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FINAL REPORT

ADVANCED DIRECT COAL LIQUEFACTION CONCEPTS

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By
D.J. Berger
R.J. Parker
P.L. Simpson

Canadian Energy Development Inc.
1500 Royal Trust Tower
Edmonton, Alberta
T5J 2Z2

and

Alberta Research Council
250 Karl Clark Road
P.O. Box 8330, Station F
Edmonton, Alberta
T6H 5X2

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Table of Contents

Page

1.0 INTRODUCTION

For most of the period since the industrial revolution began interest in the conversion of coal to liquid fuels has been dictated essentially by the availability and price of petroleum. Initially coal liquids were produced as by-products from coke manufacture, which was a requirement of the expanding steel industry, and were used mainly as chemical feedstocks. The first report of coal liquefaction by hydrogenation was by Berthelot[1] in 1869. The first studies of hydrogenative coal liquefaction were by Berguis in the period 1910 - 1927, with the first commercial plant being built by IG Farben in Germany in 1939. During World War II several plants were built in Germany due to the limited access that country had to petroleum supplies during that period. No commercial Berguis plants operate today.

After World War II petroleum shortages in the United States led to renewed interest in coal liquefaction. After major petroleum discoveries in the Middle East and elsewhere in the 1940's, however, interest waned until the 'oil shock' of 1973. In the period following 1973 with the rapidly increasing price of petroleum, and the even higher projections in the future, research on coal liquefaction took on a renewed vigour. Several demonstration plants, (eg. EDS, H-Coal) were built and operated. Technology advanced to a degree that the price at which liquid fuels produced from coal were competitive with crude oil, dropped significantly. Recent developments in two stage liquefaction technology demonstrated at Wilsonville produced coal liquids at a cost estimated to be competitive with crude oil at U.S. $33/barrel. However, since the early 1980's crude oil prices have again dropped significantly, and essentially remained below US $20/barrel in recent years. Interest in coal liquefaction research waned accordingly.

Conventional crude oil reserves in North American are, however, declining at a rapid rate, and unless alternative domestic resources are developed, increasingly larger quantities of conventional crude oil will have to be imported. This would have grave implications for the future economic well being of the continent. In Canada, heavy oil deposits in Alberta are upgraded to synthetic crude oil at the Suncor, Syncrude and Husky Lloydminster plants. This continent also possesses vast quantities of coal which have the potential to be converted to liquid fuels to replace those from conventional crudes. At current conventional crude oil prices, the production of liquid fuels from heavy oil and coal cannot be justified solely on an economic basis. Therefore, a considerable challenge exists to develop a technology which will reduce the costs of producing liquid fuels from both heavy oil and coal.

The integration of innovative steps into new advanced processes have the potential to further reduce the costs for producing liquid fuels. In this program 'Advanced Direct Coal Liquefaction Concepts', sponsored by the United States Department of Energy, (U.S. DOE), the objective is to develop a new approach to liquefaction that generates an all distillate product slate at a reduced cost of about U.S. $25/barrel of crude oil equivalent .

For this joint project, Canadian Energy Development Inc. (CED) and the Alberta Research Council (ARC) pooled their expertise in an attempt to meet the objective set by the U.S. DOE. The technical developments which provide the background to the current project are outlined below.

In the early 1980's, the Alberta Research Council embarked upon a program to evaluate the subbituminous coal resources of the Province of Alberta, as feedstocks for a variety of coal liquefaction processes. Autoclave tests of nine subbituminous coals identified the CO/steam process as an efficient method to solubilize and partially liquefy subbituminous coals[2]. Optimization of the process showed that coal solubilization was maximized for Vesta coal at 390°C, 600 psi carbon monoxide (cold) and 0.35 water/coal ratio[3]. Coal conversion dropped significantly when carbon monoxide was replaced by syngas (3:1 H_2:CO). Similar results were observed with syngas mixtures in the Highvale coal/Athabasca bitumen feedstock combination[4].

Characterization tests revealed that the majority of the products from coal liquefaction with CO/steam were non-distillable or pyridine soluble oils. The oil yield dropped rapidly after the optimum temperature (390°C) was exceeded. The process was effective for removal of up to 60% of the oxygen content of the coal. A second hydrocracking stage was, therefore, needed to upgrade the product oils to a synthetic crude oil. A hot charge/discharge unit was developed to test the two stage process[5]. Coal, solvent, water, potassium carbonate and the hydrocracking catalyst (potassium molybdate) were charged to a continuous stirred tank reactor (CSTR). The reactor was pressurized with carbon monoxide and raised to 390°C for 30 minutes to liquefy the coal. Gases and light hydrocarbons were eliminated by depressurizing the reactor and the remaining slurry was pneumatically transferred to a second preheated CSTR. Upgrading in the presence of hydrogen was typically effected at 460°C for 90 minutes. Final development of the two stage process was achieved in a continuous bench unit using a 1 litre CSTR and 2 litre CSTR in series[6].

Alberta subbituminous coals contain on average 15 - 20% ash. Any coal liquefaction process might, therefore, benefit from a deashing step. Alberta Research Council has pioneered the use of indigenous heavy oils and bitumens as bridging oils in deashing by oil agglomeration procedures. Ash reduction of up to 75% has been achieved for a variety of U.S. and Canadian subbituminous coals. ARC technology[7] has also been applied to pyrite rejection with excellent results, up to 85% reduction from eastern bituminous coals[8]. Combining a deashing step prior to coal liquefaction is a natural extension in the development of coal liquefaction. Initial tests using heavy oils and bitumen have shown that agglomerates perform as well as raw coal in coprocessing operation[9].

In 1984/85, Canadian Coal Liquefaction Corporation - the predecessor of Canadian Energy Development Inc. - performed an extensive technical and economical feasibility study on the production of synthetic crude oil from Alberta heavy oil and coal. The purpose of the study was to determine if coal/oil coprocessing and/or coal liquefaction were alternatives to heavy oil upgrading[10]. Based on the results of this study by Canadian Energy Developments Inc. (CED), a five year program was carried out from 1985 to 1990 with the objective of developing and improving coprocessing technologies for the production of synthetic crude oil from Alberta subbituminous coal and heavy oil. Two processing sequences were developed[11] and tested at the process development unit (PDU) scale (250 kg per day). CED also participated in the development of the Counterflow Reactor (CFR) through a cooperation agreement with Gesellschaft fur Kohleverflüssigung (GfK) mbH in Germany. The success of the development work at CED and at GfK lead to the Counterflow Reactor Development Project carried out by CED during 1990 to 1991[12,13].

The uniqueness of the Counterflow Reactor (CFR) technology is that the coal/heavy oil slurry is injected into the top of the reactor while the recycle gas and make up hydrogen is introduced into the bottom. Hydrogenation products are vaporized as they are formed and are withdrawn from the top of the reactor. Unconverted residue, coal, catalyst and ash particles flow downward in the reactor counter-current to the upward flowing hydrogen to promote solubilization of the coal and cracking/hydrogenation of the coal and residue. The coal/heavy oil slurry is introduced at temperatures up to 200°C below the reactor temperature (455 to 465°C) as the exothermic heat of reaction is used to raise the incoming feed slurry to reaction temperature.

Vapour products are withdrawn from the top of the reactor, cooled, condensed and separated in a cold separator. The condensed liquid product, a full range distillate hydrocarbon product (typically C_5 - 525°C), is transferred to the secondary upgrading unit. A slurry stream containing unconverted residue, unreacted coal, catalyst and ash and some vacuum gas oil product is withdrawn from the bottom of the reactor. Following depressurization in a let down system, the slurry is charged to a vacuum flash unit for recovery of vacuum gas oil.

The key advantages of the Counterflow Reactor Technology are low hydrogen recycle rates and low feed preheating requirements. Since coal and ash particles are allowed to settle naturally, superficial gas velocities inside the reactor are dictated by reaction kinetics only (maintaining a sufficiently high hydrogen partial vapour pressure) and not by the requirement to maintain the coal and ash particles in suspension (hydrodynamics). As the hot reaction products move upward counter-current to the downward flowing feed slurry, the exothermic heat of reaction is recovered efficiently inside the reactor.

The PDU study showed that distillable oil yields of up to 74 wt.% on feed (dry ash free) were obtained when coprocessing feed slurries containing about 40 wt.% Vesta subbituminous coal and 60 wt.% Cold Lake heavy vacuum tower bottoms. Continuous operation was maintained with superficial gas velocities of 2 cm/s inside the reactor, less than 1/4 of that required for the conventional up-flow bubble reactor. Coal/heavy oil slurry feed temperatures were about 150 to 200°C below the reactor temperature of approximately 455°C, thus, avoiding the problem of coking in preheater furnace tubes.

Certain aspects of the technologies developed separately by CED and ARC described above were combined for this project. A two stage liquefaction process which comprised of carbon monoxide/steam aided solubilization of subbituminous coal in the first stage and hydrocracking of the solubilized product in the second stage, both steps using the counterflow reactor system, was conceived. Deashing by oil agglomeration was an option for specific coals.

A one kilogram per hour integrated continuous flow bench scale unit was constructed at the ARC site in Devon, Alberta based on modifications to a unit located at Nisku, Alberta. The unit at Nisku had been used for both coal liquefaction and coal/oil coprocessing work. The modified unit was used to generate data which allowed a preliminary economic evaluation to be made. Laboratory and autoclave studies done prior to, and in support of the bench unit operation provided basic information to determine appropriate operating parameters for the continuous unit.

A more detailed description of the concept and the project objectives are described in the next section.

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2.0 DESCRIPTION OF EVALUATED COAL LIQUEFACTION CONCEPT AND PROJECT OBJECTIVES

2.1 DESCRIPTION OF PROCESSING CONCEPT

Figure 2.1 shows a block flow diagram of the coal liquefaction concept evaluated during this program. The overall concept consists of four principal steps:

- Feed preparation
- Coal solubilization
- Hydro-conversion and
- Coking

These steps are briefly described in the following.

2.1.1 Feed Preparation

The feed preparation section consists of an agglomeration unit and a feed slurry unit. Ground coal, coal derived solvent and water enters the oil agglomeration unit where a high portion of the inert mineral matter (ash) is removed from the coal. The deashed coal is then transferred to the slurry preparation unit where additional coal derived solvent is added to form a slurry containing about 40 wt% coal (maf). Catalysts for the coal solubilization stage and the hydroconversion stage are also mixed into the feed slurry.

2.1.2 Coal Solubilization

Slurry feed from the slurry preparation unit enters the top section of the first, solubilization counterflow reactor (CFR) and flows downwards, counter-current to the upward flowing CO and water which are injected into the bottom of the CFR. A fixed

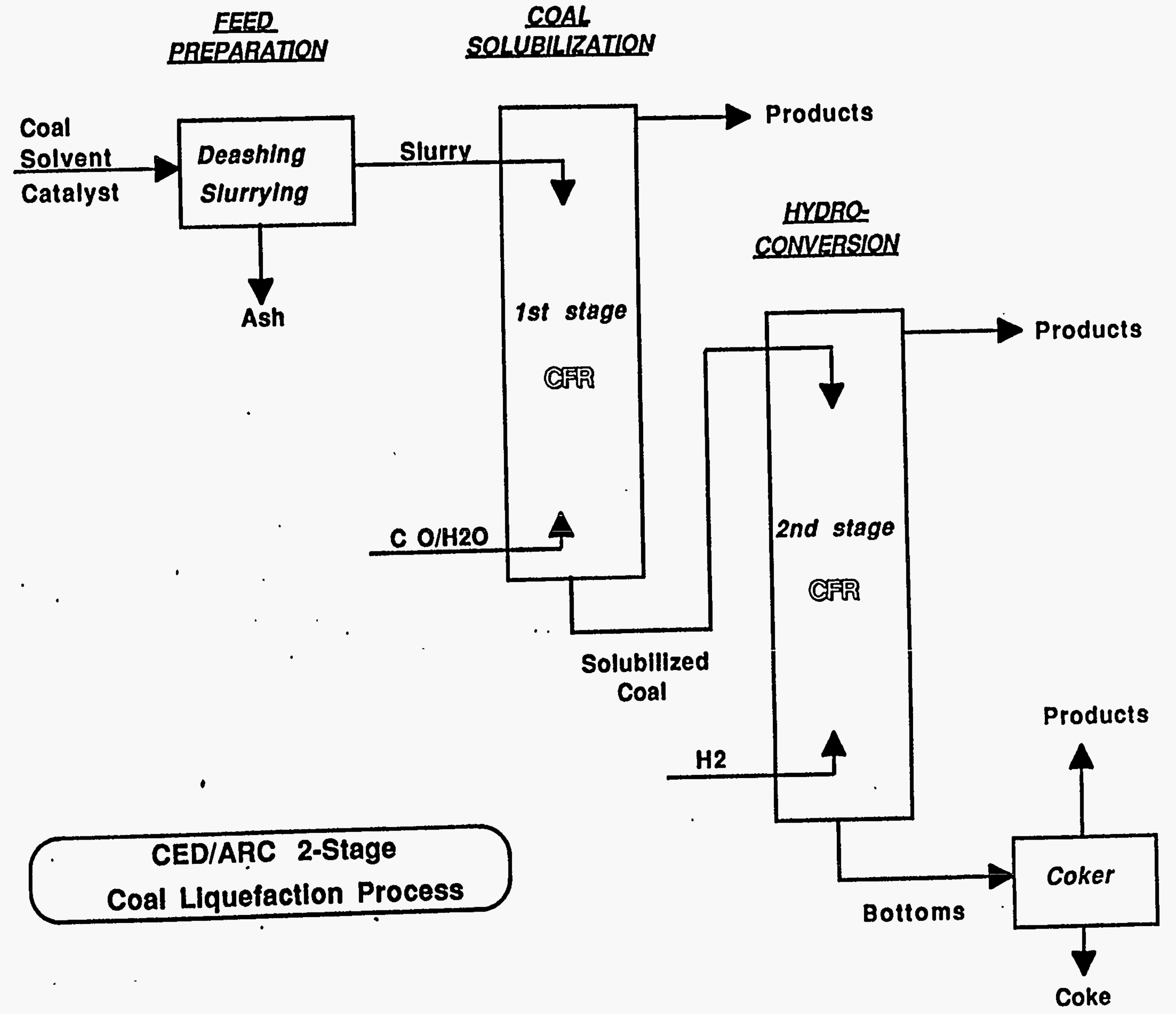

FEED PREPARATION
COAL SOLUBILIZATION
HYDRO-CONVERSION
DELAYED COKING
Coal
Solvent
Catalyst
Deashing
Slurrying
Ash
Slurry
1st stage
CFR
Products
C O/H2O
Solubilized Coal
2nd stage
CFR
Products
H2
Bottoms
Coker
Products
Coke
CED/ARC 2-Stage
Coal Liquefaction Process

Figure 2.1

liquid level is maintained inside the CFR. The upward flowing CO and water react in a shift reaction to form hydrogen and carbon dioxide. As the coal sinks slowly through the solvent against the rising gases, it is solubilized. The operating conditions are selected so that at least about 75 to 80 wt% coal (maf) are solubilized. All liquids and solids are withdrawn from the bottom of the solubilization reactor under level control, and are routed to the top of the second, hydroconversion CFR.

Gases, vaporized solvent and water vapour are removed from the top of the solubilization CFR. After cooling and condensing, the gases leave the overhead separator under back pressure control. The condensed material is withdrawn under liquid level control and separated into an oil and a water phase.

2.1.3 Hydro-Conversion

The bottoms of the solubilization reactor are injected into the top portion of the second, hydroconversion reactor and flow downwards, counter-current to the hydrogen which is injected into the bottom of the CFR. A fixed liquid level is maintained inside the CFR by level control on the bottom stream. Additional coal solubilization takes place in the upper portion of the liquid column, and as the solubilized coal and the solvent flow downward through the reactor conversion to lighter materials takes place. Non-vaporized oil, unconverted coal, ash and other solids are withdrawn from the bottom of the CFR under level control.

Gases, vaporized oil and water vapour are removed from the top of the hydroconversion CFR. After cooling and condensing, the gases leave the overhead separator under back pressure control. The condensed material is withdrawn under liquid level control and separated into an oil and water phase.

2.1.4 Coking

As one possibility to further upgrade or to generate recycle solvent, delayed coking of the bottom stream from the hydroconversion CFR is suggested. The total or a slip stream of the second stage bottom stream is therefore injected into a delayed coker to produce hydrocarbon gases, additional and lighter oil and ash.

2.2 PROJECT OBJECTIVES

The overall objective of the project is to develop a new approach to the liquefaction of coal that will produce an all distillate product slate at a cost of about U.S. $25/barrel of crude oil equivalent. Specifically, CED/ARC's objectives for Phase I were to demonstrate that counterflow reactor technology could be applied to coal liquefaction in a two stage process and to develop some preliminary economic data on this system. This was accomplished by:

1. The design, construction and operation of a 1 kg/hr coal liquefaction bench unit employing a two stage counterflow reactor system.

2. The development of a data base for the liquefaction of Black Thunder and Illinois #6 coals using autoclaves and the bench unit, from which a preliminary economic feasibility study was made.

3. The examination of the option of deashing these coals prior to liquefaction using ARC agglomeration technology.

4. The use of the knowledge and expertise gained in the Phase I work to put forward a continuing process development proposal for work in Phase II.

3.0 FEEDSTOCKS

Six coal derived oils were obtained from Wilsonville, U.S. DOE at Pittsburgh (PETC) and HRI (Table 3.1, 3.2). Small quantities were used for the autoclave program while barrel size volumes were required for bench unit tests. The initial oil shipped from Wilsonville was a V-178 product. This material was too light even for autoclave tests since its boiling range included 70% distillate. A portion of the material was subsequently distilled in the laboratory to generate 6 L of nominally +320°C solvent, which was used in the initial autoclave tests. The 5 barrel shipment of Black Thunder solvent was manufactured at Wilsonville and consisted of product (V-1074) collected during different yield periods. The individual barrels held material which was quite different in appearance and properties, especially the boiling range. In order to ensure reproducibility, solvent blends containing 25% of each barrel (2-5) were prepared and mixed for both autoclave and bench unit tests (V-1074 blend). Solvent from barrel 1 was omitted since its properties varied from the others and water was visible in the barrel.

Two samples of Illinois #6 derived solvent were ultimately obtained from HRI. One sample (LO-6282) was 5 gallons and was used for initial autoclave tests. The second sample (LO-6305) was used for the bench unit runs. The properties of the two samples were similar (Table 3.1).

Two batches of Black Thunder coal were received from Thunder Basin Coal Company and a single delivery of Illinois #6 coal was delivered from Consolidated Coal Companies. Both coals were crushed and pulverized as required for the autoclave and bench unit programs. To facilitate pulverization of the Black Thunder coal it was partially dried by spreading the coal on groundsheets and left for 1-2 days. Complete characterization of the coals was performed initially (Table 3.3) and a proximate analysis was completed on small samples for each individual autoclave test. Periodic checks on coal particle size distribution showed that little oversize material remained (i.e. > 250 μm).

Table 3.1: Properties of Coal Derived Solvents

Solvent #	V-178	V-178 (+320)	LO-6050	LO-6282	LO-6305
Coal	Black Thunder	Black Thunder	Black Thunder	Illinois #6	Illinois #6
Derivation	Wilsonville	Wilsonville	HRI	HRI	HRI
	Run 263	Run 263			
Obtained from	Wilsonville	distilled by ARC	HRI	HRI	HRI
Quantity	3 barrels	6 kg	2 x 5 gallons	5 gallons	2 barrels
Properties					
API gravity, °	12.5	10.7	18.7	14.8	14.6
Carbon %	87.7	88.3	87.6	88.5	88.6
Hydrogen %	10.2	9.5	11.3	10.5	10.7
Nitrogen %	0.71	0.96	0.21	0.08	0.13
Sulphur %	0.03	0.04	0.03	0.07	0.08
Oxygen[1] %	1.36	1.22	0.86	0.85	0.86
CCR				1.9	
Asphaltenes				2.4	1.4
Aromatics, H^1	9	8	4		
Aromatics, ^{13}C		33	15		
Cyclic H^1,	16	24	18		
Simulated Distillation	% distilled by				
IBP	200	262	183	225	237
5	244	284	239	283	285
10	261	297	262	303	305
25	289	320	300	335	337
50	326	344	339	373	374
75	355	363	374	429	427
90	375	381	409	497	495
95	386	397	431	538	539
100	414	459	487		
+525, resid				6.3	6.3

[1] by difference

Table 3.2: Properties of Black Thunder Solvent, V-1074

Solvent #	V-1074/1	V-1074/2	V-1074/3	V-1074/4	V-1074/5	V-1074 Blend
Derivation :	Black Thunder Coal, ex Wilsonville Run 263					
	Obtained from PETC Sample Bank, 1 barrel of each					
API Gravity, °						2.4
Carbon						87.8
Hydrogen						8.5
Nitrogen						0.85
Sulphur						0.05
Oxygen[1]						2.8
Simulated Distillation % distilled by						
IBP	235	241	329	330	325	256
5	271	306	352	353	349	347
10	313	352	362	364	358	360
25	371	369	375	381	375	380
50	406	414	405	404	399	404
75	435	435	430	429	424	429
90	459	469	456	453	451	458
100	508	522	513	506	536	535
Asphaltenes						12.2
Aromatics, ^{1}H						23
Aromatics, ^{13}C						54

[1] by difference

Table 3.3: Properties of Black Thunder and Illinois #6 Coals

Coal	**Black Thunder**	**Black Thunder**	**Illinois**
Obtained from	Arco	Arco	Consol
Quantity	4 barrels	3 barrels	4 barrels
Properties			
Moisture[1]	15.5	10.2	8.9
Ash	5.2	6.5	11.5
IOM	79.3	83.3	79.6
Carbon	75.7		77.7
Hydrogen	5.6		5.4
Nitrogen	1.03		1.4
Sulphur	0.43		4.2
Oxygen[2]	16.3		12.9
Particle Size Distribution, weight %			
.063-.090 mm	50.8		
.090-.125 mm	22.2		
.125-.180 mm	18.0		
.180-.250 mm	8.6		
.250-.355 mm	0.4		
d_{50}, mm	0.090		

1 coal partially dried prior to crushing

2 by difference

4.0 TEST PROGRAM

This section of the report covers all the experimental work included in Section 3.0 of the project management plan. Presented are the experimental results, and the discussions based on the results.

The first four sections cover the agglomeration studies, the autoclave program, the bench unit program and the work on residue handling. Petrographic work based on samples from both the autoclave and bench unit programs is covered in the fifth section. The final two sections present a discussion of the overall results and their implications for the proposed process concept, followed by the main conclusions stemming from the experimental work.

4.1 AGGLOMERATION TESTS

4.1.1 Black Thunder Coal

4.1.1.1 Coal Preparation

Raw Black Thunder coal (up to 5 cm top size) was crushed and pulverized to prepare samples of specific average diameter. Typically 2.5 kg of coal was passed through a laboratory crusher to reduce the particle size to a top size of about 0.5 cm. Samples which were pulverized once gave a d50 of 0.16 mm, while further pulverization reduced the d50 to 0.09 mm. The d50 was determined by a procedure developed by ARC. A dry sample (~20 g) was put onto a set of 8 cm (3 1/2") screens. The screens were vibrated for 5 minutes and subsequently the content of each screen was weighed. Results for the two samples (BT-1A, BT-1B) prepared for the agglomeration matrix program are shown in Table 4.1.1.

High moisture subbituminous coals lose water during handling, crushing and grinding. ARC has adopted a standard procedure which gives a coal with a steady state moisture level. The pulverized coal is spread thinly in a metal tray and allowed to dry overnight at room temperature. The dried coal is then stored in a sealed metal can. A proximate analysis is performed immediately and then samples are withdrawn for testing purposes.

4.1.1.2 Test Procedure

The laboratory procedure uses a cylindrical vessel, 1 litre capacity, fitted with metal baffles to aid agitation, and a mechanical stirrer. In a typical test, water (600 mL) and coal (150 g MAF) are blended at a stirring speed of 1200 rpm. The binding oil (15 - 75 g) is then added. After the coal has been wetted by the oil, the slurry changes colour at the so called 'inversion time'. This indicates that the period of growth of the

Table 4.1.1: Coal Properties - Agglomeration Tests

	BT-1	BT-1A	BT-1B
Preparation crusher/pulverization	once/once	once/once	once/three X
moisture, weight %	17.8	19.5	15.7
ash (dry basis), weight %	7.15	6.5	6.7
particle size distribution range, mm	weight %		
0.063 - 0.090	17.4	18.7	50.8
0.090 - 0.125	16.2	20.7	22.2
0.125 - 0.180	20.8	16.0	18.0
0.180 - 0.250	31.8	32.3	8.6
0.250 - 0.355	13.2	11.9	0.4
0.355 - 0.500	0.5	0.2	0
0.500 - 0.710	0.2	0.2	0
0.710 - 1.000	0		
d50, mm	.168	.160	.090

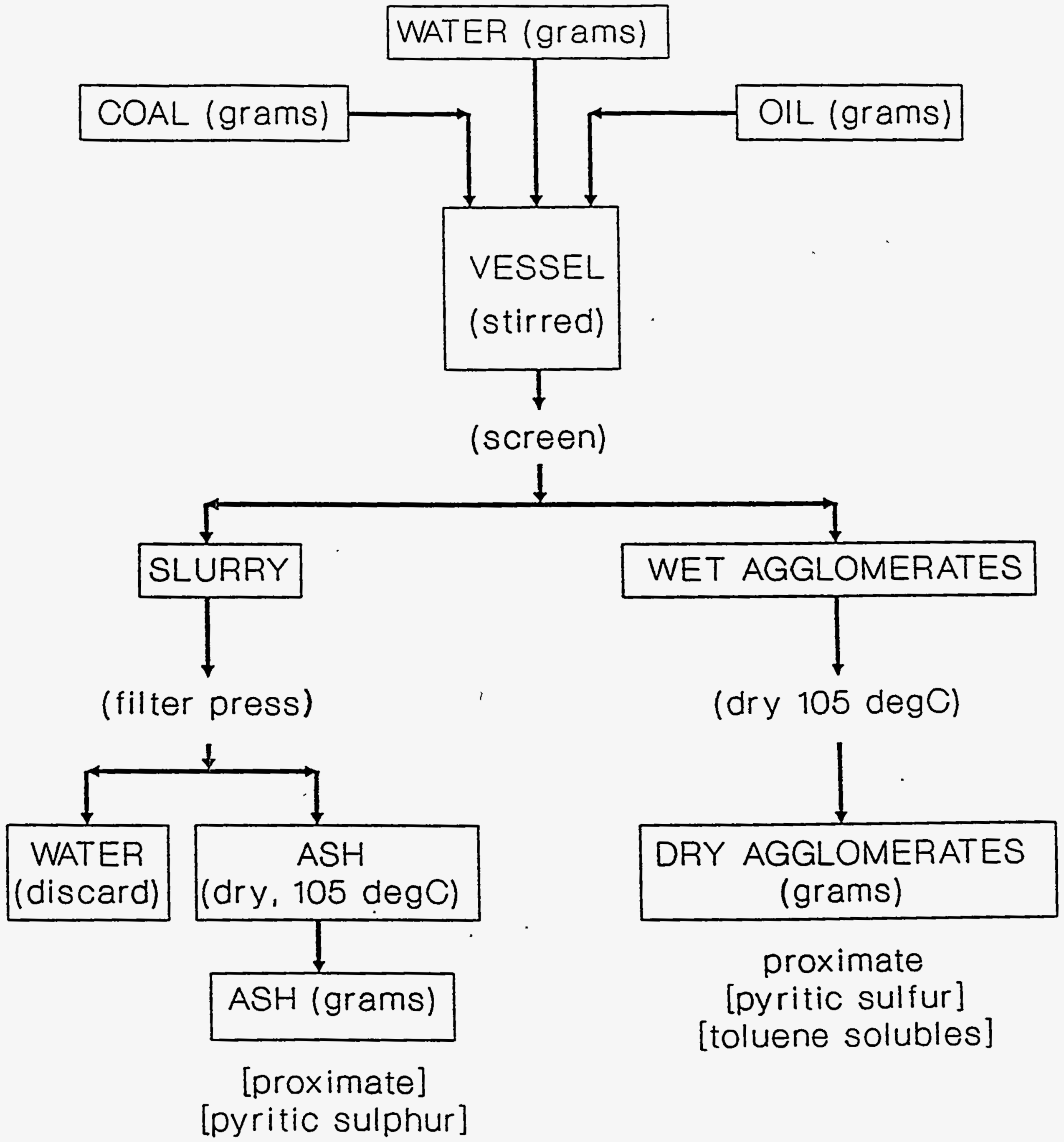
agglomerates has started. At this time the stirring rate is increased to 1800 - 2000 rpm. The test continues until the agglomerates have reached a certain size, or for a specific time (15 - 60 minutes). If the growth rate is slow, the baffles may be removed.

Upon completion of the test, stirring is stopped, and the agglomerate slurry is poured onto a 300 μm screen. The agglomerates are allowed to drain and then washed with fresh water. The work-up procedure is depicted in Figure 4.1.1. The washed agglomerates are dried to constant weight at < 50°C. The slurry water and washings are combined and pressure filtered through a wet strengthened Whatman #114 filter paper. The derived ash and filter paper are dried to constant weight at 105°C. A proximate analysis is performed on the agglomerates to determine residual moisture and ash. If desired, the oil content is found by extraction with toluene in a Soxhlet apparatus. Also, if the filtered ash shows signs of coal or oil, a proximate analysis may be performed. This procedure allows for an overall mass balance to be closed as well as balances of the ash, total hydrocarbon, coal and binder oil.

4.1.1.3 Screening Tests

It is necessary to perform screening tests on unknown coal and oils to establish the range of conditions under which agglomerates will form. The nature of the coal, i.e. rank, its ash content and the nature of the ash will determine its tendency to form agglomerates with reduced ash levels, as well as physical properties, i.e. particle size and distribution. The nature of the oil, primarily viscosity and aromaticity, influence its success as a binder or bridging liquid. The formation of mechanically robust, ash reduced agglomerates is also influenced by the operating conditions. Screening tests set the range for coal:oil ratio, coal size, stirring speed and time. Other operating variables such as coal:water ratio and temperature have been standardized and are not changed unless conditions warrant it, for example: the temperature may be raised for high viscosity oils.

Figure 4.1.1: Laboratory Agglomeration Test Procedure Schematic



Results of the screening tests are given in Table 4.1.2. In all cases the inversion time was extremely short, less than 2 minutes. Agglomerate growth was quite limited with the V-178 oil and did not proceed further after 10 - 15 minutes. Removal of the baffles and changes in stirring rate did not assist growth. In Runs 1 and 2, very small, well formed agglomerates were produced. Slightly larger agglomerates were achieved in Run 3, but some amalgamated into large amorphous lumps, usually associated with excessive oil. However, the effluent water and washings were all free of visible droplets or oil sheen. A proximate analysis on Run 3 found that 9.6 g ash remained out of a total coal ash of 10.7 g, i.e. 10% ash reduction.

Runs 4 and 5 substituted the V-178 (+320) oil under similar operating conditions. The best appearance and size was observed for the Run 5 agglomerates when the coal:oil ratio was 2:1. Run 4 duplicated Run 3, apart from the oil used, and produced a similar amalgamated product. Total ash content of these agglomerates was 9.4 g, for 12% ash reduction.

In summary, the coal derived oil could generate agglomerates from Black Thunder coal, but the ash reduction was limited. However, the Black Thunder coal has very low ash content (7%) making it a poor candidate for deashing. The screening tests did succeed in identifying the range of oil content and stirring speed for the following matrix tests.

4.1.1.4 Agglomeration Matrix Tests

A two level matrix test program was adopted to optimize agglomerate growth and ash reduction. The variables included within the matrix were oil (V-178) added (30 and 60 g), coal particle diameter (d50 BT-1B = 0.090 and BT-1A = 0.160 mm) and stirrer speed (1200 and 2000 rpm). Also, a centre point was replicated using oil added (45 g), d50 0.125 mm (50% each of the two batches) and stirring speed (1600 rpm). Other operating conditions were coal 175 g (moisture free), water 600 g (including coal

Table 4.1.2: Screening Tests

Test No.	1	2	3	4	5
Operating Conditions					
stirring speed, rpm	1800	1800[1]	2000	2000	2000
time, minutes	105	50	60	60	60
baffles removed, minutes	25	10-35[2]	no	no	no
water, g	573	573	573	573	575
coal, g	177	177	177	177	177
oil, g V-178	15	30	50		
V-178 (+320)				50	75
Results					
inversion time, minutes	< 2	.5	-	-	-
agglomerate appearance	good	good	3	3	very good
size, mm	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5

[1] Decreased to 1000 after 10 minutes and removed baffles. Resumed speed at 35 minutes and added additional 10 g oil. Still no growth.

[2] After drying 4.6% water, 4.8% ash in product.

[3] Amalgamated into lumps. 6.7% water, 4.7% ash in product.

moisture), and time 15 minutes. Agglomerate growth was monitored by withdrawing samples every 3 minutes.

The inversion time was less than 1 minute in all runs. This was observed both visually and by an increase in stirrer torque. Agglomerate size was essentially constant at about 0.3 mm. The effluent water showed no sign of oil, but did discolour on standing, indicating the presence of dissolved components from the oil and/or coal.

Hydrocarbon recovery (coal plus oil) in the agglomerates exceeded 97 weight % for all experiments (Table 4.1.3). Ash rejection was monitored by proximate analysis of the agglomerates and by the weight of residue from the pressure filtration of the water.

Agglomerate ash content was essentially constant at 5.0 ± 0.4%, which indicated that little ash was removed. This was confirmed by the pressure filtration residues which ranged from 0.3 - 0.7 g, corresponding to 2 - 6% of the ash input. Since the data were so close, no statistical interpretation was performed. Within the tested ranges no correlations could be drawn between operating parameters and ash rejection.

Again to summarize, agglomeration of Black Thunder coal by Wilsonville V-178 oil produced small, spherical agglomerates. Ash rejection, however, was minimal. A sample of agglomerates was set aside for batch autoclave testing to determine if the agglomeration process had negative impact on coal liquefaction.

4.1.2 Illinois #6 Coal

4.1.2.1 Matrix Tests

A three variable test matrix was completed to determine the effectiveness of oil agglomeration to deash Illinois #6 coal. The selected variables were coal size (d50 =

Table 4.1.3: Agglomeration Matrix Results

Run No.	Matrix Conditions			Hydrocarbon	Agglomerate	Ash Rejected	Ash Recovery
	d50	oil	rpm	Recovery, wt%	Ash content, wt% dry basis	in water, g	wt%
1	+	-	-	98	5.5	0.55	96
2	-	-	-	99	5.7	0.27	96
3	-	+	-	97	5.0	0.42	96
4	+	+	-	98	5.0	0.50	98
5	-	-	+	98	5.6	0.54	95
6	+	-	+	99	5.6	0.39	96
7	-	+	+	98	4.5	0.73	91
8	+	+	+	97	4.4	0.50	86
9	0	0	0	98	5.0	0.55	94
10	0	0	0	97	5.2	0.39	93

matrix conditions

	+	0	-
d50, mm	0.16	0.125	0.09
oil, g	60	45	30
rpm	1200	1600	2000

coal input	175 g (MF)
water	600 g (total)

100 and 160 μm), added oil (30 and 60 g) and stirrer speed (1200 and 2000 rpm). Since no process derived oil was available from Illinois #6 coal, V-178 (full range) Wilsonville Black Thunder process derived oil was substituted. Coal (200 g as received) and water loadings (600 mL) were maintained constant throughout the program. The procedure for the laboratory tests followed that described in Figure 4.1.1.

Scoping tests were initially conducted using V-178 solvent. These tests proved that coal-oil agglomerates could be made but size and growth rate were low. Also, a poorly defined inversion time was obtained. However, the procedure was successful in generating agglomerates with hydrocarbon recovery in the 96 - 98% range (Table 4.1.4). Ash levels were reduced from 13.2% in the coal to 7 - 9% in the agglomerates. Allowing for incorporation of the oil, this represented a 23 - 33% decrease in ash, to low to justify the additional cost and effort.

On an absolute basis the sulphur in the coal was reduced at best from 3.6% (MF) to 2.6% in the agglomerates. However, the inorganic sulphur of the coal was only 1.6% (pyritic and sulphitic) and so almost two thirds had been selectively eliminated.

Table 4.1.4: Agglomeration Tests on Illinois #6 Coal

	Matrix			HC Recovery	Agglomerate Analysis		% Reduction in	
	d50	oil	rpm	%	% ash	% sulphur	ash	sulphur
ILL-1	1	-1	-1	97	9.1	3.03	25	6.3
ILL-2	-1	-1	-1	97	8.7	2.94	28	9
ILL-3	-1	1	-1	96	7.8	2.62	24	5.7
ILL-4	1	1	-1	97	7.6	2.80	29	2.9
ILL-5	-1	-1	1	96	8.3	2.87	32	13.8
ILL-6	1	-1	1	97	9.3	3.18	23	2.2
ILL-7	-1	1	1	98	7.0	2.67	33	4.8
ILL-8	1	1	1	96	7.7	2.90	29	0.4
ILL-9	0	0	0	96	7.8	2.82	31	6.5
ILL-10	0	0	0	96	7.7	2.76	32	8.5

Legend	d50 coal size	-1 = 83	0 = 160	+1 = 173 um
	oil content	-1 = 30	0 = 45	+1 = 60 g
	stirrer speed	-1 = 1200	0 = 1600	+1 = 2000 rpm

4.2 AUTOCLAVE TESTS

4.2.1 Experimental Procedure

4.2.1.1 Run Procedure - Coal Solubilization Stage Only

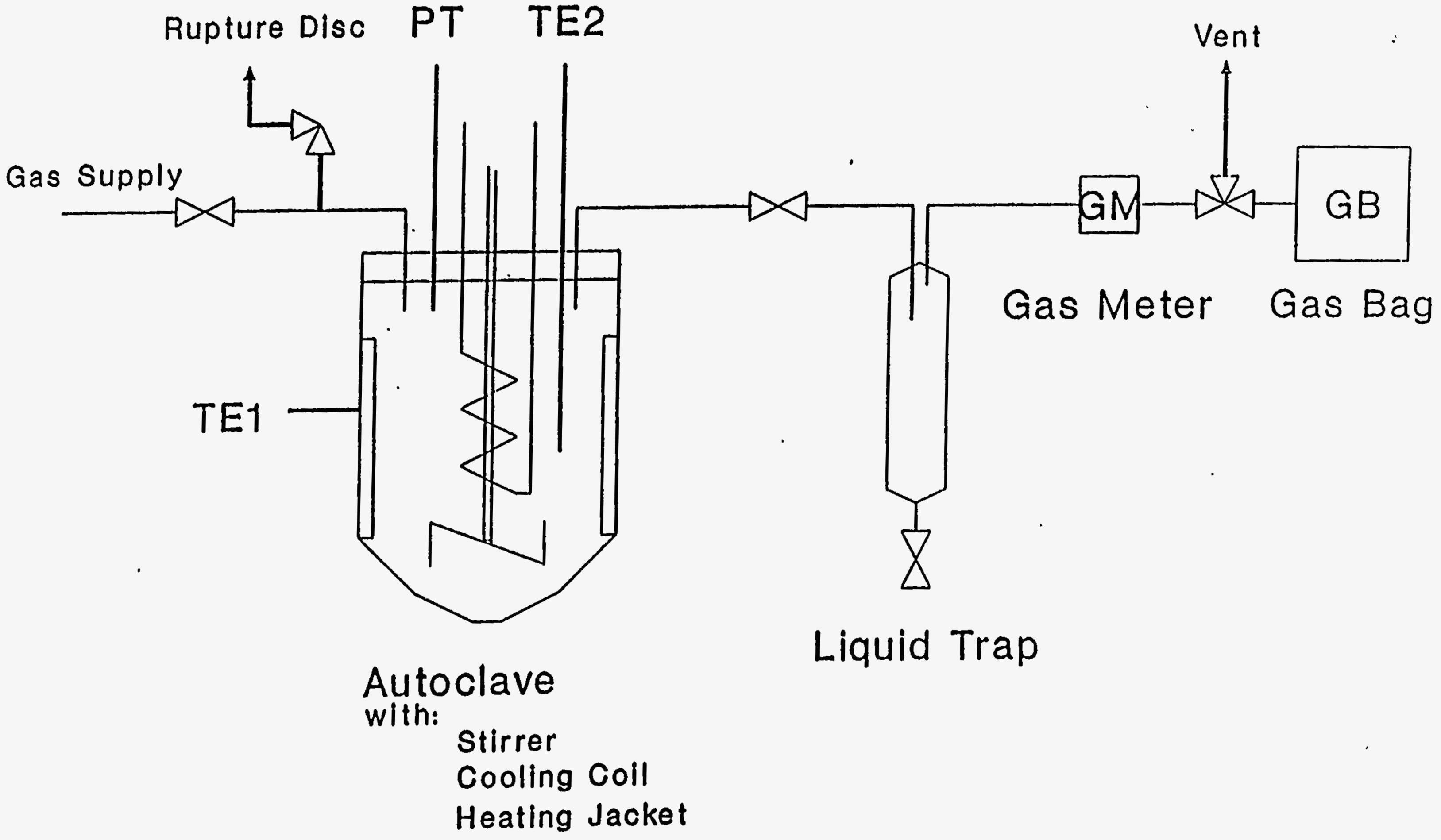
An Autoclave Engineers, 1 litre, stirred autoclave equipped with 2 half baffles was used throughout the program (Figure 4.2.1). When the unit with internals was filled with pressurized nitrogen and the gas discharged through a dry gas meter, the measured volume was 955 mL. The internals included a stirrer with multiple blades located at the bottom of the shaft, 2 half baffles, an internal cooling coil and a thermowell, which was covered by liquid during operation. Nitrogen, carbon monoxide or hydrogen were all connected to a gas supply manifold for charging or discharging gas. Product gas was cooled in a condenser filled with ice water, and collected in bags, prior to analysis.

In a typical experiment the autoclave was charged in the following sequence:

• solvent	120 g
• water, including soluble catalyst, eg. K_2CO_3	13-27 g
• coal	80 g
• other catalysts or additives	2-5 g

After sealing, the autoclave was purged with nitrogen to displace the air, then charged with the active gas, either carbon monoxide (400 - 800 psi) or hydrogen (1000 - 1100 psi). The initial gas pressure was selected so that the total pressure at operating temperature did not exceed 3200 psi. (The anticipated operating pressure of the bench unit was 2000 - 2500 psi). The weight of the contents was 225 - 250 g, and it was assumed that the density of the coal/solvent/catalyst slurry was 1.00 in order to calculate the gas charge. After charging, the autoclave was left for up to 2 hours to test for leaks.

Figure 4.2.1: Simplified Set-Up of Batch Autoclave



In a typical run the furnace was set at 75 - 100°C above the operating temperature (maximum 490°C). The internal temperature rose at 4 - 5°C/minute, requiring 80 - 100 minutes to achieve 400°C. The furnace setting was reduced as the set temperature was approached. Stirring was started at the beginning of the run, being raised in 200 rpm increments until 800 rpm was attained. Time 0 was taken when the temperature was 2°C below set point. Temperature was controlled by passing short bursts of water through the internal cooling coil, which maintained the temperature to ±2°C. Upon completion of an experiment the furnace was shut off and the autoclave contents were quenched by a continuous flow of cooling water.

When the internal temperature reached ~ 140°C, the gas was discharged through the condenser and collected in the gas bag. Initially a dry ice trap was used, but this condensed some CO_2 which was then lost during the opening of the condenser. It was therefore replaced by an ice water trap after the initial 3 or 4 tests. Two condensers were connected in series for some experiments, but this proved unnecessary since no liquid was ever collected in the second condenser. After the initial gas was collected, 75 litres of nitrogen was swept through the autoclave and collected in a second gas bag. Total time was 15 - 20 minutes each for both the discharge and nitrogen sweep. This procedure ensured complete recovery of all gases including the water soluble carbon dioxide. To prevent contamination of the gas sample the initial gas discharge was vented after passage through the dry gas meter (DGM). The DGM was protected by a water column (3 psi).

NOTE: The temperature for discharge was chosen to minimize dissolution of carbon dioxide in the product water. Dissolved carbon dioxide can effervesce when the autoclave was discharged at low temperature, resulting in carry over of a froth into the discharge lines and condenser. Also, frothing had been observed when the head was removed from the autoclave.

4.2.1.2 Run Procedure - Two Stage Operation

The procedure followed that of the one stage mode of operation, except that both first and second stage catalysts (eg. K_2CO_3 + FeS) were charged initially. When the first stage was complete the temperature of the autoclave contents was lowered to about 300°C. The gas was discharged and collected. The autoclave was then recharged with sufficient hydrogen to permit the pressure to be 2500 - 3000 psi at operating 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.

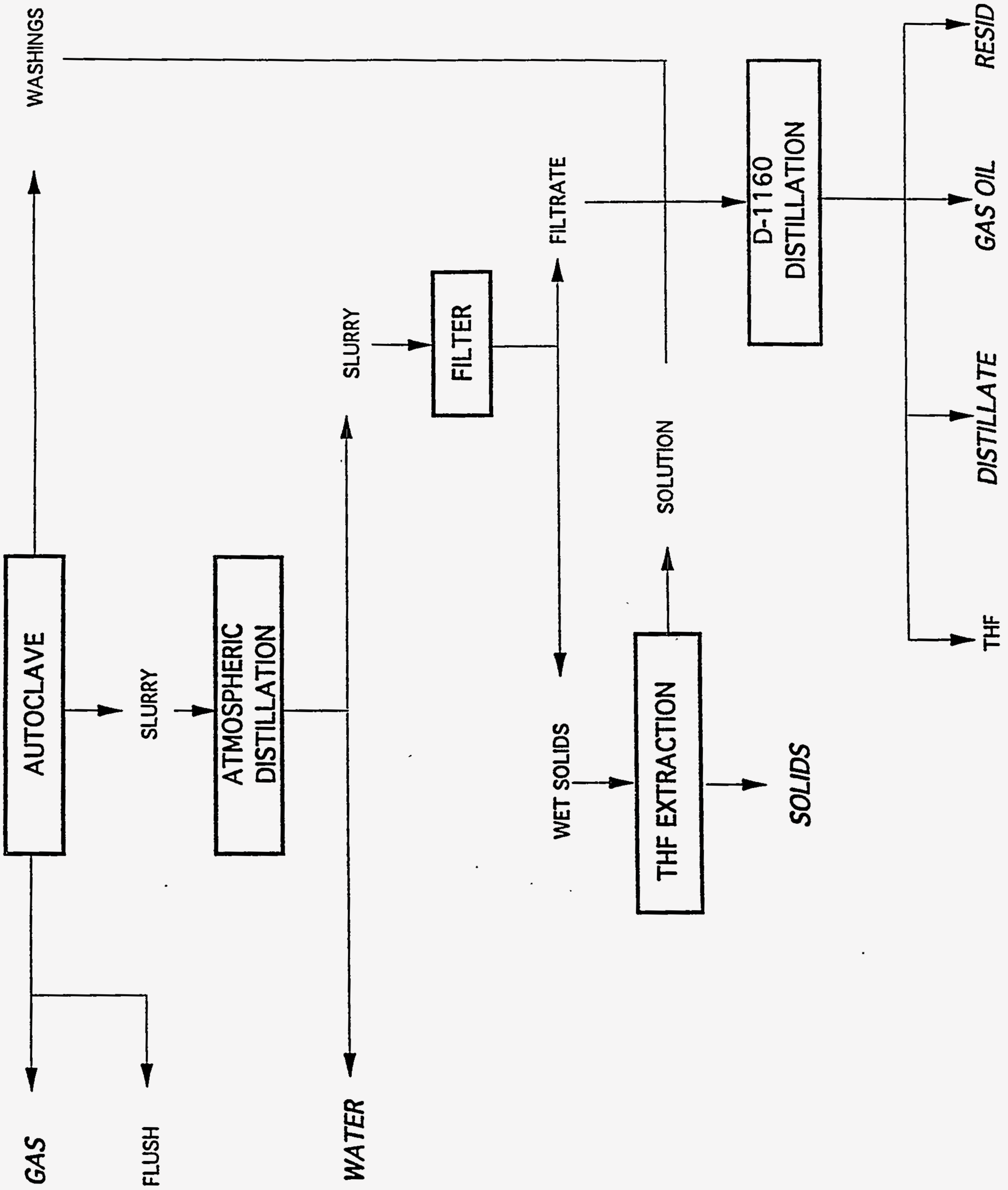
4.2.1.3 Work-Up Procedure - Distillation Method

The discharge gas and sweep gas were characterized by gas chromatography to quantify hydrocarbons, carbon oxides and hydrogen sulphide.

Liquids collected in the condenser were drained and, if necessary, separated into water and hydrocarbons (Figure 4.2.2). The contents of the autoclave were transferred to a 500 mL round bottom flask. If the product was primarily solubilized coal this was accomplished by syphoning the liquids directly into the flask. In low severity, low conversion runs much of the coal remained slurried in the solvent. In this case the slurry was removed by scraping with a spatula and added to the flask. In both cases any loose material from the autoclave head, baffles, cooling coils and stirrer was dislodged with a spatula. The autoclave interior, head, etc. were washed with tetrahydrofuran (THF) and scraped more vigorously to remove all remaining liquid and solid products. The THF was stripped off in a rotary evaporator and the remaining slurry weighed for mass balance purposes only. Finally when the autoclave and head were dry, they were wiped with a paper towel.

The main product slurry was subjected to distillation at controlled atmospheric

Figure 4.2.2: Autoclave Work Up Procedure



pressure to remove naphtha and water (maximum 200°C) initially, then D1160 vacuum distillation to recover the distillate (200 - 343°C) and gas oil (343 - 525°C) cuts. The residue was transferred to an extraction thimble and the THF soluble oils were dissolved by Soxhlet extraction (8 - 16 hours). THF was eliminated from the soluble or non-distillable oils (NDO) by rotary evaporation. The solid residue was dried and a proximate analysis performed.

Data Analysis

Overall Mass Balance Calculation

Sum of slurry + washing + condenser + wipings + gas / total charge

Ash Mass Balance Calculation

Total solids (THF insolubles) x proximate analysis (ash) / coal ash + catalyst

Product Distribution Determinations (g /100 g MAF coal)

Gas	composition
Naphtha	(includes water)
Distillate	(may include water)
Gas Oil	
Non-distillable oils	
Solids	

Washings	assigned to liquids and solids proportionately
Condenser	assigned to naphtha
Wipings	assigned to solids

Process Chemistry Calculations

Gas	CO conversion
	H_2 consumption
	Hydrocarbon gases
Liquid	net yield distillables (corrected for solvent)
	net yield non-distillable oils (THF solubles)
Solid	coal conversion

4.2.1.4 Work-Up Procedure - Solvent Extraction Method

The gases and condenser liquids were treated in the same way as in Section 4.2.1.3.

The solvent extraction procedure is shown in Figure 4.2.3. 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 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 plus additional toluene was used as the extraction medium and to recover the water from the products (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 and a proximate analysis performed. A portion of the oils was analyzed for asphaltenes by pentane precipitation.

