVERSION VS GAS UTILIZATION



3.2.4 Product Distribution

The distillation (D1160) step had proven unreliable for separating the various oil fractions, gave no information on asphaltene/preasphaltene content and failed to quantify all the water, due to solubility in THF. As an alternative it was decided to extract the oils from the product residue sequentially with toluene and THF. After removal of the toluene the asphaltenes were precipitated from a small sample and quantified. Since the mass balances on some runs were still < 96% it was decided to assign the losses exclusively to the oils. The water should have been recovered from the Dean-Stark procedure, apart from transfer losses. All of the gases were trapped and analyzed. While the solids (including asphaltenes and preasphaltenes) could be quantitatively transferred from the autoclave to the filter/thimble, the naphtha fraction might evaporate during the transfer step, which is performed at 70°C. Furthermore, naphtha components might be lost during the evaporation of the toluene from the extract solution.

The solvent, V-1074BL was quite stable as far as asphaltene content was concerned, apparently no degradation or formation of asphaltene took place under first or second stage conditions (Table 4). The tie points to the earlier work showed that most of the solubilized product from the first stage was asphaltenes. The limited data suggests that the coal dissolution was initially to preasphaltenes concurrently with some asphaltenes at low severity* (DOE-36) or to preasphaltenes followed by a rapid shift to asphaltenes. At high severity (DOE-35) the preasphaltenes have converted to asphaltenes and some oils have been formed. The trend to sequential formation of asphaltenes and oils can be seen in Figure 4. The preasphaltenes decrease at high severity since there is little remaining coal to replenish them. A sequential mechanism is therefore likely with CO_2 evolution during the primary dissolution step.

$$\text{coal} \rightarrow \text{preasphaltenes} + CO_2 \rightarrow \text{asphaltenes} \rightarrow \text{oils}$$

NOTE: See Section 3.2.6 for definition of severity index

FIGURE 4: AUTOCLAVE PROGRAM - PRODUCT YIELD DISTRIBUTION

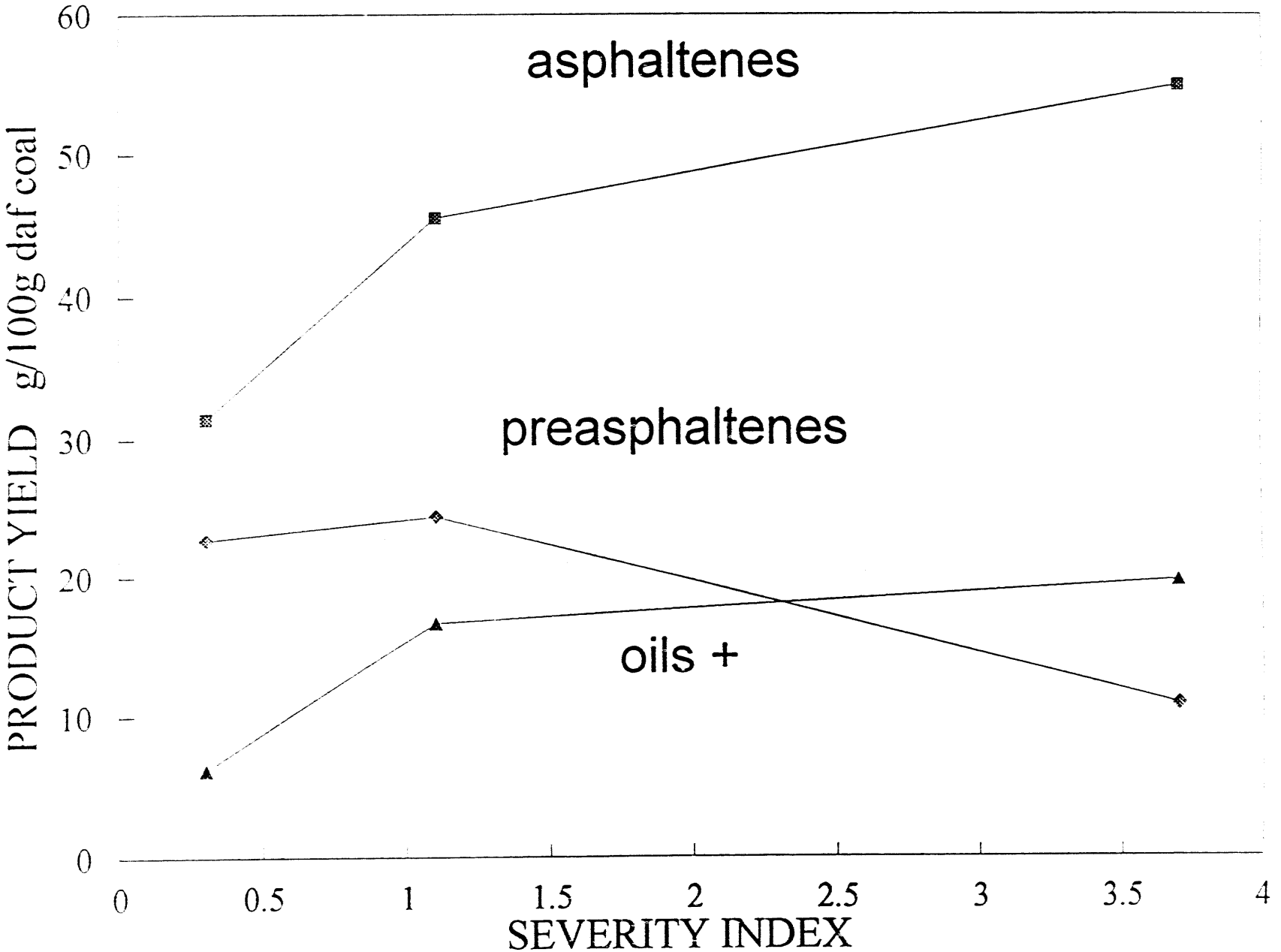


TABLE 4 AUTOCLAVE PROGRAM : PRODUCT DISTRIBUTION

RUN #	ASPHALTENES	PREASPHALT	IOM	GAS	OILS+	NOTES
A. SOLVENT STABILITY						
FEED	12.1	---	---		87.8	
DOE-29	12.1	---	---	0.8	87.1	see Table 1
DOE-30	12.2	---	---	1.3	86.5	see Table 1
B. TIE POINTS						SEV. IND.
DOE-35	54.9	10.8	11.7	2.9	19.7	3.7
DOE-36	31.4	22.7	38.9	0.8	6.2	0.3
DOE-37	45.5	24.4	12.0	1.4	16.7	1.1
C. SYNGAS						CO CONC.
DOE-41	47.8	15.3	16.7	2.0	18.2	66
DOE-42	41.9	11.8	33.1	1.7	11.5	25
DOE-43	49.9	13.6	22.1	1.5	12.9	50
DOE-44	53.0	16.7	17.8	1.5	11.0	66 +4gFe
D. TWO STAGE						
DOE-39	39.8	3.4	9.1	7.2	~40	
DOE-40	38.1	7.3	5.6	7.6	~40	
DOE-45	(30.6)*	4.0	4.7	8.1	~47	
DOE-46	33.7	5.3	5.8	11.3	~46	

YIELDS reported in g/100g coal (maf)

OILS+ includes CO_2 and H_2O

* to be repeated

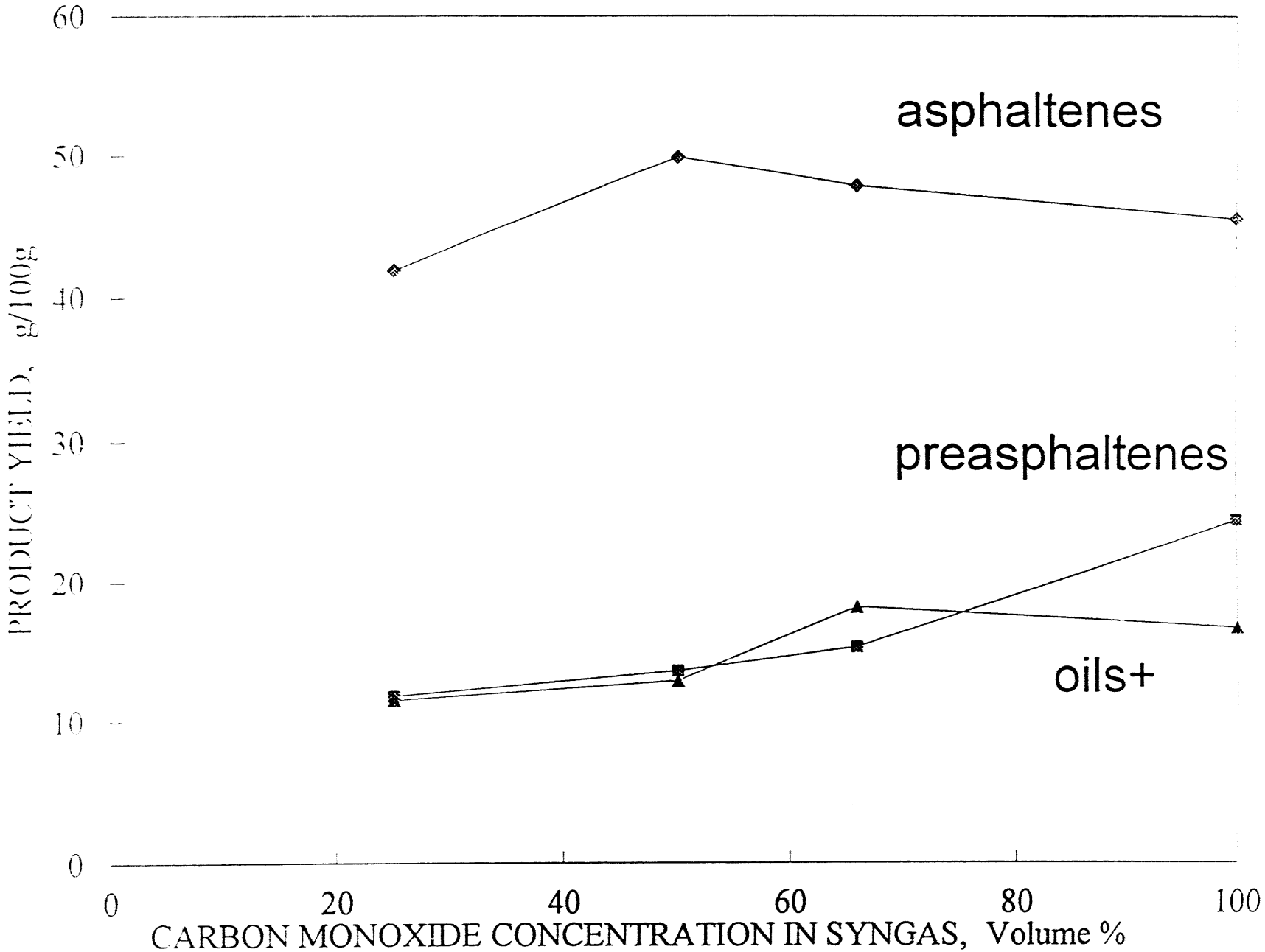
In the syngas comparison asphaltenes are similar at 46 ± 3%, omitting the FeS test (Run DOE-44). The main difference is in the preasphaltenes, which increase with CO concentration. This suggests that $CO/H_2O + K_2CO_3$ participate directly in dissolution of the preasphaltenes, while primary asphaltene dissolution may be independent of the gas composition. There is also a trend to greater oil yield with increased CO concentration, but the data is scattered (Figure 5).