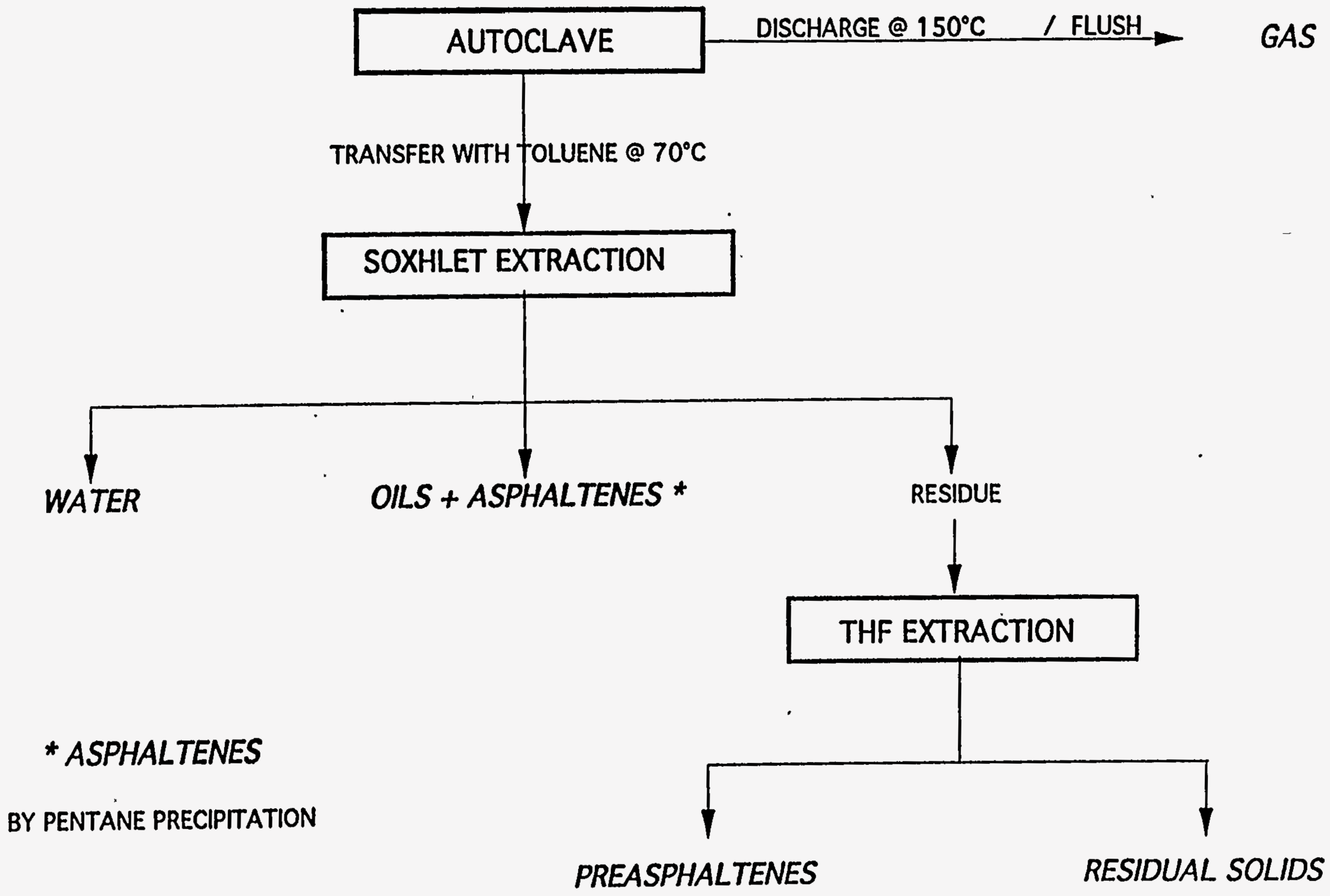


Figure 4.2.3: Extraction Procedure

4.2.2 Results

A total of 70 autoclave tests were completed, two of which were disregarded because the run was aborted or material was lost during work-up. A number of key aspects of the proposed process concept were studied in the autoclave. The results also provided a basis for decisions on the operation of the bench unit. The key aspects examined were:

(a) Thermal stability of coal derived solvents (4.2.2.1)
(b) Effects of temperature, time and initial pressure - matrix study (4.2.2.2)
(c) Effects of water gas shift reaction (WGSR) catalyst and gas composition on solubilization (4.2.2.3)
(d) Correlation of results between different solvents (4.2.2.4)
(e) Second stage catalyst effects (4.2.2.5)
(f) Impact of changing syngas composition (4.2.2.6)
(g) Simulated two stage tests in the autoclave (4.2.2.7)
(h) Illinois #6 coal solubilization (4.2.2.8)
(i) Autoclave tests on bench unit products (4.2.2.9)
(j) Process chemistry and reaction mechanism (4.2.2.10)

Runs up to DOE-31 followed the distillation work-up procedure. It was anticipated that water would be totally recovered by atmospheric distillation, but the water recoveries were often less than calculated from the WGSR. Also, mass balances were below 97% for many tests suggesting losses of light hydrocarbons in addition to the water. The distillation procedure also gave poor reproducibility for total oils and individual oil fractions. This was apparently related to the boiling range of the solvent and the instability of the 525+ oil fraction. Since the Black Thunder oils (V-178 and V-1074) were almost completely distilled by 450°C there was insufficient material to maintain an even distillation rate. Any attempt to maintain the rate required an increase in temperature, but this resulted in partially decomposition of the product leading to a loss of vacuum. The atmospheric distillation was apt to bump due to the presence of water. Distillation times were excessive since extreme care was needed to avoid bumping.

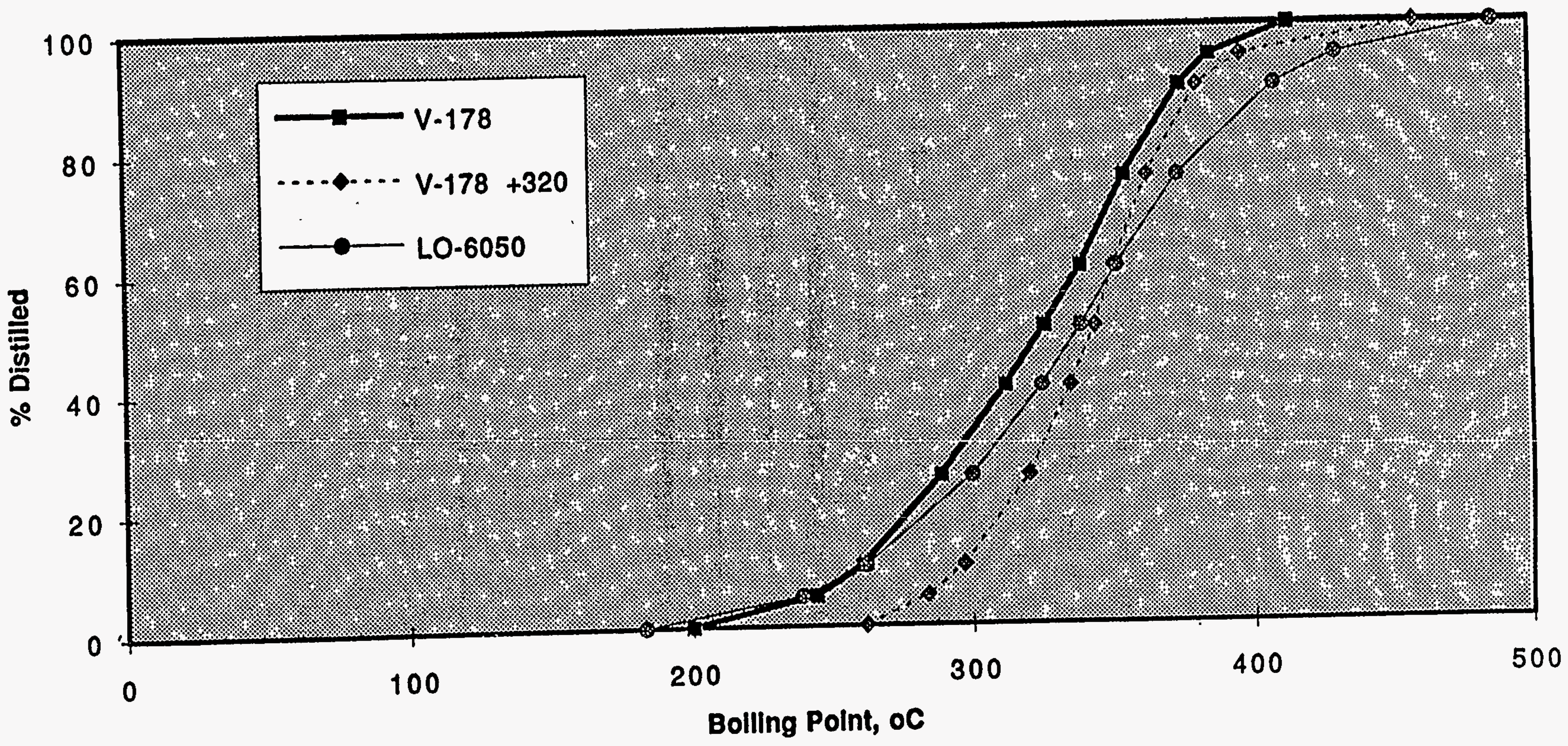
When the distillation procedure was changed to the extraction method, water recovery improved, such that, after correcting for consumption due to WGSR, mass balances were close to 100%. Overall mass balances still suffered from an inability to recover light hydrocarbons from the toluene extract. The work-up procedure did give reproducible results for unconverted coal, hydrocarbon gases, asphaltenes and preasphaltenes. Other products from the coal included pentane soluble oils, carbon oxides, and the lost hydrocarbons. These products were combined for evaluation purposes into a group defined as oils +.

Gas analyses followed the same gas chromatographic procedure throughout the experimental program. Good resolution of the individual peaks was observed throughout except in those product gases where there was little WGSR. These product gases were high in carbon monoxide and the tail from this peak interfered with the methane peak. In such cases the methane was estimated based on the average ratio of ethane/propane to methane found at similar conditions.

4.2.2.1 Solvent Stability

Several tests were completed to determine the stability of the six solvents (Tables 3.1 and 3.2) under either first or second stage conditions. In each case the solvent, gas CO or H_2, appropriate catalyst, K_2CO_3 or iron based, and water, if required, were charged to the autoclave. Following the experiment a gas analysis was performed and the solvent composition was characterized after filtration to remove the catalyst. The simulated distillation of these solvents are shown in Figure 4.2.4.

Figure 4.2.4 Simulated Distillations of Solvents



4.2.2.1.1 Black Thunder LO-6050

LO-6050 was the first solvent received, and two tests which provided general information about solvent stability were completed (Table 4.2.1). At 2 stage conditions (DOE-1) with hydrogen, the solvent showed considerable breakdown to lighter components, see simulated distillation (Figure 4.2.5). However, only a minor quantity of hydrocarbon gas (~ 1%) was produced and no light naphtha was collected in the product condenser. Both D1160 and simulated distillation illustrate the shift to lower boiling components. A marginal shift to lighter components was found at 410/30 minutes (DOE-2). The WGSR was evident (58% CO conversion) but no hydrogen was absorbed by the solvent (Δ moles CO ≡ Δ moles H_2). This solvent was very stable at first stage, but not at second stage conditions. Practically, the need for this solvent for the autoclave test program became redundant with the arrival of the V-178. No tests were, therefore, actually done with this solvent and coal.

4.2.2.1.2 Black Thunder V-178 (+320)

The early work on the Black Thunder coal utilized this solvent. This solvent also proved stable at 410°C with only marginal deterioration to gas (0.2%) or naphtha. CO conversion from this test (DOE-3) was almost identical to that in DOE-2 despite the fact that the time for the reaction was 60 minutes instead of 30 minutes in DOE-2. Overall results can be seen from the simulated distillation plots (Figure 4.2.5).

4.2.2.1.3 Black Thunder V-1074 Blend

As described earlier (Section 3), this solvent was a blend prepared from 4 barrels of Wilsonville V-1074 product. Like the other Black Thunder derived solvents it was stable at first stage conditions, (DOE-32, DOE-49), but broke down at the higher severity required for the second stage (DOE-33) (Table 4.2.1, Figure 4.2.6). Hydrocarbon gas production (2.5%) was significant at 440°C, but for all three tests the asphaltene concentration stayed essentially constant. Again, both first stage tests

Table 4.2.1 Solvent Stability

Run #	DOE-1	DOE-2	DOE-3	DOE-32	DOE-33	DOE-49
Operating Conditions						
Charge						
Solvent	LO-6050	LO-6050	V-178(+320)	V-1074	V-1074	V-1074
Catalyst	Pyrite	K_2CO_3	K_2CO_3	K_2CO_3	Pyrite	K_2CO_3/ATM
Water		yes	yes	yes		yes
Initial Pressure, psi	1100 H_2	750 CO	800 CO	800 CO	1100 H_2	600 CO
Temperature, oC	460	410	410	410	440	390
Time, minutes	60	30	60	30	60	30
Product Distribution, g/100g						
HC Gases, C1 - C5	1.2	0.6	0.2	0.8	2.5	0.1
Naphtha (RT - 182oC)	21.8	0.0	0.0			
Distillate (182 - 350oC)	40.4	61.5	48.9			
Gas Oil (350+ oC)	30.0	38.0	51.6	88.0*	85.6*	86.4*
Asphaltenes				12.1	12.2	13.4
CO Conversion, %		58	59	57		66

• Oils+

Figure 4.2.5 Stability of Solvent, LO-6050

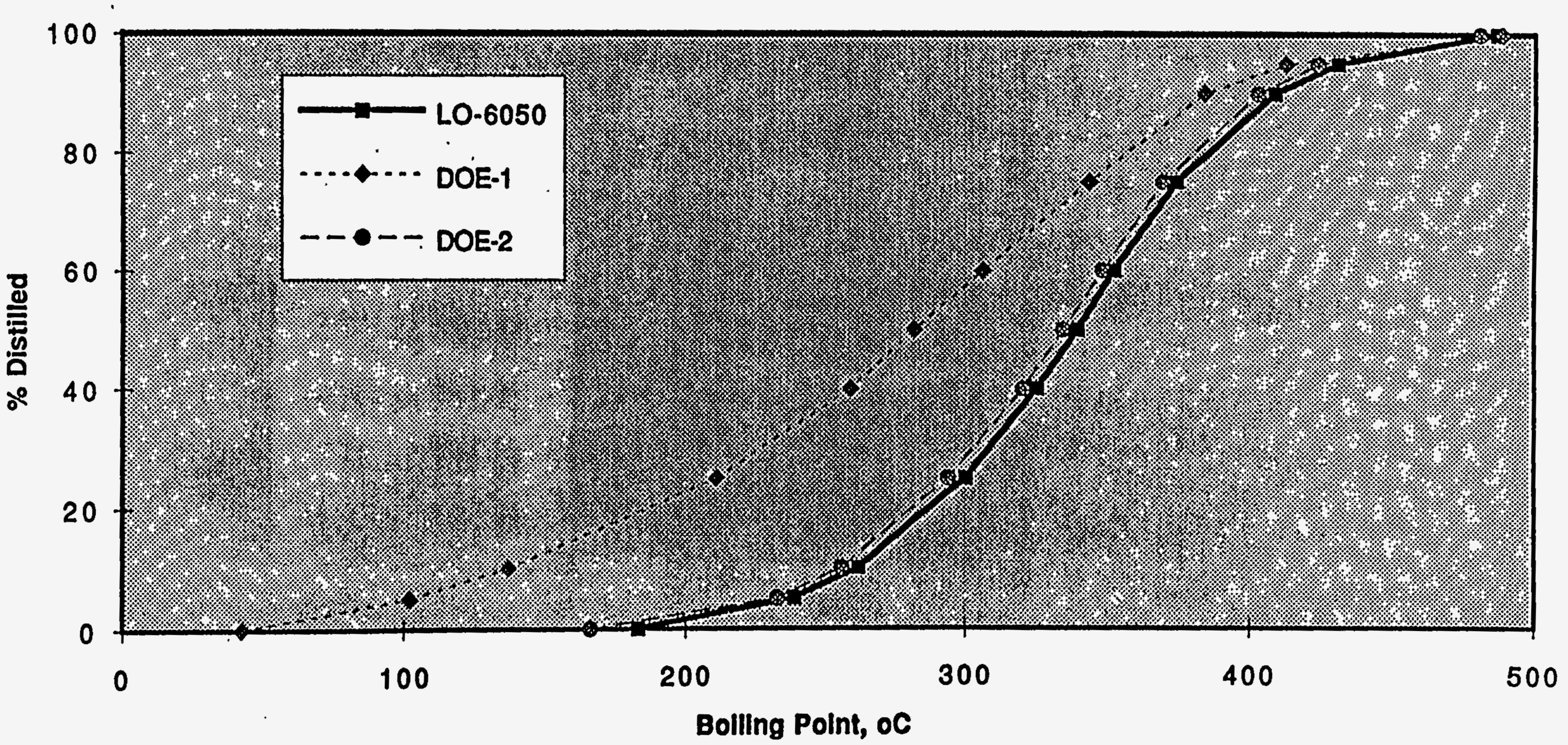
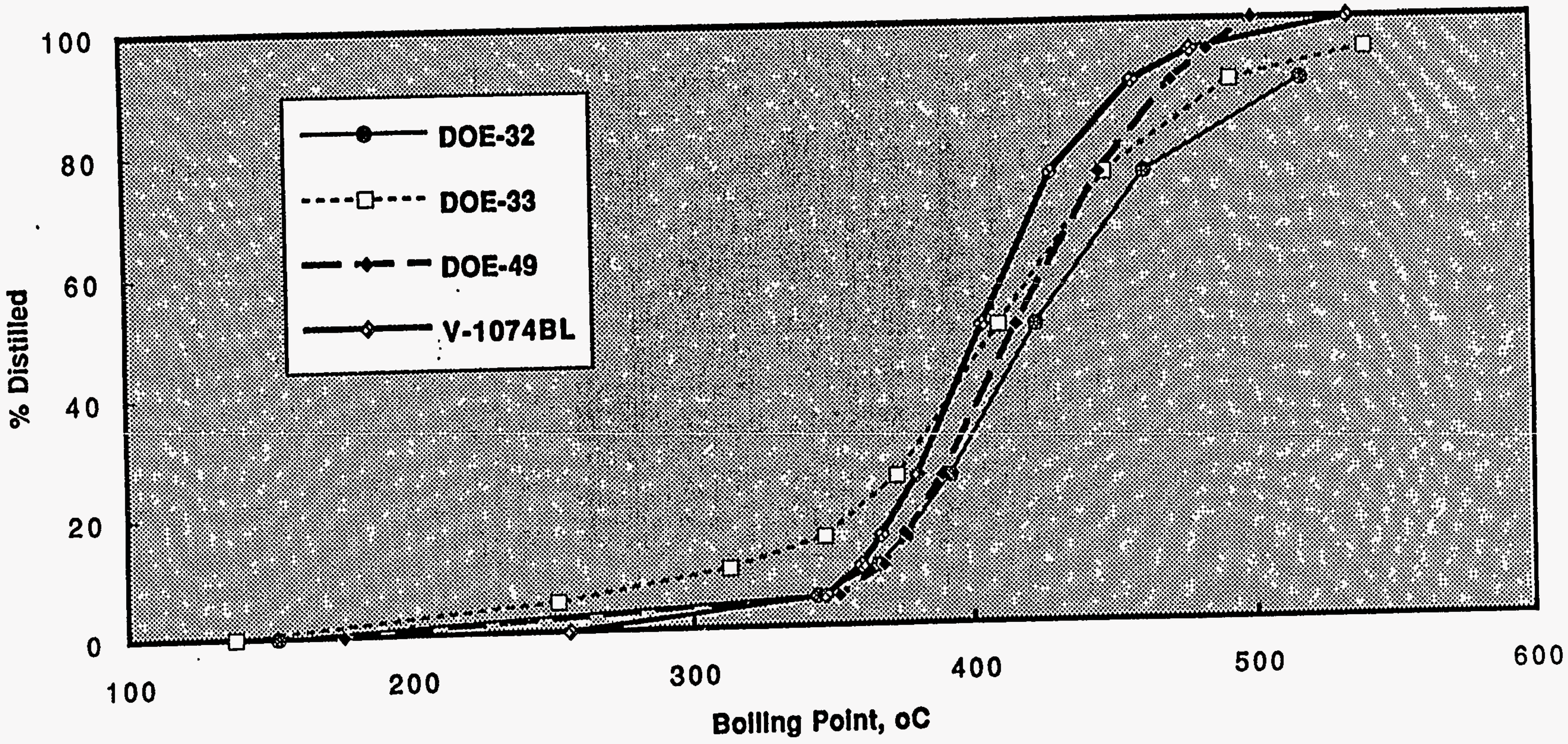


Figure 4.2.6 Stability of Solvent V-1074



gave almost stoichiometric quantities of product CO_2 and hydrogen.

4.2.2.1.4 Illinois #6, LO-6282 and LO-6305

No stability tests were performed on LO-6282. However, the stability of LO-6305 was found to be similar to Black Thunder solvents in two stage conditions (DOE-65). This can be seen in Figure 4.2.7.

4.2.2.2 Matrix Tests

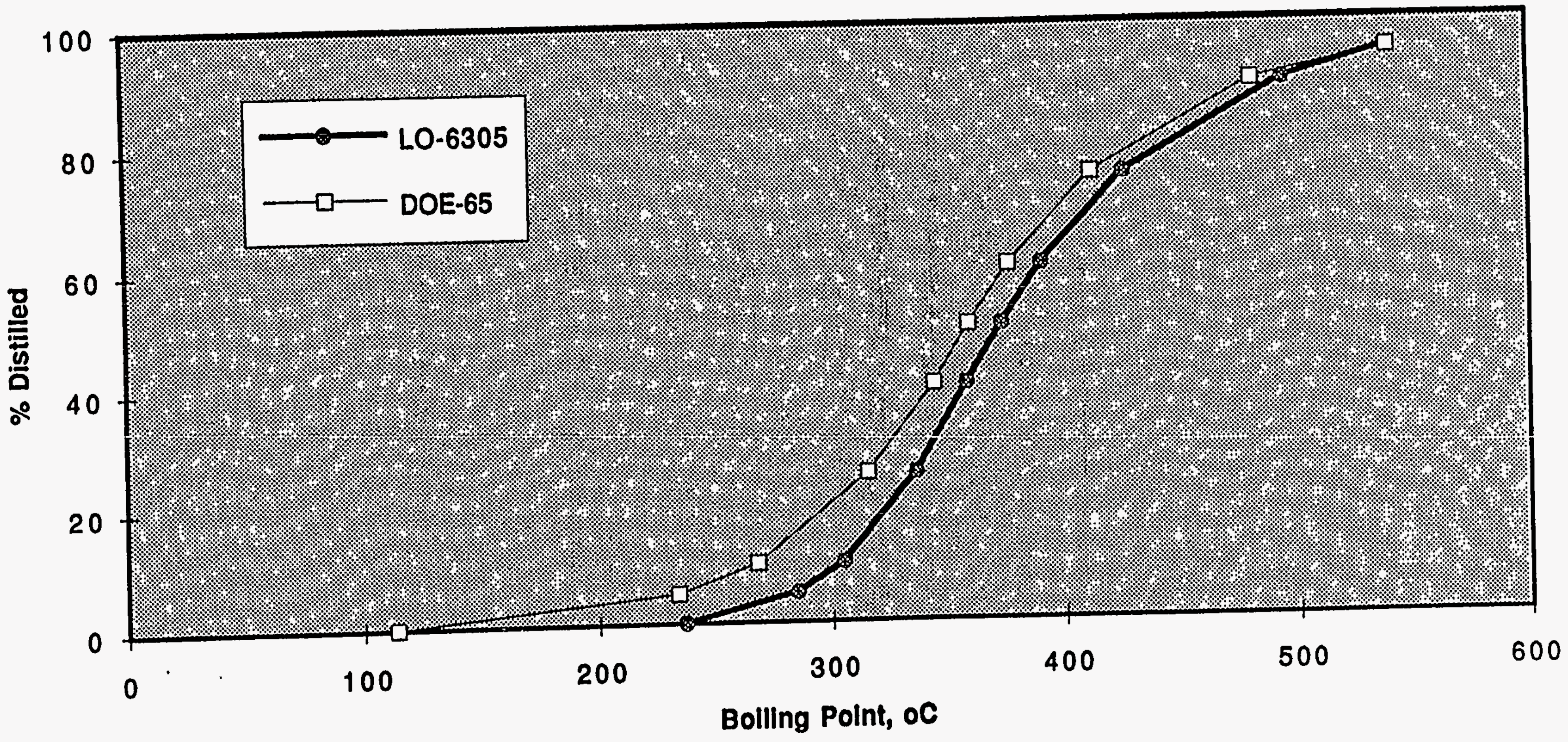
Previous work at the ARC had identified process conditions for the liquefaction of Alberta subbituminous coals in a variety of solvents. Also, a wealth of literature has indicated the preferred ranges for process variables for solubilization of U.S. coals using the CO/steam system. Using this information the following coded variables were selected to investigate the liquefaction of Black Thunder coal.

Variable	Code	+1	0	-1
Temperature, °C		410	390	370
Pressure (initial), psi CO		800	600	400
Time, minutes at temperature		60	30	0

Constants		
shift catalyst	potassium carbonate	
coal:solvent ratio (wt)	1:1.5	i.e. 40% coal
water:CO ratio (wt)	0.9:1	plus moisture in coal
charge coal	80 g	as received
solvent	120 g	

A Box-Behnken experimental design matrix was selected to test the 3 variables. This

Figure 4.2.7 Stability of Solvent LO-6305



experimental matrix is depicted in Figure 4.2.8. It required 12 experiments shown on the edge of a cube plus a centre point. Ideally each experiment should be duplicated, but the time and cost involved made this impractical. The centre point was repeated in triplicate to determine reproducibility. Ultimately additional tests were required to replace experiments which experienced difficulties during operation or work-up, or which had excessive deviation from a predicted value. Results for the matrix tests are presented in Table 4.2.2.

The original group of 15 experiments generally proceeded without problems except for DOE-12 and DOE-18. The gas sample for DOE-12 was contaminated. During DOE-18 a leak developed and the run was aborted and was replaced by the equivalent DOE-18-1. Coal conversions are shown in Figure 4.2.9. It can be seen that the coal conversion increased as the temperature and time factors are raised. The reproducibility was very good for the centre point, at 83 ± 1%. Linear and quadratic fits were performed for the data (Table 4.2.3). The linear model gave a poor fit for the centre point but identified that temperature was the prime variable in process performance. Pressure had very little effect on coal conversion. The quadratic model gave an improved fit and indicated that interaction between variables were important especially the $T * P$ and $T * t$ terms.

As a result of the statistical analysis several conditions were selected to determine reproducibility and to confirm data. The selections were made to determine reproducibility (DOE-19), to confirm suspect results (DOE-20, 21, 24) and to see if the model could predict the severity required to achieve the maximum conversion. A maximum was observed when a three dimensional surface plot was made relating coal conversion to the temperature and time variables (Figure 4.2.10). This observation was largely dependent on the result for DOE-14 since it had a relatively low coal conversion despite having the most severe matrix operating conditions. It was postulated that the high severity may have led to coke formation which would give a false low impression of coal conversion (see later).

Table 4.2.2: Matrix Tests Results

Run #	T	P	t	Conversion, %		H2 Cons	Severity
				Coal	CO	g/100g	
DOE-04	1	-1	0	76	84	1.3	3.61
DOE-05	1	1	0	89	83	2.1	3.61
DOE-06	0	0	0	83	79	1.6	1.11
DOE-07	0	1	1	85	84	2.1	2.21
DOE-08	-1	0	-1	34	33	0.9	0.105
DOE-09	-1	1	0	44	70	1.4	0.32
DOE-10	0	-1	1	76	74	1.3	2.21
DOE-11	0	-1	-1	62	42	0.6	0.037
DOE-12	0	0	0	84	73	0.1	1.11
DOE-13	1	0	-1	74	64	1.1	0.12
DOE-14	1	0	1	73	87	1.7	7.22
DOE-15	-1	-1	0	63	71	1.2	0.32
DOE-16	-1	0	1	69	65	1.2	0.64
DOE-17	0	0	0	81	79	2.1	1.11
DOE-18-1	0	1	-1	63	51	1.3	0.037

Temperature -1 = 370 0 = 390 +1 = 410 C
Pressure -1 = 400 0 = 600 +1 = 800 psi CO intial
Time -1 = 0 0 = 30 +1 = 60 minutes

Table 4.2.3: Matrix Program Statistical Evaluation

					INITIAL				REVISED		
RUN #	T	P	t		COAL CONV %	FITTED Y	RESIDUAL		COAL CONV %	FITTED Y	RESIDUAL
DOE-04	1	-1	0		76	82.6	-6.6		76	78.7	-2.7
DOE-05	1	1	0		89	83.6	5.3		89	87.7	1.3
DOE-06	0	0	0		83	70.4	12.6		83	73.2	9.8
DOE-07	0	1	1		85	79.6	5.3		85	87.7	-2.7
DOE-08	-1	0	-1		34	48.9	-14.9		34	53.2	-19.2
DOE-09	-1	1	0		44	58.1	-14.1		76	67.7	8.3
DOE-10	0	-1	1		76	78.6	-2.6		76	78.7	-2.7
DOE-11	0	-1	-1		62	61.1	0.8		62	58.7	3.3
DOE-12	0	0	0		84	70.4	13.6		84	73.2	10.8
DOE-13	1	0	-1		74	74.4	-0.4		74	73.2	0.8
DOE-14	1	0	1		73	91.9	-18.9		83	93.2	-10.2
DOE-15	-1	-1	0		63	57.1	5.8		63	58.7	4.3
DOE-16	-1	0	1		69	66.4	2.6		69	73.2	-4.2
DOE-17	0	0	0		81	70.4	10.6		81	73.2	7.8
DOE-18-1	0	1	-1		63	62.1	0.9		63	67.7	-4.7

	INITIAL	REVISED
LINEAR	12.7T + 0.5P +8.7t + 70.4	10T +4.5P + 10t + 73.2
R2	.5800	.6598
QUADRATIC	82.7 + 12.7T + 0.5P + 8.7t + 8T*P - 9T*t + 2P*t - 11T**2 - 2.8P**2 - 8.3t**2	82.6 + 10T + 4.5P + 10t - 6.5T*t + 2P*t - 6.6T**2 - 0.1P**2 - 11.1t**2
R2	.9813	.9466

Figure 4.2.8: Experimental Matrix

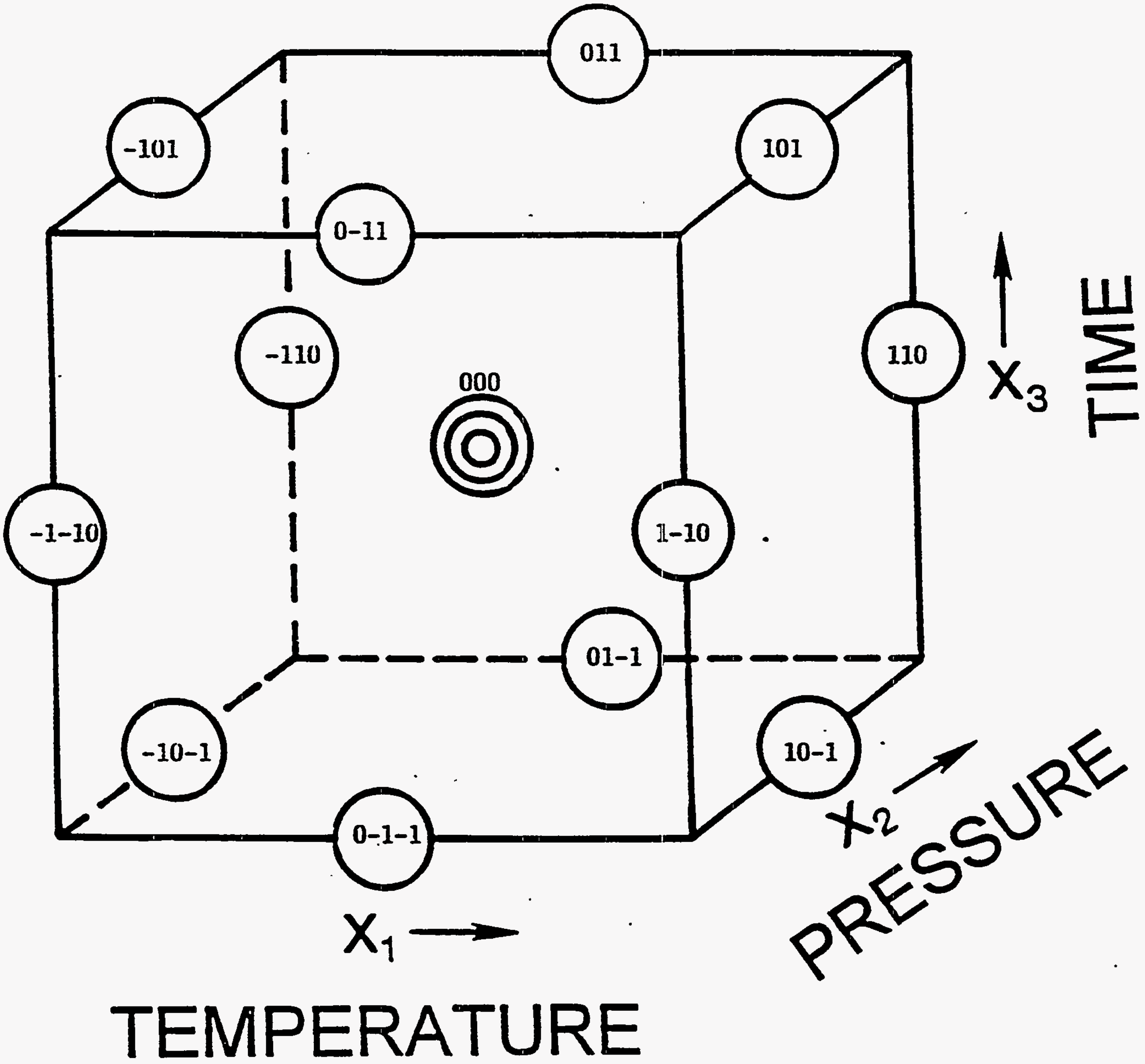


Figure 4.2.9: Matrix Tests - Coal Conversion

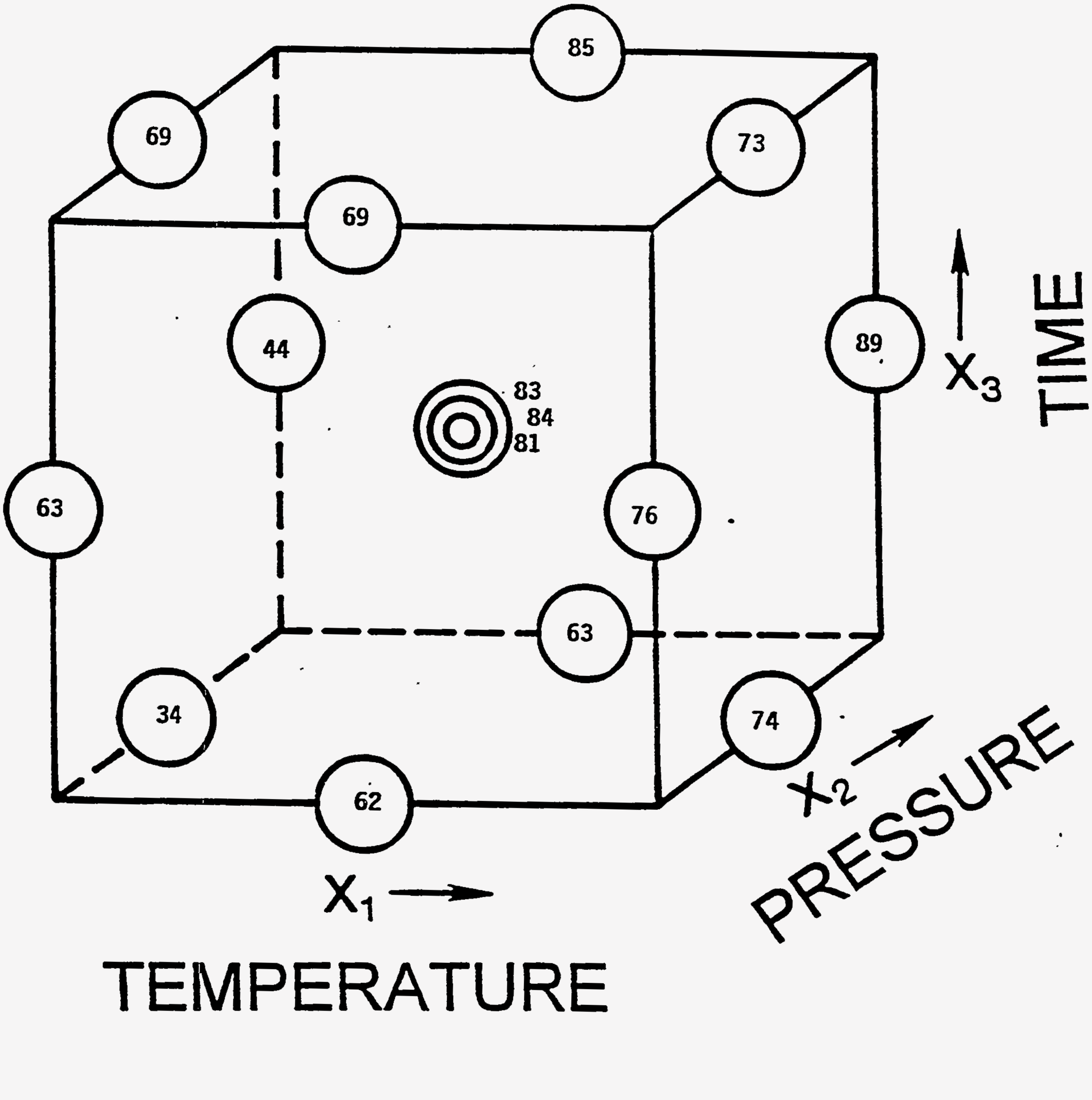
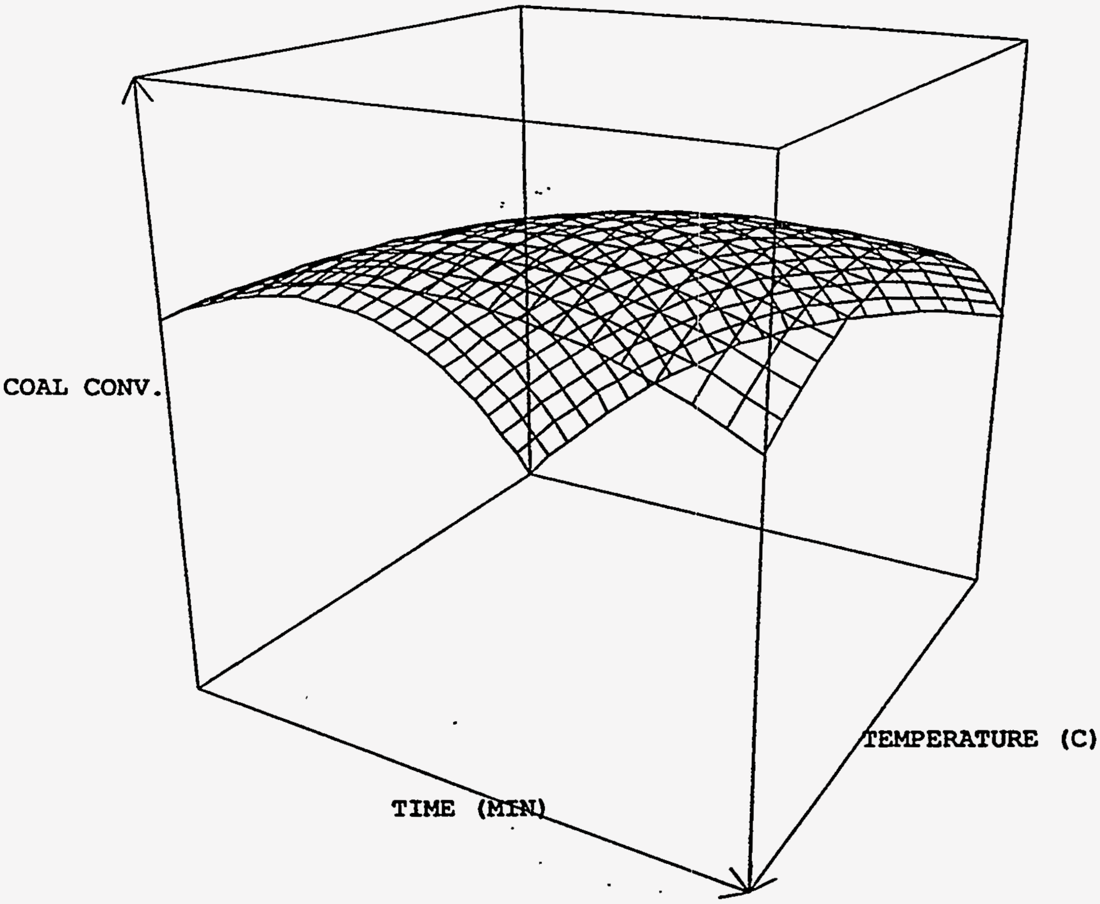


Figure 4.2.10: Coal Conversion - Temperature/Time Function



The reproducibility of the data for the repeat of DOE-05 was excellent both for coal conversion (89% in each case) and CO conversion. Gas production and hydrogen consumption did not compare quite as favourably. Also, the run where agglomerated coal was substituted for as received coal (DOE-24) confirmed the repeatability of the centre point for coal and CO conversion. The two runs which had proven suspect produced widely different coal conversion results when repeated. This was surprising since all measured gas parameters were comparable, i.e. for runs DOE-09, 20 and 23 CO conversion was 67 ± 3%, gas yield 0.5 ± .1 g/100g and hydrogen consumption 1.3 ± 0.1 g/100g. Similar variances were observed for DOE-14 and its repeat DOE-21.

Petrographic examination of the residue from DOE-14 suggested that there might have been mixing problems during the autoclave operations. The repeat value was, therefore, substituted for the matrix evaluation. Since the coal conversions for the repeats were close, and much higher than for DOE-09 it was decided to insert the medium value (76%) into the matrix. The revised statistical evaluation treatment improved the fit for the quadratic model. The linear fitted y values still indicated that the widest deviation occurred at the extremes of process severity , i.e. DOE-08 and DOE-14.

In other measures of process performance related to product gas composition the process severity (temperature and time) also was the determining factor (Figures 4.2.11 - 4.2.13). CO conversion rose in all cases with increased temperature at constant time and pressure, and with increased time at constant pressure and temperature. The trend for the pressure factor appeared to be less well defined, in some cases CO conversion as a percentage of the input rose with higher pressure and other times it was unchanged. The actual moles of CO converted are also included in Figure 4.2.14. These data are also presented in Figure 4.2.15 as a function of process severity. This plot shows that the conversion of the CO reaches a maximum or equilibrium value at a severity index of less than 1, irrespective of the initial CO pressure, however, the maximum is dependent on initial CO pressure (for definition of severity index see page 171).