The 2 stage tests were all operated at much higher severity than the previous 1 stage tests. As a result it appears that the IOM and preasphaltenes have reached a steady state base level. For the four runs, the average IOM and preasphaltenes was 6 ± 2% and 5 ± 2%, respectively. Even in the presence of a poor disposable catalyst (FeS), a high degree of asphaltene conversion had occurred yielding close to 50% oil and gas products at 430°C, (the asphaltene analysis is being checked on DOE-45 at this time) and ~ 55% at 445°C. The low values of preasphaltenes and IOM are indicative of a lack of regressive reactions in this system at temperatures as high as 445°C. Improved process performance is usually observed in continuous bench unit operations. Therefore, liquid yields could be anticipated from increased asphaltene conversion.

3.2.5 Petrographic Analysis

Petrographic analysis was carried out on a additional number of residues from the autoclave program. The results are given in the report in the Appendix. The data has yet to be examined in detail, but one point of interest is the difference in the nature of the resids where the CO conversion is low i.e. DOE-25 and DOE-26. In these runs no shift catalyst was present and the petrographic analysis shows a resid more typical of combustion rather than liquefaction.

FIGURE 5: AUTOCLAVE PROGRAM - PRODUCT YIELD VS SYNGAS COMPOSITION



3.2.6. Severity Index

The severity index is a simple kinetic model, based on first order kinetics for the coal dissolution, to describe process severity as a function of reaction temperature and time. It has been used by HRI and others[1,2] for autoclave procedures in coal liquefaction, coal/oil coprocessing and resid upgrading. Severity Index is defined as:

$$SI = t * EXP^{\frac{-53200}{R}(1/721.7 - 1/T)}$$

where	t	=	time, seconds
	T	=	temperature, deg K
	R	=	gas constant, 1.987 cals/deg.mole

3.3 Bench Unit

3.3.1 Description

A simplified schematic of the bench unit is shown in Figure 6. Feed slurry is prepared in the 50 litre vessel V-100, and is stored, heated, and recirculated with the progressive cavity pump P-100. A load cell on the 26.5 litre vessel V-110 allows for measurement of the feed rate. The progressive cavity pump P-110 circulates feed from V-110 through a loop which primes the two high pressure metering pumps P-130 and P-140 (one used as back up). The coal slurry feed passes to the counterflow reactor R-210, where the first stage coal solubilization step takes place. Carbon monoxide and steam are provided at the base of this reactor. The overhead liquids and gas are cooled and go to the

[1] Coal-Oil Coprocessing: Phase 1, EPRI AP-5105, Interim Report, March 1987.
[2] Simpson, P.L., Parker, R.J. and Beaulieu, G., AIChE Symposium Series 282, Vol. 87, 24-34, 1991.

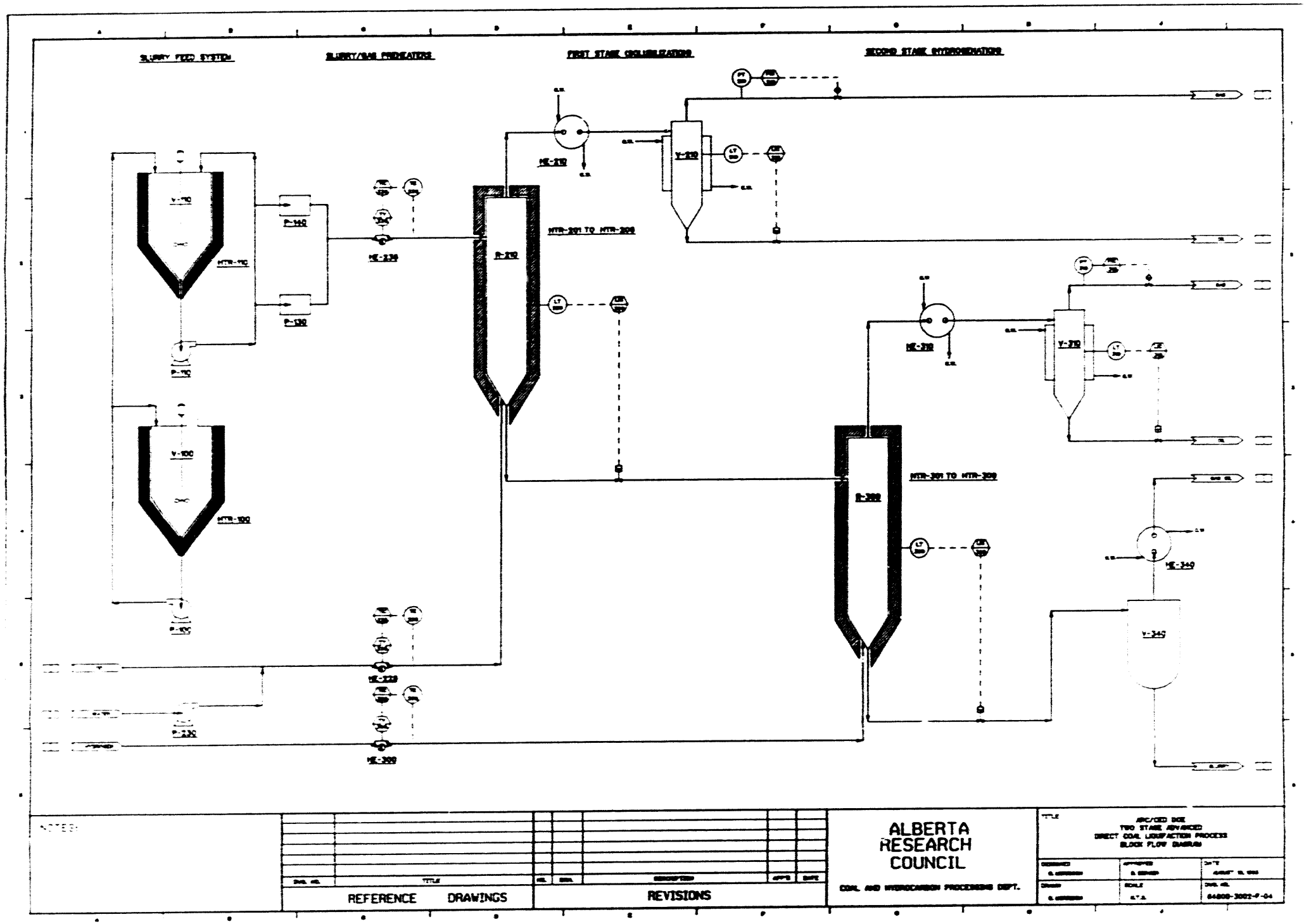

SLURRY FEED SYSTEM
SLURRY/GAS PREHEATERS
FIRST STAGE DISSOLUTION
SECOND STAGE HYDROGENATION
V-110
HTR-110
P-140
P-130
P-110
V-100
HTR-100
P-100
P-230
ME-230
ME-220
ME-200
R-210
HTR-201 TO HTR-209
ME-210
V-210
ME-310
V-310
R-300
HTR-301 TO HTR-309
ME-340
V-340
NOTES:
REFERENCE DRAWINGS
REVISIONS
ALBERTA RESEARCH COUNCIL
COAL AND HYDROCARBON PROCESSING DEPT.
TWO STAGE ADVANCED
DIRECT COAL LIQUEFACTION PROCESS
BLOCK FLOW DIAGRAM

FIGURE 6

separator V-210 where gas and liquid are separated for quantification and analysis. The bottoms product goes to the second stage counterflow reactor R-300 for the hydrocracking step. Hydrogen is provided at the bottom of this reactor and the overheads are handled as in the first stage in separator V-310. The bottoms product is collected in vessel V-340.

The unit is designed to operate with coal slurry feed rate of 1 kg/hr. Reactor R-210 has a volume of 0.7 litres and will operate at a maximum pressure of 2800 psig at an LHSV of 0.5 - 1. Reactor R-300 has a volume of 1.5 litres and is designed to operate at an LHSV of 1 - 2. The pressure in R-300 will be lower than R-210 to allow flow from the first stage reactor to the second. Maximum operating temperature of the first and second stages are 410°C and 480°C, respectively.