Figure 4.2.11: CO Conversion

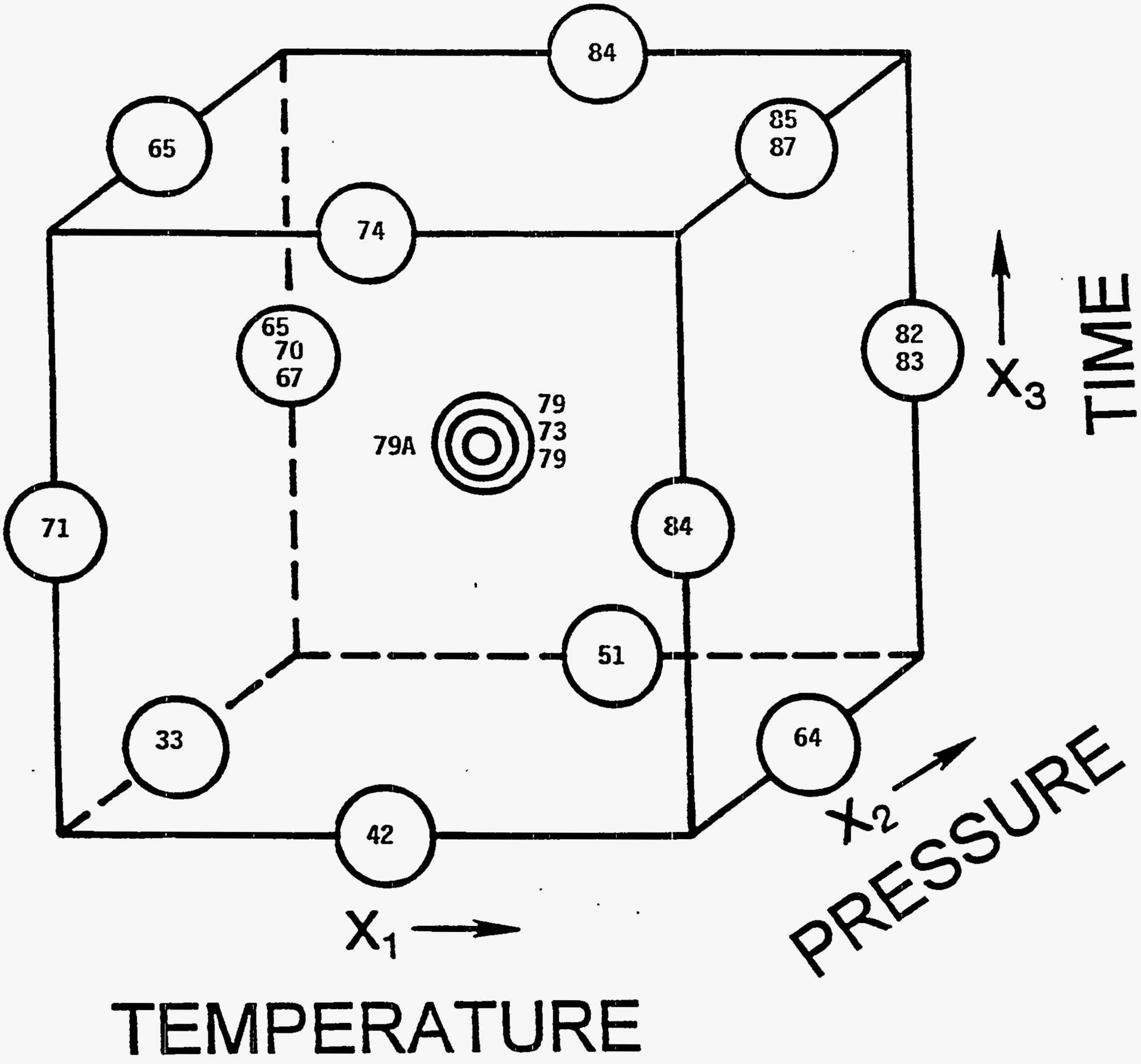


Figure 4.2.12: Gas Yield

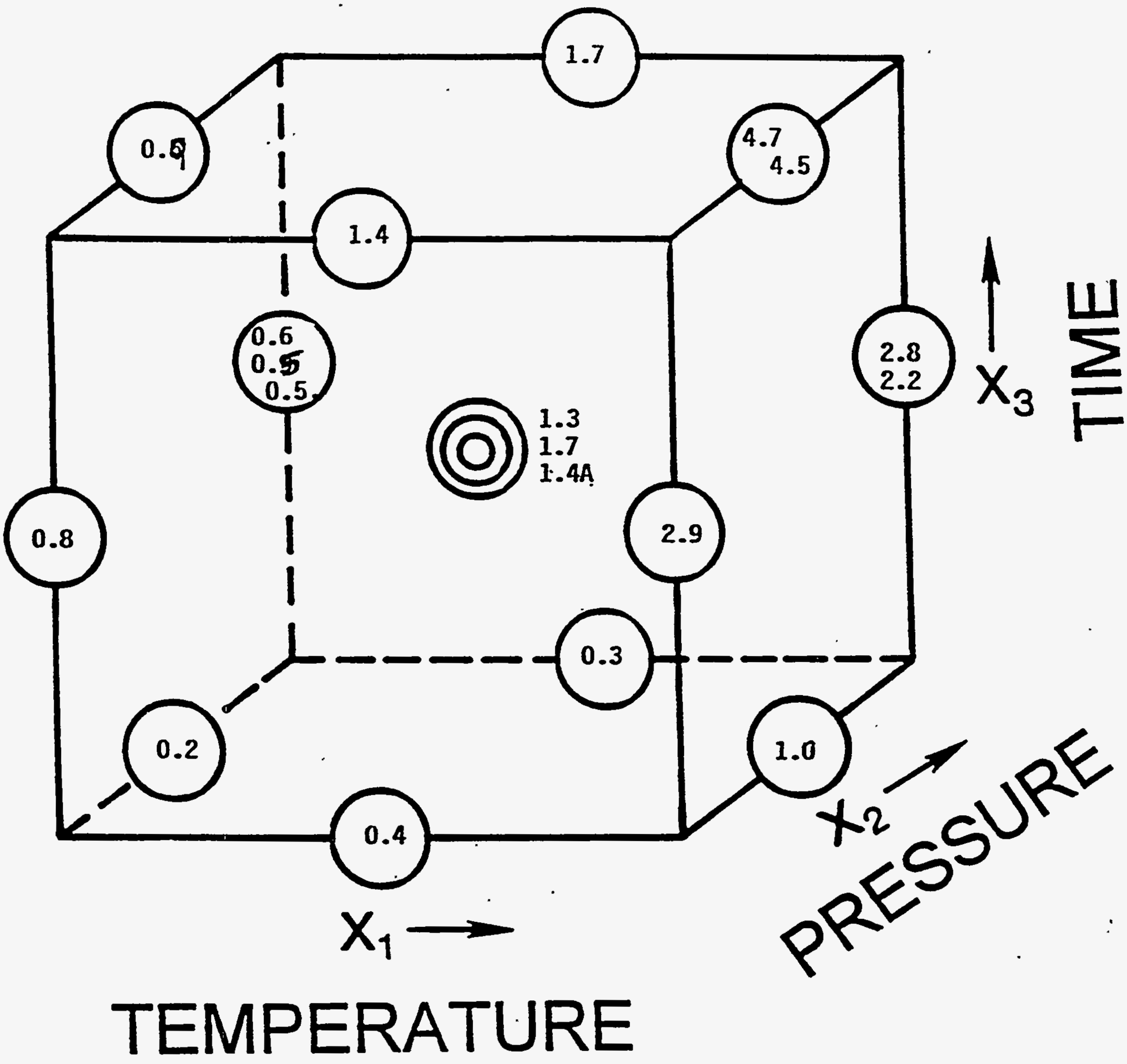


Figure 4.2.13: Hydrogen Consumption

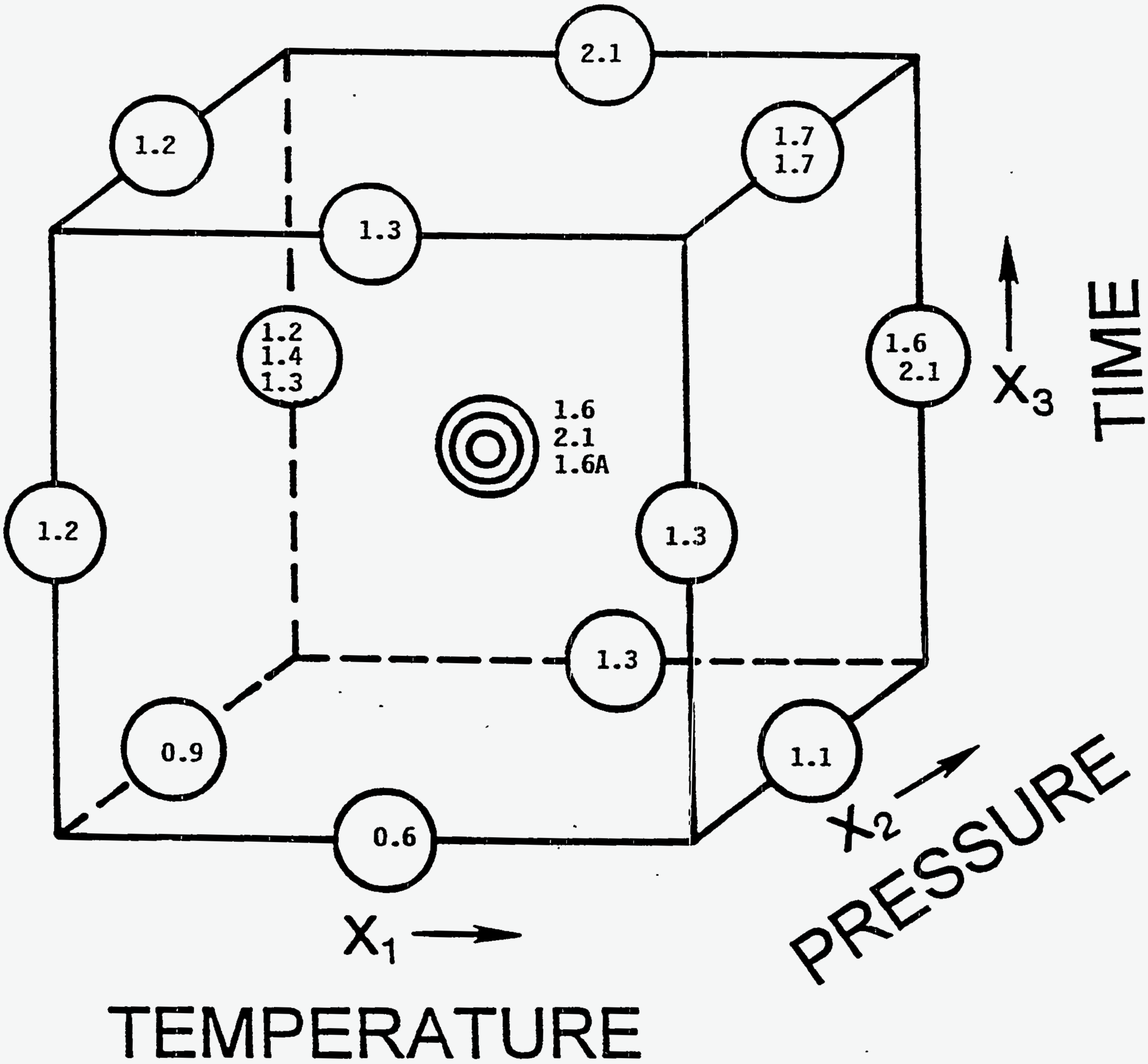


Figure 4.2.14: Moles of CO Converted

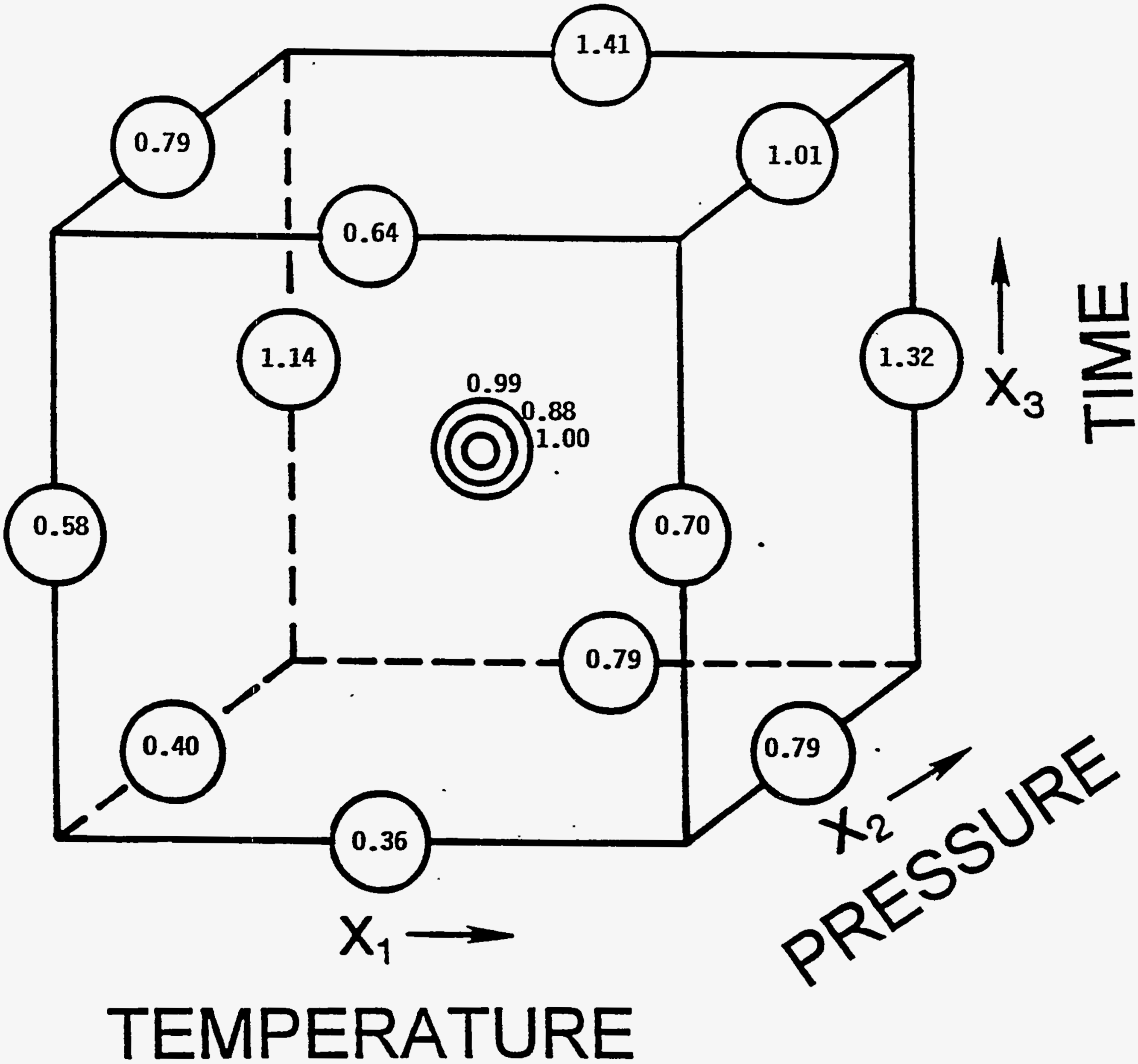
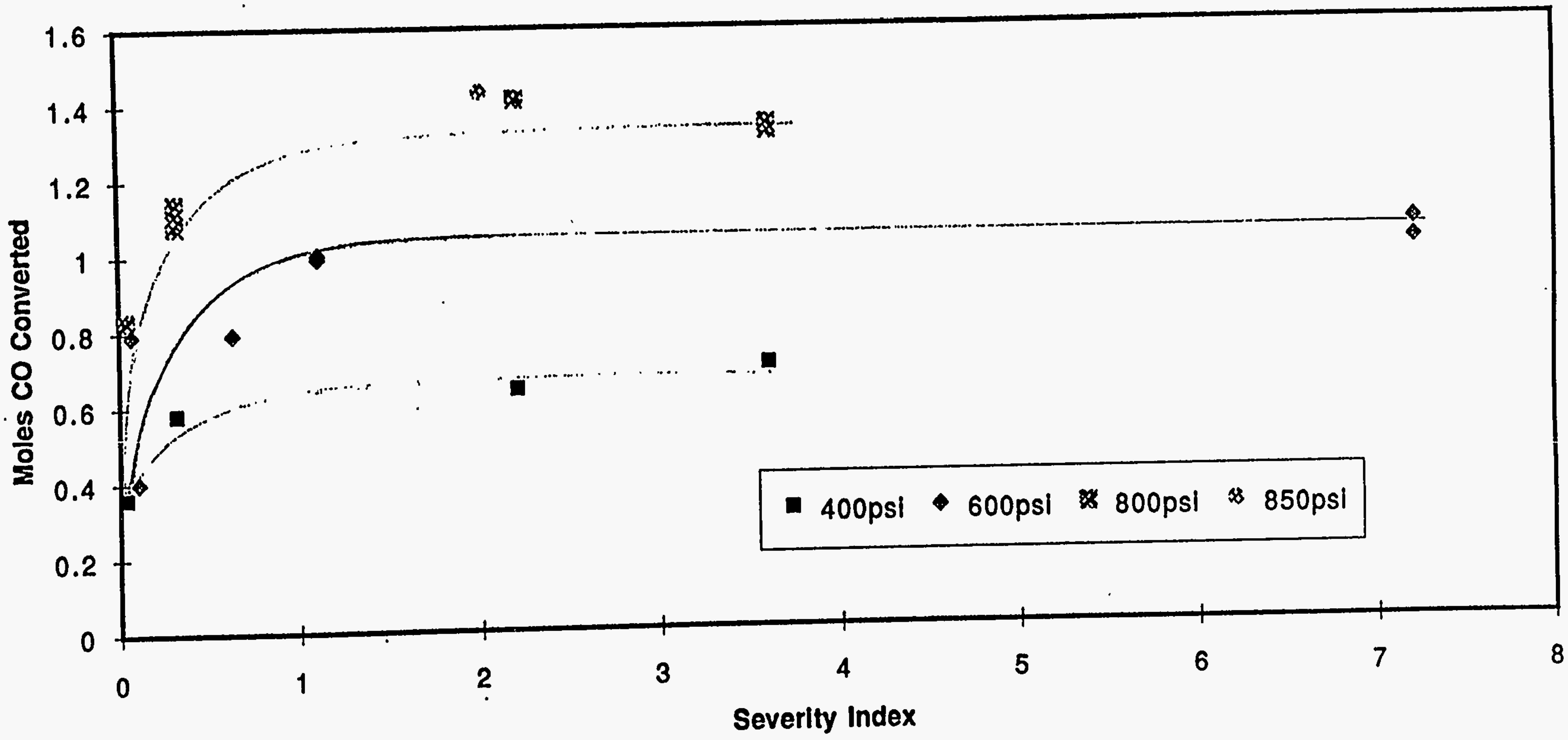


Figure 4.2.15 CO Conversion as a Function of Severity



Hydrocarbon gas production increases linearly when plotted against the severity index, with a R^2 value = .95 (Figure 4.2.16). This is consistent with first order kinetics for the thermal reaction of coal to gas. The y intercept of 0.5 can be attributed to gas production from the solvent (n 0.3 g/100g coal) plus the thermal decomposition of the coal during the heat up period. There was no effect due to pressure as can be seen from the matrix diagram (4.2.12).

Hydrogen consumption, determined as the difference between CO converted and hydrogen produced, followed the trends seen with CO conversion. The data are a little more scattered, but there is obviously higher hydrogen consumption at 800 psi than at lower initial CO pressures (Figure 4.2.17). Also the consumption reached its maximum at a severity of less than one. Absolute hydrogen consumption was generally less than 2 g/100g MAF coal. This consumption level was associated with the solubilization step and additional hydrogen consumption was needed for hydrocracking (hydroprocessing) step.

The run at the conditions selected from the initial matrix results (DOE-22) did not meet its objective of the highest coal conversion. The predicted result from the quadratic equation was 91%, which was 10% more than was actually achieved. The gas analysis and stoichiometry data have been included in the graphical presentations of the matrix results. Although only single points, each value was within the expected range for CO conversion, hydrocarbon gas production and hydrogen consumption.

The matrix results suggested that there may have been retrogressive reactions leading to coke formation at high severities. The presence of coke can be determined by petrographic examination of the residues following extraction with solvent. No coke was observed in any residues except for a single fragment in DOE-5 residue (see Section 4.5 for a complete report of the petrographic analysis).

Figure 4.2.16 Hydrocarbon Gas Yield as a Function of Severity

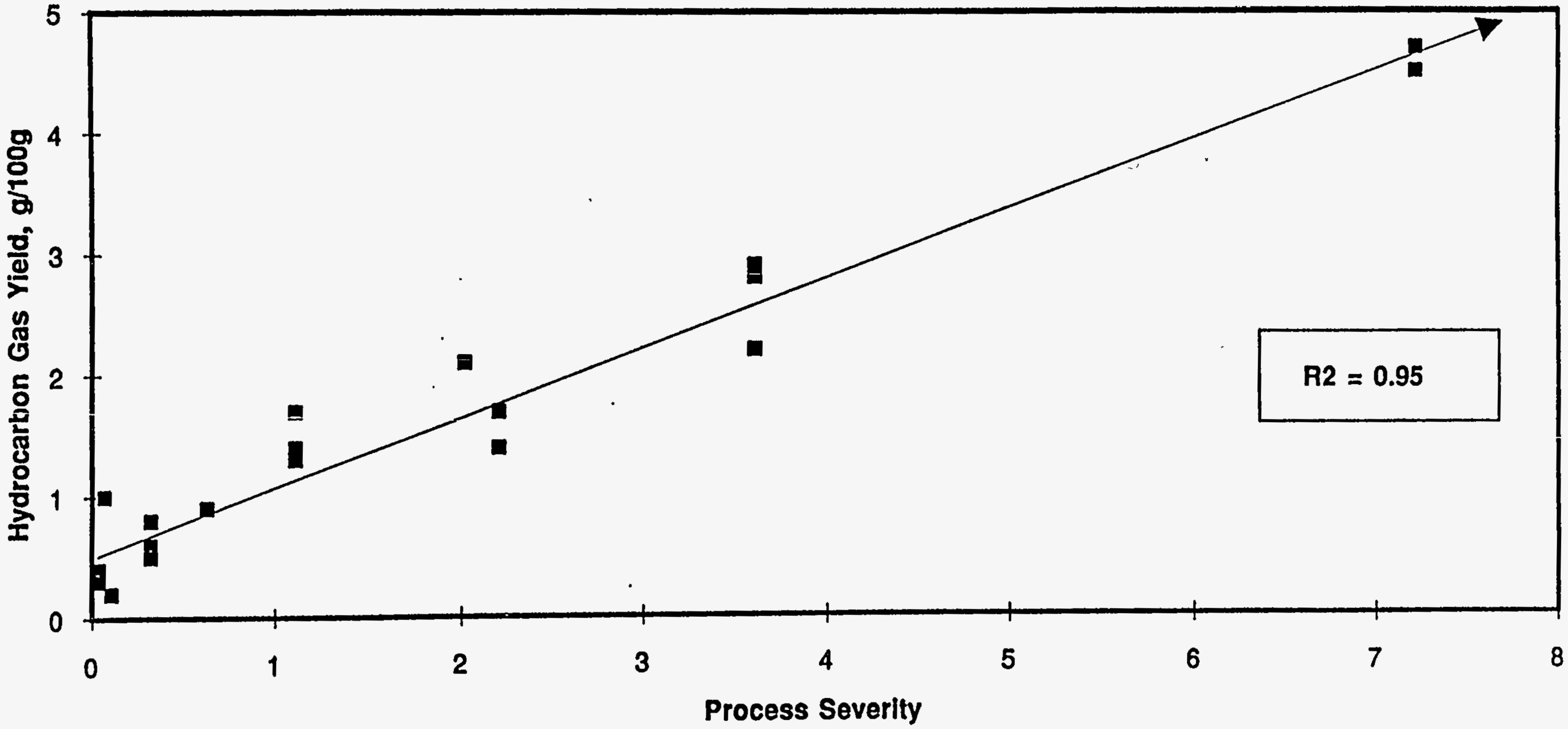
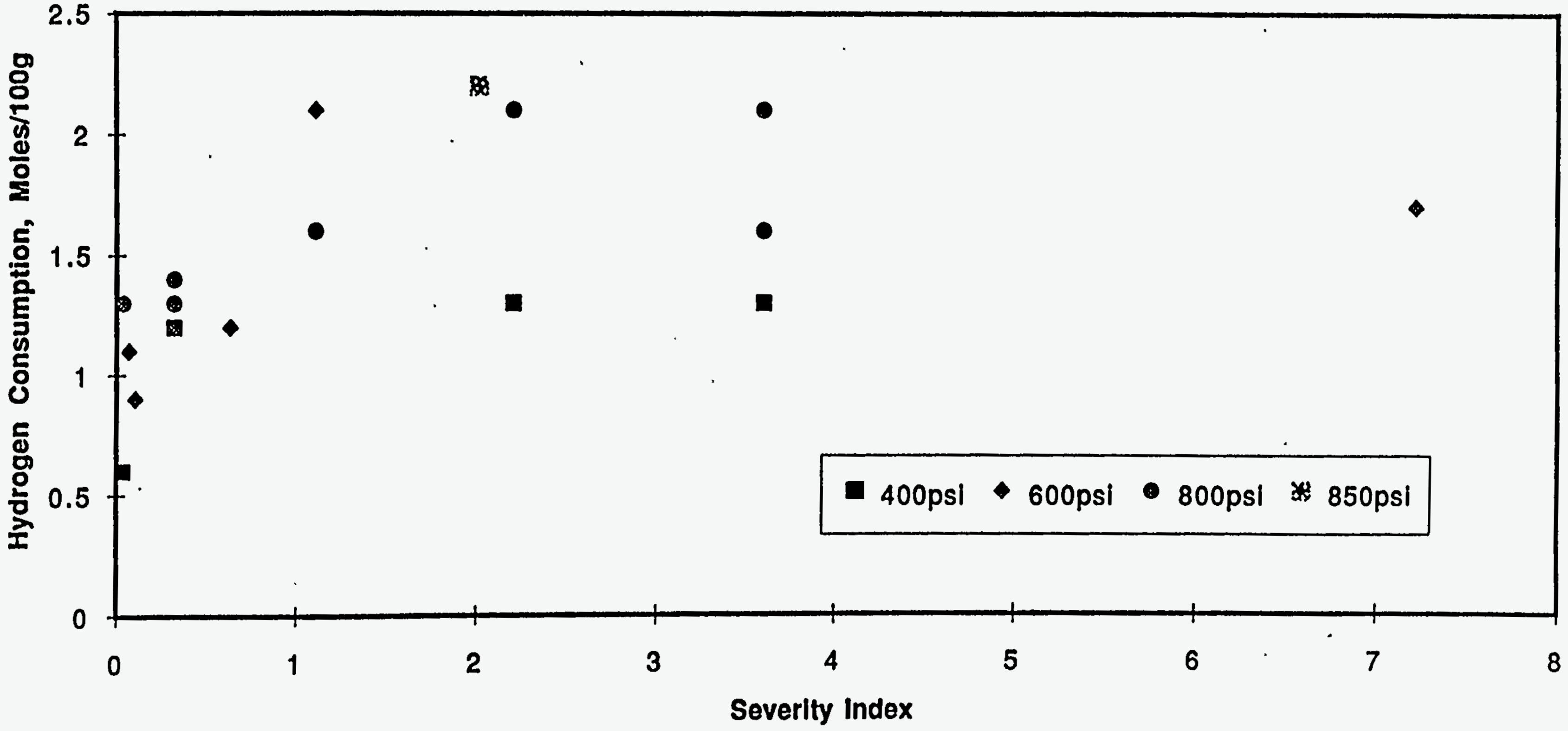


Figure 4.2.17 Hydrogen Consumption as a Function of Severity



The last experiment (DOE-24) in this section used deashed coal generated by a coal/oil agglomeration procedure (Section 4.1). Test conditions duplicated those of the centre point of the matrix program, i.e. 390°C/600 psi/30 minutes. The deashing process had reduced the ash and moisture levels in the agglomerated coal to 6.5% (dry basis) and 4.9%, respectively. The V-178 +320 solvent was employed as the binding oil in the agglomeration step. The deashed coal performed almost identically to the raw crushed coal with respect to coal conversion 83%, CO conversion 79%, hydrogen gas production 1.4 g/100g and hydrogen consumption 1.6 g/100g. The agglomeration procedure, therefore, had no detrimental effect on process performance and might improve process operability by eliminating part of the coal ash. The deashing process was not optimized, but it appeared unlikely that a major benefit could be acquired from coal/oil agglomeration of this low ash Black Thunder coal. The dewatering which was an additional accomplishment of the agglomeration step was of less importance in the two stage process which required added water for the CO/H_2O shift reaction.

The product oils from the matrix tests were characterized by atmospheric and vacuum distillation. As described in the experimental procedure, these techniques proved ineffective and did not give reproducible results. For completeness the data are presented in Table 4.2.4. The oils are separated into distillable oils (-524°C) and non-distillable oils (soluble in THF). Both values were derived from the distillation data after subtraction of the solvent distillable and non-distillable fractions, which were assumed to remain unchanged. The only inference that can be drawn from the oil distribution data is that the majority of the coal is solubilized as non-distillable oils. Also, it is likely that there is a net negative production of distillable oils in most runs indicative of regressive reactions involving the solvent.

Table 4.2.4: Matrix Tests Results - Oil Yield

Run #	T	P	t	Distillable Oil g/100g	Non-Distillable Oil g/100g
DOE-04	1	-1	0	-29.3	84.3
DOE-05	1	1	0	20.1	52.7
DOE-06	0	0	0	-2.5	74.5
DOE-07	0	1	1	14.3	67.6
DOE-08	-1	0	-1	-22.1	53.8
DOE-09	-1	1	0	-0.5	44.2
DOE-10	0	-1	1	-11.4	74.3
DOE-11	0	-1	-1	4.2	60.9
DOE-12	0	0	0	-9.7	92.6
DOE-13	1	0	-1	-9.1	79.2
DOE-14	1	0	1	-30	82.8
DOE-15	-1	-1	0	-38.6	83.6
DOE-16	-1	0	1	-25.2	89.9
DOE-17	0	0	0	-29.4	97.3
DOE-18-1	0	1	-1	-31.8	81.6

Temperature -1 = 370 0 = 390 +1 = 410 C
Pressure -1 = 400 0 = 600 +1 = 800 psi CO initial
Time -1 = 0 0 = 30 +1 = 60 minutes

4.2.2.3 Effects of Catalyst and Gas Composition, V-178 +320 Solvent

Potassium carbonate is one of the most effective WGSR catalysts as determined from earlier ARC work and literature information. Its effectiveness was compared with another shift catalyst, sodium aluminate, and an iron based catalyst, FeS and with no catalyst (Table 4.2.5, Figure 4.2.18). Very little CO conversion occurred without a catalyst or with FeS. Only aluminate gave enhanced CO conversion, although much less than K_2CO_3. The results together with later work confirm the need for a base to promote the WGSR. Despite their inability to foster the WGSR, FeS catalyst or with no catalyst comparable coal conversions to those found with effective shift catalysts were obtained. Thus, the coal solubilization step and hydrocarbon gas production are more a function of a thermal mechanism rather than CO conversion. The rider to the statement is that the presence of CO is definitely beneficial, as will be shown later.

There was a high dependence of hydrogen consumption on CO conversion. With K_2CO_3, the hydrogen consumption was close to 2g/100g MAF coal, almost double that with aluminate, while there was almost no hydrogen consumption in the absence of catalyst or with FeS. Therefore, in this system, coal conversion was not dependant on hydrogen consumption.

During the matrix tests it was observed that the quantity of CO_2 produced always exceeded that anticipated from the stoichiometry of the WGSR. In the catalyst tests this equated to about 0.6 moles/100g MAF coal and was independent of CO conversion. A similar tendency was also apparent with the reaction of water, although the data was more scattered. On average 0.45 moles/100g MAF coal of water were consumed in excess of that which reacted with the CO via the WGSR.

The effectiveness of carbon monoxide to enhance coal conversion was confirmed when the CO atmosphere was replaced by syngas or nitrogen as can be seen from Table 4.2.6 and Figure 4.2.19. In the inert nitrogen atmosphere only 50% of the coal

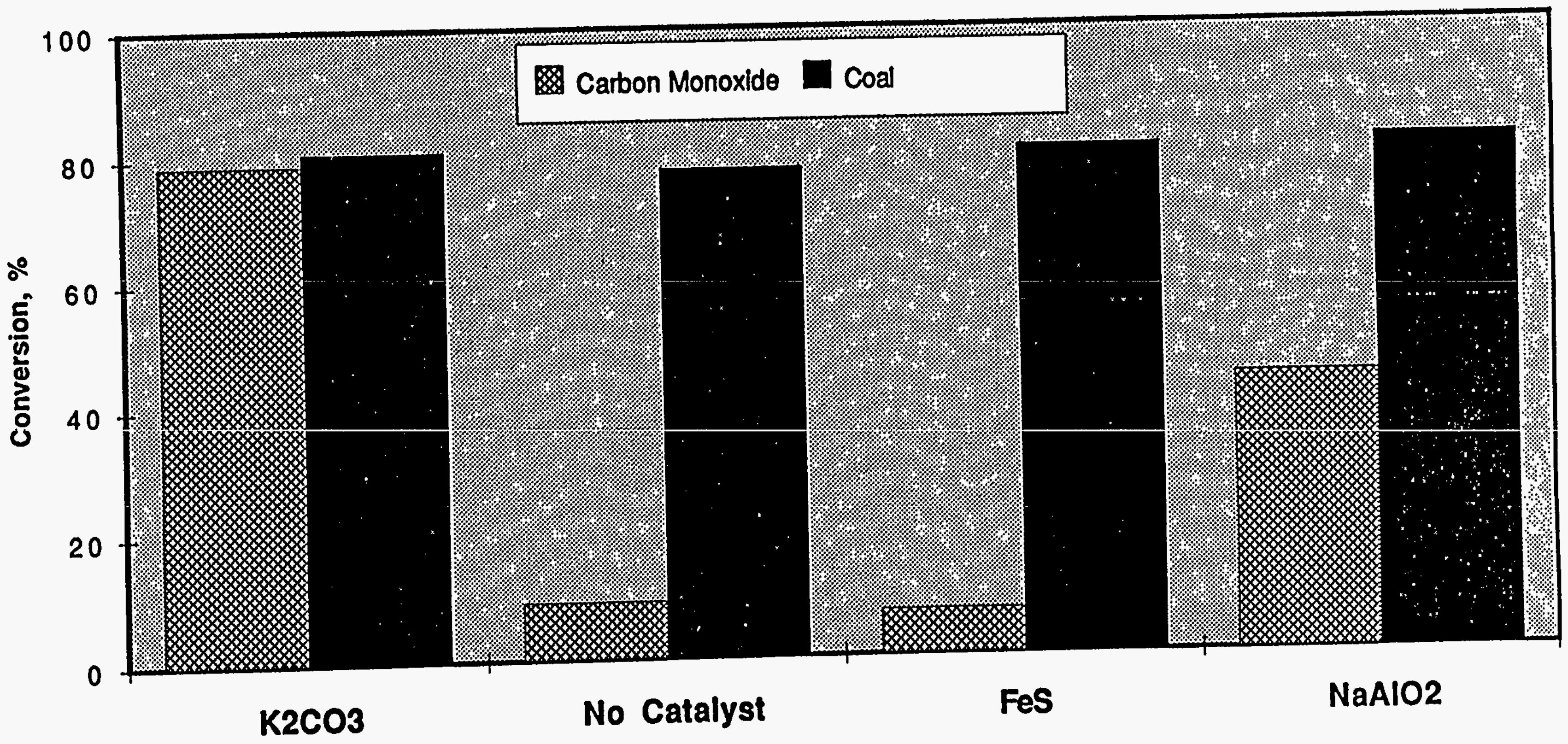
Table 4.2.5 Process Performance -- Catalysts

Run #	Catalyst	Conversion, %		HC Gas Yield	H2 Consum.
		CO	Coal	g/100g	g/100g
DOE-17	K_2CO_3	79	81	1.7	1.6*
DOE-25	No Catalyst	9	78	1.3	0.08
DOE-26	FeS	7	81	1.4	0.04
DOE-27	$NaAlO_2$	44	82	1.4	1.1

Process Conditions:		
	Temperature	390oC
	Pressure	600psi
	Time	30min

* Medium value for centerpoint runs used

Figure 4.2.18 Process Performance -- Catalysts



was converted, while the syngas (1:3 $CO:H_2$) and CO/N_2 (1:3) atmospheres were 10 - 15% below similar results with CO. In all cases the hydrocarbon gas yields were similar to those measured when using CO atmospheres, as was the excess H_2O consumption and CO_2 production. Replacing the CO by syngas (1:3, $CO:H_2$) would, therefore, result in less coal conversion in the coal solubilization stage. The effect of syngas are discussed in more detail in Section 4.2.2.6.

4.2.2.4 Process Severity, V-1074 Solvent

With the arrival of the V-1074 solvent several tests were completed to link the previous matrix program with the new solvent. At this point in the program the solvent solubility procedure was introduced for product work-up. Results of the matrix tests and V-1074 solvent tests are compared in Table 4.2.7.

At the three selected conditions the two solvents gave similar process performance in regard to coal conversion, CO conversion, hydrocarbon gas production and hydrogen consumption. The link between the tests using the two solvents was therefore established.

The majority of the coal was solubilized as asphaltenes and preasphaltenes (Table 4.2.8). There was a trend to lighter products as the process severity was raised, i.e. less preasphaltenes and more “oils +”. The asphaltenes also continued to increase with severity suggesting that the kinetics for preasphaltenes and asphaltenes was faster than for asphaltenes and “oils +”. This interpretation must be tempered by the poor reproducibility of the preasphaltene and “oils +” values at the same conditions, i.e. Runs DOE-34 and DOE-37.

Table 4.2.6 Process Performance -- Gas Composition

Run #	Gas Composition	Conversion, %		HC Gas Yield	H2 Consum.
		CO	Coal	g/100g	g/100g
DOE-17	100% CO	79	81	1.7	1.6*
DOE-29	1:3 CO : H2	83	74	1.7	0.2
DOE-30	1:3 CO : N2	90	68	1.6	1.0
DOE-31	100% N2	xx	50	1.6	0

Process Conditions:	Temperature	390oC
	Pressure	600psi
	Time	30min

* Median value from centerpoint runs used

Table 4.2.7 Solvent Comparison

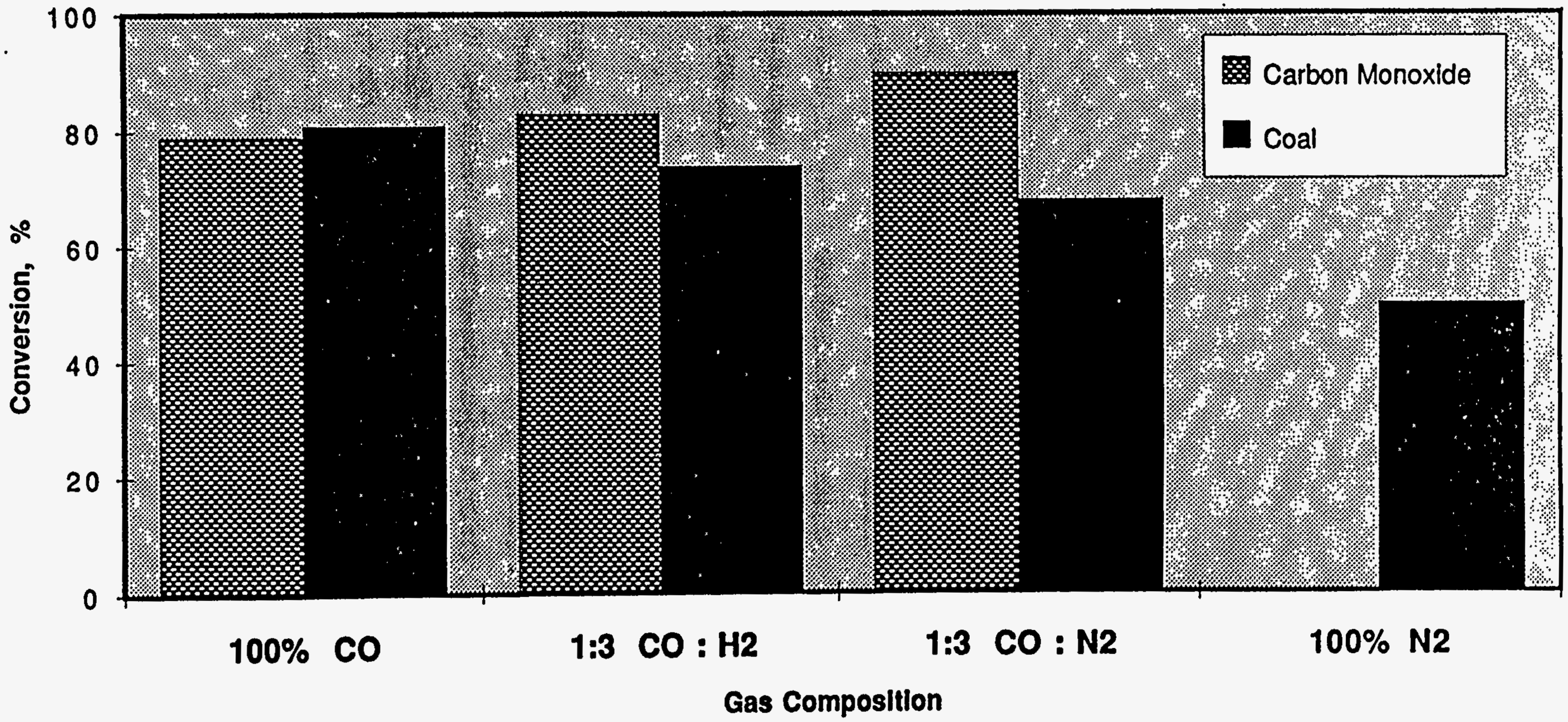
Run #	Solvent	Process Conditions			Conversion, %		HC Gas Yield	H2 Consum.
		T	P	t	CO	Coal	g/100g	g/100g
DOE-17	V-178 +320	0	0	0	79	81	1.7	1.6
DOE-34	V-1074				79	78	1.4	1.5
DOE-37	V-1074				80	82	1.4	1.6
DOE-05	V-178 +320	1	1	0	83	89	2.8	2.1
DOE-35	V-1074				82	88	3.0	1.9
DOE-15	V-178 +320	-1	-1	0	71	63	0.8	1.2
DOE-36	V-1074				70	61	0.8	1.2

Process Conditions:		-1	0	1
Temperature	oC	370	390	410
Pressure	psi	400	600	800
Time	minutes	0	30	60

Table 4.2.8 Process Severity -- Yield Distribution

Run #	Solvent	Severity	Coal Conv.	Oils+	Asphaltenes	Preasp.
			%	g/100g	g/100g	g/100g
DOE-36	V-1074	0.32	61	5.5	32.1	22.7
DOE-34	V-1074	1.11	78	19.1	48.2	9.4
DOE-37	V-1074	1.11	82	10.7	45.5	24.4
DOE-35	V-1074	3.61	88	19.3	55.0	10.8

Figure 4.2.19 Process Performance -- Gas Composition



4.2.2.5 Catalyst Activity, V-1074 Solvent

In the bench unit program several iron and molybdenum based second stage catalysts were introduced into the coal/solvent feed slurry prior to the first stage. If these catalysts were also active as shift catalysts then the aluminate or carbonate catalyst could be eliminated from the system. The earlier test without catalyst or basic salts had proven that coal conversion could be maintained without an accompanying high CO conversion. The quality of the resulting solubilized coal could now be assessed by solubility classes.

As before all the iron and molybdenum additives proved ineffective as WGSR catalysts (Table 4.2.9). Coal conversion was largely maintained but showed a tendency to decline with reduced CO conversion (Figure 4.2.20). Hydrocarbon gas production remained constant even though the coal conversions ranged from 73 - 82%. Apart from the result with potassium carbonate, the excess CO_2 was also consistent at about 0.7 moles/100g MAF coal, similar to the V-178 +320 tests. These tests confirmed that much of the process chemistry was decided by thermal rather than catalytic effects during the coal solubilization step. The key to the overall performance was the nature of the solubilized coal.

The solubility class analysis indicated that there were potentially major differences in the product state between the iron and molybdenum additives (Table 4.2.10, Figure 4.2.21). Using DOE-34 as the baseline case, the addition of ammonium tetrathiomolybdate (ATM) in combination with K_2CO_3 led to a small improvement in "oils +". In the absence of K_2CO_3, but with ATM, the yield of oils + was reduced but still substantial, i.e., 12.0 g/100g MAF coal. However, the ammonium molybdate (moly) did not upgrade any of the asphaltenes/preasphaltenes to oils +. This may have been the result of the lack of an active molybdenum species although carbon disulphide had been added. The high concentration of water in the system may have suppressed the formation of active molybdenum sulphide species. With the iron catalysts, which are

Table 4.2.9 Process Performance -- Catalysts, V-1074

Run #	Catalyst	Conversion, %		HC Gas Yield	H2 Consum.
		CO	Coal	g/100g	g/100g
DOE-34	K2CO3	79	78	1.7	1.6
DOE-51	K2CO3/ATM	79	80	1.4	1.5
DOE-53	ATM	6	73	1.3	-0.1
DOE-58	Fe2O3/CS2	20	80	1.5	0.5
DOE-59	Moly/CS2	20	75	1.5	0.3
DOE-68	Pyrite	17	77	1.5	0.3
DOE-69	Fe2O3/S	25	80	1.5	0.3

Process Conditions:	Temperature	390oC
	Pressure	600psi
	Time	30min

Table 4.2.10 Catalyst Tests -- Yield Distribution

Run #	Catalyst	Coal Conv.	Oils+	Asphaltenes	Preasp.
		%	g/100g	g/100g	g/100g
DOE-34	K2CO3	78	19.1	48.2	9.4
DOE-51	K2CO3/ATM	80	22.5	37.4	18.6
DOE-53	ATM	73	12.0	39.1	20.4
DOE-58	Fe2O3/CS2	80	0.3	42.9	34.8
DOE-59	Moly/CS2	75	0.3	46.2	26.6
DOE-68	pyrite	77	-1.7	35.8	41.3
DOE-69	Fe2O3/S	80	2.6	39.1	36.0

Figure 4.2.20 Process Performance -- Catalysts

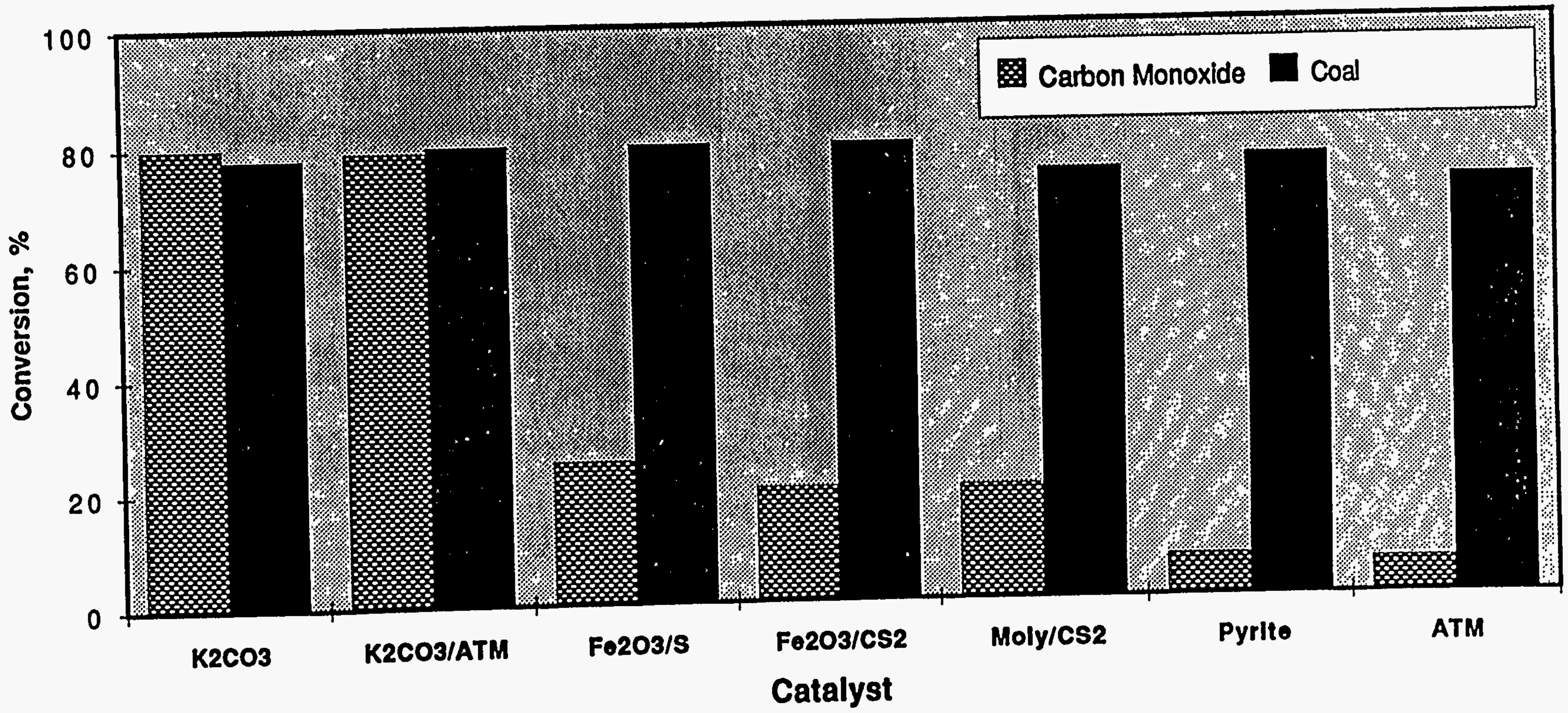
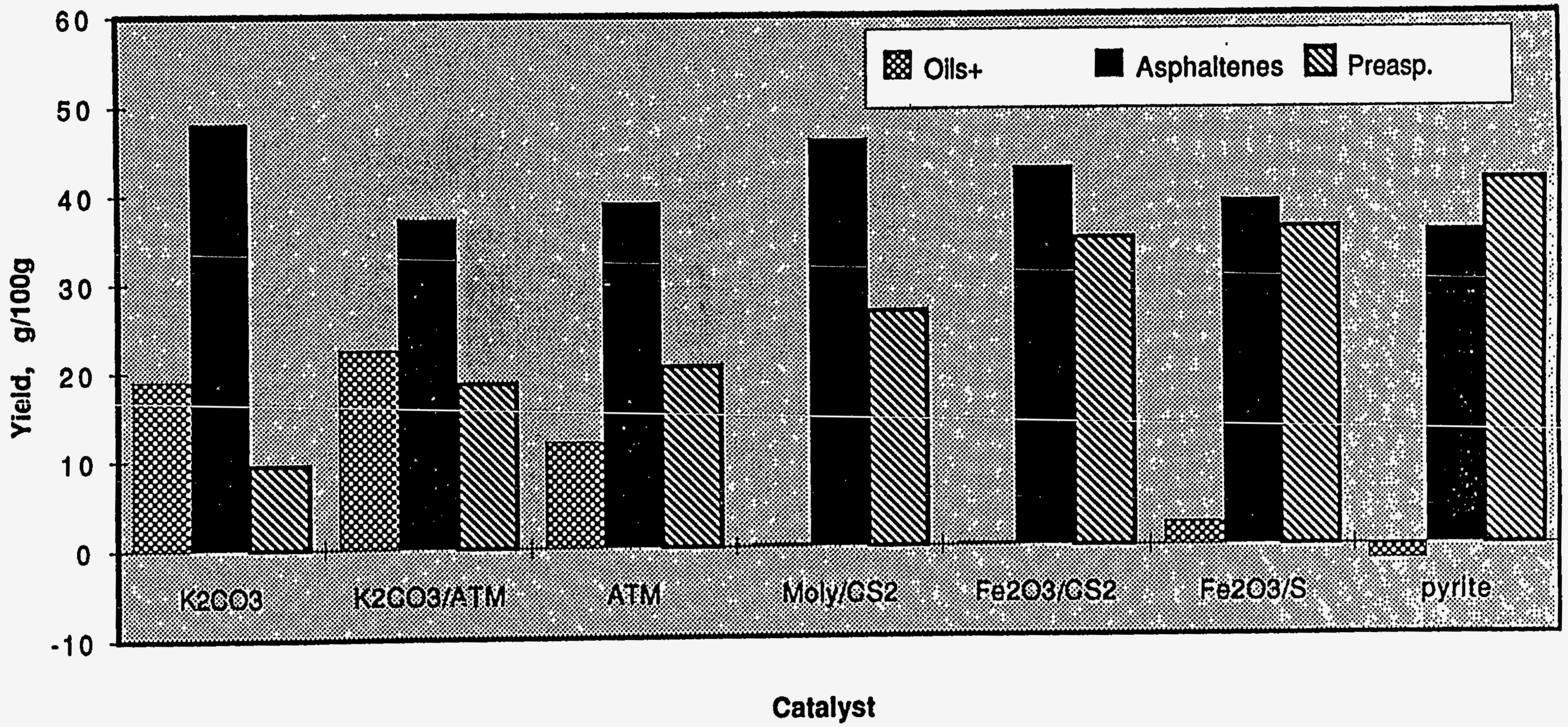
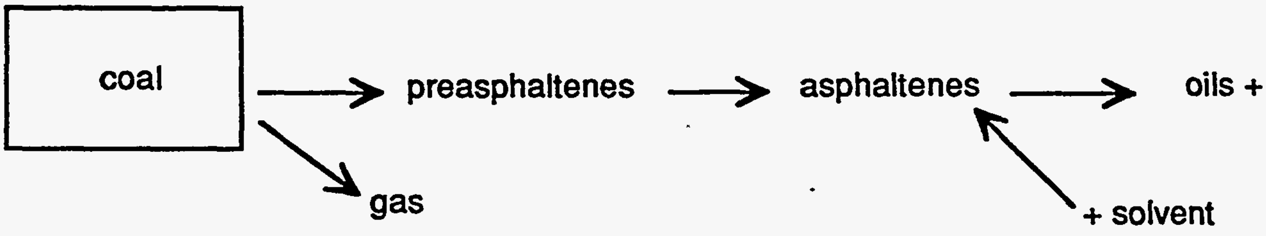


Figure 4.2.21 Catalyst -- Product Yield Distribution



usually of lower activity than molybdenum, little or no upgrading to "oils +" was found. Also, there was much less conversion of preasphaltenes to asphaltenes. These data indicate that more work is needed to identify a catalyst which is active for both first stage solubilization and second stage hydrocracking.

The comparison of catalysts was made almost exclusively at 390°C. Bench unit operations had required a higher operating temperature to obtain coal conversions in excess of 75%. A single test was, therefore, performed at 410°C with aluminate. This test is comparable with DOE-35 with K_2CO_3 apart from the higher initial pressure of CO. At 410°C there were improvements in both coal and CO conversion. The most significant development, however, was the distribution of the produced oils (Figure 4.2.22). There was a pronounced shift from oils + to asphaltenes as the result of recombination of solvent molecules or solvent-asphaltenes. The higher temperature and shift catalyst did convert a high proportion of preasphaltenes to asphaltenes. At 410°C the mechanism for coal solubilization may need to include the solvent:



4.2.2.6 Syngas Composition

Initial indications were that syngas did not perform as well as CO in first stage solubilization (DOE-29). A systematic reduction in the CO content of the syngas confirmed that there was a threshold below which there was significant loss in coal solubilization. These data are presented in Table 4.2.11 and Figures 4.2.23 and 4.2.24. With syngas with a mole ratio of CO/H_2 of 1:1 and higher, the coal conversion was within the statistical mean of the average (82 ± 6%). Only at 33% CO or in pure

Table 4.2.11 Process Performance -- Syngas Composition

Run #	Syngas	Conversion, %		H2 Cons.	HC Gas	Oils+	Asphalt.	Preasp.
		CO	Coal	g/100g	Yield g/100g			
DOE-34	100%CO	79	78	1.5	1.4	19.1	48.2	9.4
DOE-41	66%CO/33%H2	83	83	1.2	2.0	17.9	47.8	15.3
DOE-43	50%CO/50%H2	85	79	0.9	1.5	13.0	49.9	13.6
DOE-42	25%CO/75%H2	85	67	0.3	1.7	10.8	42.6	11.8
DOE-54	100%H2	^---	62	-0.9	1.5	-9.8	42.3	21.0
DOE-44*	66%CO/33%H2	84	82	1.2	1.5	11.4	52.6	16.7

Process Conditions:	Temperature	390oC
	Pressure	600psi
	Time	30min

* FeS added

Figure 4.2.22 Catalyst Performance at 410oC

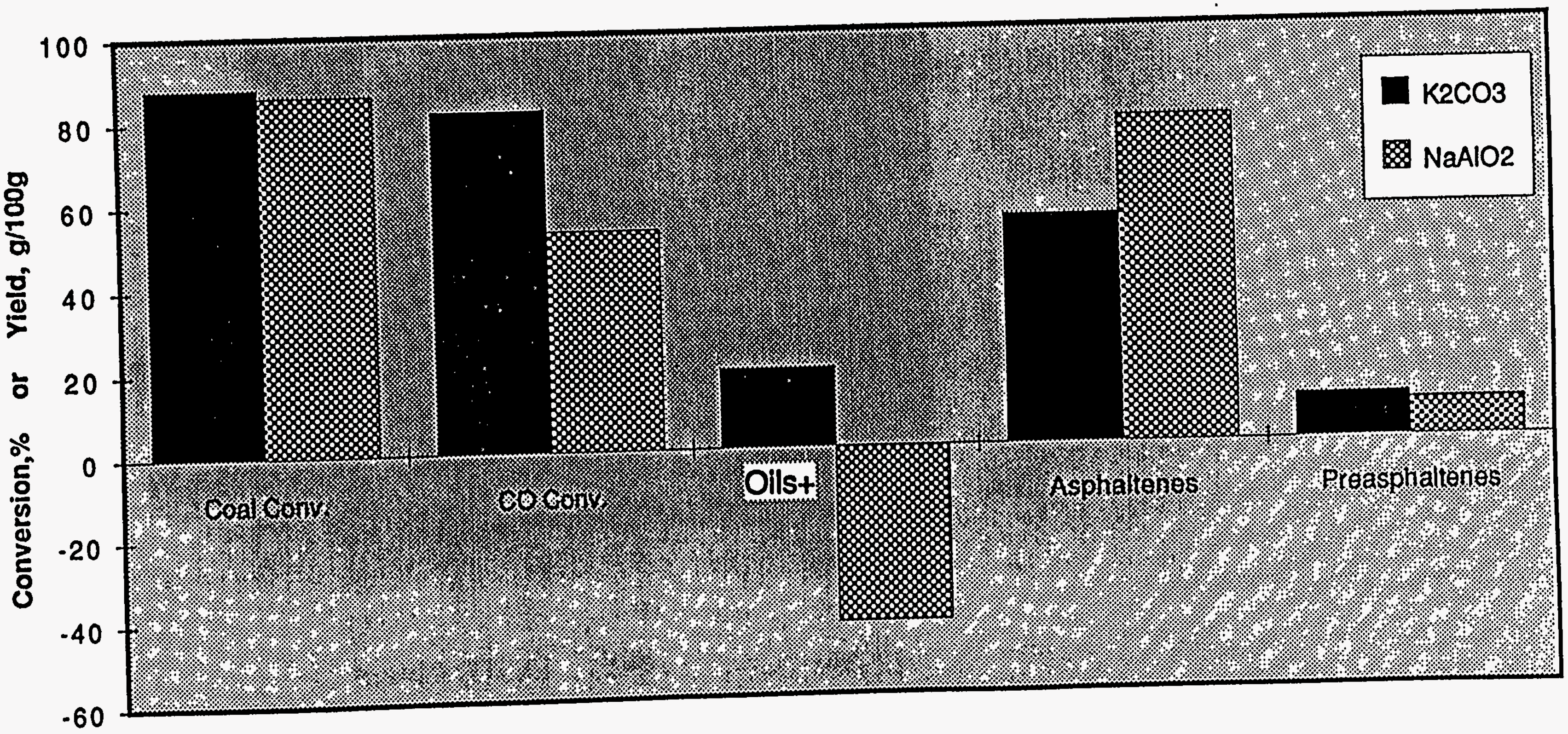


Figure 4.2.23 Process Performance -- Syngas Composition

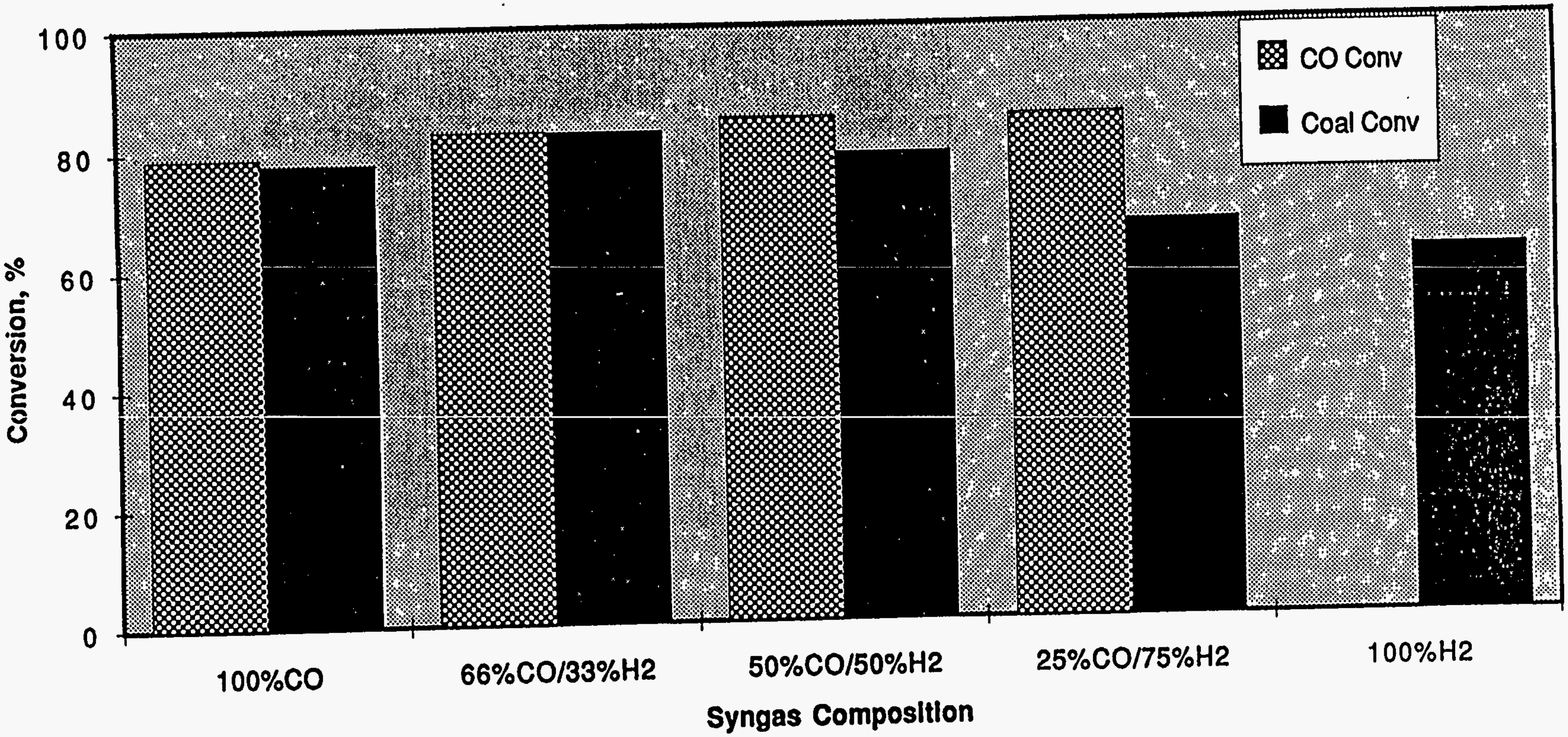
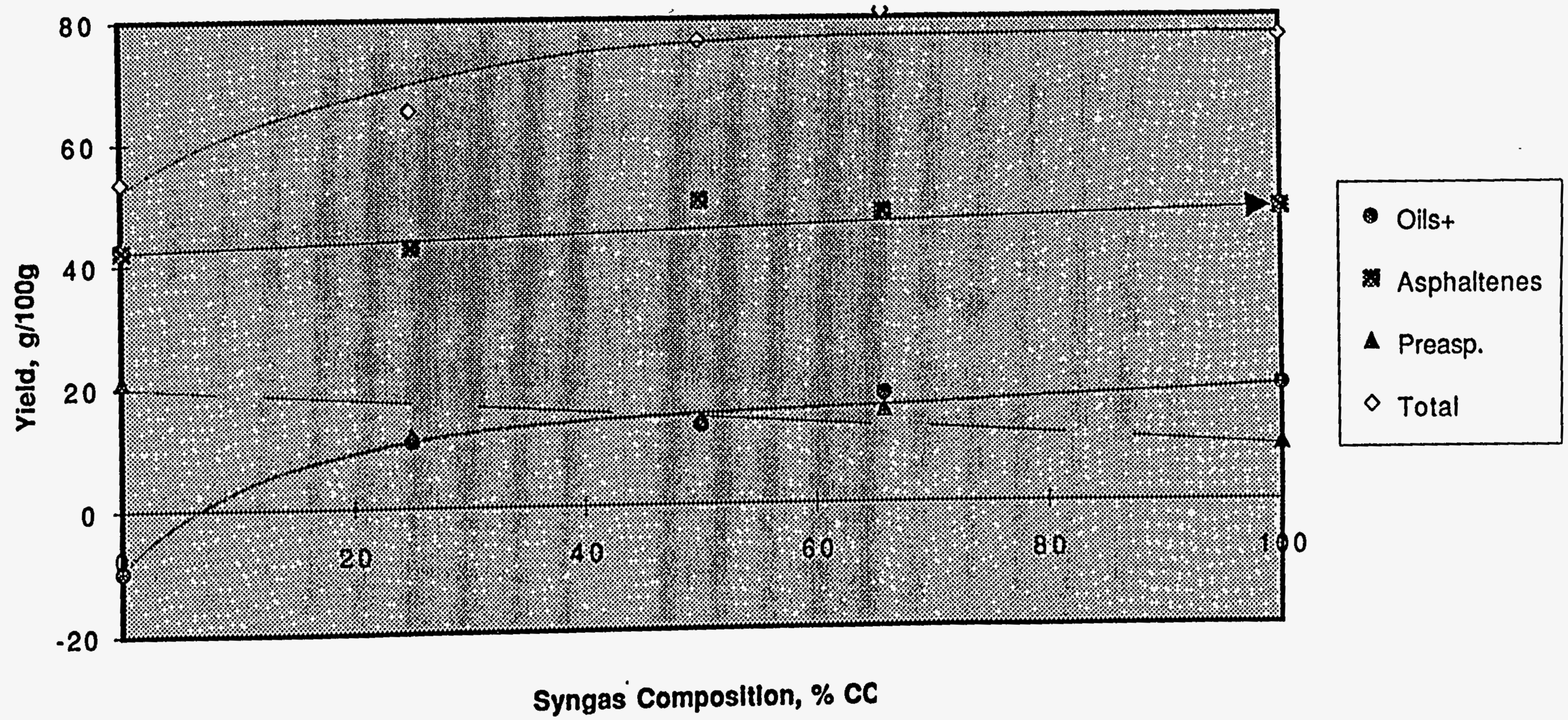


Figure 4.2.24 Process Performance -- Syngas Composition 2



hydrogen was there a significant reduction in performance. The addition of FeS had no effect on coal conversion but gave a heavier product slate. Hydrogen consumption parallelled coal conversion. In the absence of CO, hydrogen was produced, presumably from the solvent and/or coal. The results have great importance to the bench unit operation since they confirm that a syngas can be substituted for the more expensive CO. There is also potential to recycle the first stage off-gas after removal of acid gases (CO_2 and H_2S).