3.3.2 Modifications

The planned modifications to the bench unit were completed by the end of the week of April 23, 1993. The first operations on the unit commenced the week of April 26, 1993. The first objective was to operate the first stage of the unit only. During this first phase of the operation several major problems were encountered and had to be solved. These were:

1. The calibration of the gas mass flow meters at high pressure was unsatisfactory. The zero point was found to drift and calibrations were not valid from one day to the next, thus requiring considerable time for recalibrations. Considerable effort was expended on this problem, and discussions with the equipment manufacturers were of no help. Ultimately it was found that at high pressures (above 2000 psi) the mass flow meters must be mounted horizontally for proper operation. Any other orientation was not satisfactory. Horizontal mounting of the flow meters, therefore, solved the problem.

2. It was discovered that the feed pumps to the first stage reactor could not be located on the ground floor because pumping the coal/solvent slurry to the top of the first stage reactor (at the third level) at the low velocities in the high pressure feed line caused coal to settle in the feed lines and caused plugging of check valves, etc. This problem was solved by pumping the coal/solvent slurry up to the third level in a recycle loop at velocities high enough to prevent settling, and relocating the feed pumps at the third level taking feed off the recycle loop. A nitrogen injection line was also installed at the discharge of the high pressure pumps to aid flow.

3. Initially, the first stage catalyst, potassium carbonate, was added to the coal/slurry feed for pumping to the reactor. With this arrangement, the feed line rapidly plugged between the exit of the preheater and the entrance to the reactor. Potassium carbonate is hygroscopic, and it is likely that moisture was picked up in the feed system, and when it was driven off in the preheater this caused the potassium carbonate to agglomerate into larger particles, thus blocked the feed line. An extra feed pump was installed to pump potassium carbonate as an aqueous solution (15%) into the feed line just prior to the reactor, and the problem disappeared.

4. Difficulties were experienced in controlling the pressure and liquid level in the overhead receiver system when operating with a coal slurry feed. Inspection of the vessels and pipes of the overhead system suggested that waxy material was being carried downstream of the overhead product receiver vessel causing difficulties in the pressure regulator. Modifications to the overhead system were necessary to overcome these difficulties.

5. During the pressure let down from about 2500 psig to ambient pressure with carbon dioxide as a major component of the off gas, very significant cooling (Joule Thomson Effect) occurred in the pressure regulator, and because the gas stream

was also saturated with water, condensation in the regulator caused plugging and lack of pressure control. The regulator was immersed in a bath of hot water controlled at 60-70°C to solve this problem.

The modifications described above were completed by early June, and allowed us to proceed to obtain data on first stage operation of the bench unit.

3.3.3 Bench Unit Operation

The first objective of the bench unit operation was to study the first stage of the process. This involved the solubilization of coal using carbon monoxide and steam in a counterflow reactor system. We needed to determine whether the same levels of coal conversion and CO shift reaction could be achieved in the counterflow reactor when compared to the autoclave. During June four runs were completed which enabled us to compare the counterflow reactor results with autoclave results. It should be noted that a run on the bench unit is a mass balance period where the operating conditions remain unchanged for a pre-set number of hours.

In the bench unit operation, temperature was kept constant at 390°C, the pressure at 2500 psig, and the carbon monoxide flow rate at 7.5 SLPM (Table 5). The temperature and pressure conditions were selected based on the autoclave results. The carbon monoxide flow represents a five fold increase over the level used in the autoclave and was selected to ensure mixing in the counterflow reactor. In the first run (Run 1) the water feed rate was selected to keep the same carbon monoxide to water ratio as was used in the autoclave. However, this volume of water caused problems in the overhead collection system, so the rate was cut back in subsequent runs with no effect on the shift conversion. It was intended to study residence times of 30, 45 and 60 minutes, but due to a reactor volume correction, the residence times studied were actually about 20, 30 and 50 minutes.

TABLE 5

BENCH UNIT RUNS
FIRST STAGE OPERATION
Process Conditions

Run No.	**1**	**2**	**3**	**4**
Date:	June 3	June 14	June 14	June 17
Temperature (°C)	390	390	390	390
Pressure (psig)	2500	2500	2500	2500
CO Flow Rate (L/m)	7.5	7.5	7.5	7.5
Coal Slurry Feed rate (g/h)	560	650	550	295
Water Feed rate (ml/m)	8.5	2.8	3.6	4.0
Catalyst Feed rate (ml/m)	1.2	1.5	1.6	1.4
Coal/Concentration (% wt coal)	20.5	45.8	45.8	40.9
Liquid Volume (mL)	184	243	243	236
Residence Time (min)	20	22	27	48

The overhead problem in the first run did not permit a complete mass balance, but the mass balances on subsequent runs were acceptable (Table 6).