The gross solubilization of the coal does not reflect the complete picture for the effectiveness of the first stage. The nature of the solubilized coal is critical since it may impact on the ease of production of lighter oils in the second stage. Excess carbon dioxide evolution was fairly constant (0.3-0.5 moles/100g MAF coal) except for the pure H_2 run. Despite the differences in coal conversion the asphaltene yield was relatively constant at 46 ± 4 g/100g MAF coal. Preasphaltene yields were also within a narrow range 10 - 15 g/100g MAF coal with the exception of pure hydrogen. There was a pronounced trend to higher oils + yields as the concentration of CO in the syngas increased. The inability of molecular hydrogen to prevent retrogressive reactions was apparent in the net loss of distillable oils from the solvent. Evidence for retrogressive reactions also comes from production of hydrogen gas.

One test (DOE-55) was performed in CO without added water or catalyst. There was apparently no CO conversion, in fact a small production of CO was recorded. Literature reports that almost all the oxygen is lost from low rank coals as CO_2 rather than CO. There was perhaps some CO_2 produced via the WGSR since the water content of the system declined. Overall the need for added water was shown since the coal conversion was almost as low as had been found in nitrogen or hydrogen. The implication for the CFR is that the partial pressure of water must be maintained above a minimum level throughout the reaction to ensure that solubilization proceeds via a mechanism involving CO/H_2O instead of thermal loss of carbon oxides. Further work will be required to determine the water requirements, especially with syngas.

4.2.2.7 Two Stage, V-1074 Solvent

Simulated 2 stage tests all operated at standard conditions for the first stage i.e. 390°C/600 psi CO/30 minutes with K_2CO_3 catalyst. The second stage variables which were examined were: catalyst, FeS or ATM, hydrogen pressure and temperature, 430 or 445°C. As can be seen from Table 4.2.12, CO conversion, hydrogen consumption and hydrocarbon gas formation were constant for the first stage operation and were within the range observed in single stage tests.

Coal conversion improved to 93± 2% with second stage operations. This coal conversion was likely the potential limit since it matched results from Wilsonville and HRI. Examination of the solid residues did not reveal any coke or mesophase production. Process severity was not too high to induce regressive reactions. However, there was considerable hydrocarbon gas production especially at 445°C, 10 - 12g/100g MAF coal. Again, this quantity may be inflated since much may have been produced from the solvent. There was little recorded hydrogen consumption even with the molybdenum catalyst. In fact most runs exhibited very minor hydrogen production at the end of the second stage. The average gain, however, was only 0.2 g/100g MAF coal which is within the statistical limit of zero change.

Preasphaltene conversion reached an apparent upper limit in second stage tests. Only 4 ± 1 g/100g MAF coal remained at the end of second stage operation despite the additional 10% of solubilized coal. No correlation could be drawn between catalyst used or pressure, and preasphaltene yield. The conversion process was dependant entirely on severity (temperature) and appeared complete by 430°C.

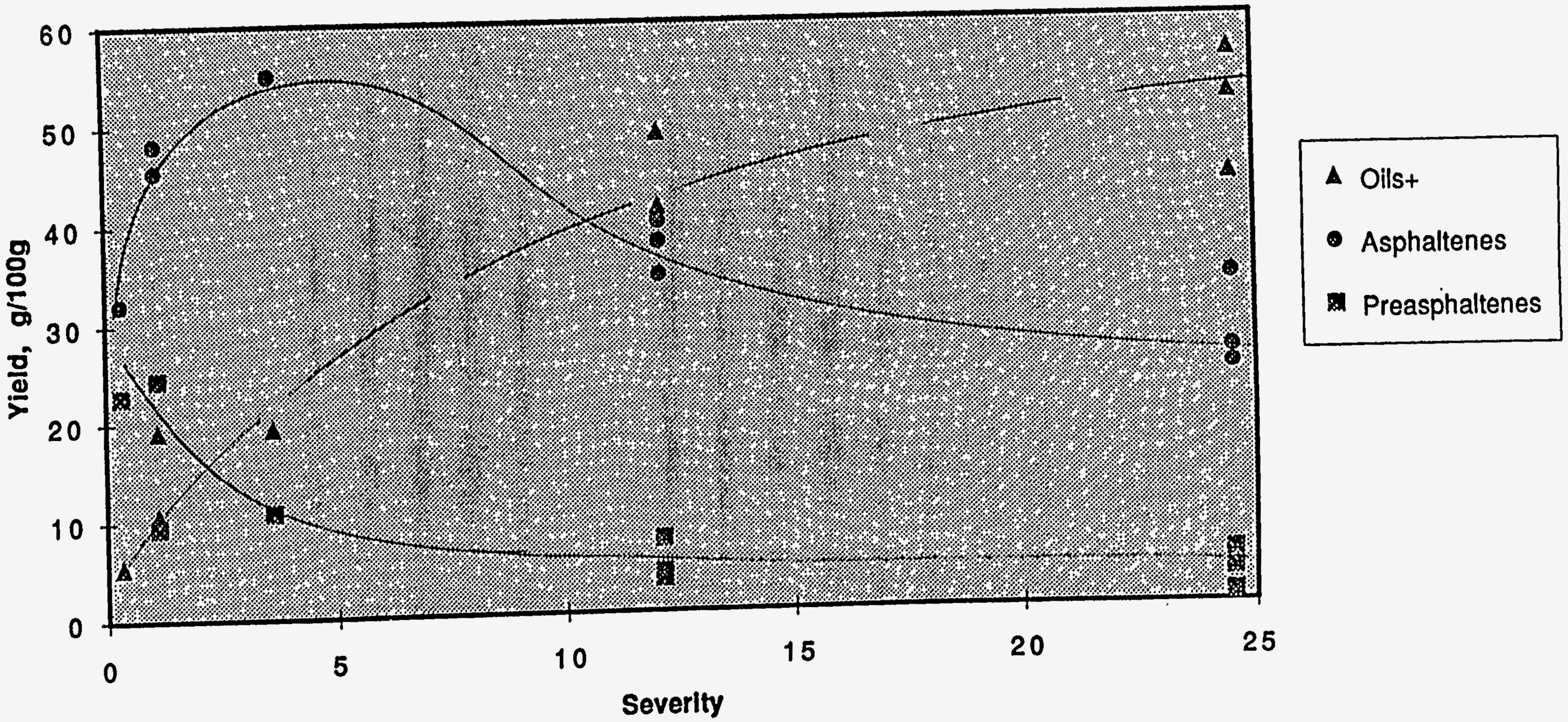
Asphaltene content of the products was between 34 and 40 g/100g MAF coal at 430°C, also considerably less than found after the first stage. As anticipated there was a progression from preasphaltenes to asphaltenes to oils + as severity increased, as depicted in Figure 4.2.25. The oils + yield did not show any further improvement at

Table 4.2.12 Simulated 2 Stage Tests

Run #	T	P	t	Conversion, %		H_2 Cons.	HC Gas	Oils+	Asphalt.	Preasp.
	oC	psi	Min	CO	Coal	g/100g	Yield g/100g			
DOE-39	0	0	0	81		1.7	0.9			
2nd ST	430	1900	30		91	-0.3	6.3	40.6	39.8	3.4
DOE-40	0	0	0	79		1.8	1.2			
2nd ST	430	2900	30		94	-0.3	6.3	41.3	37.8	7.4
DOE-45	0	0	0	79		1.5	1.3			
2nd ST	430	2800	30		95	-0.4	6.9	48.8	34.4	4.0
DOE-46	0	0	0	79		1.6	1.3			
2nd ST	445	2850	30		94	-0.1	10.0	43.9	33.7	5.3
DOE-50	0	0	0	88		1.9	0.9			
2nd ST	445	2100	30		93	0.8	8.4	56.4	26.2	0.9
DOE-52	0	0	0	79		1.5	1.5			
2nd ST	445	2300	30		93	0.2	11.6	52.1	24.5	3.4

Process Conditions:		**1st Stage**	**2nd Stage**	
	Temperature	390oC	Shown in Table	
	Pressure	600psi		
	Time	30min		
	Catalyst	K_2CO_3	Runs # 39,40,45,46	FeS
			Runs # 50,52	ATM

Figure 4.2.25 Product Yields -- One and Two Stage Tests



445°C, rather the products of asphaltene conversion were measured as hydrocarbon gas. Based on a single test (plus one with work up problems) the molybdenum (ATM) catalyst did enhance the upgrading of asphaltenes to oils + since all runs with FeS have yields of 40 - 50g vs > 52 g/100g MAF coal with ATM. There was a lack of evidence for regressive reactions at 445°C with either catalyst, this would likely have shown up as increased yields of asphaltenes at the expense of "oils +". This observation, together with the absence of coke in the solid residue, was the basis of the decision to operate the bench unit at up to 445°C.

4.2.2.8 Illinois #6 Coal

The Illinois #6 coal proved more retractable than Black Thunder coal and did not respond as well to CO/H_2O first stage treatment. At 390°C only 67% coal conversion was achieved, this rose to 81% at 425°C (Table 4.2.13 and Figure 4.2.26). It should be noted that $NaAlO_2$ catalyst was used rather than potassium carbonate. FeS (Run DOE-60) and Fe_2O_3 (Run DOE-64) were also added, since there would be iron or molybdenum based catalysts in the coal slurry feed. The coal conversion improved to 89 - 93% when hydrogen replaced the CO. [$NaAlO_2$ was inadvertently added to Run DOE-61.] It was therefore decided to use hydrogen rather than CO in the bench unit program.

Hydrocarbon gas production followed fairly closely that obtained with the Black Thunder coal (1 - 1.5 g/100g MAF coal at 390°C and > 10 at 440°C). There was a small quantity of H_2S produced in those runs without iron oxide catalyst. It was totally absent in Runs DOE-62 and 64, presumably as the result of reaction with Fe_2O_3. When another source of sulphur was present (DOE-63) to react with the Fe_2O_3, the H_2S was observed in the gas product.

Most of the solubilized Illinois coal was the preasphaltene fraction (Figure 4.2.27)

Table 4.2.13 Illinois #6 Test Results

Run #	Conditions			Catalyst	Conversion, %		H2 Cons	HC Gas	Oils+	Asphalt.	Preasp.	Notes
	T, oC	P, psi	t, min		CO	Coal	g/100g	Yield, g/100g				
Single Stage												
DOE-60	390	600	30	NaAlO2	32	67	0.4	1.1	9.2	24.3	32.4	
DOE-61	425	1000	30	FeS	H2	89	0.6	5.0	32.6	19.4	30.8	^+NaAlO2
DOE-62	425	1000	30	Fe2O3	H2	92	0.9	4.4	24.7	23.6	39.0	
DOE-64	425	600	30	NaAlO2	59	81	0.9	5.4	19.5	26.6	29.8	^+Fe2O3
Two Stage												
DOE-63	425	1100	30									
	440		30	Fe2O3	H2	93	2.2	10.7	36.2	28.2	15.9	^+DMDS
DOE-70	425	1100	30									LO-6305
	440		30	Fe2O3	H2	89	2.4	11.2	21.9	41.4	13.0	^+DMDS

Figure 4.2.26 Process Performance -- Illinois #6 Coal

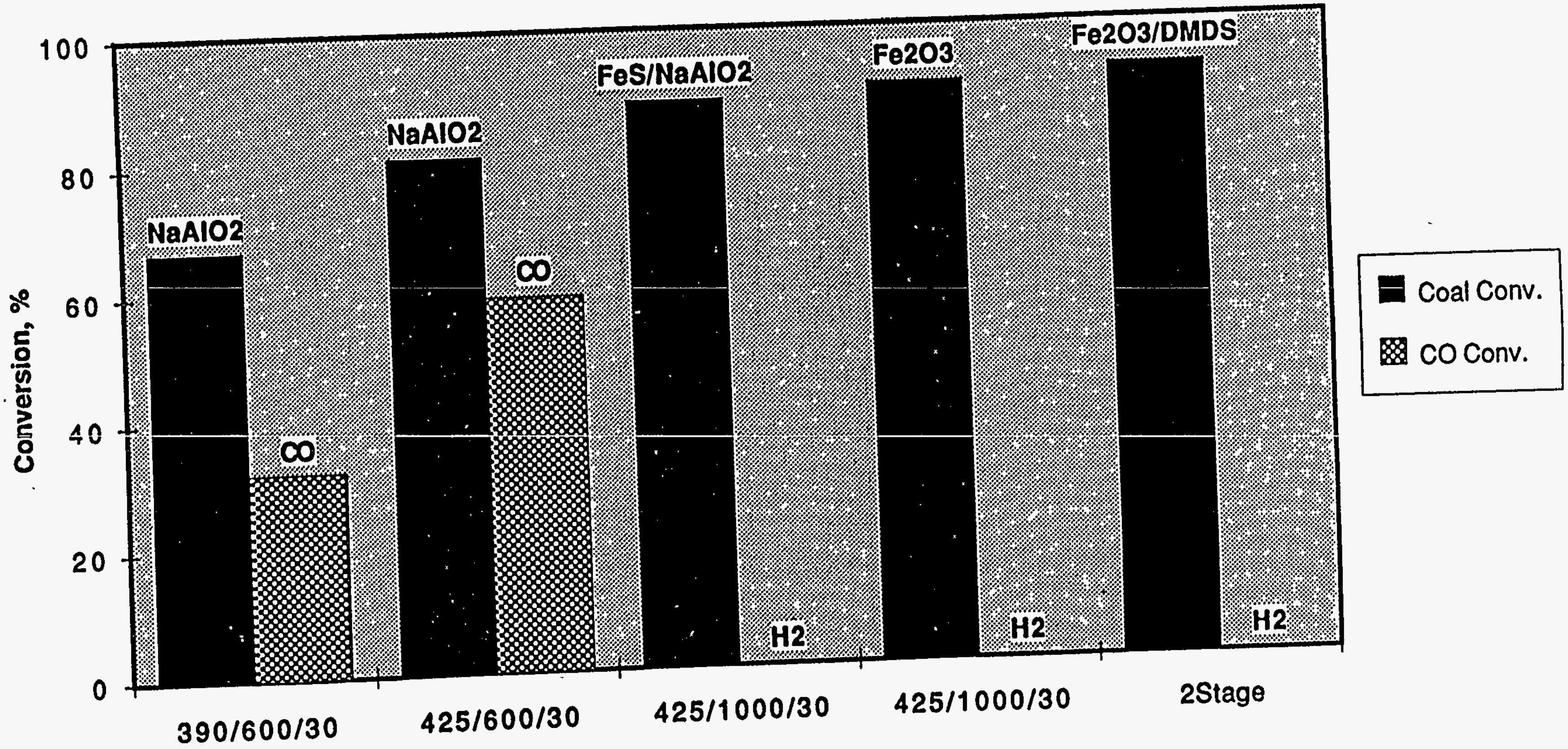
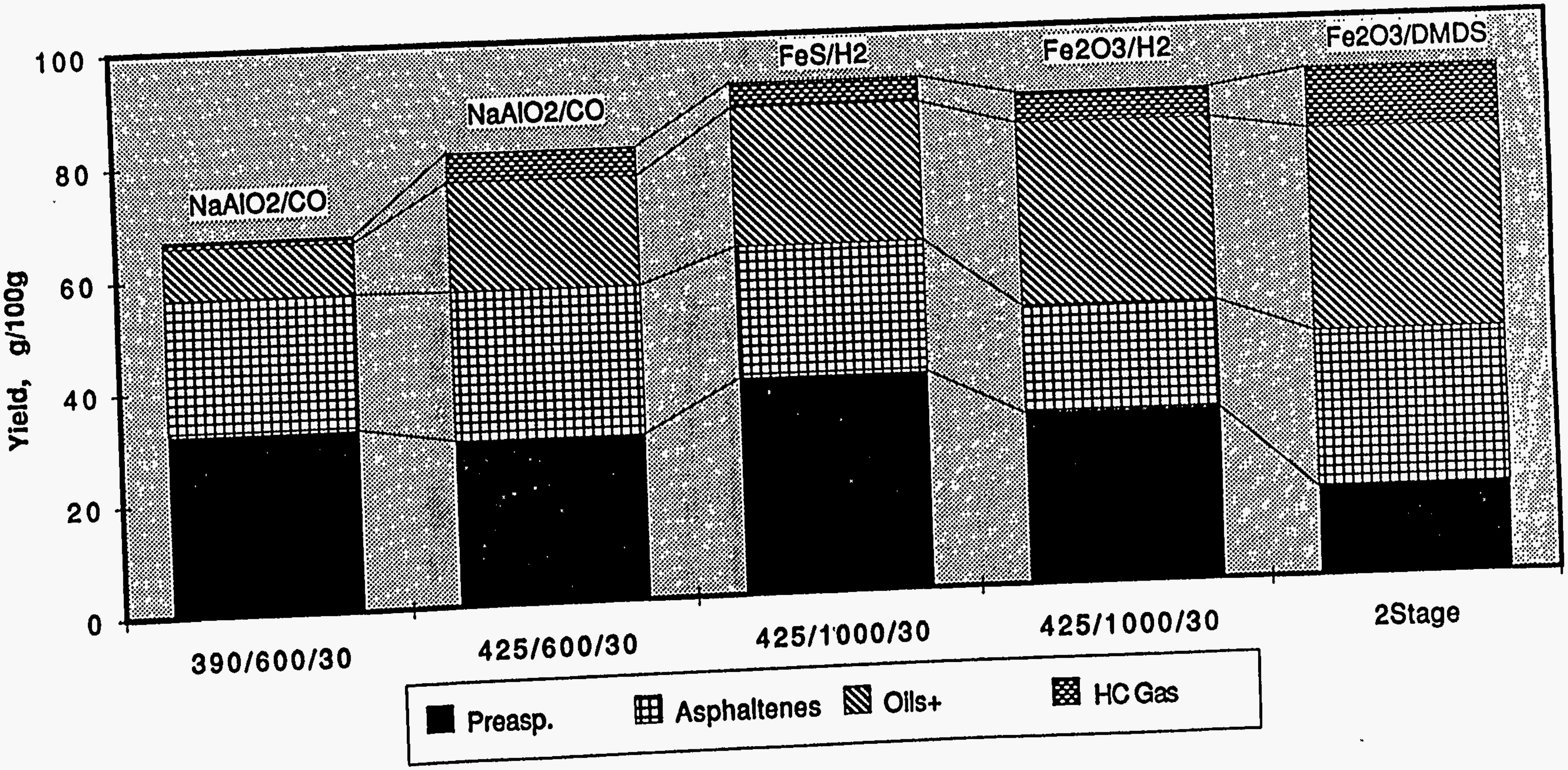


Figure 4.2.27 Yield Structure -- Illinois #6 Coal



whether the first stage used a CO or H_2 atmosphere. However, the "oils +" yield was much greater with hydrogen. Surprisingly the oils + yield after the second stage process (DOE-63) was not that different from the single stage test (DOE-61). The second stage upgraded over half the preasphaltenes but this was not reflected in oils + product, rather it resulted in additional gas and asphaltenes. The asphaltenes value (DOE-61) might be suspect in view of poor repeatability for this sample. The toluene extracts for the Illinois #6 coal often appeared to have phase separated.

The above tests utilized the small sample of Illinois #6 coal derived oil (LO-6282) which was not used in the bench unit program. In order to tie this work to the bench unit solvent (LO-6305) a single test (DOE-70) was completed which duplicated the second stage run (DOE-63). The gross measures of process performance, i.e. coal conversion, hydrocarbon gas yield and hydrogen consumption, were unchanged, as was the preasphaltene contents of the product. However, the breakdown of toluene soluble oils in classes was not repeatable. This may have been an analytical procedural problem due to the nature of the product as described earlier.

The solvent was derived from an effective hydrogen addition process and had a high hydrogen to carbon ratio (1.45:1). This may have contributed to the incompatibility of product asphaltenes. Even though the oils +: asphaltene ratio was quite different for the two solvents, the total soluble oil yield was almost identical 64.2 vs 63.3 g/100g MAF coal.

4.2.2.9 Reactivity of Bench Unit Products

Tests were performed in the autoclave on three V340 product samples from the bench unit. These samples were the bottoms product from the counterflow reactor (R-200 or R-300). The objective was to determine whether these products could be further upgraded. The results on three such products are presented in Table 4.2.14. BU-005 was the product from first stage solubilization of Black Thunder coal using carbon

Table 4.2.14 Reactivity of Bench Unit Products

Run #	Conditions				H2 Cons	HC Gas	Oils+	Asphalt.	Preasp.	IOM
	T, oC	P, psi	t, min		g/100g	Yield, g/100g				
BU-005 V-340 Bottoms										
Feedstock Composition							57.9	18.4	2.4	10.7
DOE-47	430	1200	30	H2	0	1.7				3.4
BU-16.02 V-340 Bottoms										
Feedstock Composition							63.4	17.6	1.7	6.7
DOE-66	440	1100	60	H2	0.1	3.1	68.3	13.9	1.8	2.3
BU-17.02 V-340 Bottoms										
Feedstock Composition							63.1	19.5	1.7	7.2
DOE-67	440	1100	60	H2	0.5	2.7	67.7	17.6	0.9	3.0

monoxide/steam and potassium carbonate as catalyst. BU-16.02 and BU-17.02 were products from one stage solubilization of Illinois #6 coal using hydrogen with iron oxide or ammonium molybdate catalyst, respectively. The bench unit runs are described in Section 4.3.

The product from BU-005 was partially solubilized coal, solvent and catalyst. During this period in the bench unit operation it was thought that the unit was functioning as well as had been expected. Coal conversions were however below autoclave predictions. The test (DOE-47) showed that the coal conversion could be raised from 69 to 92%. The process chemistry for the solubilization was not the limiting factor in the bench unit operations since the coal conversion matched that from other simulated second stage tests. No other characterization tests on the products were performed apart from gas analyses. This found that no additional carbon oxides were released and hydrogen consumption was zero.

The V-340 products were partially upgraded coal derived oils, catalyst, ash and solvent. The reactivity of these bottoms was measured by processing the product slurry in the autoclave with hydrogen gas. No other catalysts or additives apart from those in the feed slurry to the bench unit were present. The coal conversion in BU-16.02 and BU-17.02 were 84 and 87%, respectively. Both runs had relatively low conversion since they had only experienced the second stage conditions. The first stage at the time was not functioning suitably and was by passed. The autoclave test raised the coal conversions to 90 and 92%, both within the range of previous Illinois #6 tests. Hydrogen consumption with the iron based catalyst was insignificant , but the molybdenum catalyst added a small amount to the liquids.

The yield structure was slightly improved for both BU-16.02 and 17.02. The additional solubilized coal did not show up as preasphaltenes. This material and part of the asphaltenes were partially upgraded to oils + and gases.

4.2.2.10 Process Chemistry and Mechanisms

Hydrocarbon gas yield from the Black Thunder coal was almost totally dependent on process severity. Data from the majority of the autoclave tests, both one and two stage, are plotted against severity index (Figure 4.2.28). The results follow a clearly defined trend and are independent of gas type, pressure or coal conversion. 24 runs were completed at the standard conditions 390°C/600 psi/30 minutes. The hydrocarbon gas produced was 1.5 ± 0.2%, as can be seen from Figure 4.2.29. There was no correlation between coal conversion and hydrocarbon gas production. Gas production was, therefore, the result of a thermal degradation of the coal and the solvent.

No solvent stability tests of Black Thunder solvent were done at 390°C, however at 410°C, V-178 and V-1074 gave 0.6 and 0.8 g/100g gas respectively. In the data interpretation no correction was made for the contribution of the solvent to gas production. This correction would correspond to 0.9 - 1.2 g/100g coal at 410°C. The range for the reported gas production at this severity was 2.5 - 2.9 g/100g coal for V-178+320 and 3.0 - 3.5 g/100g coal for V-1074. Thus, the solvent contributed approximately one third to the gas yield.

Coal conversion was earlier reported to be at a maximum at a process severity index of greater than 1, for the Matrix series. This observation was reinforced by repeat tests and tie point tests for the V-1074 solvent (Figure 4.2.30). In order to calculate a severity index for the matrix condition of time = -1, a nominal value of 1 minute was used. This ignored the contribution of the heat-up period. Overall the coal conversions found in the autoclave exceeded those in the bench unit (see Section 4.6), which brings the residence time equivalence into question.

Figure 4.2.28 Hydrocarbon Gas Yield as a Function of Process Severity

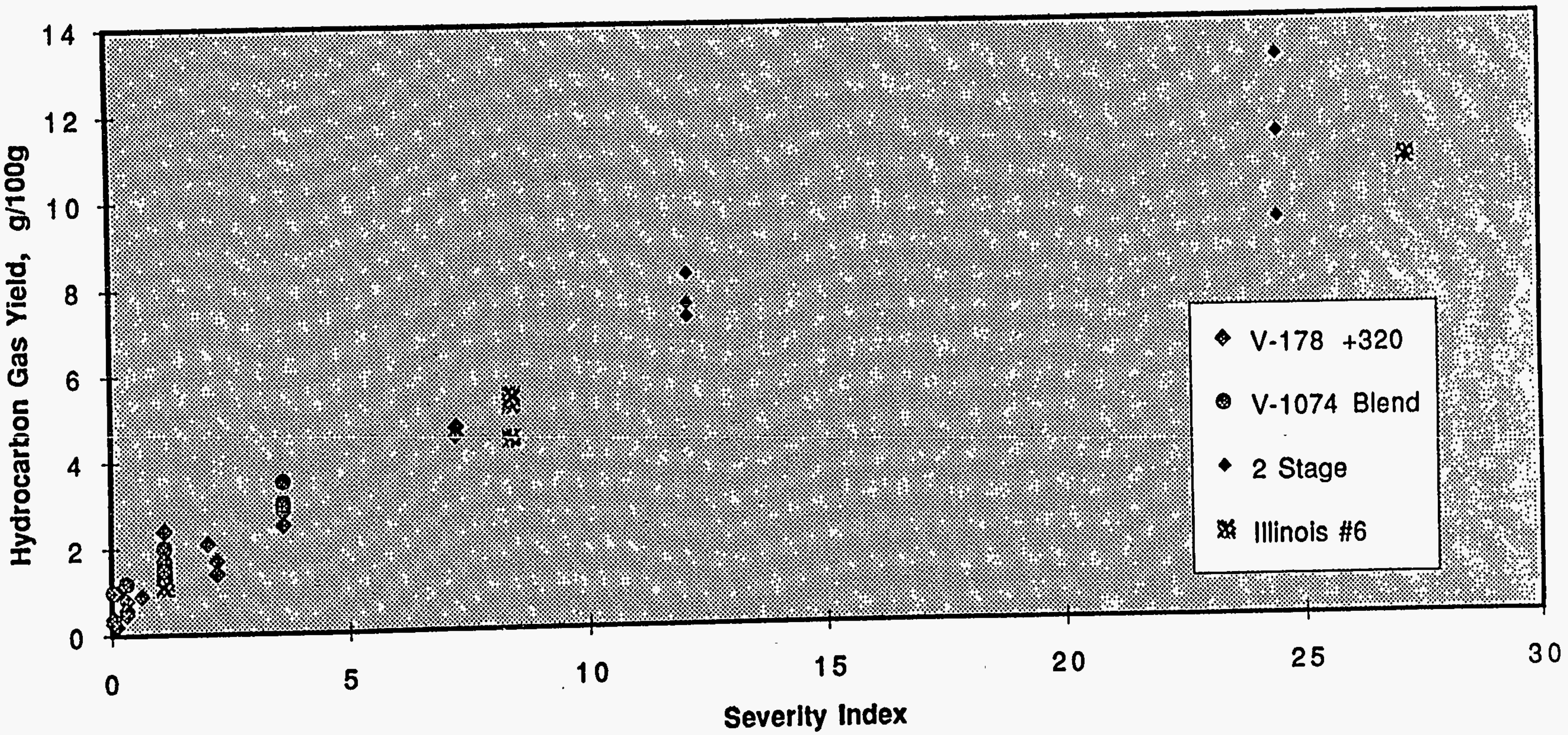


Figure 4.2.29 Hydrocarbon Gas Production as a Function of Coal Conversion

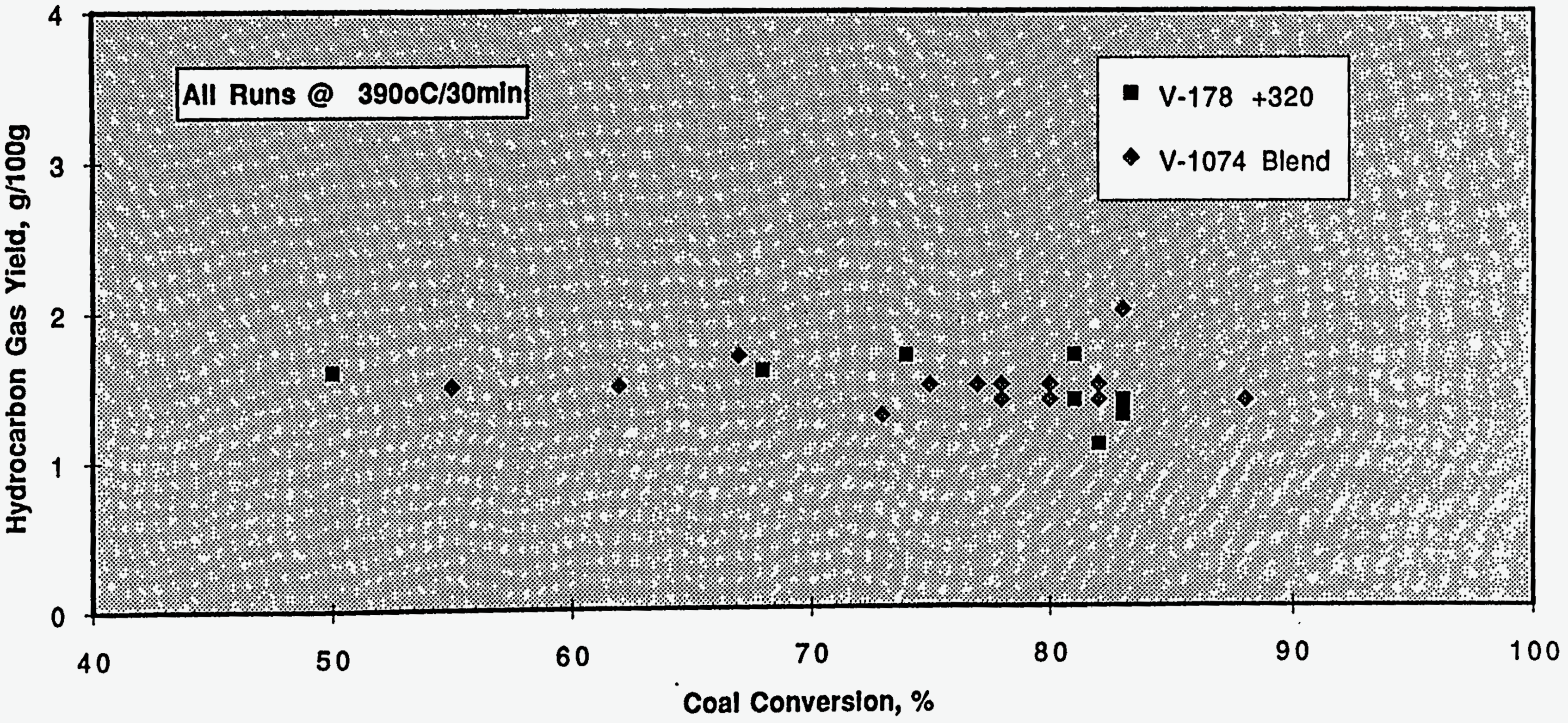
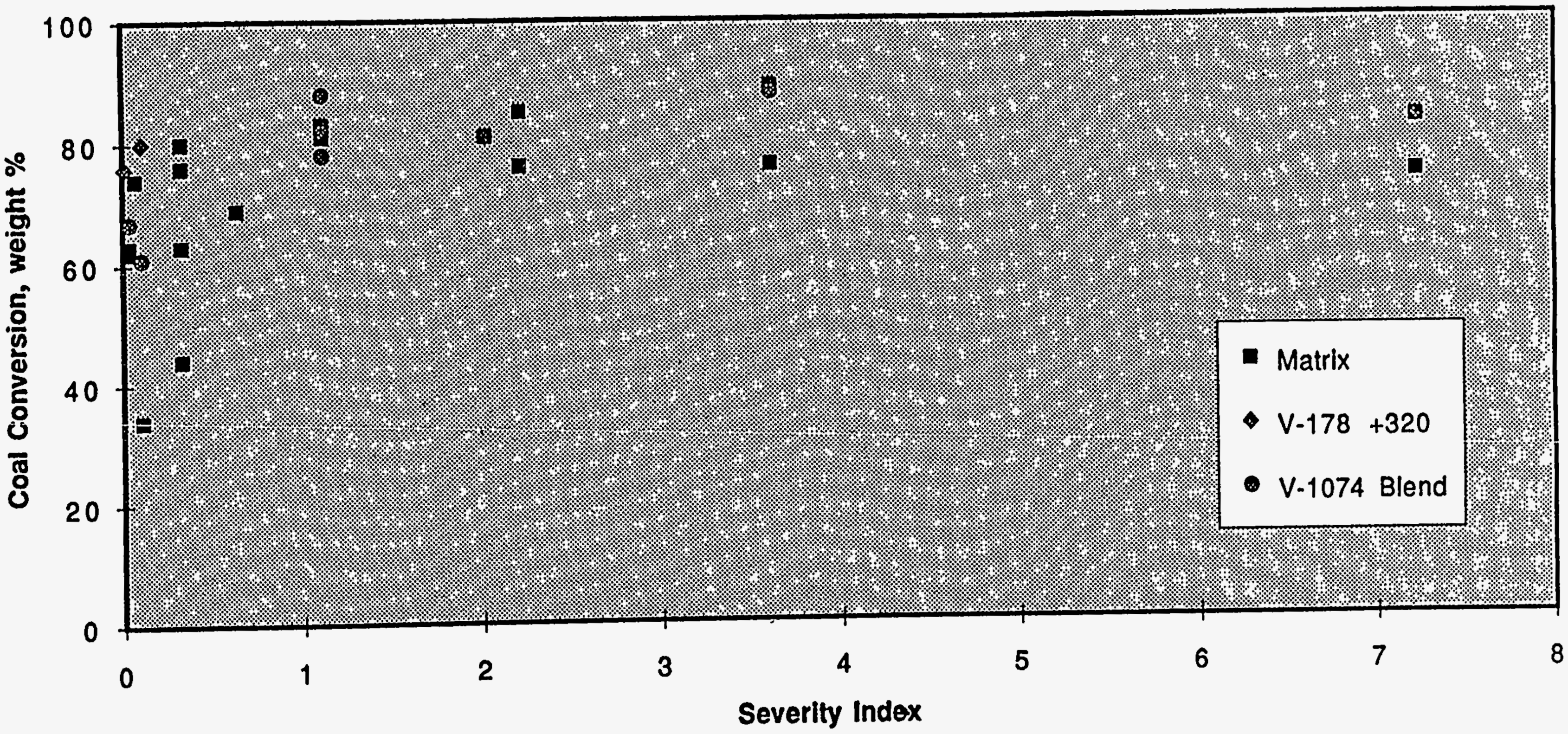


Figure 4.2.30 Coal Conversion as a Function of Severity



The formation of asphaltenes, preasphaltenes and pentane soluble oils was dependent on both thermal and catalytic processes. The data is limited since no class analyses were performed on the matrix tests. With the V-1074 solvent conversion of coal to asphaltenes was a linear function of severity index. The data for the preasphaltenes is more scattered but there is a decrease with severity indicating that the preasphaltenes are reactive. The mechanism in the CO/H_2O solubilization with K_2CO_3 shift catalyst was therefore:

In addition to hydrocarbon gases the Black Thunder coal generated an excess of carbon dioxide over and above that which could be assigned to the WGSR. There was also an excess of water consumption during the autoclave tests and its relationship to excess CO_2 was constant (Figure 4.2.31). The water must, therefore, be included in the mechanism for coal solubilization. Ross[1] has depicted this mechanism as:

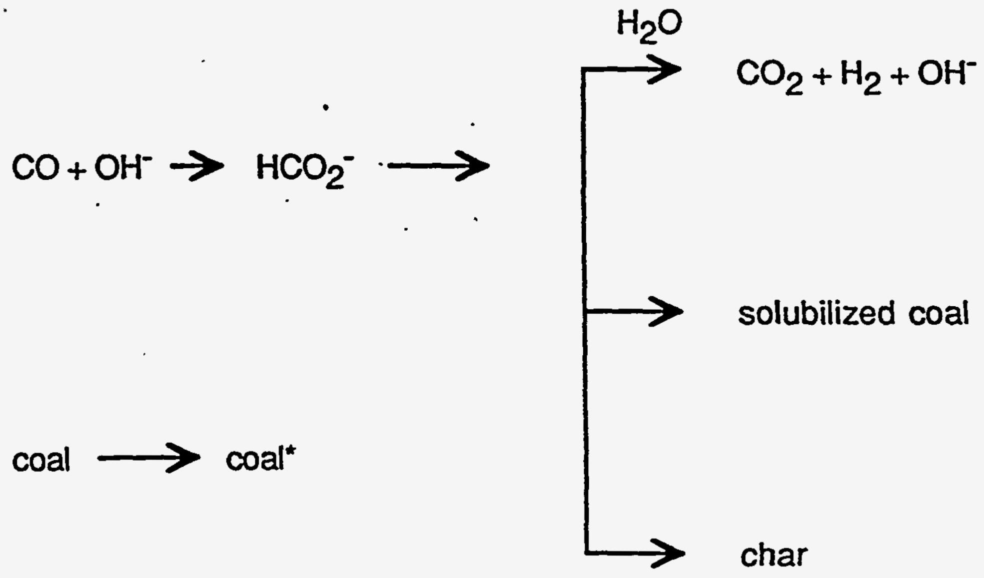
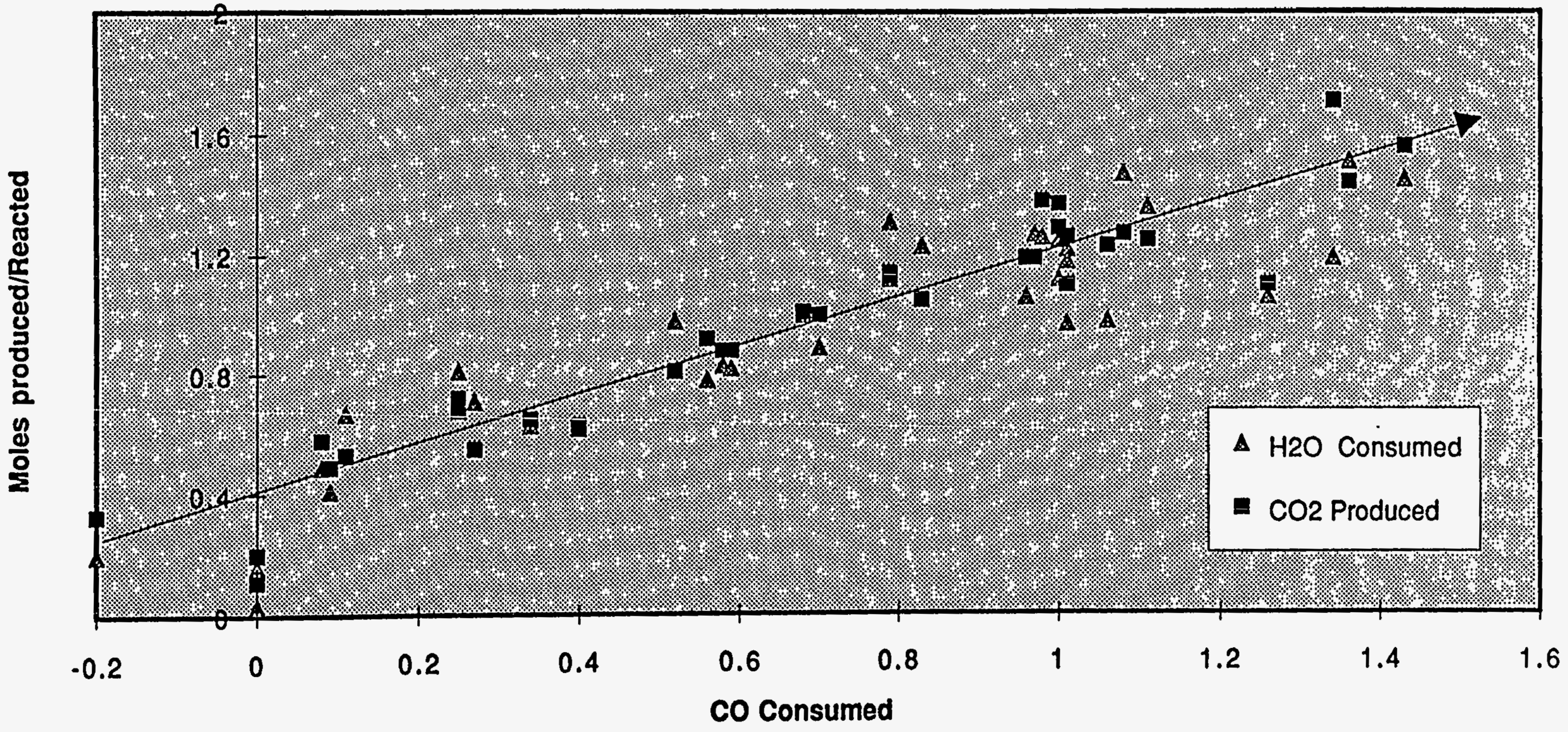


Figure 4.2.31 Water Gas Shift Reaction -- CO Consumption



where the coal is thermally activated in parallel with the WGSR. In this study the stoichiometry of the WGSR was not the simple relation found in the gas phase reaction. When the data for all the runs was assessed it was found that:

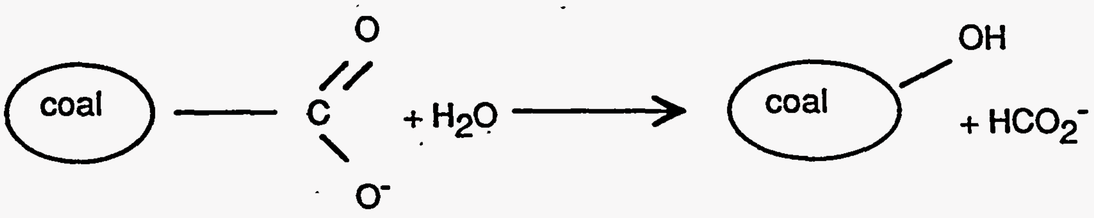
a) there was a 1:1 relationship between moles water reacted and moles CO_2 produced (Figure 4.2.32).

b) the CO_2 production exceeded the CO consumed by about 0.6 moles/100g MAF coal

c) hydrogen production was half of the CO consumption (Figure 4.2.33).

Thermal treatment of Black Thunder coal will generate both CO and CO_2, with the latter predominating. Saini[2] has reported this CO_2 production to be 7 - 9 g/100g MAF (0.16 - 0.20 moles/100g) during liquefaction in tetralin or methylnaphthalene. Serio[3] titrated coal and found 0.24 moles carboxylate group per 100 g coal. This would account for a significant portion of the excess CO_2 produced in the autoclave tests. The total H_2O consumed is equivalent to moles CO_2 from the WGSR + CO_2 from coal. Therefore, a mechanism for the removal of carboxylate from the coal must involve the participation of water, such as:

1a)



$$\text{coal}-C(=O)O^- + H_2O \longrightarrow \text{coal}-OH + HCO_2^-$$

1b)

$$HCO_2^- + H_2O \longrightarrow CO_2 + H_2 + OH^-$$

The net change in oxygen content of the coal would be 1 atom per mole of excess CO_2 or about 0.6 atoms/100 g coal (~10g).

Figure 4.2.32 Water Consumed vs. Carbon Dioxide Produced

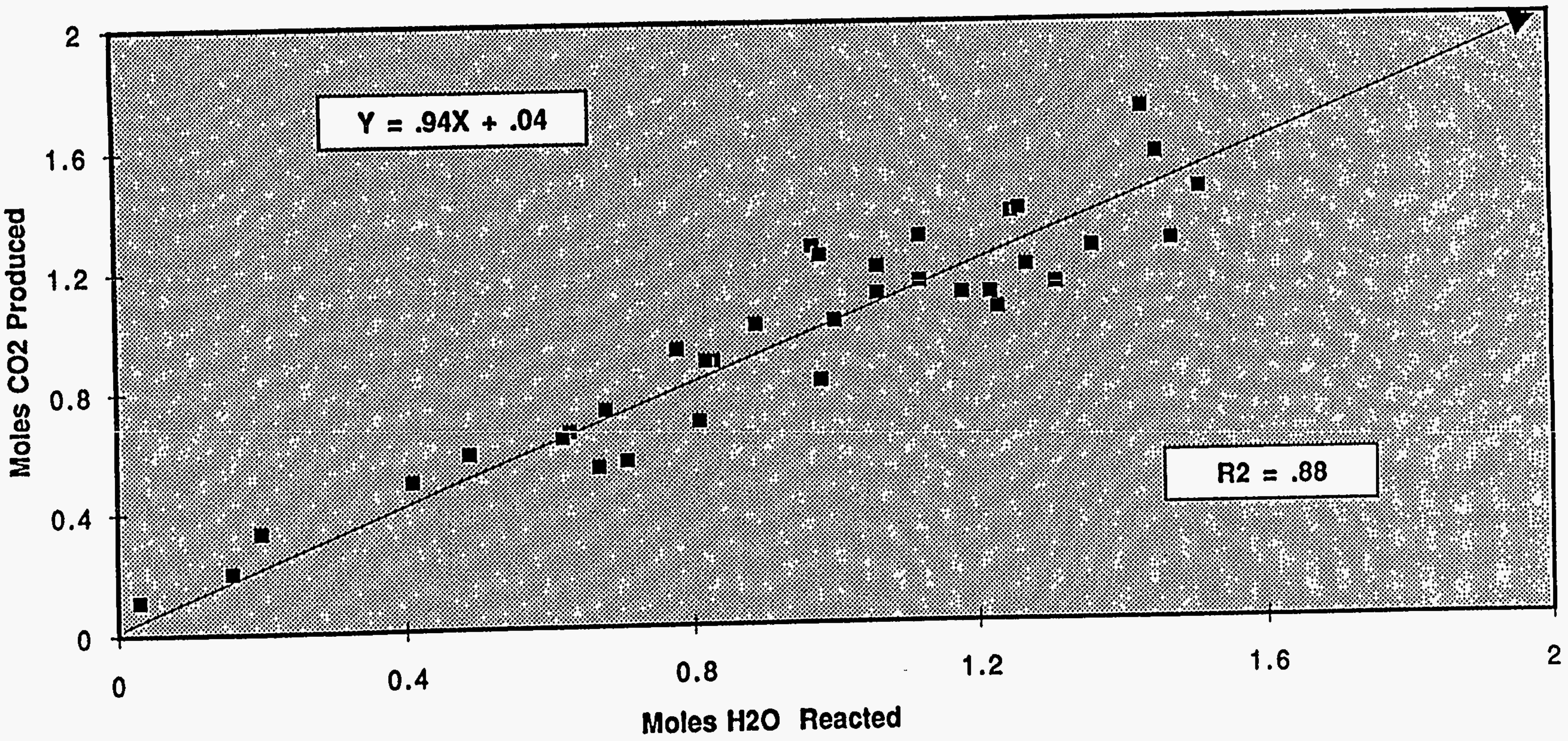
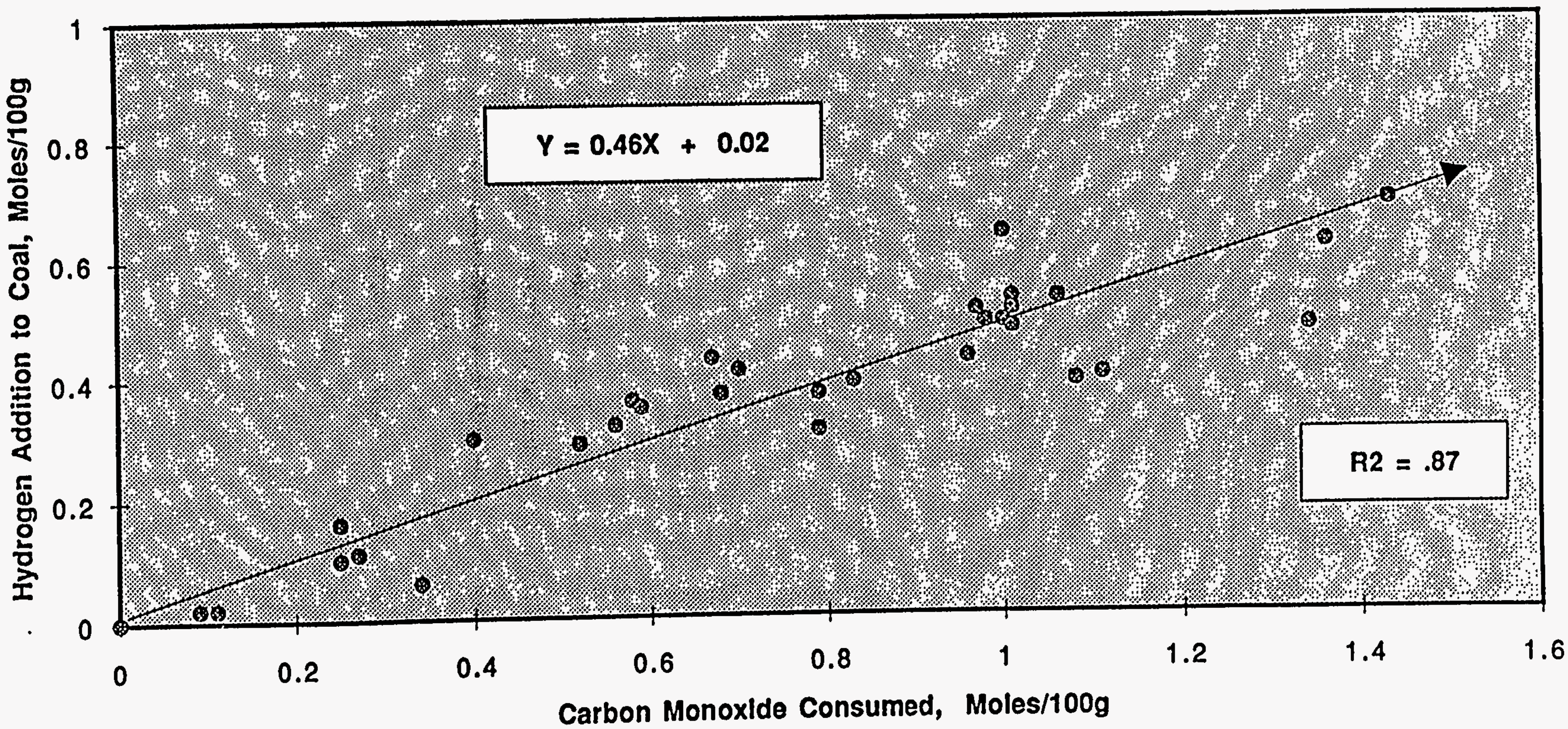


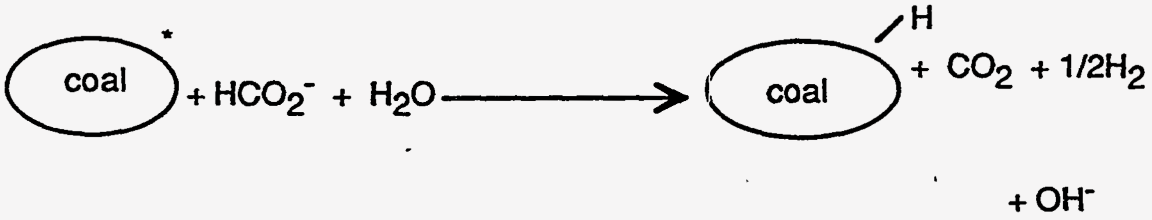
Figure 4.2.33 Hydrogen Addition as a Function of CO Consumption



The remaining CO_2 is derived from the WGSR which also is a source of hydrogen. There is hydrogen addition to the coal perhaps simultaneously with the liberation of the CO_2. Since the hydrogen production was only half the CO consumed it suggests that one atom of hydrogen is added to the coal while one atom eventually forms molecular hydrogen.

2a)

2b)



4.2.3 Conclusions

4.2.3.1 Black Thunder Coal

1) Coal solubilization in CO/steam is dependant on process severity i.e. temperature and time, and to a lesser extent CO pressure, maximum conversion with CO/steam was about 90%.

2) Coal conversion was largely independant of CO conversion in the presence of a high quality solvent, but the nature of the products was defined by CO conversion; ranking of tested catalyst $K_2CO_3 \gg NaAlO_2 \gg$ Fe or Mo based catalysts.

3) Substituting syngas for pure CO gave comparible performance as long

as the CO partial pressure was greater than 2/3 of the total.

4) The molar carbon dioxide yield exceeded that derived from the water gas shift by an amount equal to the molar water consumption. This was attributed to base hydrolysis of carboxylic groups. Hydrogen addition to the coal was directly proportional to the CO consumed.

5) Hydrocarbon gas yield was purely thermal in origin and was independant of the gas pressure and composition, nature of WGS catalyst, nature of solvent or coal conversion.

6) The main products from solubilization with CO/steam were asphaltenes and preasphaltenes, however, much of this material was converted to oils in a following hydroconversion stage. At the same time coal conversion was raised to 93 - 95%.

4.2.3.2 Illinois #6 Coal

1) Hydrogen gas out performed CO/steam in first stage solubilization.

2) Higher temperatures are required to achieve equivalent solubilization of Illinois #6 coal (vs Black Thunder).

4.2.3.3 Bench Unit Products

1) Further upgrading of the V-340 bottoms to oils was possible without the onset of coke formation.

4.2.4 References

1. Ross *et al*, in Coal Science, Vol. 3, Academic Press, Inc. Orlando, Florida, 1984.

2. Saini *et al*, Preprints, Division of Fuel Chemistry, 205th ACS National Meeting, Denver, Colorado, March 28 to April 2, 1993.

3. Serio *et al*, Preprints, Division of Fuel Chemistry, 205th ACS National Meeting, Denver, Colorado, March 28 to April 2, 1993.

4.3 BENCH UNIT PROGRAM

4.3.1 Description of Bench Unit

The continuous bench unit (BU) designed and built for this program originated as a one stage up-flow reactor system located at the Nisku facilities of the Alberta Research Council (ARC). As the Nisku facility was shut down, the unit was moved to the ARC Devon High Head Laboratory, and was converted into a two stage integrated system. The original plan for this program was to use a stirred autoclave for the first, coal solubilization stage of the process, and a counterflow reactor for the second, hydroconversion stage. However, the opportunity existed to apply the counterflow reactor system for the first stage also. This option was designed and built into the bench unit when it was reassembled in Devon. The following is a description of the BU in the configuration used for most of the test runs. Modifications of the BU for individual test runs will be described in Section 4.3.2 Operation.

The BU is designed for a nominal feed rate of 1 kg/hr. The design pressure and design temperature are 20.8 MPa and 500°C, respectively. The unit is very flexible as the two reactor stages can be operated as individual stages or directly coupled in series. As it was anticipated that the residence time in the second reactor would be twice the residence time in the first reactor, the second stage reactor has about twice the volume of the first stage reactor. As results from the tests became available, this proved to be a limiting factor for the operation and the performance of the first, solubilization stage. Although the operating pressure of each stage is controlled separately, the pressure in the second stage must be higher than the pressure in the first stage.

A computerized PC based control system (Camile) is installed in a separate control room where the operators monitor and control the operation. The Camile keeps a record of all significant operating parameters throughout a test run. These "trending curves" are used to evaluate the overall run and particularly each individual mass balance period.

Figure 4.3.1 represents a simplified process flow diagram of the BU. The BU consists of three main sections:

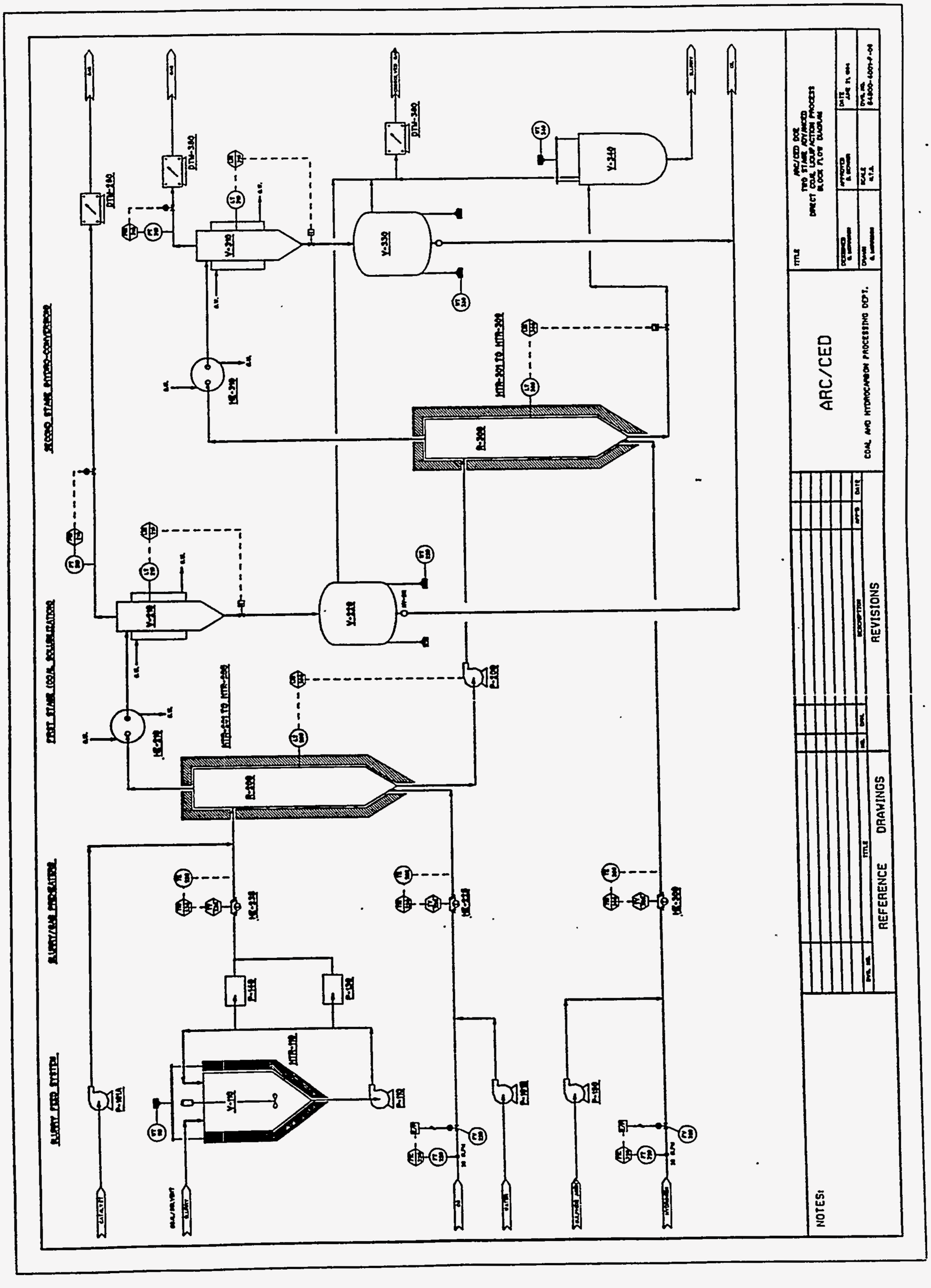
- the slurry feed system
- the coal solubilization stage and
- the hydroconversion stage

In its present configuration, the BU is not equipped with a solvent recovery and recycle system, i.e. the coal derived solvent must be provided externally. It is anticipated that for Phase II of this program a solvent recovery and recycle system would be installed in order to demonstrate the CFR coal liquefaction process in bench unit runs over extended periods of time (one to two months of continuous operation).

4.3.1.1 Slurry Feed System

The slurry feed system contains all facilities required to provide the feed slurry, catalyst, water and sulphiding agent to the reactor stages. Weighed amounts of coal, solvent and catalysts (if required) are mixed in a mixing vessel to prepare a homogeneous slurry feed with the desired coal concentration. Sufficient slurry is prepared to last for at least one mass balance period including the line-out period of the BU. The prepared slurry feed is manually transferred to the slurry feed tank V-110 (volume of about 26 litres) which is maintained at a constant temperature by an electrical heater. Tank V-110 is suspended from a strain gauge balance (WT-110) which is monitored and recorded by the control system and allows the determination of the slurry feed rate.

Figure 4.3.1


SLURRY FEED SYSTEM
SLURRY/GAS PREHEATING
FIRST STAGE COAL SOLUBILIZATION
SECOND STAGE HYDRO-CONVERSION
CATALYST
COAL/SOLVENT SLURRY
WATER
HYDROGEN
GAS
SLURRY
OIL
V-110
HTR-110
R-200
R-300
V-210
V-220
V-310
V-330
V-340
NOTES:
REFERENCE DRAWINGS
REVISIONS
ARC/CED
COAL AND HYDROCARBON PROCESSING DEPT.
TITLE
ARC/CED DOE
TWO STAGE ADVANCED
DIRECT COAL LIQUEFACTION PROCESS
BLOCK FLOW DIAGRAM
DATE
SCALE
N.T.S.
DWG. NO.

Pump P-110 circulates the feed slurry to maintain a uniform mixture and to prevent settling of the coal or catalysts. One of the high pressure displacement pumps P-130 or P-140 takes a slip stream of the circulating slurry and raises its pressure to the operating pressure of the first stage counterflow reactor R-200. The displacement of these pumps (adjusted manually) sets the feed rate to the reactor system.

The feed system also provides high pressure displacement pumps for the injection of water (P-161B) and a catalyst solution (P-161A) into the first stage, and for the injection of a sulphiding agent (P-150) into the second stage. The respective rates of injection are determined from level readings taken on burets attached to the suction side of each pump.

4.3.1.2 Coal Solubilization Stage

The coal solubilization stage consists of preheaters HTR-235 and HTR-225, the first stage solubilization reactor R-200, the overhead cooler/condenser HE-210, the overhead separator V-210, and the overhead product receiver vessel V-220. The solubilization reactor R-200 is designed for counterflow operation and has an internal volume of about 0.8 litres.

The temperature of the slurry feed stream from P-130 (or P-140) is raised to the reactor feed temperature in electrical preheater HTR-235. Just before the slurry feed enters the solubilization reactor R-200, catalyst solution (if required) is injected. Carbon monoxide flow controlled via FIC-220 and water are combined, heated to the desired temperature in the electrical heater HTR-225 and then injected into the bottom of R-200. Facilities are provided to replace the carbon monoxide gas with hydrogen gas. The temperature in R-200 is controlled by five separately controlled heating zones along the height of the reactor and monitored via three internal thermocouples.

The slurry feed flows downward through the reactor, counter-current to the carbon monoxide and water injected into the bottom of R-200. As the CO and water react to form hydrogen and carbon dioxide, the coal is solubilized. Level controller LIC-200 maintains the liquid level in R-200 at the desired height by controlling the withdrawal rate of the stream that is removed from the bottom of R-200 with interstage pump P-200. Gases and vaporized products leave the top of R-200 via cooler/condenser HE-210.

The overhead condensate is separated from the uncondensed material in vessels V-210, removed under level control (LIC-210) and collected in the overhead product receiver vessel V-220. Vessel V-220 is suspended from the strain gauge balance WT-220 which is monitored and recorded by the Camile. Dissolved gases from V-220 are combined with the dissolved gases from the hydroconversion stage and are metered in dry gas meter DTM-360.

The uncondensed stream leaves V-210 via back-pressure controller PIC-210 which controls the operating pressure in R-200. The gas stream is measured in dry gas meter DTM-260, and a slip stream is analyzed in an on-line gas chromatograph.

4.3.1.3 Hydroconversion Stage

The hydroconversion stage consists of the hydroconversion reactor R-300, the hydrogen heater HTR-300, the overhead cooler/condenser HE-310, the overhead separator V-310, the overhead product receiver vessel V-330, and the bottoms receiver vessel V-340. The hydroconversion reactor R-300 is designed for counterflow operation and has an internal volume of about 1.6 litres.

After interstage pump P-200 raises the pressure to the operating pressure of the second stage, the bottom stream from the solubilization reactor R-200 is injected into the top of the hydroconversion reactor R-300. Hydrogen under flow control (FIC-320) and at a temperature adjusted in the heater HTR-300 is injected into the bottom of R-300. The temperature in R-300 is controlled by eight separately controlled heating zones along the height of the reactor and monitored via eight internal thermocouples.

The first stage bottoms stream flows downward through R-300, counter-current to the hydrogen and is converted to lighter materials. Level controller LIC-300 maintains the liquid at the desired height in R-300 by controlling the withdrawal rate of the stream that is removed from the bottom of R-300 via a constant volume let-down system. The bottom stream containing unconverted coal, ash and other solids and oil that is not vaporized under the conditions prevailing in R-300 is collected in the receiver vessel V-340. Vessel V-340 is suspended from a strain gauge balance (WT-340) which is monitored and recorded by the Camile. Dissolved gases from V-340 are combined with the dissolved gases from V-220 and V-330 and are measured in dry gas meter DTM-360.

Gases and vaporized conversion products leave the top of R-300 via cooler/condenser HE-310. The overhead condensate is separated from the uncondensed material in vessel V-310, removed under level control (LIC-310) and collected in overhead receiver vessel V-330. Vessel V-330 is suspended from a strain gauge balance (WT-330) which is monitored and recorded by the Camile. Dissolved gases from V-330 are combined with the dissolved gases from V-220 and V-340 and are metered in a dry gas meter DTM-360. Gas samples are taken periodically for GC analysis.

The uncondensed stream leaves V-310 via back-pressure controller PIC-310 which controls the operating pressure in R-300. The gas stream is measured in the dry gas meter DTM-350, and a slip stream is analyzed by an on-line gas chromatograph.

4.3.2 Operation and Work-Up

4.3.2.1 Operation

The design, relocation and reconstruction of the bench unit was completed at the end of April 1993. Commissioning of the unit started at that time, and the experimental program was completed exactly twelve months later at the end of April 1994. During this twelve month period, some eighteen (18) runs were completed covering about forty five (45) different operation conditions (see Table 4.3.1). The following describes chronologically the operation of the bench unit and the modifications made during the twelve month operating period. Section 4.3.3 presents and discusses the results of the bench unit tests in detail.

Most of the bench unit work (DOE-BU-001 to DOE-BU-015) was carried out with Black Thunder subbituminous coal from Wyoming and Black Thunder derived solvent from the Wilsonville operation. The final three runs (DOE-BU-016 to DOE- BU-018) were carried out with Illinois #6 coal and Illinois #6 derived solvent from the HRI pilot plant operation.

4.3.2.2 Tests With Black Thunder Coal

Autoclave tests with Black Thunder coal confirmed that solubilization was best achieved in a carbon monoxide/water steam environment using potassium carbonate as the preferred catalyst (see Chapter 4.2 Autoclave Tests, 4.2.2 Black Thunder Coal). It was, therefore, decided to perform the first two bench unit runs (DOE-BU-001 and-002) using the solubilization reactor R-200 only with potassium carbonate mixed into the coal/solvent feed slurry. Almost immediately after the feed slurry was introduced into the bench unit, major plugging problems were encountered in between the slurry feed tank V-110 and the first stage reactor R-200. Numerous attempts using mechanical changes to the bench unit failed to solve this plugging problem.

Analysis determined that the major portion of the material causing the plugs was in fact potassium carbonate. Eventually, this problem was overcome when the potassium carbonate was injected as a 15 wt.% aqueous solution into the slurry feed line immediately upstream of the counterflow reactor R-200. It was speculated that due to its hygroscopic nature, water absorption caused the potassium carbonate to form agglomerated solids in the lines causing the plugging. Because of these plugging problems, no worthwhile data could be collected during those first two bench unit runs.

TABLE 4.3.1 BENCH UNIT OPERATIONS

DOE RUN #	YIELD PERIODS	DATES	FIRST STAGE CONDITIONS				SECOND STAGE CONDITIONS			
			TEMPERATURE (C)	PRESSURE (MPa)	WHSV	CATALYST	TEMPERATURE (C)	PRESSURE (MPa)	WHSV	CATALYST
BLACK THUNDER COAL						(CO/H2O)				(H2)
BU-003	YP-01	JUNE 3,1993	386	17.24	2.06	CARBONATE	NONE			
BU-004	YP-01,YP-02	JUNE 14,1993	395	17.24	1.89,1.60	CARBONATE	NONE			
BU-005	YP-001	JUNE 17,1993	396	17.24	0.9	CARBONATE	NONE			
BU-008	YP-01,YP-02	SEPTEMBER 8-9,1993	395	10.34	2.24,2.19	NONE	434	17.24	0.94,0.92	ATM
BU-009	YP-01	SEPTEMBER 13,1993	395	10.34	2.01	NONE	434	17.24	0.59	ATM
BU-009	YP-02,YP-03	SEPTEMBER 16,1993	395,394	10.34	1.99,2.04	ALUMINATE	443	17.24	0.59,0.6	ATM
BU-009	YP-04,YP-05	SEPTEMBER 17,1993	391,392	10.34	1.95,1.92	NONE	442	17.24,13.79	0.74,0.72	ATM
BU-010	YP-01,-YP-04	OCTOBER 19-21,1993	390-392,410-412	10.34,15.17	2.62-1.74	ALUMINATE	NONE			
BU-011	YP-01,-YP-03	OCTOBER 26,1993	410-412	10.34	1.49-1.18	ALUMINATE	NONE			
BU-012	YP-01,-YP-04	NOVEMBER 9-11,1993	409-410	10.34	2.07-1.55	ALUMINATE	408-433	17.24	1.50-0.91	Fe2O3/DMDS
BU-013	YP-01	NOVEMBER 16,1993	411	10.34	2.2	ALUMINATE	425	17.24	1.47	PYRITE
BU-013	YP-02	NOVEMBER 18,1993	409	10.34	1.75	ALUMINATE	425	17.24	1.18	ATM
BU-013	YP-03	NOVEMBER 18-19,1993	411	10.34	2.15	ALUMINATE	424	17.24	1.44	ATM/DMDS
BU-013	YP-04	NOVEMBER 19,1993	412	10.34	2.35	ALUMINATE	424	17.24	1.58	AHM/DMDS
BU-014	YP-01,-YP-04	DECEMBER 7-10,1993	410-411	10.34	1.79-1.73	ALUMINATE	430-445	17.24	1.07-1.04	Fe2O3/DMDS
BU-015	YP-01,-YP-06	DECEMBER 14-17,1993	409-412	10.34	2.29-1.74	ALUMINATE	430-440	17.24	1.20-0.85	AHM/DMDS
ILLINOIS #6 COAL						(H2)				(H2)
BU-016	YP-01,YP-02	MARCH 24-25,1994	428,440	17.24	0.92,0.80	Fe2O3/DMDS	NONE			
BU-017	YP-01,-YP-03	MARCH 28-29,1994	428-442	17.24	1.06-0.88	AHM/DMDS	NONE			
BU-018	YP-01,-YP-03	APRIL 27-28,1994	422-428	17.24+	1.55-1.40	AHM	430-440	17.24	0.90-0.81	AHM
BU-018	YP-04,YP-05	APRIL 28-29,1994	415,417	17.24+	1.79,1.64	Fe2O3	431,440	17.24	0.80,0.86	Fe2O3

CARBONATE	POTASSIUM CARBONATE, K_2CO_3
ALUMINATE	SODIUM ALUMINATE, $NaAlO_2$
Fe2O3	IRON OXIDE, Fe_2O_3
DMDS	DIMETHYL DISULPHIDE, CH_3SSCH_3
AHM	AMMONIUM HEPTAMOLYBDATE, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$
ATM	AMMONIUM TETRATHIOMOLYBDATE, $(NH_4)_2MoS_4$

With the modified system of catalyst injection, three bench unit runs (DOE-BU-003 to -005) were performed during June 1993. Only the first stage, solubilization reactor R-200 (one stage mode) was used for these runs, and conditions were selected based on autoclave tests. Reactor pressure was maintained at 17.24 MPa, temperature at 395°C (for DOE-BU-003 the temperature was lower) and the weighted hourly space velocity (WHSV) ranged from 1.9 to 0.9. The slurry feed for these runs contained about 40 wt.% coal, except DOE-BU-003 where it was 16% wt coal.

During DOE-BU-003 difficulties were encountered in the pressure let down system as frequent plugging of the back pressure regulator PIC-210 occurred. It was observed that the outside of the regulator iced up. This clearly indicated that the temperature of the off gas dropped below the freezing point of water during the expansion to atmospheric pressure due to the large amount of carbon dioxide (product of the shift reaction) in the off-gas. Installing the pressure regulator in a hot water bath prevented this freezing problem in subsequent runs.

Although coal solubilizations obtained in DOE-BU-003 to DOE-BU-005 were found to be lower than those achieved in the autoclave, it was decided to proceed to the two stage, integrated operation of the bench unit.

The original design and construction of the bench unit was based on the concept to operate the first stage at a higher pressure than the second stage. This would allow the transfer of the first stage reactor bottoms stream to the top of the second stage reactor via control valves which are controlled by the liquid level in the first stage reactor. During run DOE-BU-006 it soon became clear that smooth operation using this system was not attainable. Either no material flowed between the two reactors or all material from the first reactor was dumped into the second reactor. Changing the control valves or the pressure difference between the two reactors did not solve the problem. It was speculated that the small size of the control valve(s) may be the cause of the problem, as ash, catalyst or coal particles may temporarily block the flow and then, as the control valve opens, release suddenly.

A major decision was, therefore, reached to change the design concept and to operate the first stage at a lower pressure than the second stage. Autoclave tests showed that coal solubilization would not be effected significantly by lowering the operating pressure of the solubilization reactor to around 10 MPa. Therefore, the transfer pump P-200 was installed between the two stages to raise the pressure of the first stage bottom stream to the second stage operating pressure and to control the liquid level in the solubilization reactor (variable speed drive).

With the transfer pump P-200 installed, severe plugging problems in the check valves of P-200 prevented a successful continuous operation during DOE-BU-007. Analysis of the plugs once again implicated the potassium carbonate. As a result, both runs, DOE-BU-006 and DOE-BU-007 did not yield any useful data. However, the modifications made to solve the difficulties and the operating experience gained during these two runs laid the foundation for the successful operation of the bench unit for the subsequent runs.

With the experience from DOE-BU-007, it was apparent that an alternative first stage catalyst had to be found for the continuous operation of the bench unit. Autoclave studies determined that sodium aluminate, although less active than potassium carbonate, was the best available replacement. At that time, however, only a limited amount of sodium aluminate was at hand, and the Department of Energy suggested to examine ammonium tetrathiomolybdate (ATM) as a second stage catalyst which might also have some first stage activity. The first two successful two stage runs, DOE-BU-008 and DOE-BU-009 were carried out with ammonium tetrathiomolybdate as first and second stage catalyst for all but two yield periods during which sodium aluminate was added as an additional, first stage catalyst. The addition of aluminate was shown to be clearly beneficial for carbon monoxide conversion, coal solubilization and pentane soluble oil yield. Sodium aluminate was, therefore, used as first stage catalyst for all subsequent runs, where carbon monoxide/steam was used for the first stage. Starting with DOE-BU-008, the bench unit was operated continuously for about five (5) days at a time.

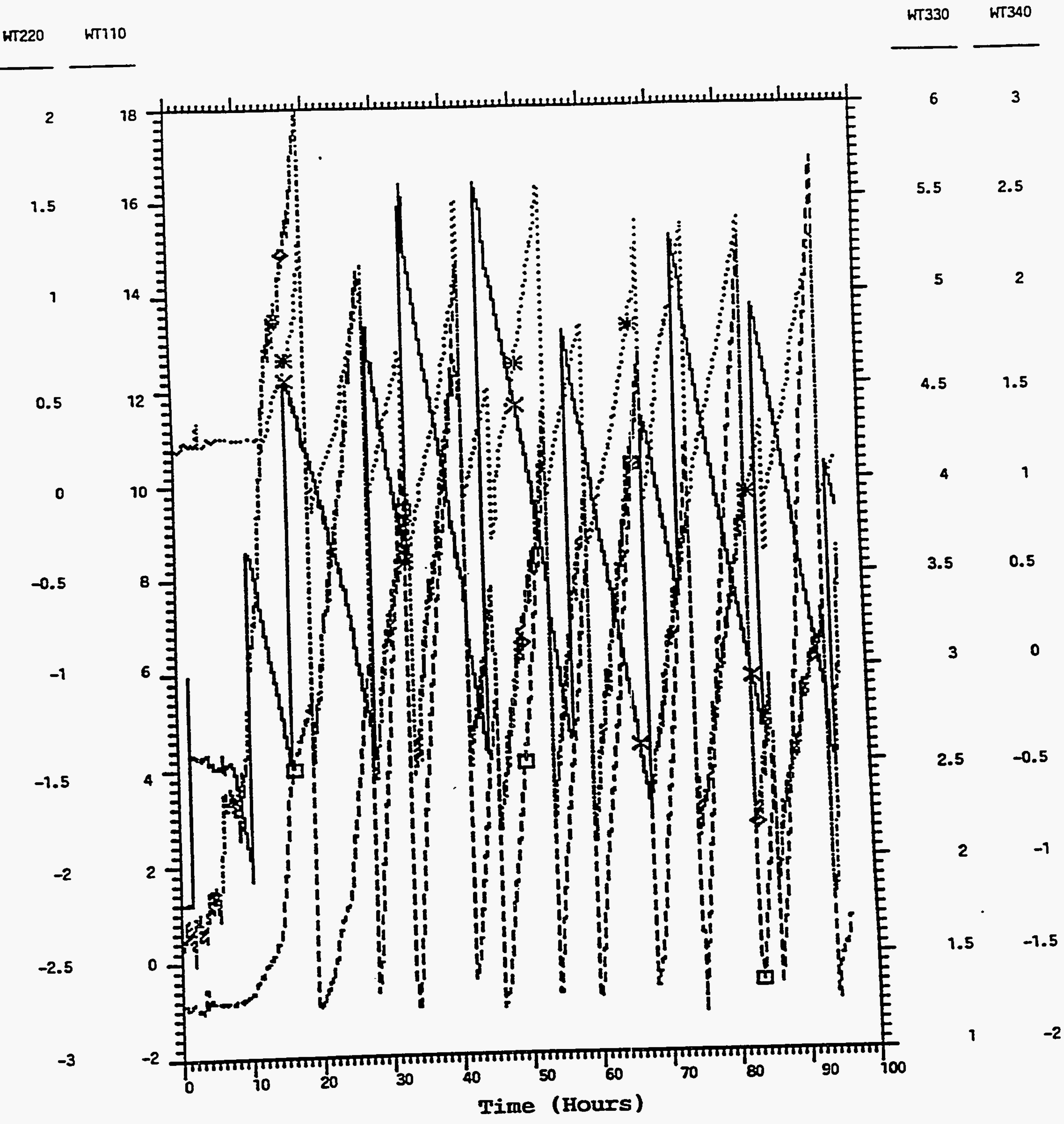
While DOE-BU-007 and DOE-BU-008 successfully demonstrated continuous two stage operation using the counterflow reactor system, the coal conversions and pentane soluble oil yields on a MAF coal basis were relatively low. It was decided, therefore, to reexamine first stage operation, this time using sodium aluminate as catalyst. During runs DOE-BU-010 and DOE-BU-011 different reactor temperatures and space velocities were studied. As a result of these runs, carried out in October 1993, first stage conditions with sodium aluminate as catalyst were fixed at 410°C, 10.34 MPa and WHSV of 1.5 to 2.0 for all subsequent runs with Black Thunder subbituminous coal. These conditions gave coal conversions of 75 to 80 wt% which were regarded "optimum" for the operation of the second stage. There now remained the task of improving second stage operating conditions to increase coal conversion and oil yields.

Runs DOE-BU-012 and DOE-BU-013 were important in two respects: firstly, it was decided to add the first stage catalyst (sodium aluminate) directly into the feed slurry as had been initially attempted with potassium carbonate, instead of being added as an aqueous solution. The addition of sodium aluminate during the preparation of the feed slurry proved successful, and in fact led to much higher carbon monoxide conversions by shift reaction in the first stage. Secondly, several second stage catalysts were tried. Iron oxide or ammonium molybdate with dimethyl disulphide addition were chosen as the most promising. Coal conversion and oil yields were still relatively low, but operating temperatures in the second stage reactor were only 425°C.

In the final bench unit runs with Black Thunder coal carried out in December 1993 (DOE-BU-014 and DOE-BU-015), second stage reactor temperatures were raised to 430 and 440°C. Under these conditions coal conversions reached target values of above 90% with corresponding increases in oil yield.

Clearly, integrated two stage operation using counterflow reactors for both stages was demonstrated on a once through basis using Black Thunder coal. Figure 4.3.2 is an

Figure 4.3.2



Input File: C:\CAMILE\RUN-15\RUN15-8.DAT
Starting Time: 11-DEC-93 8:58:34

X —— WT110 (KGS)
✱ ···· WT220 (KGS)
□ – – WT330 (KGS)
◇ -·-· WT340 (KGS)

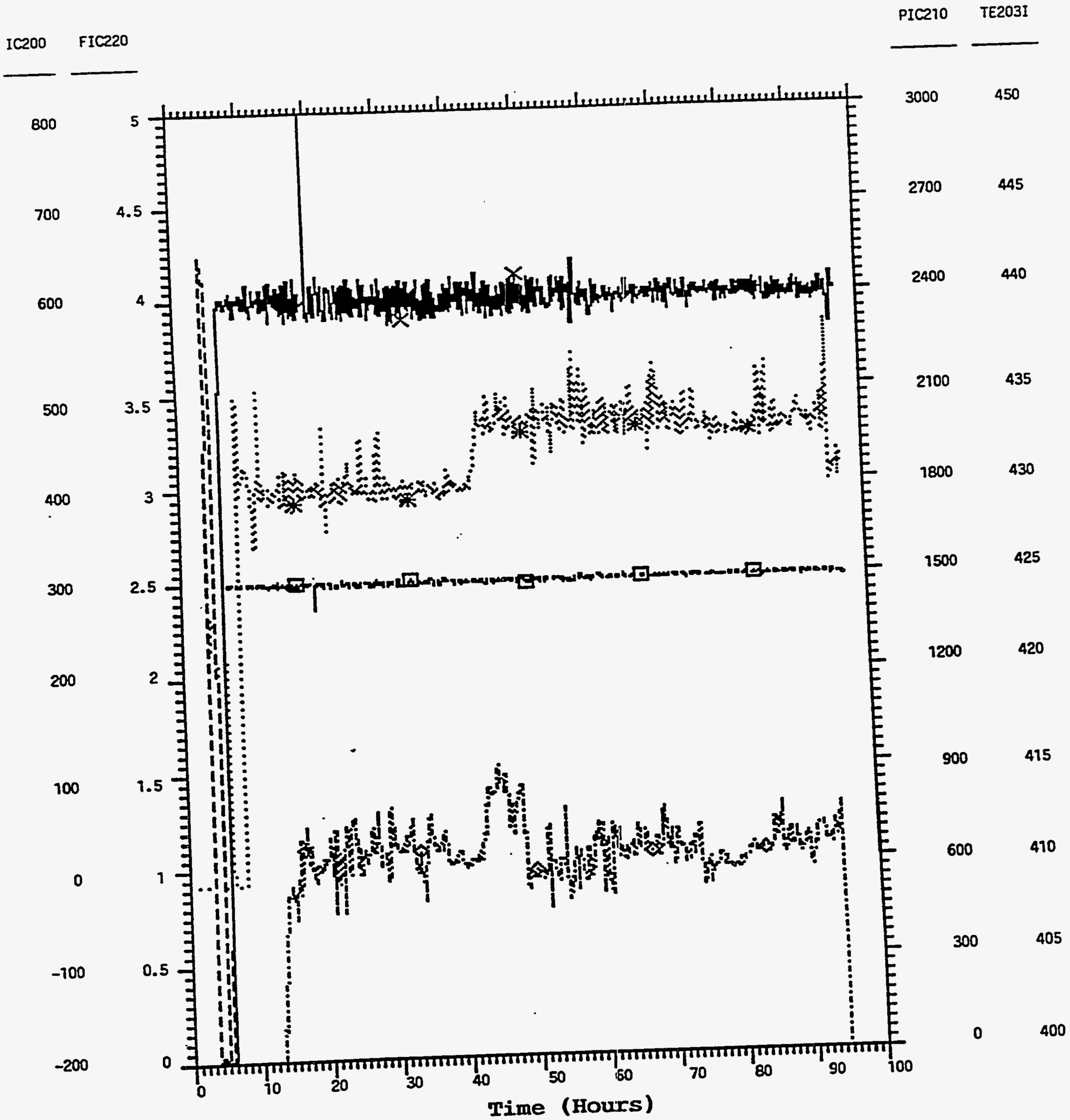
example of the typical "saw-teeth" shape for the weights of the feed vessel (WT-110), and the product receiver vessels (WT-220, WT-330 and WT-340). Figures 4.3.3 and 4.3.4 show first and second stage operating conditions (pressure, temperature and liquid level), respectively. These curves are print-outs of trending curves stored by the computerized control system for run DOE-BU-015 and clearly shows the smooth and continuous operation of the bench unit. Further optimization of the operating conditions and the demonstration of solvent recycle is envisioned for Phase II of this program.

4.3.2.3 Tests With Illinois #6 Coal

Bench unit operation with Illinois #6 was delayed until the receipt of Illinois #6 coal derived solvent from HRI in March 1994. Autoclave tests showed this coal to be much less reactive than Black Thunder coal, and as expected, to be less responsive to solubilization with carbon monoxide/steam than with hydrogen. Nevertheless, at the end of March 1994, first stage bench unit runs using the counterflow reactor were attempted using both carbon monoxide/steam with sodium aluminate catalyst and hydrogen with ammonium molybdate catalyst. In both cases, the check valves of the transfer pump P-200 between the two stages plugged. This time the analysis indicated that the plugging material was non converted coal. As attempts to solubilize Illinois #6 coal at higher temperatures in the first stage reactor R-200 did not succeed, it was concluded that the reactor R-200 was too small, i.e. insufficient height for successful operation. It is postulated that the height of the liquid level in reactor R-200 does not provide sufficient settling time for Illinois #6 coal to solubilize.

Consequently, two one stage runs were carried out (DOE-BU-016 and DOE-BU-017) using the second stage reactor R-300 with about twice the height of the reactor R-200, thus, offering longer settling, i.e. solubilization time for the coal. Using hydrogen, coal conversions in the 80% range were achieved at temperatures of up to 440°C and WHSV of around 0.9. No further attempts were made to increase coal conversion in one stage by increasing reactor temperature or decreasing WHSV. Instead, it was

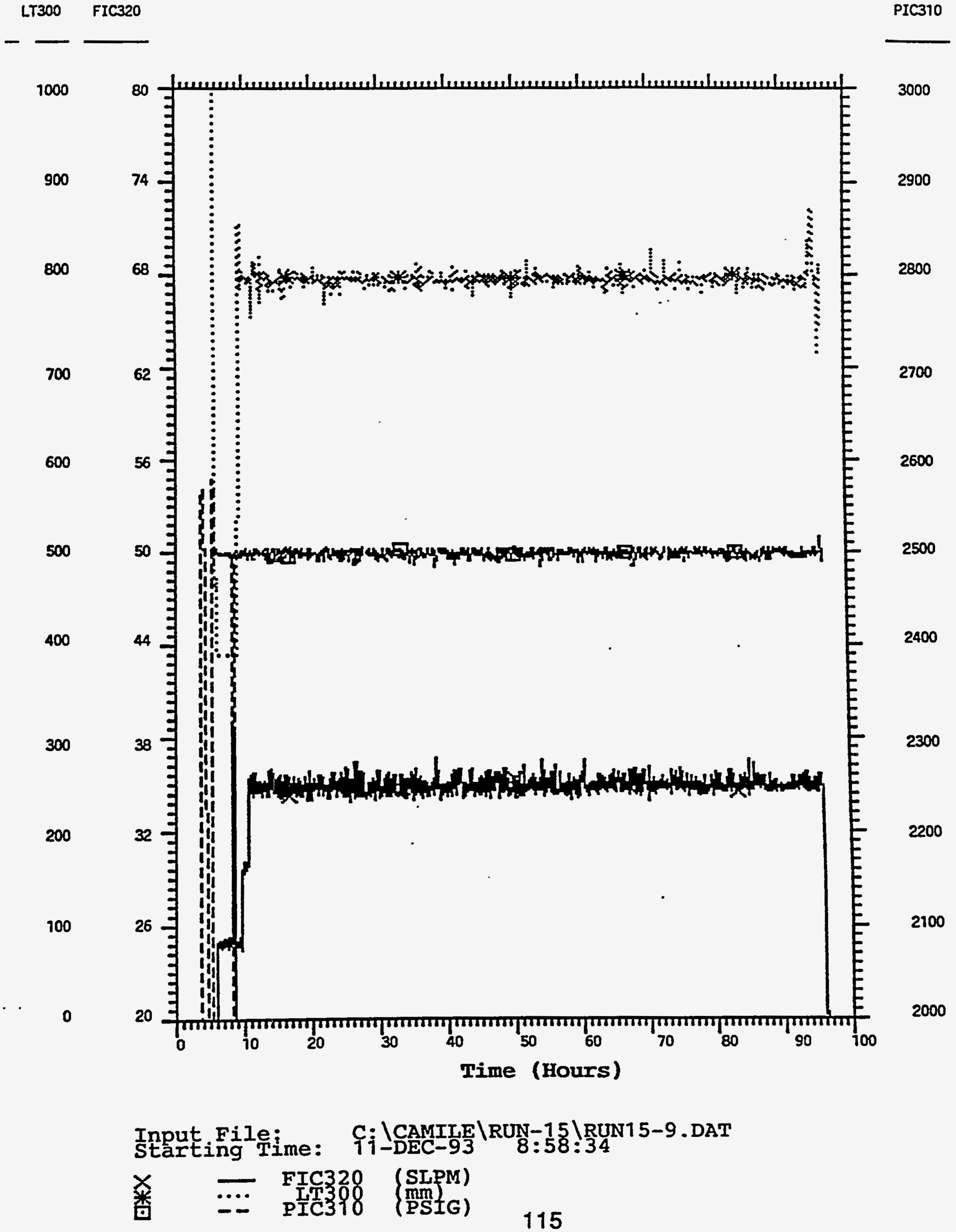
Figure 4.3.3



Input File: C:\CAMILE\RUN-15\RUN15-12.DAT
Starting Time: 11-DEC-93 8:58:34

X ——— FIC220 (SLPM)
✱ ····· LIC200 (mm)
⊡ – – PIC210 (PSIG)
◈ –·–· TE203I (DEG C)

Figure 4.3.4



LT300
FIC320
PIC310
1000
900
800
700
600
500
400
300
200
100
0
80
74
68
62
56
50
44
38
32
26
20
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
0
10
20
30
40
50
60
70
80
90
100
Time (Hours)
Input File: C:\CAMILE\RUN-15\RUN15-9.DAT
Starting Time: 11-DEC-93 8:58:34
X — FIC320 (SLPM)
✱ .... LT300 (mm)
□ -- PIC310 (PSIG)

decided to revisit the original two stage bench unit concept and to replace the first stage counterflow reactor (R-200) with a flow-through, stirred autoclave.

In April 1994, the final bench unit run (DOE-BU-018) was therefore performed with a flow-through, stirred autoclave as the first stage reactor and the counterflow reactor R-300 as the second stage. Hydrogen was used in both stages, and iron oxide or ammonium molybdate were the catalysts. Coal conversions of around 95% were obtained with this system. As with Black Thunder coal, further optimization particularly the use of a larger first stage counterflow reactor is envisaged for Phase II.

4.3.2.4 Mass Balance Procedure

During the eighteen bench unit runs, forty five different operating conditions were tested. For each of these operating conditions a mass balance was performed around the bench unit. The numerical work-up of these mass balances was performed using a LOTUS spreadsheet program. The following provides a description of how the data for the mass balances were collected and processed. Table 4.3.2, Sheet 1 to 7, shows an example of the set of print outs for each mass balance period.