Data on the shift reaction are shown in Table 7. In the autoclave, at a reaction temperature of 390°C a cold carbon monoxide pressure of 600 psig, and a residence time of 30 minutes, the carbon monoxide conversion was about 80%. The feed to the autoclave contained 200 gm of 40% coal slurry with 1.25 moles of carbon monoxide. The conversion of carbon monoxide, therefore, was 0.5 moles/100gm of slurry feed or 1.6 moles/100gm MAF coal. In this system, 1.6 moles/100gm MAF coal of available hydrogen is produced by the shift reaction. Typically, at these conditions 0.5 - 1 moles of hydrogen are consumed in the coal solubilization process per 100gm MAF coal, i.e. about half of that available.

As explained earlier, the carbon monoxide fed to the bench unit represented a five fold excess over that provided in the autoclave (3 - 3.5 moles/100gm coal slurry). Therefore, although the carbon monoxide conversions were only 10 - 15% in the bench unit, the amount converted per 100gm of feed slurry was about the same as that observed in the autoclave i.e. 0.4 - 0.6 moles/100gm feed slurry. The amount of available hydrogen, therefore, also remained the same on a comparative basis, and in fact the hydrogen consumption data were also comparable to those obtained in the autoclave, with the exception of Run 4 which was low. Since these numbers are greatly affected by minor changes in the gas analysis, this is probably due to a slight error in that analysis. The same observation also applies to the apparent excess of carbon dioxide which is also comparable to the autoclave results.

Coal conversions for the four bench unit runs ranged from 68% to 79% (Table 8). Ash balances were about 70% which is consistent with autoclave data. Coal conversions in the bench unit appear to be somewhat lower than in the autoclave at equivalent residence times (see Figure 7). This may be due to difference in gas/liquid contact in the two units, however, this is not a key issue since further coal conversion is expected in the second

TABLE 6

BENCH UNIT RUNS
FIRST STAGE OPERATION
Mass Balance

Run No.	1	2	3	4
Input:				
Coal/Oil Slurry (g)	560	1300	1100	590
Water (g)	584	481	583	628
Potassium Carbonate (g)	18	26	28	25
Carbon Monoxide (g)	562	1125	1125	1125
Total	**1724**	**2932**	**2836**	**2368**
Output:				
Liquid Product (g)	460	950	920	433
Product Gas (g)	613	1205	1276	1290
Dissolved Gas (g)	41	26	9	1
Overhead Liquid (g)	N/A	600	600	600
Total	**N/A**	**2781**	**2805**	**2324**
Mass Balance	**N/A**	**95**	**99**	**98**

TABLE 7

BENCH UNIT RUNS

FIRST STAGE OPERATION

Gas Balances

Run No.	1	2	3	4
INPUT:				
CO Moles	20.1	40.2	40.2	40.2
H_2O Moles	32.4	26.7	32.4	34.9
Output:				
CO Moles	17.2	34.2	35.4	36.5
CO_2 Moles	3.2	6.2	6.1	5.9
H_2 Moles	1.9	2.5	2.6	3.5
CO Conversion (%)	14.4	14.9	11.9	9.2
Excess CO_2 (Moles)	0.3	0.2	1.3	2.2
Hydrogen Uptake (Moles)	1.0	3.5	2.2	0.2
Hydrogen Cons. (mole/100g) MAF coal	1.1	0.75	0.55	0.1
CO Converted (mole/100g) feed	0.52	0.46	0.44	0.62