Sheet No.: 1 - Measurements

Description of the feed, operating conditions, readings from strain gauge balances and gas meters, liquid levels in the reactor(s), etc. are input in Sheet 1. The numerical value for each input is taken from log sheets kept by the bench unit operators (an example is shown in Table 4.3.3) and cross checked with corresponding trending curves from the Camile (examples are shown in Figures 4.3.5 to 4.3.7). Feed composition, i.e. wt% maf coal is calculated as the fraction of IOM in the feed (maf basis) from Sheet No. 7. "Measured Volume %" in the box labelled "Measured Gas Compositions" are averages calculated in Sheet No. 4 from GC analysis. Total gas volume is calculated by difference from dry gas meter readings before and after a mass balance period, and is then converted to standard conditions to give the "Net

Table 4.3.2 (Sheet 1)

UN No.: DOE-BU-014

M.B.No.: YP-03/ C1

	Date	Time	Date	Time
TART:			Dec. 09, 93	21:00
ND:			Dec. 10, 93	05:00
URATION (hours):				8.00

Feed:	Type	Wt% (maf)
Coal	BTH	41.81%
Solvent	V-1074	58.19%
Catalyst 1	Aluminate	2.00%
Catalyst 2	FeO+DMDS	2.00%
Other		

OPERATING PARAMETERS:		
EED TANK WI-110):	(G)	
Start of Mass Balance		14600.00
End of Mass Balance		7710.00
Rate	(G/HR)	861
FIRST STAGE:		
Operating Pressure:	(MPa)	10.34
Feed Temp.:	(C)	
Reactor Temp.:	(C)	
TE-201I	(BTTM)	410
TE-202I		411
TE-203I		411
TE-204I	(Top)	389
Liquid Level	(mm)	540
Separator Temperature:	(C)	47
CO-Feed Rate:	(L/MIN)	4.03
Water Feed Rate:	(ML/MIN)	1.22
Temperature:	(C)	180
Catalyst Feed:	(ML/MIN)	
Liquid Product (WI-220):	(G)	
Start of Mass Balance		
End of Mass Balance		522.10
Nitrogen Rate:	(L/MIN)	3.93
SECOND STAGE:		
Operating Pressure:	(MPa)	17.24
Feed Temp.:	(C)	140
Reactor Temp.:	(C)	
TE-301I	(BTTM)	438
TE-302I		440
TE-303I		440
TE-304I		438
TE-305I		438
TE-306I		438
TE-307I		434
TE-308I	(Top)	432
TE-309I	(VAP)	432
Liquid level	(mm)	900
Separator Temperature:	(C)	45
Hydrogen Feed Rate:	(L/MIN)	34.08
Temperature:	(C)	398
Liquid Product (WI-330):	(G)	
Start of Mass Balance		1240
End of Mass Balance		5360
Bottoms Product (V-340):	(G)	
Start of Mass Balance		-480
End of Mass Balance		1460
Sulfiding Agent	(mL/HR)	10.47

MEASURED GAS COMPOSITIONS				
NAME	MW	Measured Volume %		
		Product Gas 11	Product Gas 21	Dissolved Gas 22
Hydrogen	2.02	4.28	99.18	34.81
CO2	44.01	13.03	0.08	22.30
CO	28.01	23.81	0.37	8.21
H2S	34.08			
Methane	16.04	0.50	0.94	0.56
Ethylene	28.05		0.03	0.48
Ethane	30.07		0.25	0.48
Propane	44.01		0.18	1.53
Propylene	42.08			
i-Butane	58.12		0.01	0.14
n-Butane	58.12		0.08	1.25
i-Butene	56.11			
n-Butene	56.11			
C2-Butene	56.11			
i-Pentane	72.15			
n-Pentane	72.15		0.11	3.34
Nitrogen	28.02			
TOTAL		41.61	101.24	73.1045

Gas Meter Readings	DTM-260	DTM-360	DTM-350
Start of M.B. : (L)	5653.0	3703.0	8314.0
End of M.B. : (L)	10593.0	21350.0	8316.0
Total : (L)	4940.0	17647.0	2.0
Temperature: (C)	22.7	22.1	23.7
Meter Pressure : (mmHg)	694	699	699
Standard Volume: (L)	4165	15016	2
Nitrogen to R-200: (L)	1886		
Net Gas Out: (L)	2279	15016	2

Run Conditions			
Basis: MAF		First Stage	Second Stage
Pressure	Mpa	10.3	17.2
Temperature	deg C	411	439
Catalyst		Aluminate	FeO+DMDS
Feed	wt % maf coal	41.81%	
WHSV	(kg / hr) / l	1.76	1.06
CO Rate	kg / kg maf coal	0.92	
	moles / 100g maf coal	3.27	
consumed	moles / 100g maf coal	1.06	
Water Rate	kg / kg maf coal	0.92	
	moles / 100g maf coal	5.08	
Hydrogen	kg / kg maf coal		0.56
	moles / 100g maf coal		27.79
consumed	wt % maf coal	1.35%	5.63%

Table 4.3.2 (Sheet 2)

RUN No.: DOE-BU-014 M.B.No.: YP-03/ C1

OVERALL MASS BALANCE

Material In:		Grams		Material Out:		Grams
	Feed Slurry	6890			First Stage Liquid:	522
	CO-Gas:	2416			First Stage Product Gas:	3072
	Water:	585			Second Stage Liquid:	4120
	Hydrogen:	1475			Second Stage Reactor Bottoms:	1940
	Catalyst:				Second Stage Product Gas:	1717
	S-Agent	84			Dissolved Gas:	2
TOTAL IN:		11449		TOTAL OUT:		11372
	Catalyst mf	276			OVERALL BALANCE:	99.3%

WATER BALANCE

TOTAL IN:	816	TOTAL OUT:	988
		WATER BALANCE:	121.1%

Coal Conversion	wt.% maf	92.4%
Ash Balance	wt.%	139.7%

PRODUCT YIELDS

Description	Total Gross			Total Net	
	[grams]		wt. % maf feed	[grams]	wt. % maf coal
	measured	normalized			
H2O	172.53	176.07	2.79%	176.07	6.67%
COx	260.30	265.64	4.21%	265.64	10.06%
H2S					
C1 to C3	228.16	232.84	3.69%	232.84	8.82%
C4 +	89.53	91.37	1.45%	91.37	3.46%
Oil	4469.38	4561.07	72.24%	1332.09	50.46%
Asphaltene	885.66	903.83	14.32%	459.34	17.40%
Preasphalt.	65.78	67.13	1.06%	67.13	2.54%
IOM	195.64	199.66	3.16%	199.66	7.56%
Total	6366.98	6497.60	102.92%	2824.13	106.98%

Simulated Distillation Profile THF-Extract						Crude Sim. Dist. (Comp. Sample)				
Fraction	Feed	Product				Feed	Product			
		Total Gross		Total Net			Total Gross		Total Net	
			normalized					normalized		
[deg C]	[grams]	[grams]	[grams]	[grams]	wt. % maf coal	[grams]	[grams]	[grams]	[grams]	wt. % maf coal
C4 - 182		144.33	147.29	147.29	5.58%		89.53	91.37	91.37	3.46%
182 - 343	146.94	1428.82	1458.13	1311.19	49.67%	66.12	902.67	921.19	855.06	32.39%
343 - 524	3526.53	3544.24	3616.95	90.42	3.43%	3082.04	3616.94	3691.14	609.10	23.07%
524+		588.61	600.68	600.68	22.75%	525.31	1096.85	1119.36	594.05	22.50%
TOTAL	3673.47	5705.99	5823.05	2149.58	81.43%	3673.47	5705.99	5823.05	2149.58	81.43%
IBP - 524	3673.47	5117.39	5222.37	1548.90	58.67%	3148.16	4609.14	4703.69	1555.53	58.92%

Table 4.3.2 (Sheet 3)

RUN No.: DOE-BU-014 M.B.No.: YP-03/C1

GAS ANALYSIS

Name	First Stage Product Gas (DTM-260)							Second Stage Product Gas (DTM-360)							Dissolved Gas (DTM-330)						
	Number of Samples: 1							Number of Samples: 6							Number of Samples: 2						
	vol.%	vol.%	vol.%	vol.%	vol.%	vol.%	Av.vol.%	vol.%	vol.%	vol.%	vol.%	vol.%	vol.%	Av.vol.%	vol.%	vol.%	vol.%	vol.%	vol.%	vol.%	Av.vol.%
Hydrogen	4.275						4.275	100.046	99.953	99.798	97.710	97.641	99.931	99.180	31.289	38.321					34.805
CO2	13.029						13.029	0.081	0.091	0.061	0.076	0.085	0.097	0.082	22.497	22.095					22.296
CO	23.812						23.812	0.335	0.352	0.371	0.388	0.398	0.392	0.372	8.066	8.361					8.214
H2S																					
Methane	0.495						0.495	0.989	0.961	0.888	0.883	0.888	1.010	0.936	0.580	0.536					0.558
Ethylene								0.031	0.030	0.032	0.030	0.030	0.030	0.031	0.911	0.058					0.485
Ethane								0.241	0.237	0.256	0.257	0.258	0.251	0.250	0.060	0.898					0.479
Propane								0.198	0.193	0.201	0.199	0.119	0.199	0.185	1.541	1.523					1.532
Propylene																					
I-Butane								0.012	0.015	0.011	0.011	0.010	0.016	0.013	0.145	0.143					0.144
n-Butane								0.084	0.082	0.084	0.085	0.083	0.084	0.084	1.257	1.244					1.251
I-Butene																					
n-Butene																					
C2-Butene																					
I-Pentane																					
n-Pentane								0.110	0.107	0.110	0.110	0.110	0.109	0.109	3.280	3.404					3.342
Nitrogen																					
TOTAL	41.611						41.611	102.127	102.021	101.812	99.747	99.620	102.119	101.241	69.626	76.583					73.105

RUN No.: DOE-BU-014 M.B.No.: YP-03/ C1

GAS CALCULATIONS

Name	Mol.Weight	First Stage Product Gas (DTM-260)				Second Stage Product Gas (DTM-360)				Dissolved Gas (DTM-350)			
		Average Mol Weight:		16.53 (g/mole)		Average Mol Weight:		2.56 (g/mole)		Average Mol Weight:		23.37 (g/mole)	
		Volume		Weight (norm.)		Volume		Weight (norm.)		Volume		Weight (norm.)	
		meas. %	norm. %	(G)	%	meas. %	norm. %	(G)	%	meas. %	norm. %	(G)	%
Hydrogen	2.02	4.28	10.27	21.10	0.69	99.18	97.96	1325.93	77.24	34.81	47.61	0.07	4.12
CO2	44.01	13.03	31.31	1401.30	45.62	0.08	0.08	23.84	1.39	22.30	30.50	1.01	57.44
CO	28.01	23.81	57.22	1629.96	53.06	0.37	0.37	69.02	4.02	8.21	11.24	0.24	13.47
H2S	34.08												
Methane	16.04	0.50	1.19	19.42	0.63	0.94	0.92	99.38	5.79	0.56	0.76	0.01	0.52
Ethylene	28.05					0.03	0.03	5.66	0.33	0.48	0.66	0.01	0.80
Ethane	30.07					0.25	0.25	49.75	2.90	0.48	0.66	0.01	0.84
Propane	44.01					0.18	0.18	53.84	3.14	1.53	2.10	0.07	3.95
Propylene	42.08												
i-Butane	58.12					0.01	0.01	4.81	0.28	0.14	0.20	0.01	0.49
n-Butane	58.12					0.08	0.08	32.18	1.87	1.25	1.71	0.08	4.25
i-Butene	56.11												
n-Butene	56.11												
C2-Butene	56.11												
i-Pentane	72.15												
n-Pentane	72.15					0.11	0.11	52.21	3.04	3.34	4.57	0.25	14.12
Nitrogen	28.02												
TOTAL		41.61	100.00	3071.78	100.00	101.24	100.00	1716.63	100.00	73.10	100.00	1.76	100.00

First Stage Shift Reaction

		CO	+ H2O	= CO2	+ H2
Stochiom.	[moles]	28.06	28.06	28.06	28.06
Produced	[moles]			3.78	-17.62
Total	[moles]	28.06	28.06	31.84	10.45
Stochiom.	[grams]	786.08	505.72	1235.10	56.69
Produced	[grams]			166.19	-35.59
Total	[grams]	786.08	505.72	1401.30	21.10

Hydocarbon Gases

		First	Second	Dissolved	Total
C1 to C3	[grams]	19.42	208.63	0.11	228.16
C4 +	[grams]		89.20	0.33	89.53
Total	[grams]	19.42	297.83	0.44	317.69

Hydrogen

		First	Second			Total
		Up-Take	In	Out	Up-Take	Up-Take
Hydrogen	[grams]	35.59	1474.66	1326.01	148.66	184.24

Table 4.3.2 (Sheet 4)

Table 4.3.2 (Sheet 5)

RUN No.: DOE-BU-014 M.B.No.: YP-03/ C1

Liquid / Slurry Stream Analysis

		Coal	Solvent	Feed	V-220	V-340 (BTTMS)	V-330	Comp. Sample
Type		BTH	V-1074					
Total Feed / Product				6890	522	1940	4120	
Total Sample	[grams]			53.71	14.7	56.15	60.92	
Water	[grams]			1.8	8.7	0.1	2.5	
Oils+Asphaltenes	[grams]			28.64	5.97	42.92	55.09	
Oils	[wt%] calc	100.00%	87.90%	87.90%	94.57%	77.71%	85.41%	
Asphaltene	[wt%]		12.10%	12.10%	5.43%	22.29%	14.59%	
Pre-Asphaltenes	[grams]					1.16	0.38	
Insolubles	[grams]			23.54		13.23	3.36	
IOM	[wt%] calc			87.29%		35.73%	12.40%	
Ash	[wt%]			11.58%		63.52%	86.60%	
Moisture	[wt%]			1.13%		0.75%	1.00%	
			Cr.S.D.	D-2887		Cr.S.D.	D-2887	Cr.S.D.
Distill. THF-Extract	[wt.%]							
IBP - 182	deg C				6.88%	1.38%	0.53%	
182 - 343			1.80%	4.00%	37.24%	6.48%	33.65%	14.40%
343 - 524			83.90%	96.00%	55.88%	65.64%	65.82%	57.70%
524+			14.30%			26.50%		27.90%
Elemental Analysis:	[wt.%]			IBP - 182	182 - 343	343 - 524	524+	
Carbon		75.70%	87.80%	84.40%	85.20%	88.30%	87.50%	
Hydrogen		5.60%	8.50%	13.20%	10.00%	8.90%	6.70%	
Nitrogen		1.03%	0.85%	0.25%	0.66%	0.76%	1.35%	
Sulphur		0.43%	0.05%	0.11%	0.05%	0.05%	1.20%	
Oxygen (diff)		17.24%	2.80%	2.04%	4.09%	1.99%	3.25%	

Table 4.3.2 (Sheet 6)

RUN No.: DOE-BU-014 M.B.No.: YP-03/ C1

	Feed	Products V-220	V-340 (BTTMS)	V-330
	-------- In grams of analysis sample --------			
Total Sample	53.71	14.70	56.15	60.92
Water	1.80	8.73	0.10	2.50
Oils+Asphaltenes	28.64	5.97	41.76	54.71
Oils	25.17	5.64	32.19	46.68
Asphaltenes	3.46	0.32	9.57	8.04
Pre-Asphaltenes			1.16	0.38
Insolubles	23.27		13.13	3.33
IOM	20.58		4.79	0.45
Ash	2.70		8.34	2.88
TOTAL	53.71	14.7	56.15	60.92
	-------- In wt% of analysis sample --------			
Water	3.35%	59.40%	0.18%	4.10%
Oils+Asphaltenes	53.32%	40.60%	74.37%	89.81%
Oils (on fraction)	87.90%	94.57%	77.09%	85.31%
(on total)	46.86%	38.40%	57.33%	76.62%
Asphalt. (on fract.)	12.10%	5.43%	22.91%	14.69%
(on total)	6.45%	2.20%	17.04%	13.19%
Pre-Asphaltenes			2.07%	0.62%
Insolubles	43.33%		23.39%	5.46%
IOM (on fraction)	88.42%		36.48%	13.40%
(on total)	38.31%		8.53%	0.73%
Ash (on fraction)	11.58%		63.52%	86.60%
(on total)	5.02%		14.85%	4.73%
TOTAL	100.00%	100.00%	100.00%	100.00%
	-------- In grams of feed / product --------			
Total Feed / Product	6890	522	1940	4120
Water	230.9	310.1	3.5	169.1
Oils+Asphaltenes	3673.5	212.0	1442.8	3700.3
Oils (on fraction)	3229.0	200.5	1112.3	3156.6
(on total)	3229.0	200.5	1112.3	3156.6
Asphalt. (on fract.)	444.5	11.5	330.5	543.6
(on total)	444.5	11.5	330.5	543.6
Pre-Asphaltenes			40.1	25.7
Insolubles	2985.6		453.7	225.0
IOM (on fraction)	2639.9		165.5	30.1
(on total)	2639.9		165.5	30.1
Ash (on fraction)	345.7		288.2	194.8
(on total)	345.7		288.2	194.8
TOTAL (as is)	6890.0	522.1	1940.0	4120.0
TOTAL (MAF)	6313.4	212.0	1648.4	3756.1

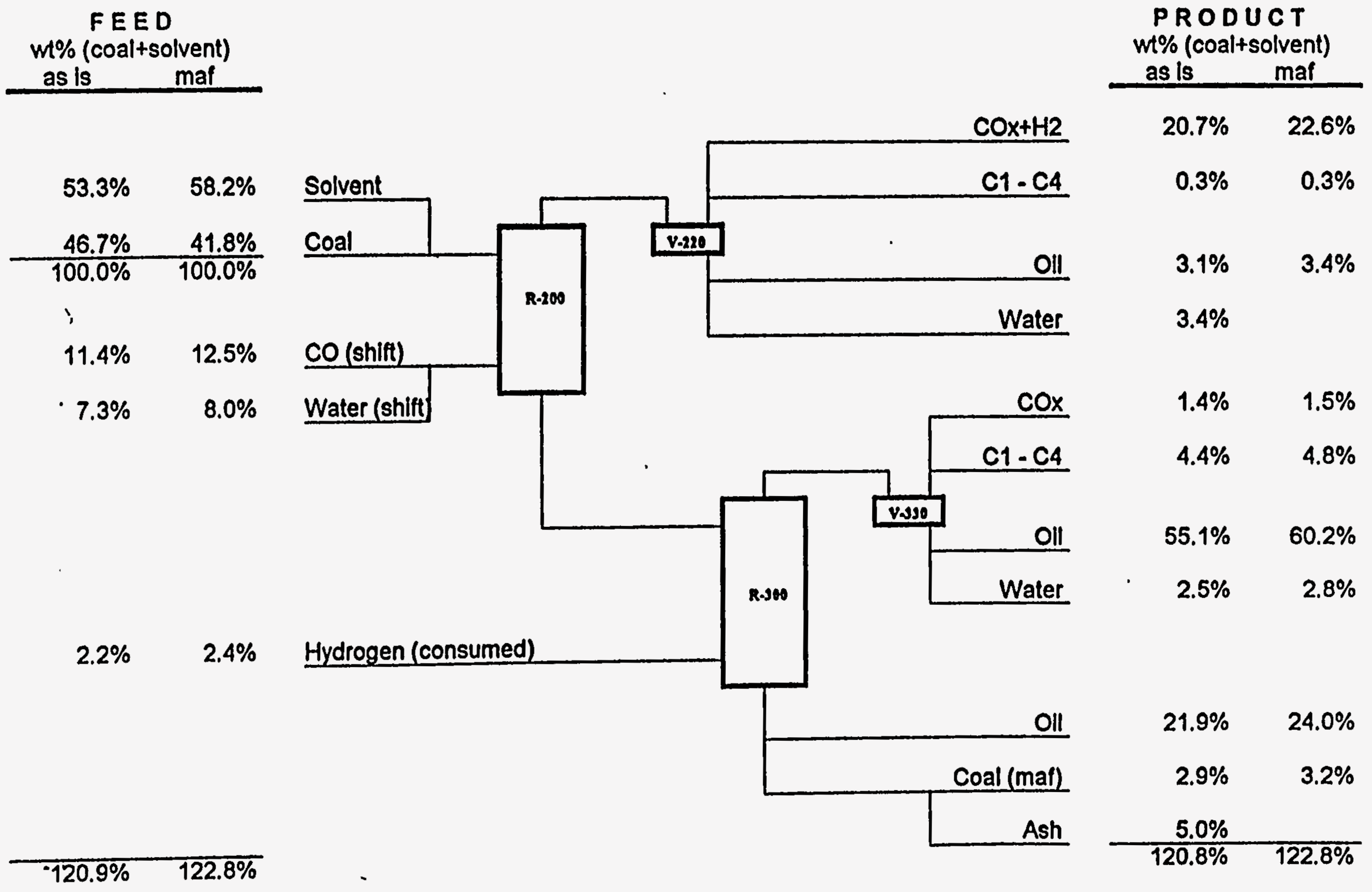
Distillation Profile THF-Extract						D-1160		
Fractions deg C	Feed	Products V-220	V-340 (BTTMS)	V-330	Total	Feed	Product Comp. Sample as is	corr.
IBP - 182		14.58	20.48	19.75	54.80			
182 - 343	146.94	78.94	96.09	1253.79	1428.82	66.12	902.67	902.67
343 - 524	3526.53	118.45	973.36	2452.43	3544.24	3082.04	3616.94	3616.94
524+			558.46	30.15	588.61	525.31	1748.92	1096.85
TOTAL	3673.47	211.98	1648.37	3756.11	5616.46	3673.47	6268.52	5616.46

Feed	Products (nomalized) V-220	V-340 (BTTMS)	V-330	Total	Feed	Products (nomalized) V-220	V-340 (BTTMS)	V-330	Total
-------- In wt% of total feed (as is) --------					-------- In wt% of total feed (MAF) --------				
3.42%	3.42%	0.05%	2.50%	5.97%				2.79%	2.79%
53.28%	3.14%	21.36%	54.77%	79.26%	58.19%	3.43%	23.32%	59.81%	86.56%
46.83%	2.97%	16.46%	46.72%	66.15%	51.15%	3.24%	17.98%	51.03%	72.24%
6.45%	0.17%	4.89%	8.05%	13.11%	7.04%	0.19%	5.34%	8.79%	14.32%
		0.59%	0.38%	0.97%			0.65%	0.42%	1.06%
43.30%		5.44%	2.47%	7.91%					
38.29%		2.45%	0.45%	2.90%	41.81%		2.68%	0.49%	3.16%
5.01%		2.99%	2.02%	5.01%					
100.00%	6.56%	27.44%	60.12%	94.12%					
					100.00%	3.43%	26.64%	63.50%	93.58%

Table 4.3.2 (Sheet 7)

PROCESS YIELD STRUCTURE

RUN No.: DOE-BU-014 M.B. No.: YP-03/ C1



Remarks:

Table 4.3.3

DOE BENCH UNIT HOURLY LOG SHEET

TOOK FEED SAMPLE BEFORE YP.

RUN NUMBER: DOE BU-015 YIELD PERIOD: 03 DATE: DEC 15/93

TIME:	0700	0800	0900	10:00	11:00	12:00	13:00	14:00	15:00
WT110	14.72	14.07	13.20	12.40	11.62	10.82	9.88	8.93	7.92
RATE		650	870	800	780	800	940	950	
WT220	-0.29		.25	.412	.64	.84	1.08	1.28	1.58
RATE				170	180	200	240	200	
WT330	1.29	1.39	1.78	2.16	2.52	2.87	3.34	3.73	4.22
RATE			390	380	360	350	470	390	
FIC220	0	248	483	716	967	1206	1451	1690	1932
RATE			235	233	251	239	245	239	
FIC320	0	2166	4216	6321	8417	10494	12627	14712	16826
RATE			2050	2105	2096	2077	2133	2085	
FIC460	0	240	467	702	933	1164	1402	1632	1866
RATE			227	235	231	231	238	230	
DTM260	6043	6677	7328	7950	8580	9163	9749	10312	10886
RATE			651	621	630	583	586	563	
DTM360	5709	7920	10195	12350	14543	16690	18650	20770	22960
RATE			2275	2155	2193	2147	1960	2120	
DTM350	7825	7822	7842	7849	7857	7865	7878	7869	7878
RATE			10	7	8	8	* 13	1	
V161A	1784	1738	1698	1648	1600	1556	1511	1467	1425
DIFF.			40	50	52	44	45	44	
X 2.017			81/1.3	101/1.7	105/1.7	89/1.5	91/1.5	89/1.5	
V161B	91.3	86.1	81.0	75.9	71.0	65.9	60.4	55.0	49.5
DIFF			5.1	5.1	5.1	5.1	5.5	5.4	
X 1.802			9.8	9.3	9.8	9.8	10.6	10.4	
WT340	-.83	-.69	-.32	-0.07	.20	.38	.58	.93	1.34
			370	250	270	180	200	370	

Figure 4.3.5

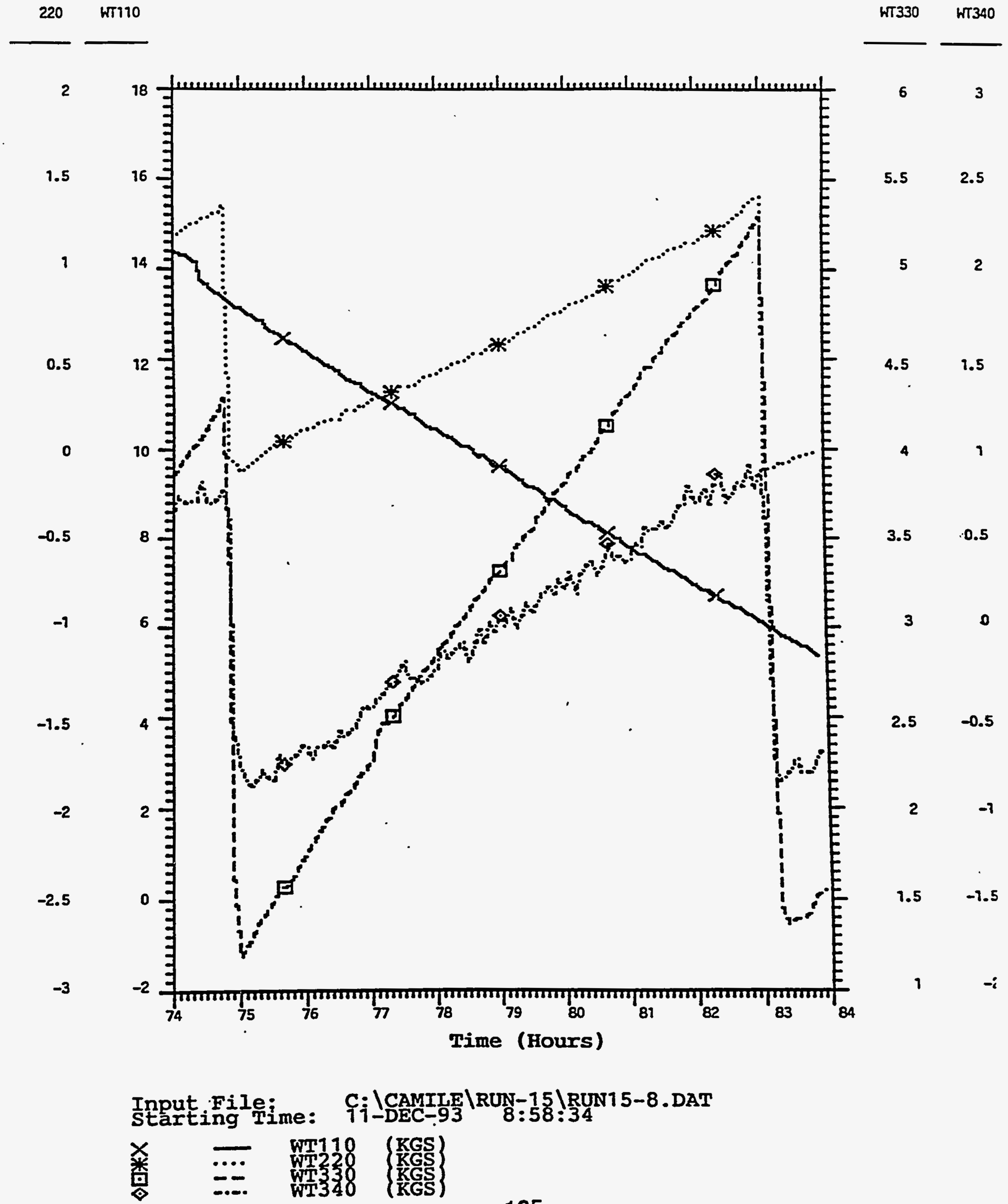

220
WT110
WT330
WT340
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
18
16
14
12
10
8
6
4
2
0
-2
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
74
75
76
77
78
79
80
81
82
83
84
Time (Hours)
Input File: C:\CAMILE\RUN-15\RUN15-8.DAT
Starting Time: 11-DEC-93 8:58:34
WT110 (KGS)
WT220 (KGS)
WT330 (KGS)
WT340 (KGS)

Figure 4.3.6

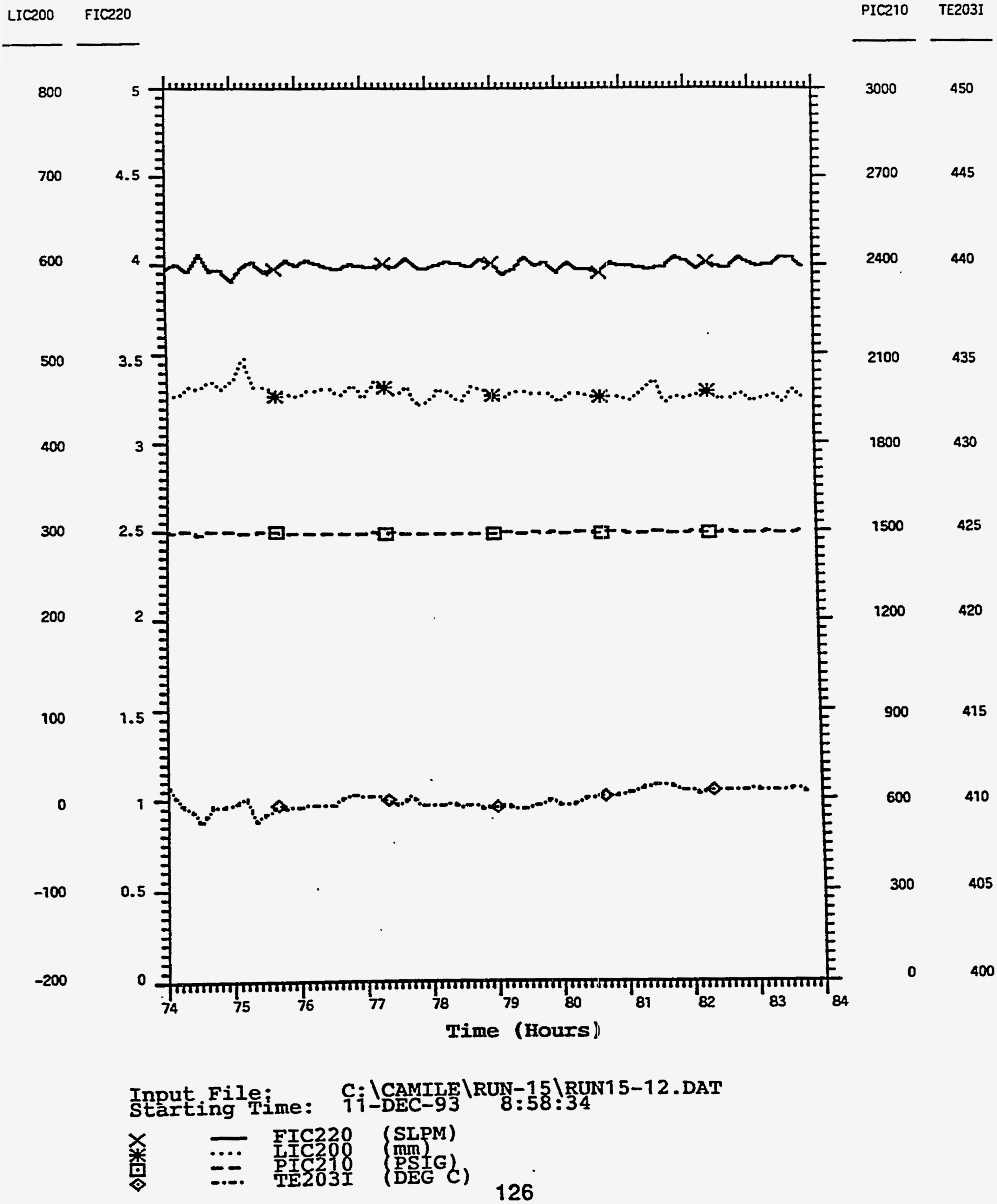
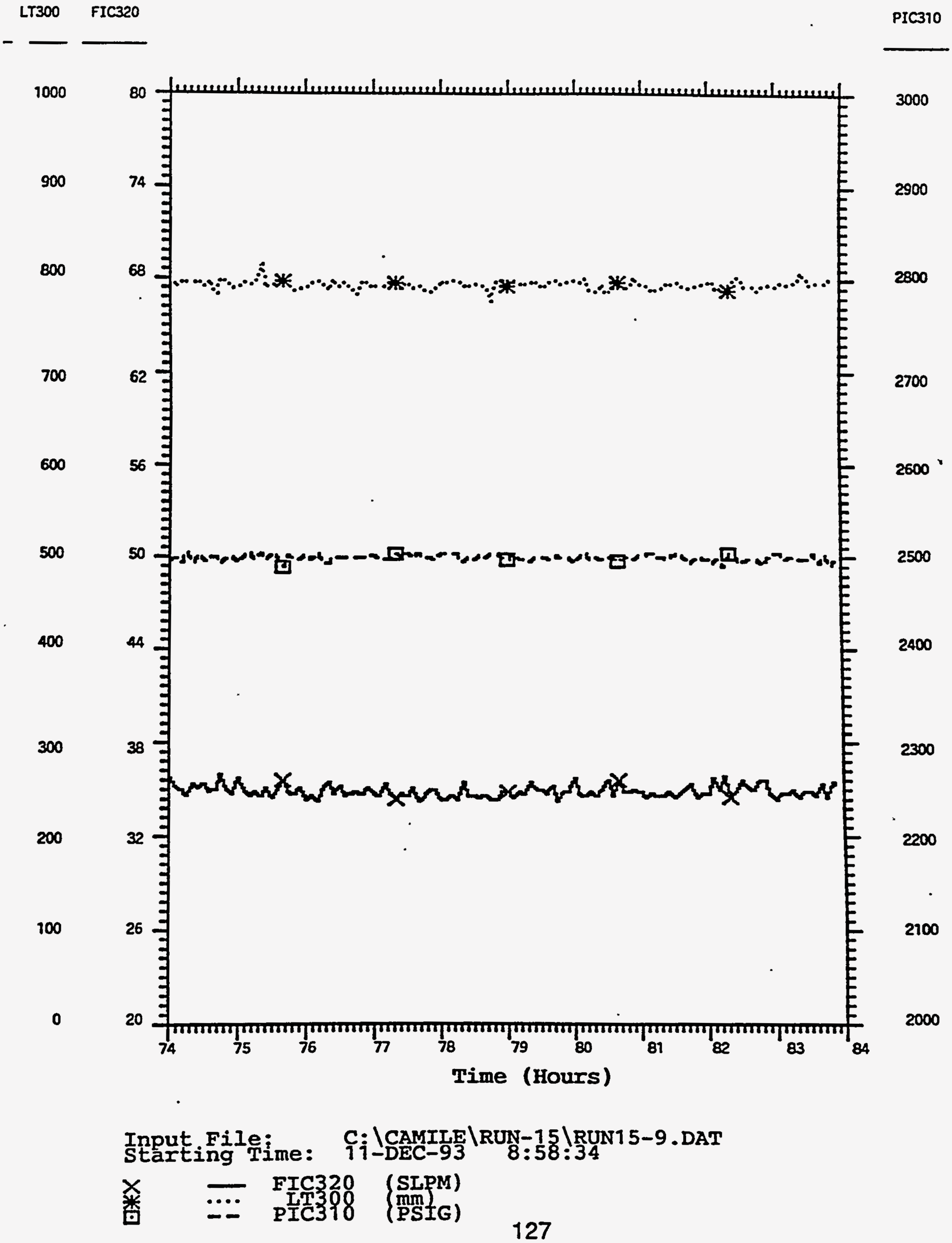

LIC200
FIC220
PIC210
TE203I
800 700 600 500 400 300 200 100 0 -100 -200
5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0
3000 2700 2400 2100 1800 1500 1200 900 600 300 0
450 445 440 435 430 425 420 415 410 405 400
74 75 76 77 78 79 80 81 82 83 84
Time (Hours)
Input File: C:\CAMILE\RUN-15\RUN15-12.DAT
Starting Time: 11-DEC-93 8:58:34
X —— FIC220 (SLPM)
✱ .... LIC200 (mm)
□ -- PIC210 (PSIG)
◇ -.-. TE203I (DEG C)

Figure 4.3.7


LT300
FIC320
PIC310
1000
900
800
700
600
500
400
300
200
100
0
80
74
68
62
56
50
44
38
32
26
20
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
74
75
76
77
78
79
80
81
82
83
84
Time (Hours)
Input File: C:\CAMILE\RUN-15\RUN15-9.DAT
Starting Time: 11-DEC-93 8:58:34
FIC320 (SLPM)
LT300 (mm)
PIC310 (PSIG)

Gas Out". Values in the box labled "Run Conditions" are calculated from operating conditions and physical dimensions of the bench unit.

Sheet No.: 2 - Mass Balances

This sheet summarizes the quantity of each individual stream used to calculate the overall mass balance. The weights of the gas streams are calculated from the corresponding volumetric flows and the average molecular weights calculated in Sheet No. 4. Besides the overall mass balance, the water balance and ash balance is also shown, as well as the coal conversion. The ash balance and coal conversions are calculated using IOM and ash values calculated in Sheet No. 6 from analytical data. Although overall mass balances closed within ±5% for most mass balance periods, it was very difficult to obtain consistent water balances. To improve this, the water balance was forced to close around the first stage, i.e. it was assumed that all free water injected into the first stage minus water consumed in the shift reaction (from Sheet No. 4) is collected in the first stage overhead receiver (V-220). Data from first stage autoclave tests support this assumption as oxygen in the feed does not appear to be converted to water in the first stage.

Sheet No. 2 also summarizes the key performance parameters calculated from mass balance data and analytical data (Sheet No. 3 for GC-gas analysis and Sheet No. 5 for liquid analysis). The box labelled "Product Yields" summarizes the yields of individual product fractions. To normalize the measured amount of products, it is assumed that the amount of Total Gross Product is equal to the sum of maf feed (from Sheet No. 6) plus total hydrogen up-take (from Sheet No. 4). The net yields are calculated by subtracting the amount contained in the feed from the respective normalized gross product fraction. It must be emphasized that the calculation of the net yields assumes that the solvent, i.e. its composition and boiling point curve does not change during the processing in the bench unit.

Sheet No.: 3 - Gas Analysis

Sheet No. 3 lists GC gas analysis of the product gas streams and calculates the averages for each stream.

Sheet No.: 4 - Gas Calculations

Three calculations are performed in this sheet:

1) The measured, average gas compositions are normalized and converted into weight based compositions. Yields of C1 to C3 and C4+ are summarized for each stream.

2) The shift reaction in the first stage is evaluated assuming that all the CO consumed, i.e. the difference between the input CO and that measured in the first product gas (DTM-260), is converted via the shift reaction.

3) The Total Hydrogen Up-Take is determined from as the sum of hydrogen produced in the shift reaction minus hydrogen in the first stage gas plus hydrogen injected into the second stage minus hydrogen in the second stage and dissolved gas.

Sheet No.: 5 - Liquid Analysis

Sheet No. 5 summarizes the analysis of the feed and liquid products. Note that the amount of water in V-220 is a calculated value to force the water balance around the first stage. The amount of "oil + asphaltenes", however, is a measured value. The percent of "moisture" indicated for the "Insolubles" is solvent (THF) residual and not water. Calculations in Sheet No. 6 is corrected for this moisture content.

Sheet No.: 6 - Liquid Calculations

With the liquid analysis from Sheet No. 5 and mass balance data from Sheet No. 1 and 2, component distribution of the liquid product streams is calculated to give measured amounts of product components based on solubility and boiling range. Also, the normalized percent yield of each product steam is determined based on total and maf feed.

Sheet No.: 7 - Process Yield Structure

This sheet summarizes in a simple process flow diagram of the bench unit all feed and product streams (on percent basis).

4.3.3 Test Results

A compilation of the data for all of the bench unit runs, together with the mass balances and numerical work up based on these mass balances are given in the Appendix. An analysis of the results is described in the next sections.

4.3.3.1 Black Thunder Coal

A summary of the key data from all the bench unit mass balance periods on Black Thunder coal is provided in Tables 4.3.4 to 4.3.8. Interpretation of these data with respect to coal solubilization and two stage liquefaction is provided below.

4.3.3.1.1 Coal Solubilization

Carbon monoxide/steam has been shown to be particularly effective in the solubilization of low rank coals. Most of the work on carbon monoxide/steam solubilization has been performed in autoclaves, and to our knowledge, no one has

Table 4.3.4

SUMMARY OF BENCH UNIT TEST RUNS

(forced water balance and kept oil in V-220 as measured)

RUN No.:		DOE-BU-003	DOE-BU-004		DOE-BU-005
M.B.No.:		YP-01/C1	YP-01/C1	YP-02/C1	YP-01/C1
Coal		BTH	BTH	BTH	BTH
wt % maf		16.37%	39.62%	40.03%	36.13%
First Stage:					
Feed Rate	(kg / hr) / l WHSV	2.06	1.89	1.60	0.90
Pressure	Mpa	17.24	17.24	17.24	17.24
Temperature	deg C	386	395	395	396
Catalyst		Carbonate	Carbonate	Carbonate	Carbonate
CO Rate	kg / kg maf coal	6.50	2.36	2.81	6.01
	moles / 100g maf coal	23.19	8.41	10.02	21.46
consumed	moles / 100g maf coal	3.77	1.21	1.29	2.85
Water Rate	kg / kg maf coal	6.50	2.36	2.81	6.01
	moles / 100g maf coal	36.07	13.08	15.58	33.37
Hydrogen	wt % maf coal	3.08%	1.40%	1.30%	2.10%
Second Stage:					
Feed Rate	(kg / hr) / l WHSV				
Pressure	Mpa				
Temperature	deg C				
Catalyst					
Hydrogen	kg / kg maf coal				
	moles / 100g maf coal				
consumed	wt % maf coal				
Coal Conversion (wt % maf coal)		51.38%	58.91%	63.68%	69.19%
Product Yield (wt % maf coal)					
	H_2O				
	CO_x	9.40%	8.88%	11.73%	12.98%
	H_2S				
	C1 to C3				
	Pentane soluble (incl. C4)	-9.36%	14.88%	31.64%	23.47%
	Asphaltenes	45.05%	28.86%	15.15%	28.04%
	Preasphaltenes	9.37%	7.67%	6.47%	6.80%
	IOM	48.62%	41.09%	36.32%	30.81%
TOTAL		103.08%	101.40%	101.30%	102.10%

NOTE:

Table 4.3.5

SUMMARY OF BENCH UNIT TEST RUNS

(forced water balance in V-200 and kept oil as measured)

RUN No.:		DOE-BU-008		DOE-BU-009			
M.B.No.:		YP-01/C1	YP-02/C1	YP-01/C1	YP-02/C1	YP-04/C1	YP-05/C1
Coal		BTH	BTH	BTH	BTH	BTH	BTH
wt % maf		29.93%	31.92%	27.48%	38.34%	38.34%	37.10%
First Stage:							
Feed Rate	(kg / hr) / l WHSV	2.24	2.19	2.01	1.99	1.95	1.92
Pressure	Mpa	10.34	10.34	10.34	10.34	10.34	10.34
Temperature	deg C	395	395	395	395	391	392
Catalyst					Aluminate		
CO Rate	kg / kg maf coal	2.91	2.81	3.38	2.36	2.50	2.41
	moles / 100g maf coal	10.39	10.01	12.07	8.41	8.92	8.62
consumed	moles / 100g maf coal	0.31	0.36	0.25	0.75	0.39	0.32
Water Rate	kg / kg maf coal	2.91	2.81	3.38	2.36	2.50	2.41
	moles / 100g maf coal	16.15	15.58	18.78	13.08	13.88	13.40
Hydrogen	wt % maf coal	0.46%	0.57%	0.35%	1.03%	0.63%	0.48%
Second Stage:							
Feed Rate	(kg / hr) / l WHSV	0.94	0.92	0.59	0.59	0.74	0.72
Pressure	Mpa	17.24	17.24	17.24	17.24	17.24	13.79
Temperature	deg C	434	434	434	443	442	442
Catalyst		ATM	ATM	ATM	ATM	ATM	ATM
Hydrogen	kg / kg maf coal	0.89	0.96	0.93	0.32	0.36	0.36
	moles / 100g maf coal	44.50	47.84	46.28	15.80	17.85	18.03
consumed	wt % maf coal	2.70%	2.76%	2.87%	1.59%	2.31%	2.09%
Coal Conversion (wt % maf coal)		77.36%	78.76%	80.93%	81.53%	73.24%	74.58%
Product Yield (wt % maf coal)							
	H2O	8.85%	13.44%	5.58%	1.91%	1.50%	2.17%
	COx	7.83%	4.37%	12.60%	6.56%	7.50%	7.99%
	H2S						
	C1 to C3	9.93%	10.79%	11.90%	8.83%	10.54%	7.94%
	Pentane soluble (incl. C4)	10.03%	15.91%	13.83%	39.77%	7.03%	-4.45%
	Asphaltenes	40.96%	33.66%	35.97%	26.74%	42.71%	35.28%
	Preasphaltenes	2.91%	3.92%	4.27%	0.35%	6.91%	28.23%
	IOM	22.64%	21.24%	19.07%	18.47%	26.76%	25.42%
TOTAL		103.16%	103.33%	103.21%	102.63%	102.94%	102.58%

NOTE:

Table 4.3.6

SUMMARY OF BENCH UNIT MASS BALANCES
(forced water balance and kept V-220 oil as measured)

RUN No.:		DOE-BU-010				DOE-BU-011		
M.B.No.:		YP-01/C1	YP-02/C1	YP-03/C1	YP-04/C1	YP-01/C1	YP-02/C2	YP-03/C1
Coal		BTH	BTH	BTH	BTH	BTH	BTH	BTH
wt % maf		36.48%	37.93%	36.06%	36.06%	36.40%	37.51%	39.64%
First Stage:								
Feed Rate	(kg / hr) / I WHSV	1.74	1.78	2.00	2.13	1.18	1.20	1.49
Pressure	Mpa	10.34	15.17	10.34	10.34	10.34	10.34	10.34
Temperature	deg C	392	390	410	412	410	411	410
Catalyst		Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate
CO Rate	kg / kg maf coal	1.42	1.38	1.25	2.28	1.75	3.07	2.39
	moles / 100g maf coal	5.08	4.92	4.47	8.14	6.26	10.95	8.52
consumed	moles / 100g maf coal	0.42	0.55	0.44	0.82	0.82	1.30	1.10
Water Rate	kg / kg maf coal	1.42	1.38	1.25	2.28	1.75	3.07	2.39
	moles / 100g maf coal	7.90	7.65	6.95	12.66	9.74	17.03	13.25
Hydrogen	wt % maf coal	-0.89%	-0.76%	0.56%	1.11%	1.04%	1.60%	1.36%
Second Stage:								
Feed Rate	(kg / hr) / I WHSV							
Pressure	Mpa							
Temperature	deg C							
Catalyst								
Hydrogen	kg / kg maf coal							
	moles / 100g maf coal							
consumed	wt % maf coal							
Coal Conversion (wt % maf coal)		54.93%	61.68%	67.88%	67.94%	66.63%	75.89%	72.86%
Product Yield (wt % maf coal)								
	H2O							
	COx	10.81%	9.79%	10.99%	8.42%	11.05%	11.35%	11.35%
	H2S							
	C1 to C3	0.20%	0.27%	0.44%	0.10%	0.67%	0.99%	0.80%
	Pentane soluble (incl. C4)	4.74%	10.98%	15.34%	8.66%	11.79%	20.91%	16.47%
	Asphaltenes	30.91%	33.13%	31.35%	43.39%	35.92%	36.06%	36.79%
	Preasphaltenes	7.38%	6.75%	10.32%	8.50%	8.24%	8.18%	8.81%
	IOM	45.07%	38.32%	32.12%	32.06%	33.37%	24.11%	27.14%
TOTAL		99.11%	99.24%	99.24%	100.56%	101.04%	101.60%	101.36%

Table 4.3.7

SUMMARY OF BENCH UNIT TEST RUNS

(forced water balance in V-200 and kept oil as measured)

RUN No.:		DOE-BU-012				DOE-BU-013			
M.B.No.:		YP-01/ C1	YP-02/ C1	YP-03/C1	YP-04/C1	YP-01/C1	YP-02/C1	YP-03/C1	YP-04/C1
Coal		BTH	BTH	BTH	BTH	BTH	BTH	BTH	BTH
wt % maf		39.47%	40.12%	39.25%	38.63%	37.15%	38.30%	36.74%	40.62%
First Stage:									
Feed Rate	(kg / hr) / IWHSV	1.91	2.07	1.55	1.91	2.20	1.75	2.15	2.35
Pressure	Mpa	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34
Temperatu	deg C	410	410	410	409	411	409	411	412
Catalyst		Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate
CO Rate	kg / kg maf coal	1.12	0.98	1.32	1.17	0.99	1.24	1.04	0.90
	moles / 100g maf coal	3.98	3.49	4.72	4.17	3.53	4.43	3.70	3.20
consumed	moles / 100g maf coal	0.82	0.73	0.89	0.87	1.35	0.84	0.76	0.89
Water Rate	kg / kg maf coal	1.12	0.98	1.32	1.17	0.99	1.24	1.04	0.90
	moles / 100g maf coal	6.19	5.43	7.34	6.49	5.50	6.88	5.75	4.98
Hydrogen	wt % maf coal	1.15%	1.05%	1.22%	1.23%	2.15%	1.18%	1.09%	1.17%
Second Stage:									
Feed Rate	(kg / hr) / IWHSV	1.12	1.21	0.91	1.50	1.47	1.18	1.44	1.58
Pressure	Mpa	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24
Temperatu	deg C	408	424	433	426	425	425	424	424
Catalyst		FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	Pyrite	ATM	ATM+DMDS	Moly+DMDS
Hydrogen	kg / kg maf coal	0.64	0.60	0.81	0.66	0.61	0.74	0.62	0.54
	moles / 100g maf coal	31.71	29.72	40.21	32.83	30.49	36.64	31.04	26.86
consumed	wt % maf coal	7.17%	6.43%	8.30%	6.28%	5.12%	6.70%	6.84%	6.17%
Coal Conversion (wt % maf coal)		80.73%	86.43%	83.69%	81.78%	78.71%	75.61%	75.26%	77.02%
Product Yield (wt % maf coal)									
	H2O	4.49%	4.50%	5.63%	3.98%	6.87%	1.16%	4.25%	4.59%
	COx	11.92%	11.85%	12.05%	11.40%	13.42%	13.14%	13.81%	12.09%
	H2S				3.33%	0.35%		1.52%	1.58%
	C1 to C3	2.71%	5.45%	5.72%	4.39%	4.65%	5.09%	5.34%	5.19%
	Pentane soluble (incl. C4)	40.00%	52.02%	52.15%	42.05%	30.73%	31.65%	30.13%	36.33%
	Asphaltenes	24.65%	15.83%	11.84%	19.28%	25.18%	27.60%	23.30%	19.40%
	Preasphaltenes	5.27%	4.26%	5.82%	4.85%	4.79%	4.86%	4.85%	5.18%
	IOM	19.27%	13.57%	16.31%	18.22%	21.29%	24.39%	24.74%	22.98%
TOTAL		108.32%	107.48%	109.52%	107.50%	107.27%	107.88%	107.93%	107.35%

NOTE:

Table 4.3.8

SUMMARY OF BENCH UNIT TEST RUNS

(forced water balance in V-200 and kept oil as measured)

RUN No.:		DOE-BU-014				DOE-BU-015					
M.B.No.:		YP-01/ C1	YP-02/ C1	YP-03/ C1	YP-04/ C1	YP-01/ C1	YP-02/ C1	YP-03/ C1	YP-04/ C1	YP-05/C1	YP-06/C1
Coal		BTH	BTH	BTH	BTH	BTH	BTH	BTH	BTH	BTH	BTH
wt % maf		39.80%	41.98%	41.81%	41.81%	38.42%	40.61%	42.94%	44.70%	41.88%	41.62%
First Stage:											
Feed Rate	(kg / hr) / IWHSV	1.77	1.79	1.76	1.73	1.62	2.29	1.74	1.86	1.83	1.85
Pressure	Mpa	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34
Temperature	deg C	411	411	411	410	411	412	412	409	411	411
Catalyst		Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate
CO Rate	kg / kg maf coal	0.96	0.90	0.92	0.94	1.22	0.84	0.92	0.82	0.89	0.87
	moles / 100g maf coal	3.42	3.22	3.27	3.34	4.34	3.01	3.29	2.93	3.17	3.12
consumed	moles / 100g maf coal	1.09	0.99	1.06	1.09	1.38	0.99	1.08	0.96	1.02	1.01
Water Rate	kg / kg maf coal	0.96	0.90	0.92	0.94	1.22	0.84	0.92	0.82	0.89	0.87
	moles / 100g maf coal	5.32	5.00	5.08	5.20	6.75	4.68	5.11	4.56	4.93	4.85
Hydrogen	wt % maf coal	1.35%	1.18%	1.35%	1.37%	1.71%	1.28%	1.37%	1.23%	1.28%	1.27%
Second Stage:											
Feed Rate	(kg / hr) / IWHSV	1.06	1.07	1.06	1.04	0.85	1.20	1.04	1.11	1.10	1.11
Pressure	Mpa	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24
Temperature	deg C	430	435	439	445	430	434	435	429	440	436
Catalyst		FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS
Hydrogen	kg / kg maf coal	0.58	0.55	0.56	0.57	0.74	0.51	0.56	0.50	0.54	0.53
	moles / 100g maf coal	29.02	27.30	27.79	28.35	36.88	25.56	27.89	24.94	26.94	26.52
consumed	wt % maf coal	5.78%	5.29%	5.63%	5.50%	2.61%	7.13%	6.12%	6.18%	6.39%	6.33%
Coal Conversion (wt % maf coal)		91.54%	92.51%	92.44%	93.74%	82.63%	89.78%	92.34%	91.36%	92.46%	93.16%
Product Yield (wt % maf coal)											
H2O		6.19%	6.02%	6.67%	7.80%	2.40%	5.15%	4.64%	5.30%	3.62%	4.88%
COx		13.51%	14.54%	10.06%	10.19%	16.88%	10.64%	12.60%	9.25%	11.37%	11.40%
H2S											
C1 to C3		7.15%	7.70%	8.82%	10.77%	7.04%	7.17%	7.26%	5.47%	7.13%	6.72%
C4 - 182		5.99%	4.43%	3.46%	7.22%	7.05%	6.47%	6.53%	5.82%	6.51%	6.94%
182 - 343		35.09%	34.73%	32.39%	36.76%	41.63%	41.35%	43.92%	42.29%	51.77%	46.85%
343 - 524		9.37%	16.12%	23.07%	8.42%	1.27%	11.19%	6.43%	14.69%	4.02%	1.88%
IBP - 524		50.44%	55.28%	58.92%	52.41%	49.95%	59.01%	56.88%	62.79%	62.29%	55.66%
524+		29.84%	22.95%	22.50%	25.71%	28.06%	26.43%	26.11%	24.59%	23.26%	28.94%
TOTAL		107.13%	106.48%	106.98%	106.88%	104.32%	108.40%	107.49%	107.42%	107.67%	107.60%
Yields based on Solubility											
Pentane soluble (incl. C4)		50.79%	51.78%	53.92%	55.46%	45.57%	57.64%	59.33%	60.74%	62.62%	61.06%
Asphaltenes		17.71%	15.63%	17.40%	13.94%	12.09%	14.72%	14.05%	16.08%	13.29%	14.45%
Preasphaltenes		3.31%	3.33%	2.54%	2.47%	2.97%	2.87%	1.96%	1.92%	2.11%	2.25%
IOM		8.46%	7.49%	7.56%	6.26%	17.37%	10.22%	7.66%	8.64%	7.54%	6.84%
TOTAL		80.28%	78.22%	81.43%	78.12%	78.00%	85.45%	82.99%	87.39%	85.55%	84.60%
NOTE:											

attempted to carry out the solubilization in counterflow reactors. In a two stage process where carbon monoxide and steam are used in the first stage for solubilization, followed by hydrocracking in the second stage where hydrogen is used, two counterflow reactors in series was considered an attractive scheme.

Autoclave tests on the Black Thunder coal and the Black Thunder derived solvent to be used in the bench unit study indicated that potassium carbonate was the best catalyst, and the preferred conditions of temperature, pressure and residence time were 390°C, 4.1 MPa cold CO, and 30 minutes respectively. These conditions provided a starting point for our work in the counterflow reactor on the continuous bench unit.

In the autoclave, the conditions outlined above gave coal conversions of 80% and above. Figure 4.3.8 shows coal conversion obtained on the bench unit in single stage operation at various conditions with both aqueous carbonate and aqueous aluminate catalyst. Because of the operational problems described earlier, the preferred catalyst for the bench unit was aluminate at a reactor pressure of 10.34 MPa. Under these conditions an operating temperature of 410° (with a WHSV of 1.0 - 1.5 (40 - 60 mins. residence time)) was required to obtain conversions approaching 80%. Clearly the thermal exposure of the coal is less in the counterflow reactor under equivalent conditions. Catalyst dispersion, less efficient mixing, and the impact of having excess water due to introducing the catalyst as a solution may all be factors in the observed lower coal conversions in the counterflow reactor.