TABLE 8

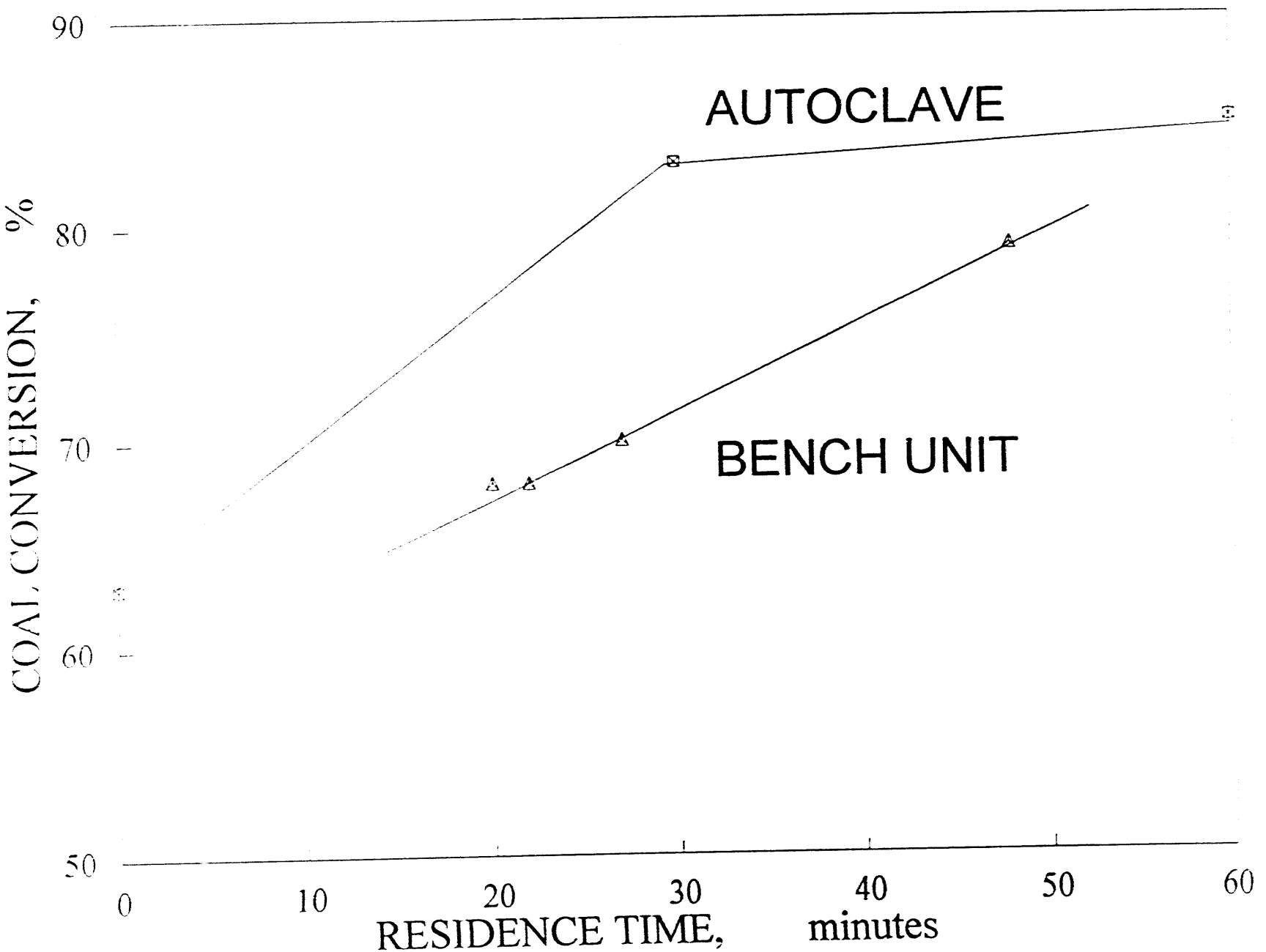
BENCH UNIT RUNS

FIRST STAGE OPERATION

Coal Conversion/Ash Balance

Run No.	1	2	3	4
Coal Conversion (% wt)	68	68	70	79
Ash Balance (% wt)	N/A	71	70	70

FIGURE 7: PROCESS PERFORMANCE - BENCH UNIT VS AUTOCLAVE



stage.

For the two stage runs, a temperature of 390°C, pressure of 2500 - 2700 psig and a residence time of 45 minutes in the first stage would provide a coal conversion of 75 - 80%, considered sufficient for processing in the second stage.

3.3.4 Next Steps

Further work on the first stage operation of the bench unit maybe needed to confirm the results obtained so far, and explore the effect of other variables, but the priority now is to demonstrate two stage operation and obtain data on the overall process. At the end of June, therefore, the unit was modified to allow for direct transfer of first stage product to the second stage reactor, in preparation for two stage operation in July.

FUTURE WORK

During the next quarter, it is anticipated that the following items will be completed:

1. Two stage autoclave tests with a more active catalyst system, e.g. ammonium tetrathiomolybdate in the second stage will carried out.

2. An autoclave test will be performed to determine whether ammonium tetrathiomolybdate can be used as a shift catalyst in the first stage.

3. The bench unit will be commissioned for two stage operation. Three separate weeks of operation in the two stage mode are scheduled. In these tests the objective will be to collect data at nine different operating conditions in the second stage, while conditions are held fixed in the first stage

APPENDIX

PETROGRAPHIC CHARACTERIZATION OF LIQUEFACTION RESIDUES OF BLACK THUNDER COAL

by

Thomas Gentzis

June 1993

RESULTS AND DISCUSSION

Following an optical examination of the residues, it becomes apparent that the suite can be subdivided into four groups.

- The first group consists of samples DOE-21-SD, DOE-27-SD and DOE-28-SD, which contain the lowest volume percentage of vitroplast (Table 1). Vitroplast content ranges from 2.7% to 5.0%, fusinite ranges from 33.6% to 42.0% and semifusinite is in the 1.6% to 10.3% range. Sample DOE-27-SD shows the highest percentage of granular residue (an admixture of vitroplast, mineral matter, broken inertodetrinite) (40.6%), followed by sample DOE-28-SD (7.3%). The latter sample contains 41.3% clay mineral matter and sample DOE-21-SD, 57.0% clays.

- The second group consists of samples DOE-29-SD, DOE-30-SD and DOE-31-SD, which show the highest amount of unconverted vitroplast (Table 1). Vitroplast content ranges from 60.7% to 75.7%, no granular residue was identified in any of the three samples, fusinite content is in the 7.3% to 19.3% range and clays in the 4.0% to 11.0% range. Vitroplast shows devolatilization vacuoles (range of vacuoles is from 3.7% to 10.3%) and semifusinite is present in small amounts (1.0% to 4.0%).