Carbon monoxide conversion, as might be expected, was found to be independent of liquid residence time, but dependent on the catalyst system used. Figure 4.3.9 shows that sodium aluminate introduced as a solid into the feed was most effective in promoting carbon monoxide conversion. In the autoclave potassium carbonate gave carbon monoxide conversions of about 80% compared to 44% for sodium aluminate at the standard conditions (390°C, 4.1 MPa CO, 30 mins.). At 410°C with sodium

FIGURE 4.3.8

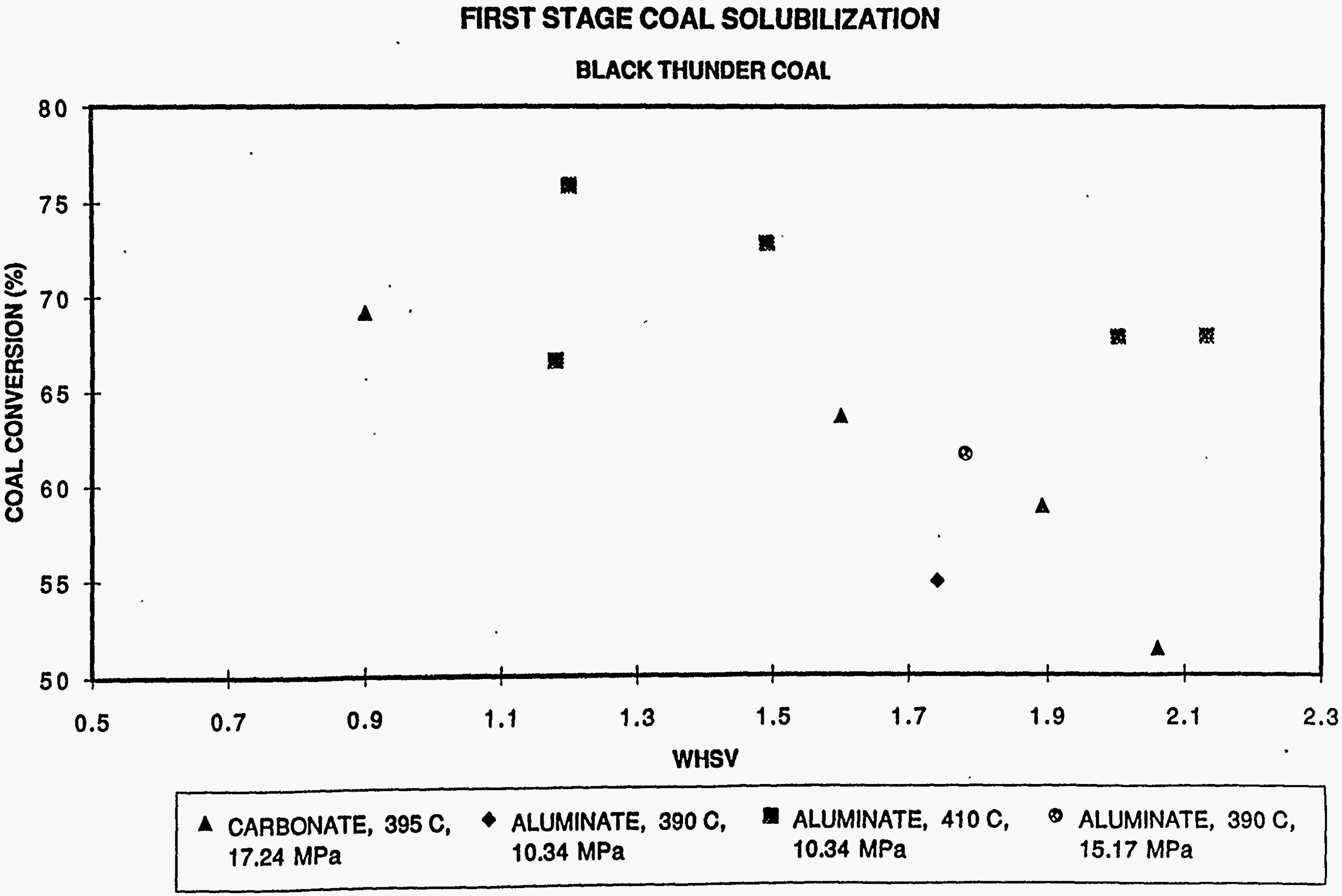
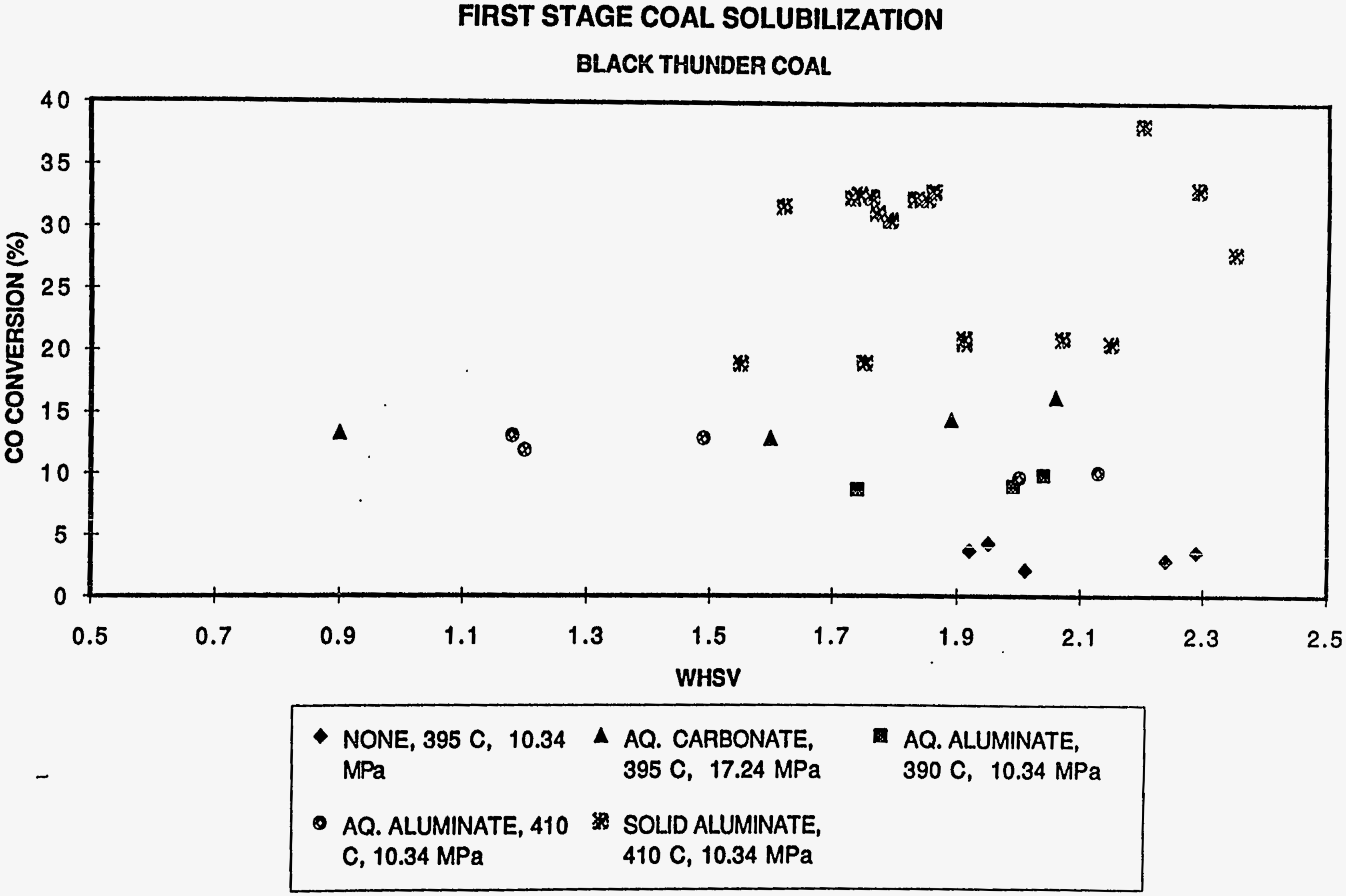

FIRST STAGE COAL SOLUBILIZATION
BLACK THUNDER COAL
COAL CONVERSION (%)
80
75
70
65
60
55
50
0.5
0.7
0.9
1.1
1.3
1.5
1.7
1.9
2.1
2.3
WHSV
▲ CARBONATE, 395 C, 17.24 MPa
◆ ALUMINATE, 390 C, 10.34 MPa
■ ALUMINATE, 410 C, 10.34 MPa
⊗ ALUMINATE, 390 C, 15.17 MPa

FIGURE 4.3.9


FIRST STAGE COAL SOLUBILIZATION
BLACK THUNDER COAL
CO CONVERSION (%)
40
35
30
25
20
15
10
5
0
0.5
0.7
0.9
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5
WHSV
◆ NONE, 395 C, 10.34 MPa
▲ AQ. CARBONATE, 395 C, 17.24 MPa
■ AQ. ALUMINATE, 390 C, 10.34 MPa
⊗ AQ. ALUMINATE, 410 C, 10.34 MPa
※ SOLID ALUMINATE, 410 C, 10.34 MPa

aluminate, the carbon monoxide conversions rose only slightly to near 50%. In the counterflow reactors the gas residence times are much lower than in the autoclave, so the carbon monoxide conversions are not unexpectedly lower. In terms of carbon monoxide consumed per 100 g MAF coal, however, the two systems are comparable (1.0 - 1.5 moles/100 g MAF coal) when solid aluminate is used.

A general relationship appears to exist between carbon monoxide conversion and hydrogen consumption in the coal solubilization step as shown in Figure 4.3.10. There is some scatter in the data but the trend is clear. Hydrogen consumption is significant because the higher consumption would indicate less opportunity for retrograde reactions which would lower coal solubility or conversion.

In Figures 4.3.11 and 4.3.12, a comparison is made between aqueous carbonate and aqueous aluminate on yield structure and product quality on solubilization. The reactor conditions are not exactly equivalent, but the results indicate that while the overall yield structures are not dissimilar, the carbonate catalyzed product contains significantly more pentane soluble oil and less asphaltene than the aluminate catalyzed product. A similar comparison was made with aqueous aluminate catalyst and two different reactor temperatures 392°C and 410°C (Figures 4.3.13 and 4.3.14). The higher temperature shows significantly higher liquid yields and conversion (lower IOM) with only a slight increase in gas and water yield. The liquid product also contains a larger amount of pentane soluble oil at the higher temperatures.

These results suggest that while potassium carbonate would be a preferred catalyst in bench unit operation, sodium aluminate is a viable alternative, particularly if introduced in a solid form into the feed, and if operated at a reaction temperature of 410°C.

FIGURE 4.3.10

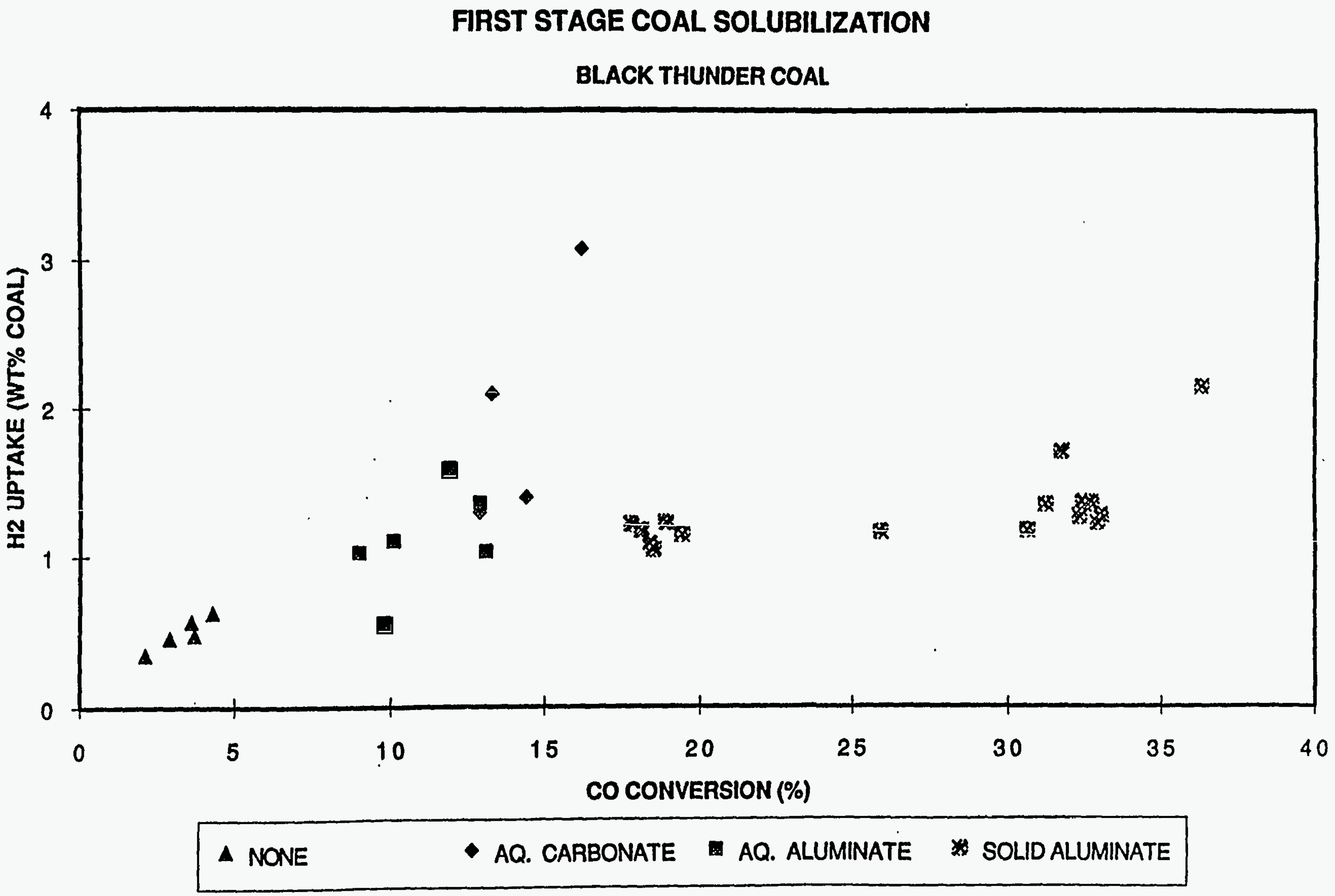

FIRST STAGE COAL SOLUBILIZATION
BLACK THUNDER COAL
H2 UPTAKE (WT% COAL)
0
1
2
3
4
0
5
10
15
20
25
30
35
40
CO CONVERSION (%)
▲ NONE
◆ AQ. CARBONATE
■ AQ. ALUMINATE
※ SOLID ALUMINATE

FIGURE 4.3.11

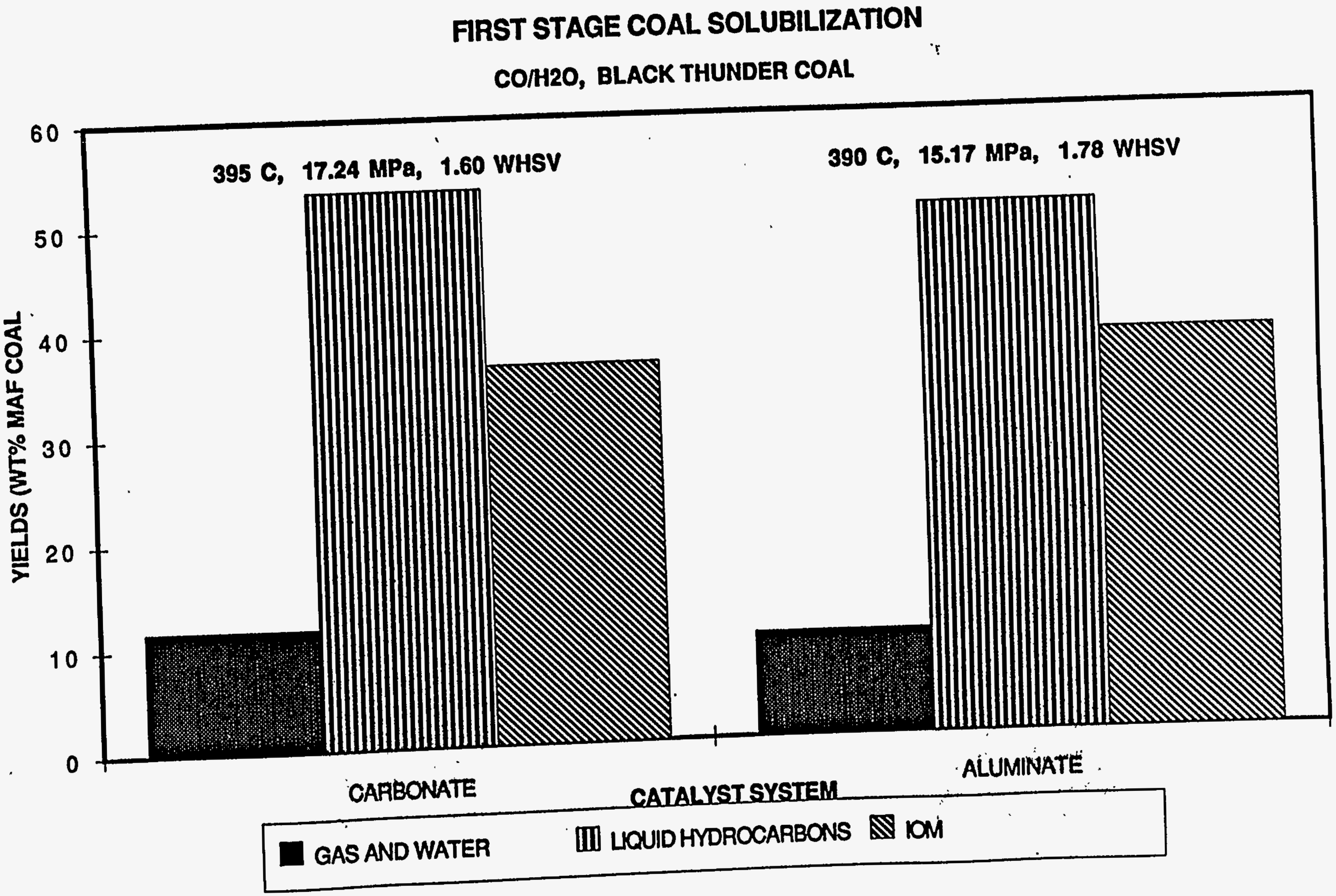

FIRST STAGE COAL SOLUBILIZATION
CO/H2O, BLACK THUNDER COAL
395 C, 17.24 MPa, 1.60 WHSV
390 C, 15.17 MPa, 1.78 WHSV
YIELDS (WT% MAF COAL
60
50
40
30
20
10
0
CARBONATE
ALUMINATE
CATALYST SYSTEM
GAS AND WATER
LIQUID HYDROCARBONS
IOM

FIGURE 4.3.12

FIRST STAGE COAL SOLUBILIZATION

CO/H2O, BLACK THUNDER COAL

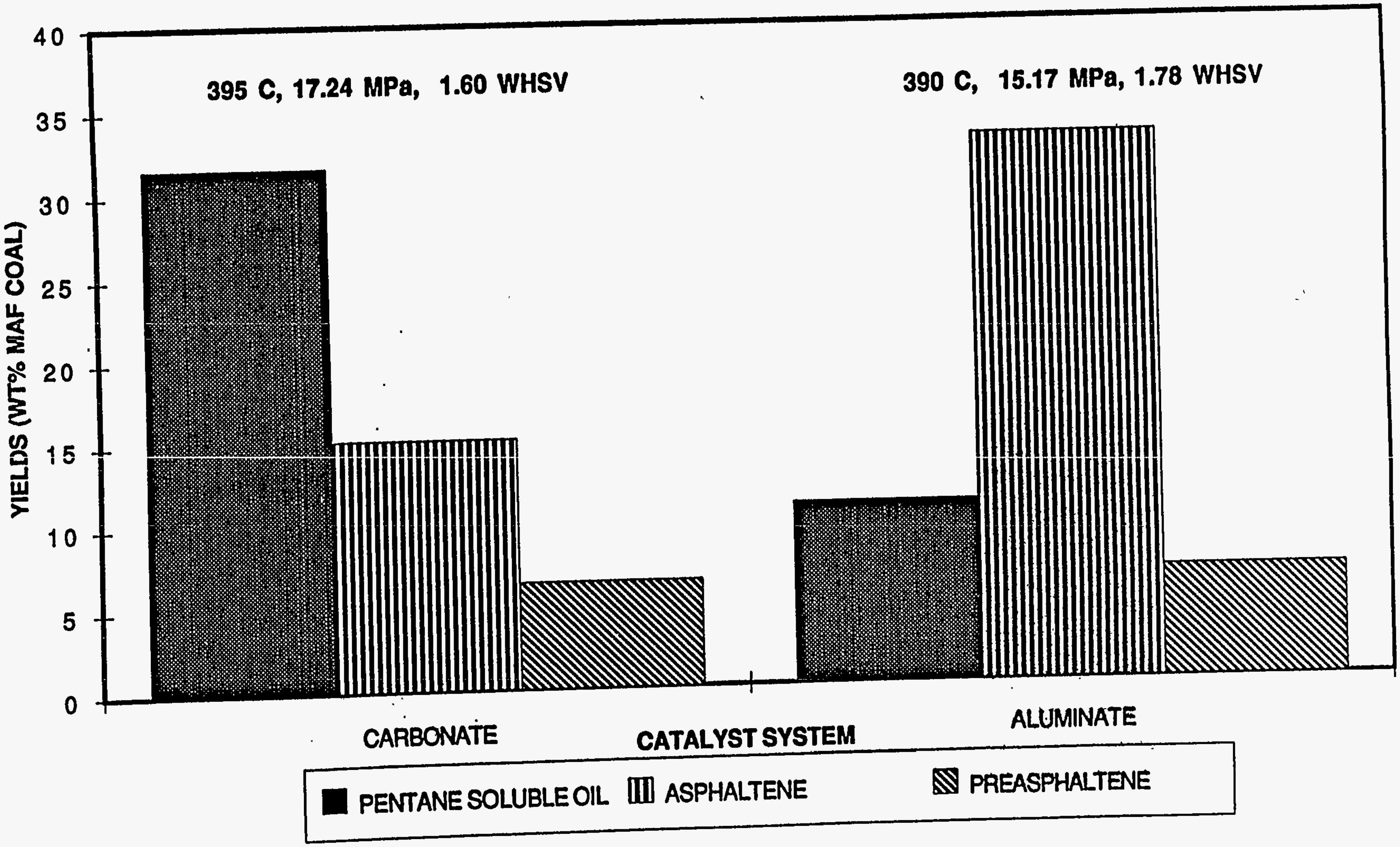


FIGURE 4.3.13

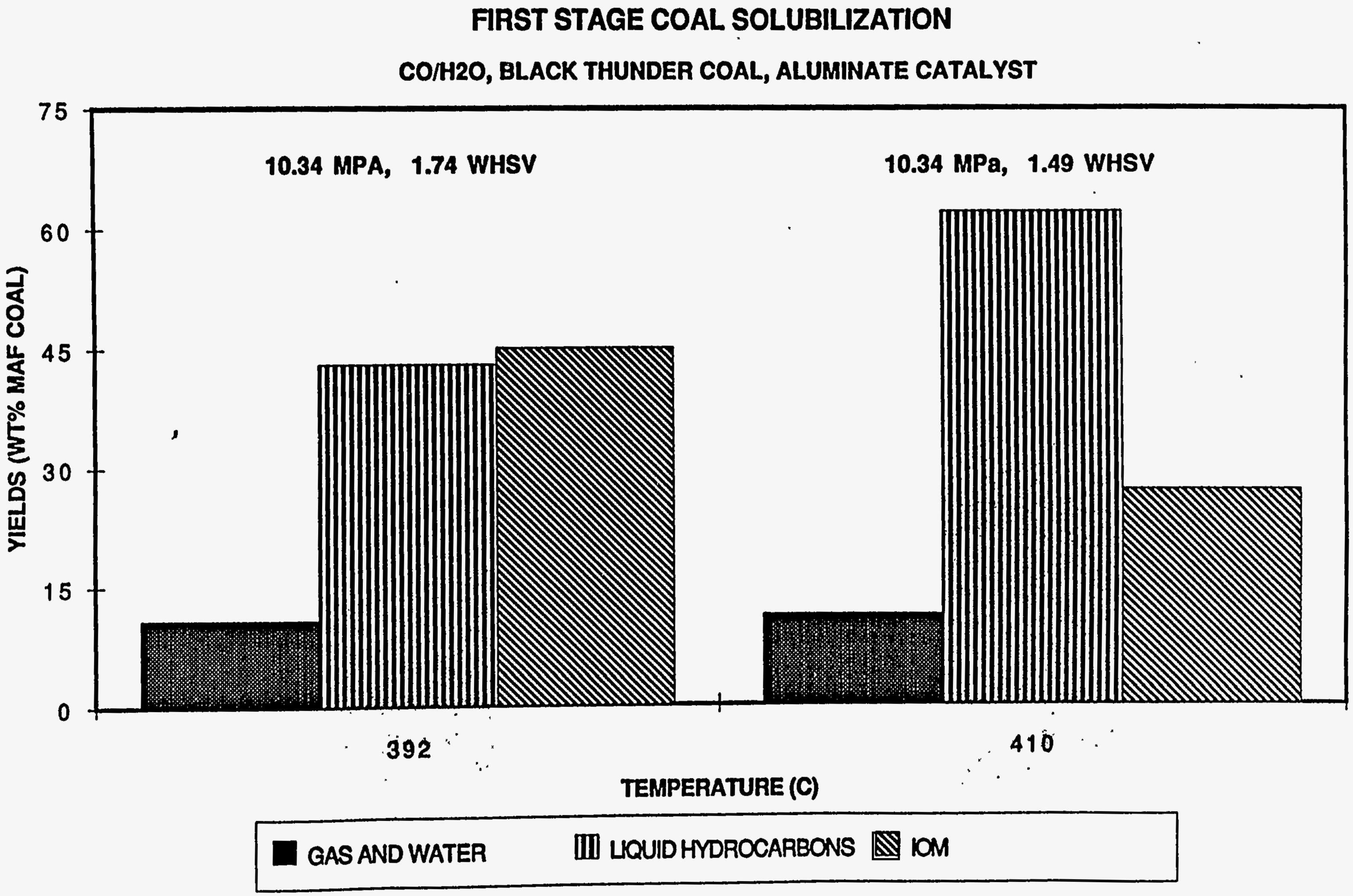
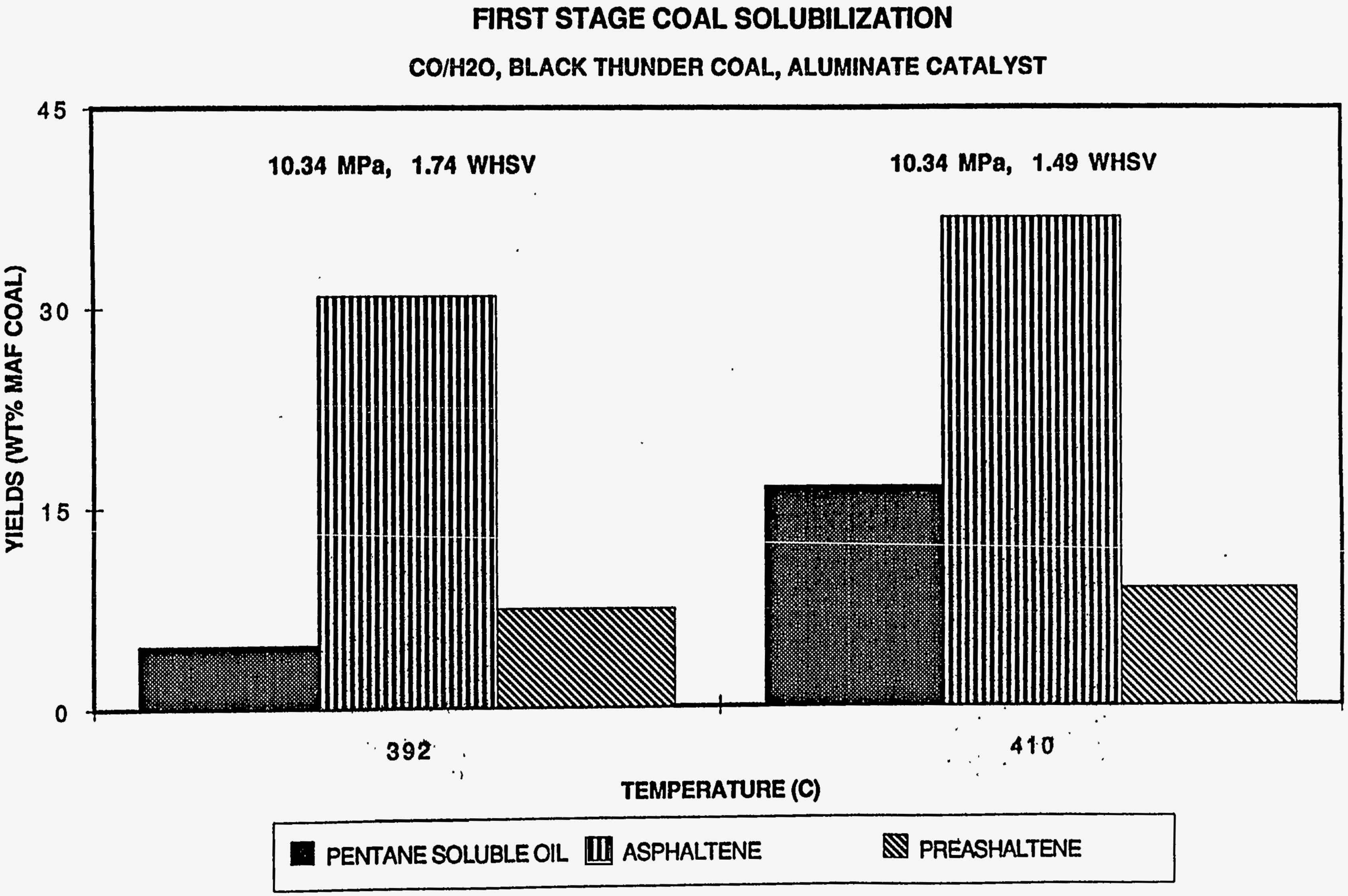

FIRST STAGE COAL SOLUBILIZATION
CO/H2O, BLACK THUNDER COAL, ALUMINATE CATALYST
10.34 MPA, 1.74 WHSV
10.34 MPa, 1.49 WHSV
YIELDS (WT% MAF COAL)
75
60
45
30
15
0
392
410
TEMPERATURE (C)
GAS AND WATER
LIQUID HYDROCARBONS
IOM

FIGURE 4.3.14


FIRST STAGE COAL SOLUBILIZATION
CO/H2O, BLACK THUNDER COAL, ALUMINATE CATALYST
10.34 MPa, 1.74 WHSV
10.34 MPa, 1.49 WHSV
YIELDS (WT% MAF COAL)
45
30
15
0
392
410
TEMPERATURE (C)
PENTANE SOLUBLE OIL
ASPHALTENE
PREASHALTENE

4.3.3.1.2 Two Stage Liquefaction

The initial two stage liquefaction operations (DOE-008 and DOE-009) were performed under non-ideal first stage conditions i.e. no catalyst, or aqueous aluminate catalyst at low temperature (390°C). After it was determined that potassium carbonate could not be used as a first stage catalyst due to operational problems, the alternate catalyst, sodium aluminate was only available in a very limited quantity at the time of these runs. As a result, most mass balance periods were carried out with no first stage catalyst, and only one satisfactory period had aluminate as catalyst. Ammonium tetrathiomolybdate was added to the feed slurry as second stage catalyst in these initial runs. Autoclave tests showed, however, that this compound had little shift catalyst activity. All subsequent two stage liquefaction operations (DOE-012 to DOE-015) were carried out at fixed first stage conditions using solid sodium aluminate as catalyst mixed directly into the feed slurry. These conditions were determined to be the best for first stage operation using bench unit equipment, and only conditions in the second stage reactor were varied in these subsequent runs.

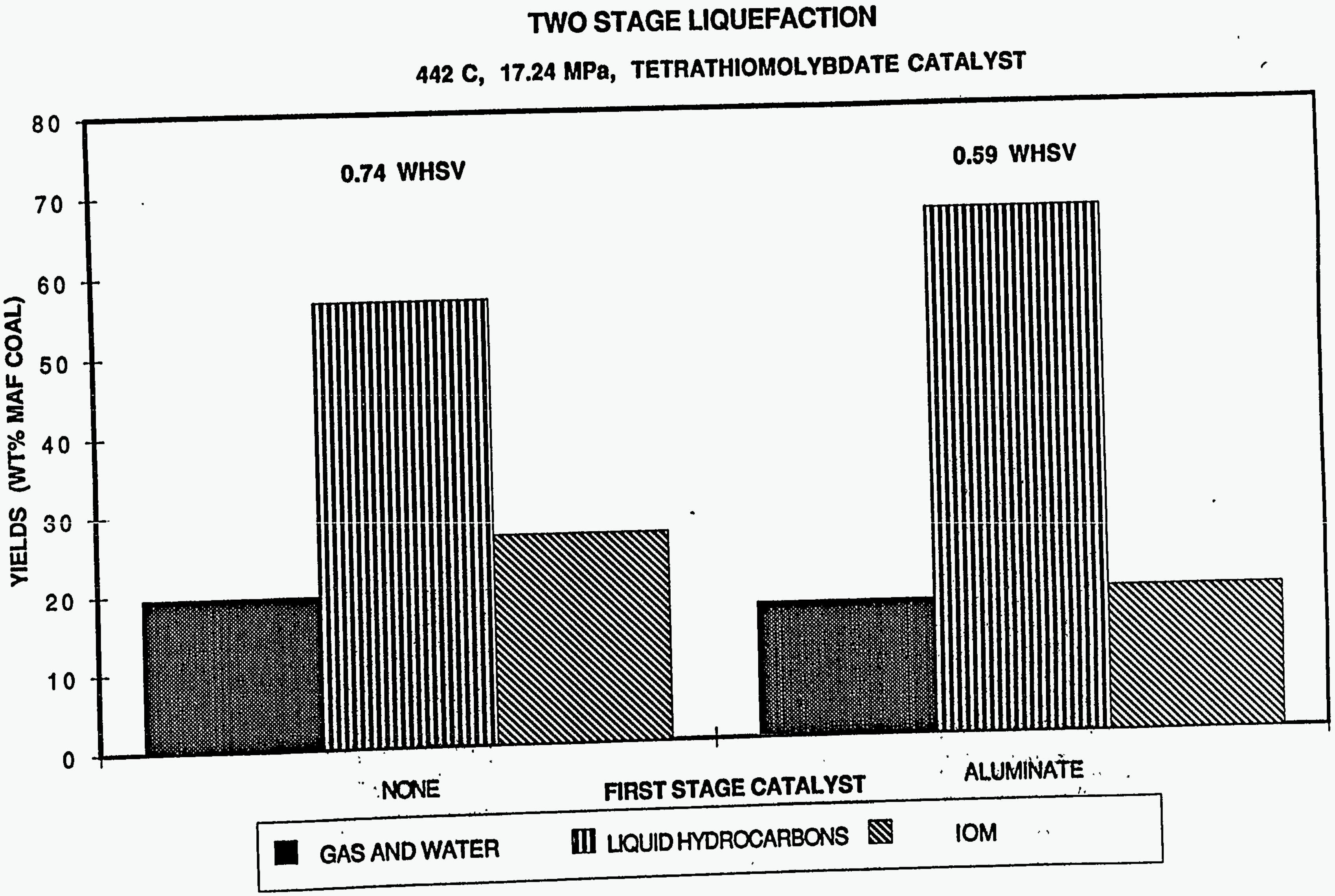
Despite limited data, the initial operations (DOE-008 and DOE-009) did confirm:

a. The presence of a first stage catalyst (aluminate) resulted in improved overall product quality from two stage operation.

b. Higher pressure in the second stage reactor resulted in improved product quality.

In Figures 4.3.15 and 4.3.16, product yields are compared with aluminate present and in its absence in first stage operations. In the final product more pentane soluble oil and less asphaltene are observed in the case where a catalyst is used. This is consistent with a large hydrogen consumption resulting from increased carbon monoxide conversion.

FIGURE 4.3.15



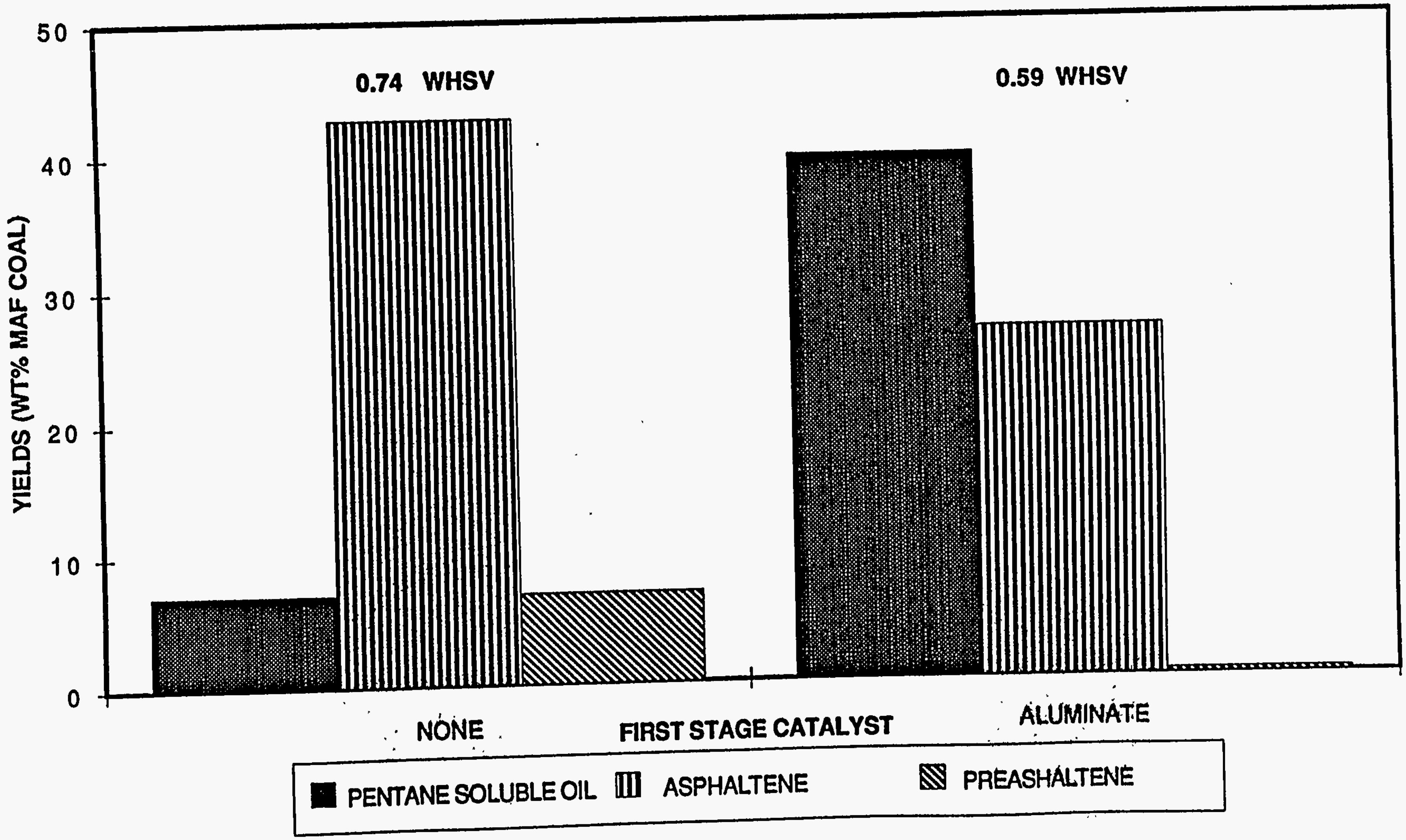
TWO STAGE LIQUEFACTION

442 C, 17.24 MPa, TETRATHIOMOLYBDATE CATALYST

FIGURE 4.3.16

TWO STAGE LIQUEFACTION

442 C, 17.24 MPa, TETRATHIOMOLYBDATE CATALYST



Lower pressure in the second stage reactor resulted in lower pentane soluble oil yield and higher preasphaltene yield in the final product. This comparison is illustrated in Figures 4.3.17 and 4.3.18. The highest pressure, 17.24 MPa, was used in second stage operation for all subsequent runs.

The effect of second stage reactor temperature on product yields was examined in DOE-BU-012. Iron oxide with DMDS was used as catalyst. In the first stage, sodium aluminate was added to the feed slurry directly as a solid, and operating conditions were fixed as close as possible to 410°C, 10.34 MPa, 1.5 WHSV, and a CO flow rate of 4 L/min. Variability in the feed flow rate and liquid level in the reactors led to some variability of space velocity, but although no big differences were observed in gas yield and coal conversion, a steady increase of pentane soluble oil at the expense of asphaltene was observed with increasing second stage reactor temperature. This is shown in Figures 4.3.19 and 4.3.20.

Four different catalysts were evaluated in DOE-BU-013. Figure 4.3.21 shows a comparison of yield structure for four different catalysts at similar operating conditions. Iron oxide/DMDS and ammonium molybdate/DMDS appeared to give somewhat higher pentane soluble oil yields than pyrite and ammonium tetrathiomolybdate so the final bench unit runs on Black Thunder coal were carried out with these catalysts.

The bench unit tests on Black Thunder coal concluded with Runs DOE-BU-014 and DOE-BU-015. These runs represented the best conditions for the liquefaction of Black Thunder coal using the counterflow reactor system. These runs were, therefore, analyzed in more detail than previous runs. Nine mass balance periods were performed, four using iron oxide/dimethyldisulphide as second stage catalyst and five with ammonium molybdate and dimethyldisulphide as catalyst.

The product yields on an MAF coal basis are shown in Figure 4.3.22. The results show THF extractables (C_4 - preasphaltenes) yields in the 70 - 80 wt% range with

FIGURE 4.3.17

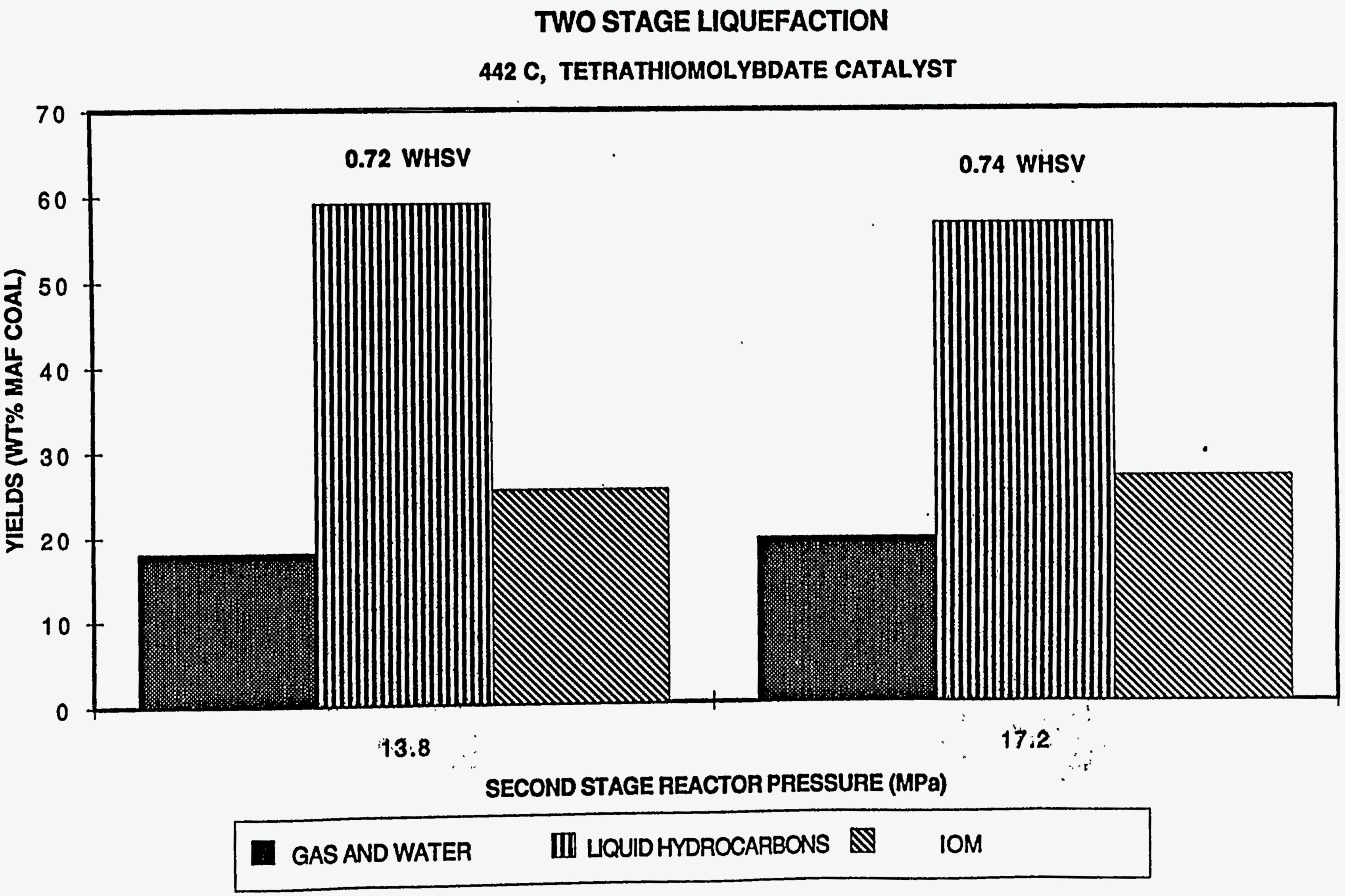

TWO STAGE LIQUEFACTION
442 C, TETRATHIOMOLYBDATE CATALYST
YIELDS (WT% MAF COAL)
70
60
50
40
30
20
10
0
0.72 WHSV
0.74 WHSV
13.8
17.2
SECOND STAGE REACTOR PRESSURE (MPa)
GAS AND WATER
LIQUID HYDROCARBONS
IOM

FIGURE 4.3.18

TWO STAGE LIQUEFACTION

442 C, TETRATHIOMOLYBDATE CATALYST

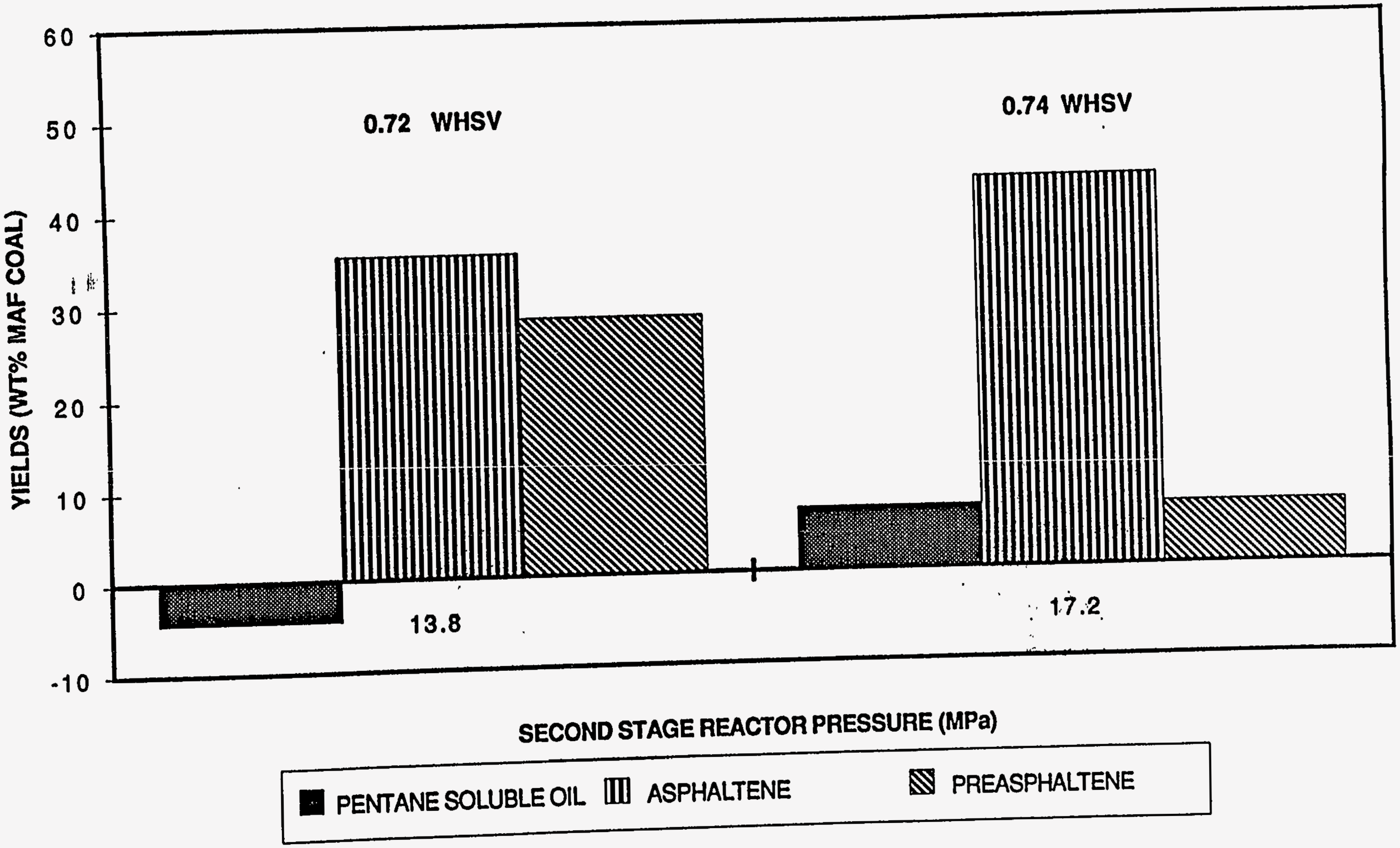


FIGURE 4.3.19

TWO STAGE LIQUEFACTION

BLACK THUNDER COAL, IRON OXIDE/DMDS CATALYST, 17.24 MPa

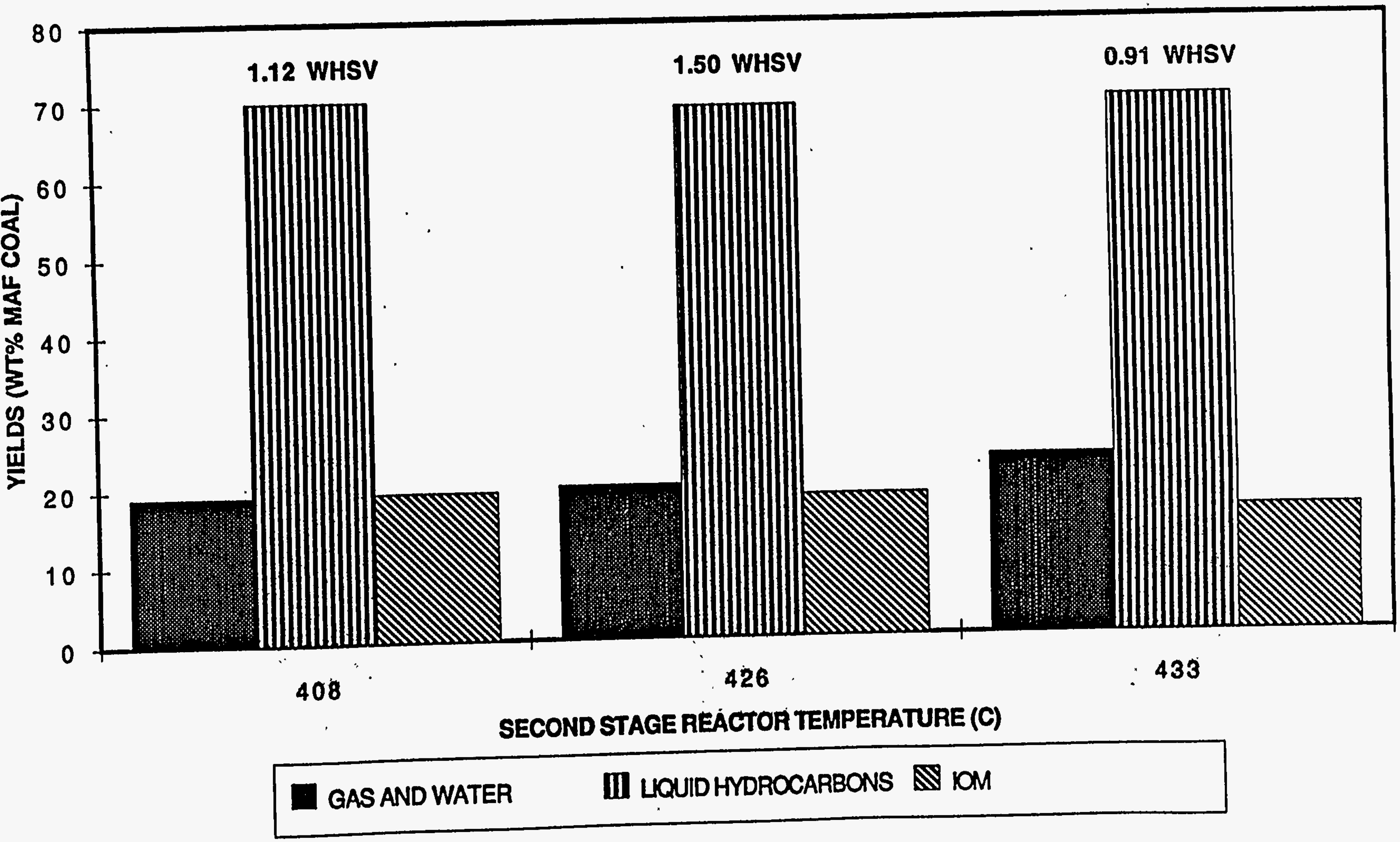
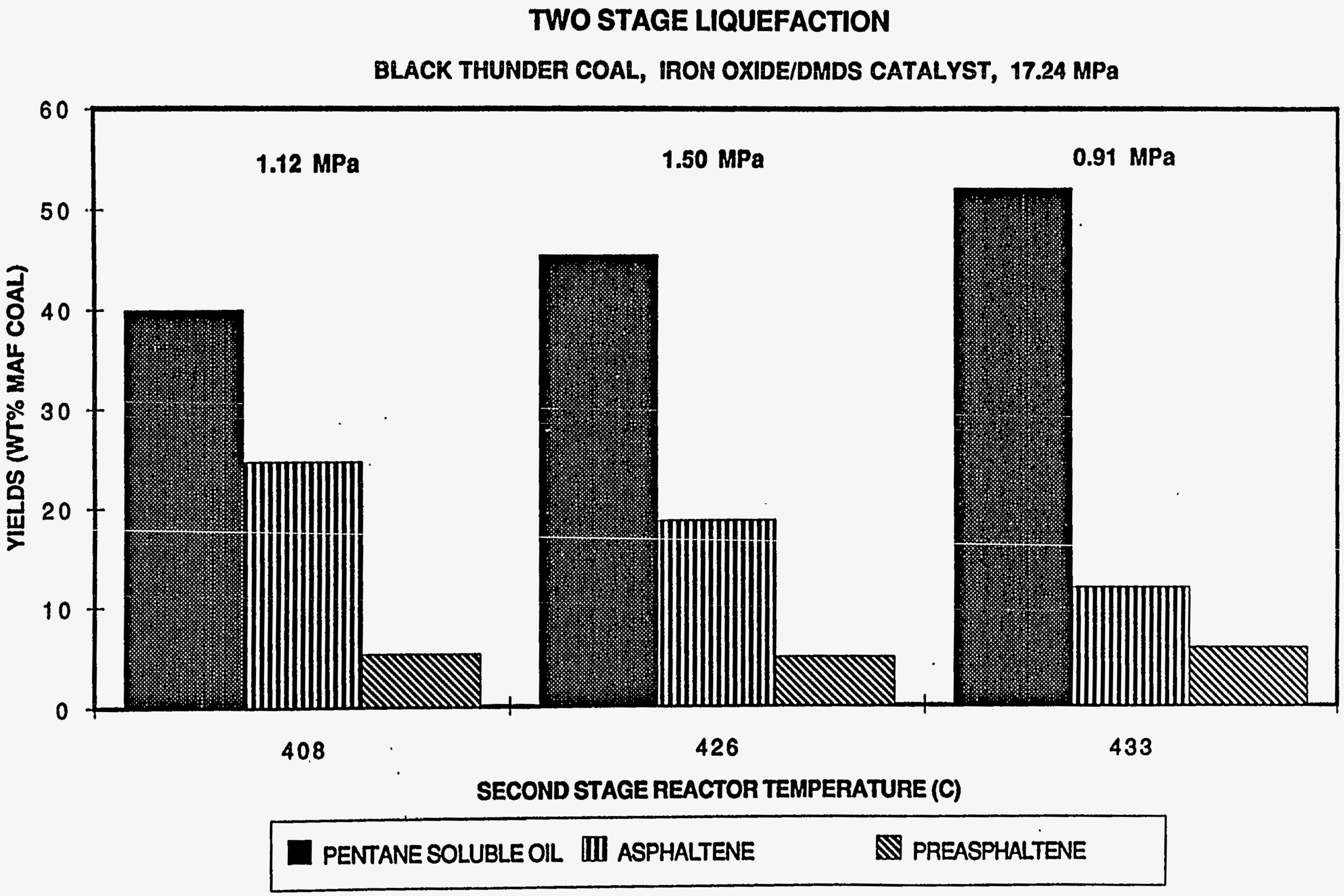