- The third group of samples consists of samples DOE-25-SD and DOE-26-SD, which are dominated by rounded and semi-rounded cenosphere particles. Cenosphere content is in the 52.3% to 59.3% range and the presence of large quantities of devolatilization vacuoles (13.3% and 14.0%) indicates the highly explosive devolatilization rate of the coal particles, similar to coal combustion. No vitroplast was present in the two samples, semifusinite content was virtually identical (9.0% and 9.3%), fusinite ranges from 7.7% to 17.0%, clay mineral matter is low (1.7% and 2.3%), which is the lowest of any other sample, but pyrite content is the hight (14.6%) in sample DOE-26-SD.

- Finally, the fourth group of samples (DOE-23-SD and DOE-24.SD) has a very similar vitroplast content (26.3% and 27.0%) and fusinite content (35.0% and 36.3%) Clay content is between 17.0% and 27.0%, semifusinite ranges from 0.3% to 9.3% and sample DOE-23-SD contains 11.0% granular residue. Therefore, in terms of unconverted vitroplast, these two samples fall 'in between' the first and the second groups, which show the lowest and the highest vitroplast content, respectively.

TABLE 1

POINT-COUNTING* OF LIQUEFACTION RESIDUES

Sample No.	Organic Matter Type (vol.%)								Experimental Conditions	Conversion %
	Vitroplast	Cenospheres	Vacuoles	Granular Residue	Semi-Fusinite	Fusinite	Pyrite	Clays		
DOE-21-SD	2.7	0.0	0.0	0.6	1.6	36.7	1.3	57.0	410°C Highest Severity	83
DOE-23-SD	27.0	0.0	6.7	11.0	0.3	35.0	0.7	17.0	370°C	76
DOE-24-SD	26.3	0.0	0.0	0.0	9.3	36.3	1.0	27.0	390°C Agglomerates	83
DOE-25-SD	0.0	59.3	13.3	0.0	9.3	17.0	1.0	1.7	390°C No catalyst little CO Conv.	78
DOE-26-SD	0.0	52.3	14.0	0.0	9.0	7.7	14.6	2.3	390°C FeS	81
DOE-27-SD	5.0	0.0	4.0	40.6	10.3	33.6	2.0	4.3	390°C Catalyst $NaAlO_2$	82
DOE-28-SD	2.7	0.0	0.0	7.3	5.7	42.0	1.0	41.3	390°C	89
DOE-29-SD	00.7	0.0	3.7	0.0	4.0	19.3	1.3	11.0	390°C 1:3 Syngas CO,H_2	73 approx.
DOE-30-SD	71.0	0.0	7.0	0.0	3.3	14.6	0.0	4.0	390°C CO,N 1:3	66 approx.
DOE-31-SD	75.7	0.0	10.3	0.0	1.0	7.3	0.7	5.0	390°C N	48 approx.

*Based on 300 points, under a combination of plane-polarized and cross-polarized light.

TABLE 2

Group	Samples	Characteristics	Comments
Two	DOE-29-SD DOE-30-SD DOE-31-SD	• Highest vitroplast (unconverted coal) • One coke fragment seen • Lowest conversion	• Can be further liquefied • Temperature too severe?
Four	DOE-23-SD DOE-24-SD	• Intermediate vitroplast • Intermediate conversion	• Some potential for further liquefaction
One	DOE-21-SD DOE-27-SD DOE-28-SD	• Lowest vitroplast • Highest conversion	• Cannot be liquefied further. Could be too costly for an additional small conversion percentage.
Three	DOE-25-SD DOE-26-SD	• No vitroplast, high cenosphere content (explosive devolatilization) • Combustion process prevailed?	• Something went wrong with experimental procedure? Looks more like combustion rather than liquefaction.

Conversion Order

Highest DOE-28-SD>21>27>24>23>29>30>DOE-31-SD Lowest

TABLE 3

Sample DOE-9

Vitroplast	Inertinite	Granular Residue	Mineral Matter	Conversion %
78.6	20.3	0	1.0	44

Sample DOE-23

Vitroplast	Vacuoles	Granular Residue	Inertinite	Mineral Matter	Conversion %
27.0	6.7	11.0	35.3	18.0	76

Sample DOE-14

Vitroplast	Inertinite	Granular Residue	Inertinite	Mineral Matter	Conversion %
30.3	31.0	0	0	58.3	73

Sample DOE-21

Vitroplast	Granular Residue	Inertinite	Mineral Matter	Conversion %
2.7	0.6	38.3	58.3	83

Sample DOE-17

Vitroplast	Inertinite	Mineral Matter	Conversion %
35.6	39.0	25.3	81

Sample DOE-28

Vitroplast	Inertinite	Mineral Matter	Conversion %
2.7	47.7	42.3	88

END

DATE
FILMED
1/11/94