FIGURE 4.3.20



TWO STAGE LIQUEFACTION

BLACK THUNDER COAL, IRON OXIDE/DMDS CATALYST, 17.24 MPa

FIGURE 4.3.21

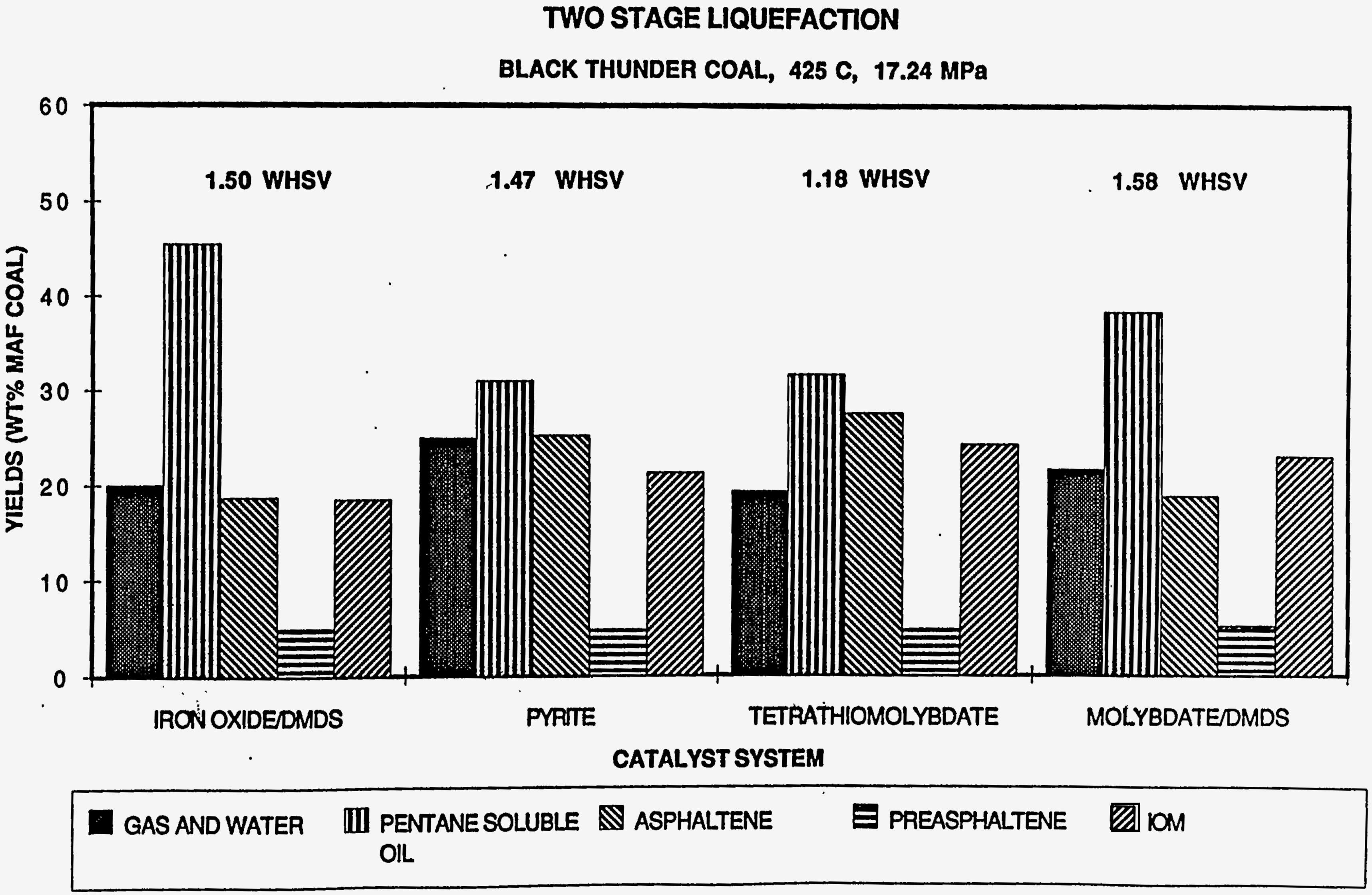
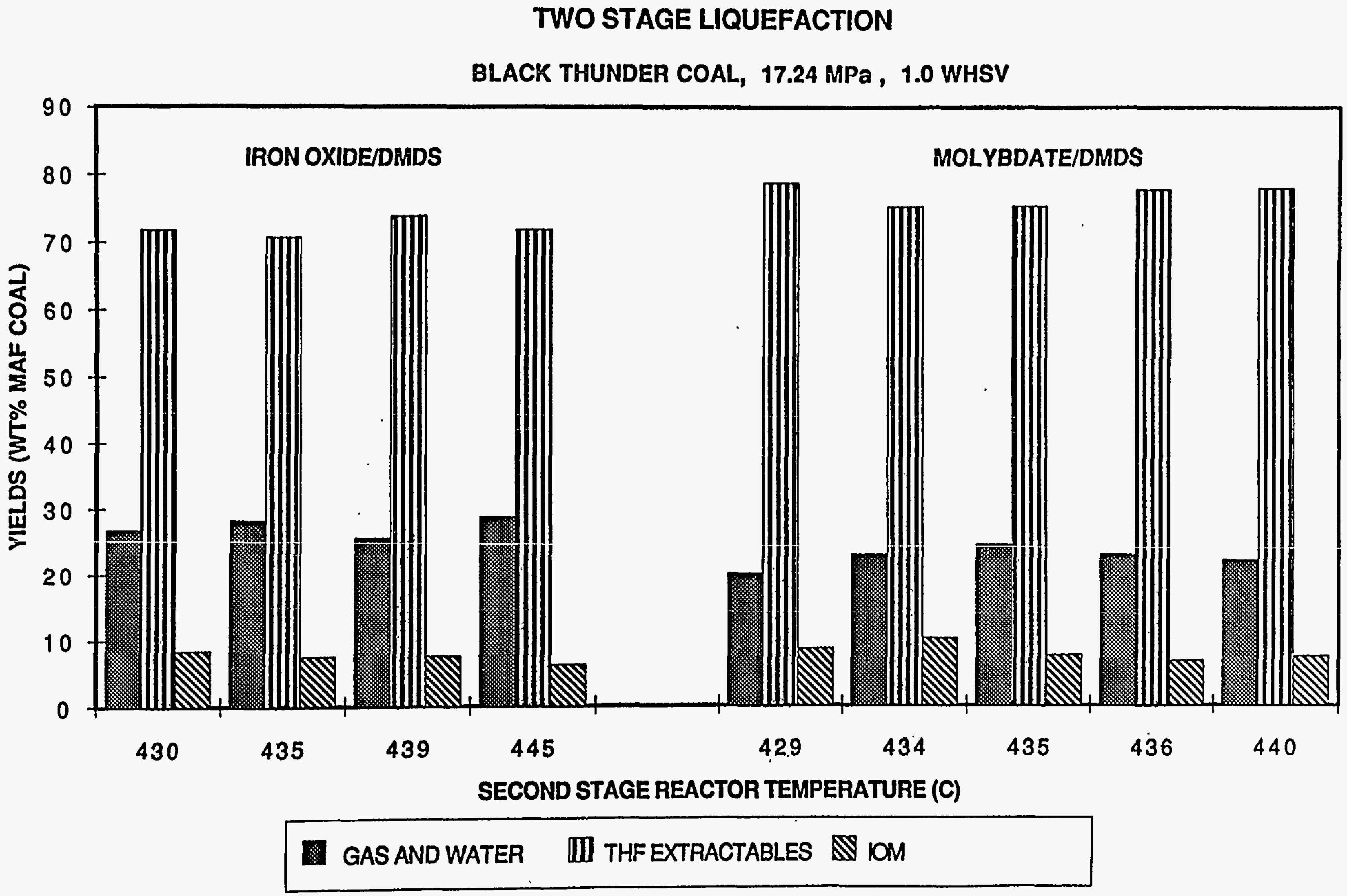

TWO STAGE LIQUEFACTION
BLACK THUNDER COAL, 425 C, 17.24 MPa
YIELDS (WT% MAF COAL)
0
10
20
30
40
50
60
1.50 WHSV
1.47 WHSV
1.18 WHSV
1.58 WHSV
IRON OXIDE/DMDS
PYRITE
TETRATHIOMOLYBDATE
MOLYBDATE/DMDS
CATALYST SYSTEM
GAS AND WATER
PENTANE SOLUBLE OIL
ASPHALTENE
PREASPHALTENE
IOM

FIGURE 4.3.22



TWO STAGE LIQUEFACTION
BLACK THUNDER COAL, 17.24 MPa , 1.0 WHSV
IRON OXIDE/DMDS
MOLYBDATE/DMDS
YIELDS (WT% MAF COAL)
0
10
20
30
40
50
60
70
80
90
430
435
439
445
429
434
435
436
440
SECOND STAGE REACTOR TEMPERATURE (C)
GAS AND WATER
THF EXTRACTABLES
IOM

molybdenum catalyst. As expected these were slightly higher than with the iron oxide catalyst. Conversely, the iron oxide catalyst gave slightly higher gas and water yields. The conditions in the first stage were kept constant for all these runs, the only variable apart from catalyst was the temperature of the second stage reactor. Between 430°C and 445°C (determined earlier to be the optimum range) temperature did not appear to have a major effect, but the IOM did tend to be lower at higher temperatures, as would be expected.

The gas and water yields are broken down into water, carbon oxides and hydrocarbon gas in Figure 4.3.23..

Some variability in the data is shown here, but the data suggests:

1. Hydrocarbon gas yields increase with temperature with iron oxide catalyst.
2. Water yields are slightly higher with iron oxide catalyst.

The breakdown of the THF extractables on the basis of solubility is shown in Figure 4.3.24. This data indicates that ammonium molybdate catalyst does give slightly higher oil yields (pentane soluble) than iron oxide. Oil yields also tend to increase with temperature while asphaltene yields (toluene soluble) decrease. Preasphaltene yields (THF soluble fraction) are low and fairly constant at 2 - 3 wt%.

In general, the distillable oil would be expected to be most of the pentane soluble oil, while most of the asphaltene fraction and the preasphaltene fraction would be expected to be non-distillable. The V-1074 solvent provided from Wilsonville, for instance, was 87.9% pentane soluble oil and 12.1% asphaltene.

Figure 4.3.25 shows a comparison of the distillable oil yield with the pentane soluble oil yields determined by extraction. The results show that the distillable oil yields are indeed in fairly good agreement with the pentane soluble oil yields obtained by

FIGURE 4.3.23

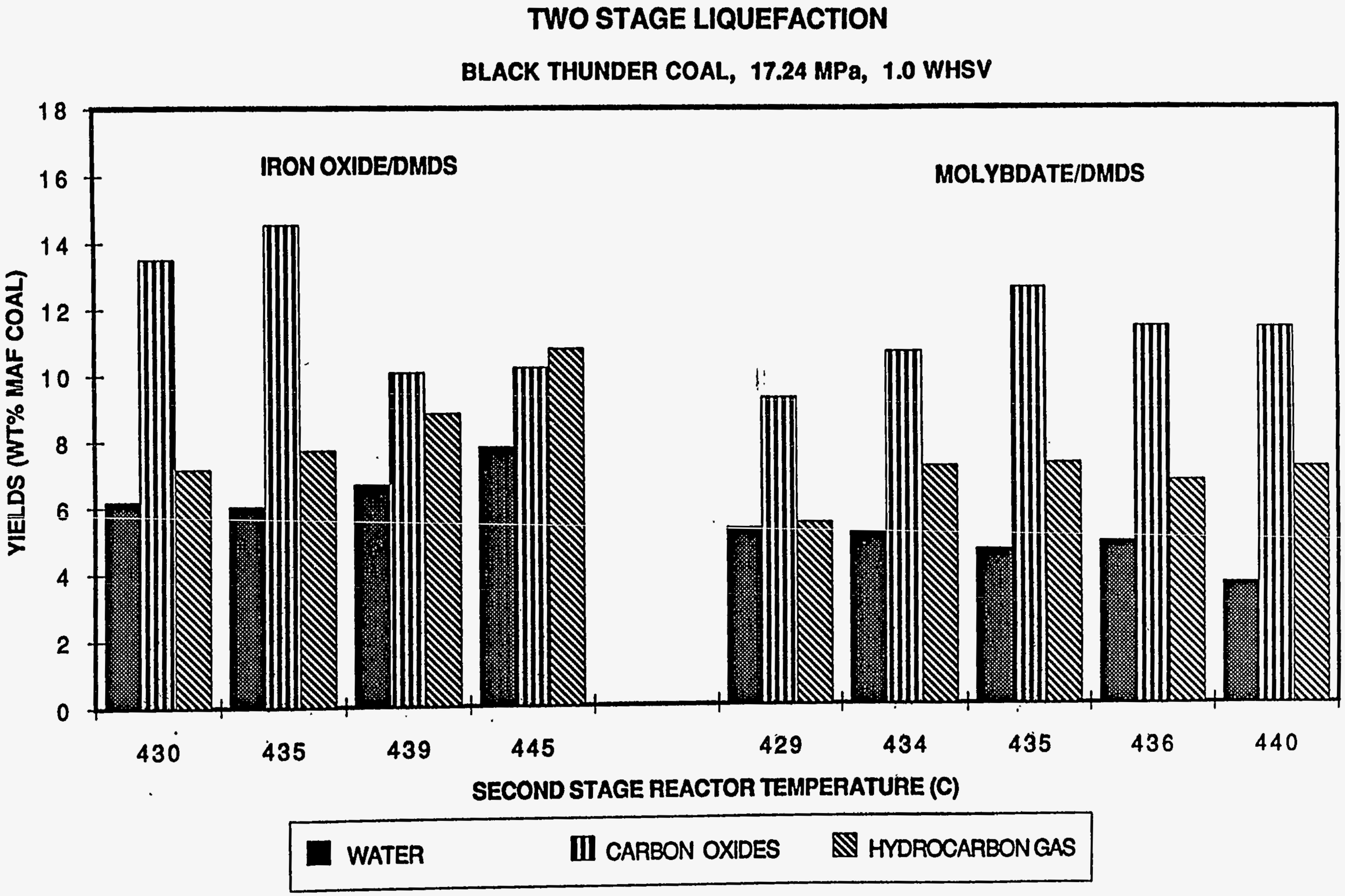

TWO STAGE LIQUEFACTION
BLACK THUNDER COAL, 17.24 MPa, 1.0 WHSV
IRON OXIDE/DMDS
MOLYBDATE/DMDS
YIELDS (WT% MAF COAL)
0
2
4
6
8
10
12
14
16
18
430
435
439
445
429
434
435
436
440
SECOND STAGE REACTOR TEMPERATURE (C)
WATER
CARBON OXIDES
HYDROCARBON GAS

FIGURE 4.3.24

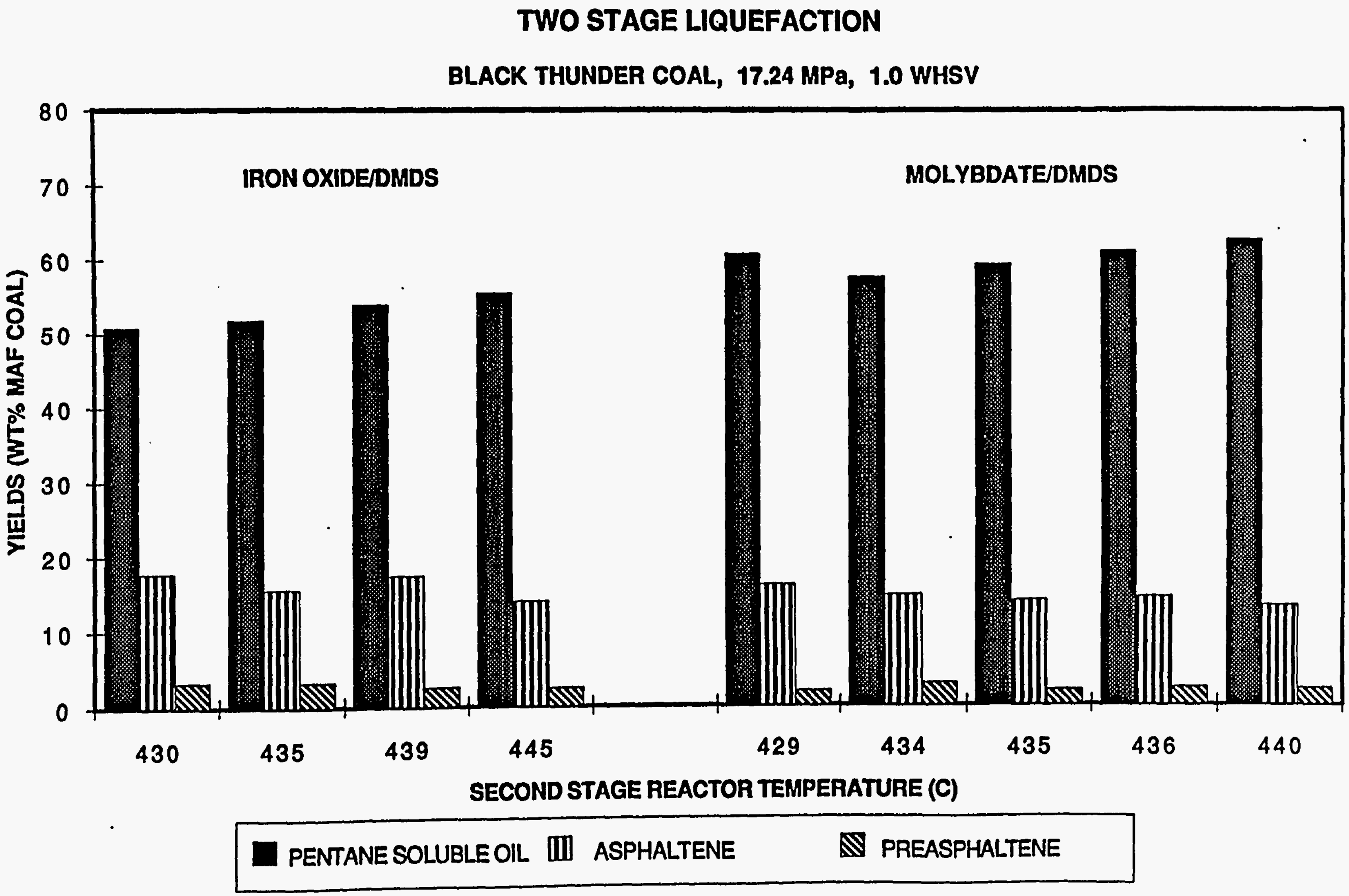
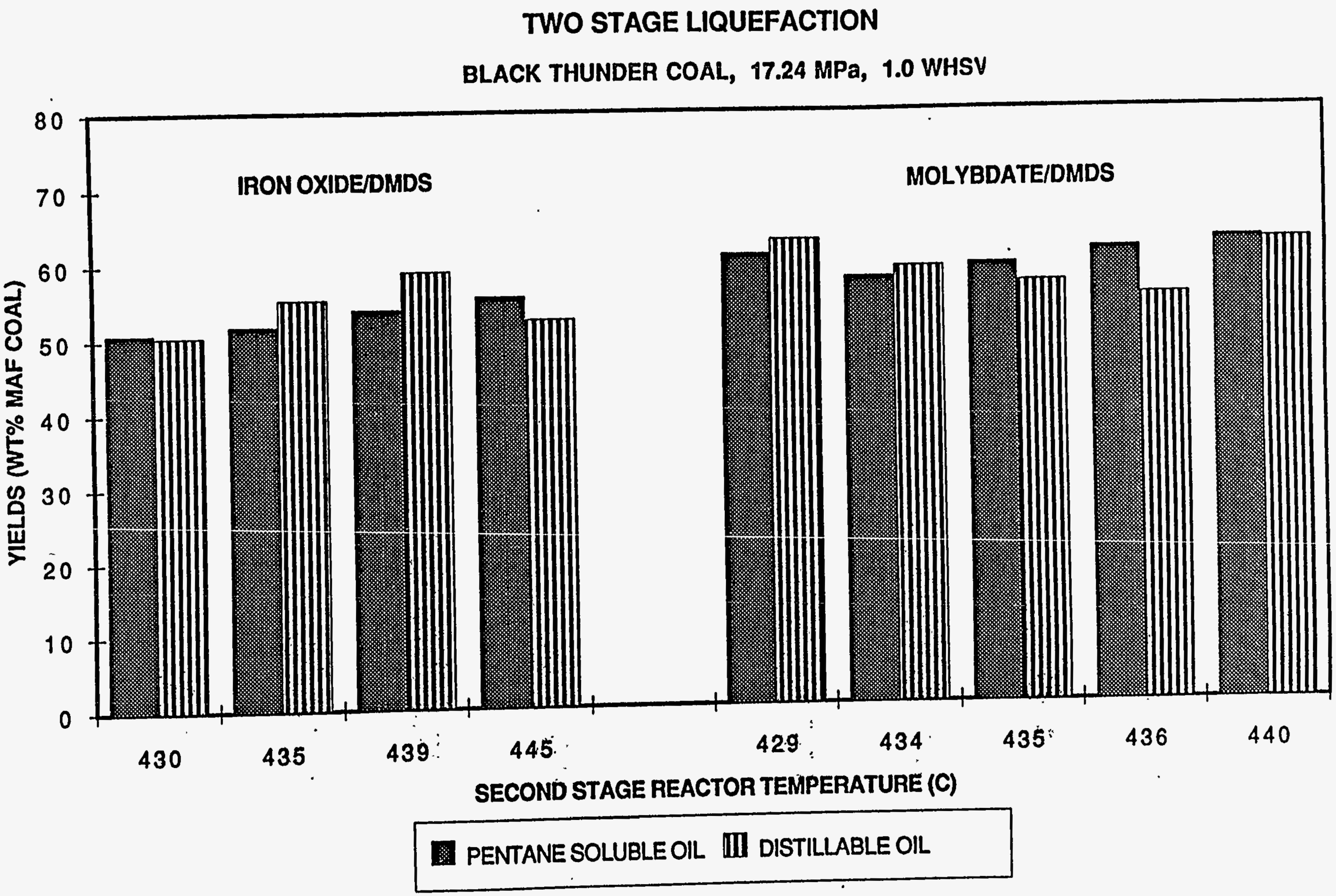

TWO STAGE LIQUEFACTION
BLACK THUNDER COAL, 17.24 MPa, 1.0 WHSV
IRON OXIDE/DMDS
MOLYBDATE/DMDS
YIELDS (WT% MAF COAL)
80
70
60
50
40
30
20
10
0
430
435
439
445
429
434
435
436
440
SECOND STAGE REACTOR TEMPERATURE (C)
■ PENTANE SOLUBLE OIL
▥ ASPHALTENE
▧ PREASPHALTENE

FIGURE 4.3.25


TWO STAGE LIQUEFACTION
BLACK THUNDER COAL, 17.24 MPa, 1.0 WHSV
YIELDS (WT% MAF COAL)
80
70
60
50
40
30
20
10
0
IRON OXIDE/DMDS
MOLYBDATE/DMDS
430
435
439
445
429
434
435
436
440
SECOND STAGE REACTOR TEMPERATURE (C)
PENTANE SOLUBLE OIL
DISTILLABLE OIL

extraction. Distillable oil yields of about 55 wt% based on MAF coal were obtained using iron oxide as catalyst, but with molybdate these yields were increased to 60 - 65%. A value of 62% was taken for the economic study.

It has to be remembered that the bench unit was operated in the once through mode with no recycle of bottoms material. It is expected, therefore, that significantly higher distillable oil yields would be achieved with bottoms recycle. If all the pentane soluble oil fraction was converted to distillable oil, and 25% of the asphaltene fraction to distillable oil, yields close to 70% wt based on MAF coal should be achieved. This would be at least comparable with other technologies that use recycle.

The elemental balances for Runs DOE-BU-014, YP3 and DOE-BU-015, YP5 are shown in Tables 4.3.9 and 4.3.10, respectively. The carbon balances are only slightly high, and as mentioned earlier the oxygen balances are quite good indicating the validity of the procedures used to measure shift reaction and water balance. The sulphur balances are variable in percentage terms, but in actual quantities are quite close considering the difficulties in accurately measuring all sulphur in small pilot plants. The nitrogen balances are low in both cases, but acceptable considering that we know some ammonium bicarbonate is formed and deposits in the second stage product gas line and is not accounted for. Also, the produced water was not analyzed for ammonia or hydrogen sulphide. One problem area appears to be the hydrogen balances which are low in both cases. It is not clear at the moment whether this is due to analytical or measurement error, but might suggest that the stated hydrogen consumptions are conservatively high.

4.3.3.2 Illinois #6 Coal

A summary of the key data from all the bench unit mass balance periods on Illinois #6 coal are shown in Tables 4.3.11 and 4.3.12. Interpretation of the results is provided below.

Table 4.3.9

ELEMENTAL BALANCE

RUN No.: DOE-BU-014 M.B.No.: YP-03/ C1

COMPONENT (1)	Mass Balance (2)	CARBON		HYDROGEN		NITROGEN		SULPHUR		OXYGEN		ELEMENT BALANCE
		In (1)	In (2)	In (1)	In (2)	In (1)	In (2)	In (1)	In (2)	In (1)	In (2)	
FEED												
Coal	41.81%	75.70%	31.65%	5.60%	2.34%	1.03%	0.43%	0.43%	0.18%	17.24%	7.21%	
Solvent	58.19%	87.80%	51.09%	8.50%	4.95%	0.85%	0.49%	0.05%	0.03%	2.80%	1.63%	
CO	12.45%	42.90%	5.34%							57.10%	7.11%	
Water	8.01%			11.00%	0.88%					87.20%	6.98%	
Hydrogen	2.35%			100.00%	2.35%							
TOTAL FEED	122.82%		88.08%		10.52%		0.93%		0.21%		22.93%	122.67%
PRODUCT												
CO2	22.65%	27.30%	6.18%							72.70%	16.47%	
CO	1.12%	42.90%	0.48%							57.10%	0.64%	
H2S				5.90%				94.10%				
Water	2.79%			11.00%	0.31%					87.20%	2.43%	
Hydrogen	0.33%			100.00%	0.33%							
CH4	1.92%	75.00%	1.44%	25.00%	0.48%							
C2H6	0.90%	80.00%	0.72%	20.00%	0.18%							
C3H8	0.87%	81.80%	0.71%	18.20%	0.16%							
C4+	1.45%	83.00%	1.20%	17.00%	0.25%							
IBP - 182		84.40%		13.20%		0.25%		0.11%		2.04%		
182 - 343	14.59%	85.20%	12.43%	10.00%	1.46%	0.66%	0.10%	0.05%	0.01%	4.09%	0.60%	
343 - 524	58.47%	88.30%	51.63%	8.90%	5.20%	0.76%	0.44%	0.05%	0.03%	1.99%	1.16%	
524+	17.73%	87.50%	15.51%	6.70%	1.19%	1.35%	0.24%	1.20%	0.21%	3.25%	0.58%	
TOTAL PRODUCT	122.82%		90.31%		9.56%		0.78%		0.25%		21.88%	122.77%
COMPONENT BALAN	100.00%		102.52%		90.80%		84.30%		119.34%		95.39%	100.08%

TABLE 4.3.10

ELEMENTAL BALANCE

RUN No.: DOE-BU-015 M.B.No.: YP-05/C1

COMPONENT (1)	Mass Balance (2)	CARBON		HYDROGEN		NITROGEN		SULPHUR		OXYGEN		ELEMENT BALANCE
		In (1)	In (2)	In (1)	In (2)	In (1)	In (2)	In (1)	In (2)	In (1)	In (2)	
FEED												
Coal	41.88%	75.70%	31.70%	5.60%	2.35%	1.03%	0.43%	0.43%	0.18%	17.24%	7.22%	
Solvent	58.12%	87.80%	51.03%	8.50%	4.94%	0.85%	0.49%	0.05%	0.03%	2.80%	1.63%	
CO	11.97%	42.90%	5.13%							57.10%	6.83%	
Water	7.70%			11.00%	0.85%					87.20%	6.71%	
Hydrogen	2.68%			100.00%	2.68%							
TOTAL FEED	122.35%		87.87%		10.81%		0.93%		0.21%		22.40%	122.21%
PRODUCT												
CO2	22.07%	27.30%	6.02%							72.70%	16.04%	
CO	1.50%	42.90%	0.64%							57.10%	0.86%	
H2S				5.90%				94.10%				
Water	1.52%			11.00%	0.17%					87.20%	1.32%	
Hydrogen	0.33%			100.00%	0.33%							
CH4	1.13%	75.00%	0.85%	25.00%	0.28%							
C2H6	0.92%	80.00%	0.74%	20.00%	0.18%							
C3H8	0.93%	81.80%	0.76%	18.20%	0.17%							
C4+	1.45%	83.00%	1.20%	17.00%	0.25%							
IBP - 182	1.27%	83.90%	1.07%	13.30%	0.17%	0.23%	0.00%	0.78%	0.01%	1.79%	0.02%	
182 - 343	22.73%	84.80%	19.27%	9.90%	2.25%	0.61%	0.14%	0.23%	0.05%	4.46%	1.01%	
343 - 524	50.45%	86.90%	43.84%	9.70%	4.89%	0.76%	0.38%	0.11%	0.06%	2.53%	1.28%	
524+	18.05%	84.40%	15.24%	7.30%	1.32%	1.05%	0.19%	0.13%	0.02%	7.12%	1.29%	
TOTAL PRODUCT	122.35%		89.64%		10.01%		0.71%		0.14%		21.82%	122.32%
COMPONENT BALANCE	100.00%		102.01%		92.58%		77.21%		67.49%		97.42%	100.09%

Table 4.3.11

SUMMARY OF BENCH UNIT TEST RUNS					
RUN No.:	DOE-BU-016		DOE-BU-017		
M.B.No.:	YP-01/ C1	YP-02/ C1	YP-01/ C1	YP-02/ C1	YP-03/ C1
Coal	Illinois#6	Illinois#6	Illinois#6	Illinois#6	Illinois#6
wt % maf	32.56%	32.56%	39.80%	38.15%	39.87%
First Stage:					
Feed Rate (kg / hr) / I WHSV					
Pressure Mpa					
Temperatu deg C					
Catalyst					
CO Rate kg / kg maf coal					
moles / 100g maf coal					
consumed moles / 100g maf coal					
Water Rate kg / kg maf coal					
moles / 100g maf coal					
Hydrogen wt % maf coal					
Second Stage:					
Feed Rate (kg / hr) / I WHSV	0.92	0.80	1.06	0.94	0.88
Pressure Mpa	17.24	17.24	17.24	17.24	17.24
Temperatu deg C	428	440	428	442	431
Catalyst	FeO+DMDS	FeO+DMDS	Moly+DMDS	Moly+DMDS	Moly+DMDS
Hydrogen kg / kg maf coal	0.69	0.79	0.57	0.67	0.69
moles / 100g maf coal	34.22	39.55	28.37	33.30	34.34
consumed wt % maf coal	3.50%	4.55%	2.47%	2.46%	1.82%
Coal Conversion (wt % maf coal)	82.85%	87.42%	86.01%	87.83%	89.36%
Product Yield (wt % maf coal)					
H2O	-0.74%	0.40%	-0.90%	0.18%	0.01%
COx	1.09%	1.04%	0.89%	0.75%	0.69%
H2S	0.76%	1.30%	1.75%	1.73%	1.22%
C1 to C3	5.97%	9.17%	4.32%	6.56%	3.90%
Pentane soluble (incl. C4)	30.76%	35.36%	41.87%	40.89%	40.94%
Asphaltenes	44.32%	41.90%	36.77%	35.82%	39.45%
Preasphalt.	4.19%	2.81%	3.78%	4.35%	4.97%
IOM	17.15%	12.58%	13.99%	12.17%	10.64%
TOTAL	96.42%	92.64%	96.41%	93.24%	96.01%

NOTE:

Table 4.3.12

SUMMARY OF BENCH UNIT TEST RUNS

RUN No.:		DOE-BU-018				
M.B.No.:		YP-01/ C1	YP-02/ C1	YP-03/ C1	YP-04/ C1	YP-05/ C1
Coal		Illinois#6	Illinois#6	Illinois#6	Illinois#6	Illinois#6
wt % maf		34.04%	37.08%	38.59%	37.88%	38.14%
First Stage:						
Feed Rate	(kg / hr) / I WHSV	1.48	1.40	1.55	1.79	1.64
Pressure	Mpa					
Temperature	deg C	428	425	422	417	415
Catalyst						
CO Rate	kg / kg maf coal					
	moles / 100g maf coal					
consumed	moles / 100g maf coal					
Water Rate	kg / kg maf coal					
	moles / 100g maf coal					
Hydrogen	wt % maf coal					
Second Stage:						
Feed Rate	(kg / hr) / I WHSV	0.96	0.91	1.42	1.16	1.06
Pressure	Mpa	17.24	17.24	17.24	17.24	17.24
Temperature	deg C	430	439	440	440	431
Catalyst		Moly	Moly	Moly	Iron Oxide	Iron Oxide
Hydrogen	kg / kg maf coal	1.04	1.02	0.88	0.80	0.86
	moles / 100g maf coal	51.78	50.79	43.74	39.65	42.86
consumed	wt % maf coal	4.52%	4.20%	3.46%	3.89%	2.95%
Coal Conversion (wt % maf coal)		**95.03%**	**95.16%**	**94.57%**	**93.17%**	**92.99%**
Product Yield (wt % maf coal)						
H2O		6.15%	2.74%	7.21%	6.84%	4.90%
COx		0.99%	0.87%	0.71%	1.85%	1.28%
H2S			0.02%	0.02%		
C1 to C3		6.86%	8.33%	6.33%	7.33%	5.67%
C4 - 182		12.65%	12.46%	10.18%	12.16%	18.25%
182 - 343		31.00%	33.16%	36.75%	32.74%	30.19%
343 - 524		-6.12%	2.44%	4.42%	-0.54%	0.25%
IBP - 524		37.53%	48.05%	51.35%	44.36%	48.69%
524+		52.99%	44.43%	37.84%	43.51%	42.41%
TOTAL		104.52%	104.20%	103.46%	103.89%	102.95%
Yields based on Solubility						
Pentane soluble (incl. C4)		47.56%	60.07%	50.06%	43.60%	47.77%
Asphaltenes		37.13%	26.81%	32.83%	36.23%	34.88%
Preasphaltenes		0.86%	0.52%	0.87%	1.21%	1.45%
IOM		4.97%	4.84%	5.43%	6.83%	7.01%
TOTAL		90.52%	92.24%	89.19%	87.87%	91.11%
NOTE:						

4.3.3.2.1 Coal Solubilization

The initial intent was to study the solubilization of Illinois #6 coal in the counterflow reactor system using CO/steam and then hydrogen in separate operations and complete a comparison. Literature work and our own autoclave studies suggested that unlike subbituminous coals, such as Black Thunder, coal solubilization of bituminous coals is more effectively accomplished using hydrogen. When operational problems occurred running CO/steam solubilization with Illinois #6 coal in the first counterflow reactor, the decision was made to concentrate on hydrogen only in both one stage and two stage operation. One stage operation (DOE-BU-016 and DOE-BU-017) was carried out in the second stage counterflow reactor only. Two stage operation (DOE-BU-018) was performed by using a continuous autoclave (CSTR) as first stage and then directing the total product from the autoclave to the second stage counterflow reactor.

4.3.3.2.2 Comparison of One and Two Stage Operation

The effects on product slate of two stage operation as opposed to one stage only are illustrated in Figures 4.3.26 - 4.3.29. The conditions in the counterflow reactor are the same in each comparison, the difference is that in the two stage operation a CSTR reactor operating at a target temperature of 425°C, a target space velocity of 1.5 and nominally 17.24 MPa pressure (controlled by second stage reactor pressure) precedes the CFR. Two different catalysts, iron oxide and ammonium molybdate and two different temperatures 430 and 440°C were used. In each case the trends are the same. Two stage operation shows higher coal conversion (lower IOM) higher pentane soluble oil yields and lower asphaltene and preasphaltene yields. Hydrocarbon gas yields are relatively constant.

These data confirm the benefits of two stage operation. The results of the two stage operations are shown in bar graph form in Figures 4.3.30 and 4.3.31. The results

FIGURE 4.3.26

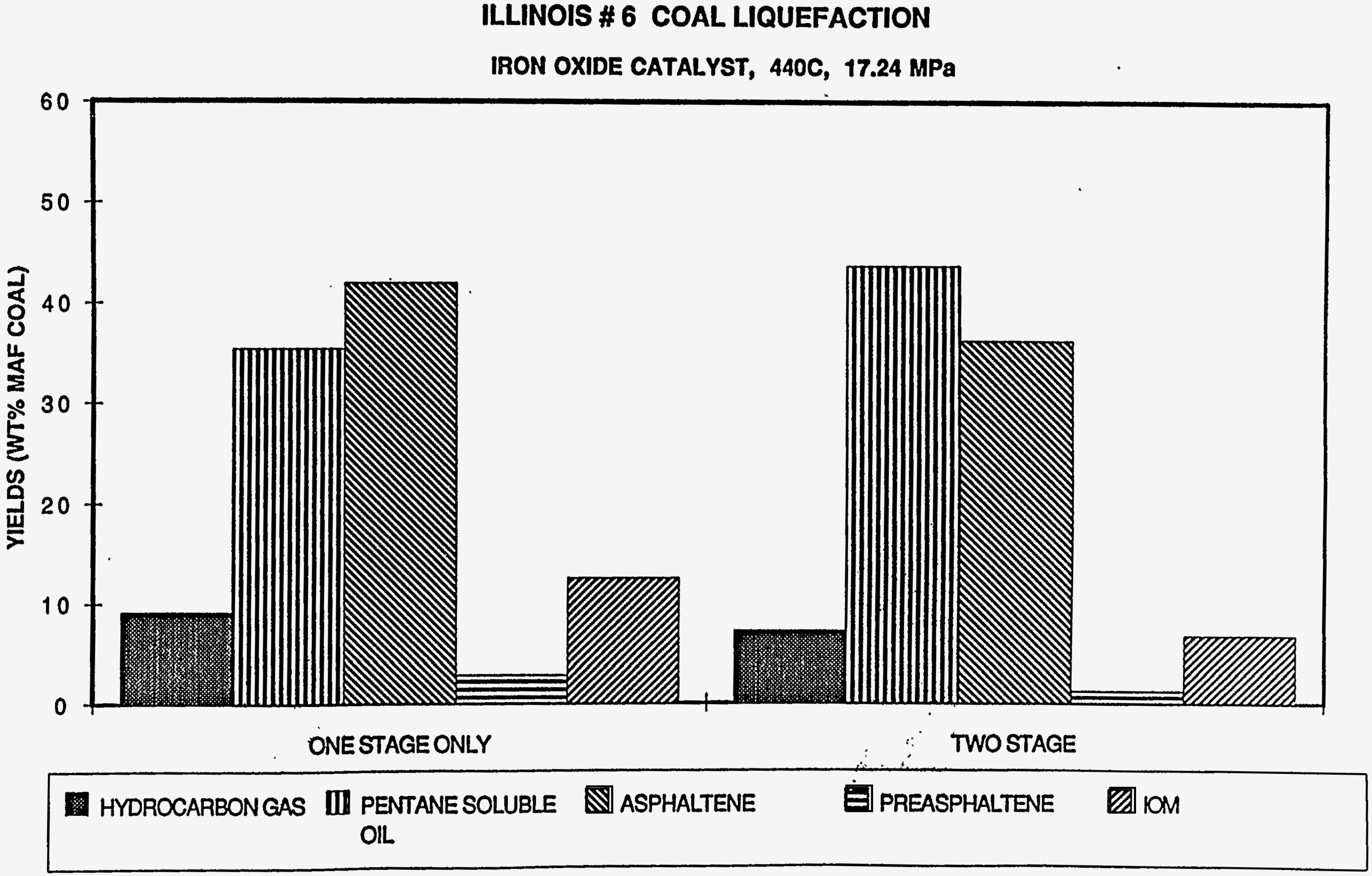

ILLINOIS # 6 COAL LIQUEFACTION
IRON OXIDE CATALYST, 440C, 17.24 MPa
YIELDS (WT% MAF COAL)
60
50
40
30
20
10
0
ONE STAGE ONLY
TWO STAGE
HYDROCARBON GAS
PENTANE SOLUBLE OIL
ASPHALTENE
PREASPHALTENE
IOM

FIGURE 4.3.27

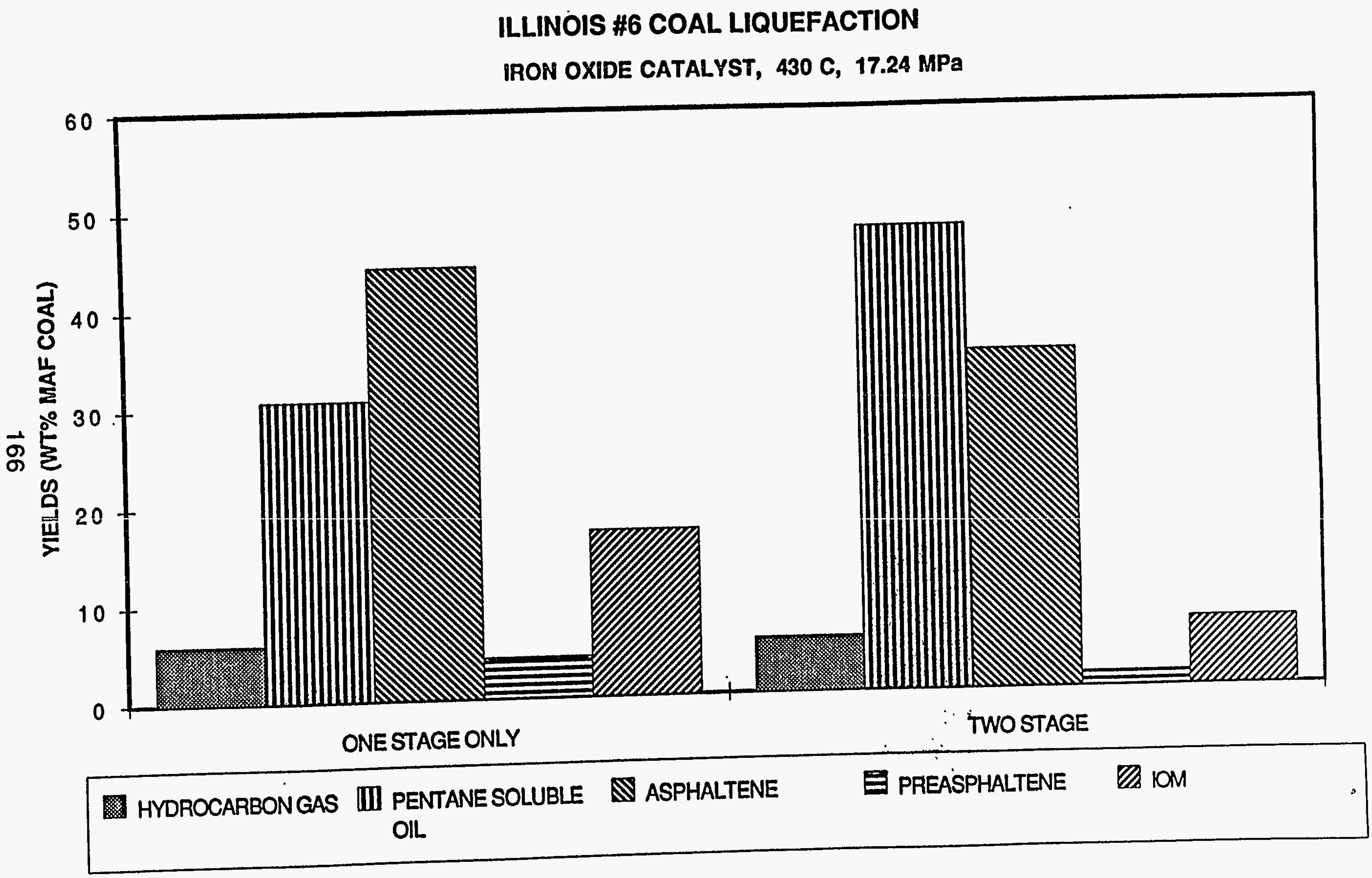
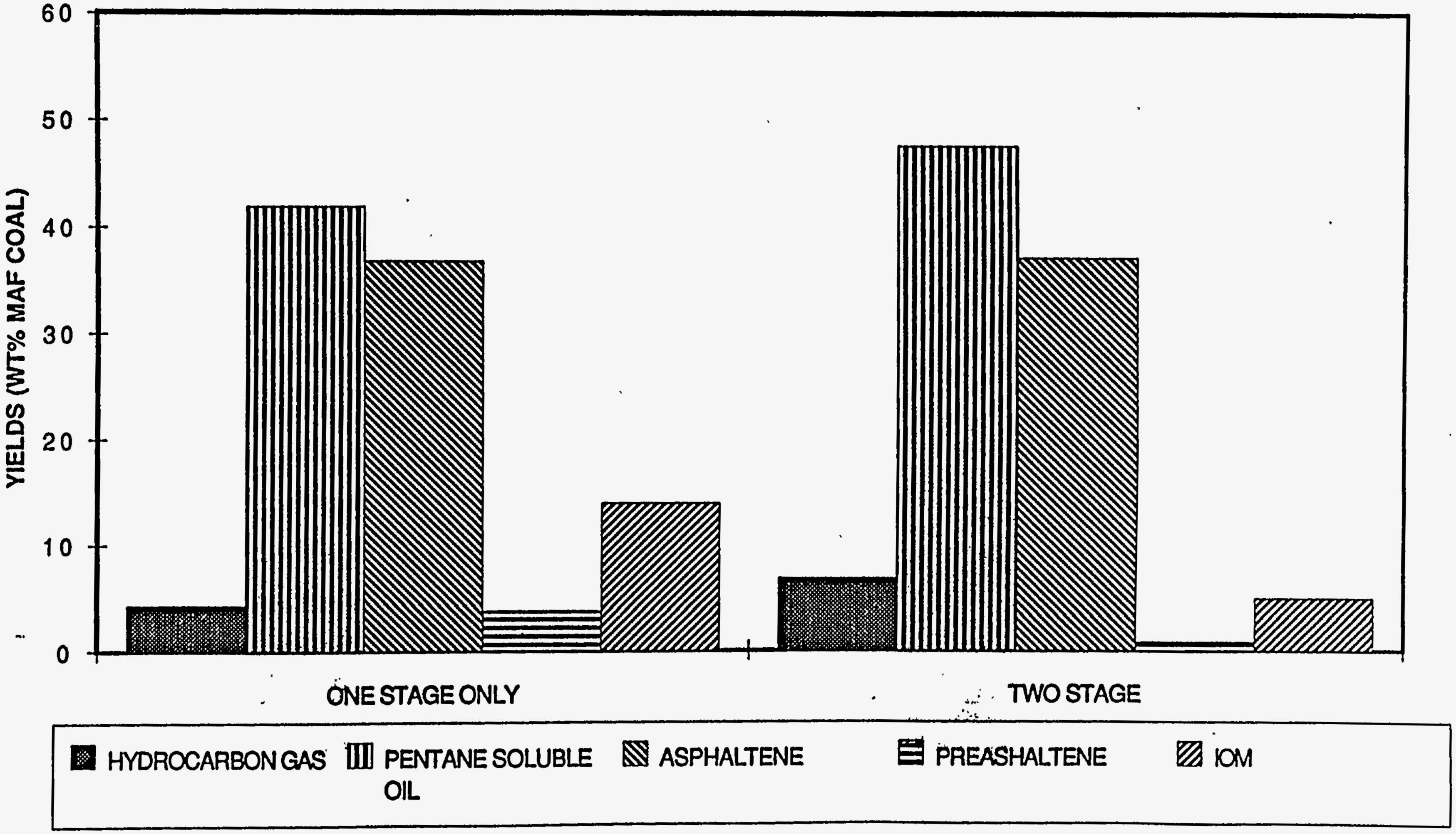

ILLINOIS #6 COAL LIQUEFACTION
IRON OXIDE CATALYST, 430 C, 17.24 MPa
YIELDS (WT% MAF COAL)
60
50
40
30
20
10
0
ONE STAGE ONLY
TWO STAGE
▩ HYDROCARBON GAS
▥ PENTANE SOLUBLE OIL
▧ ASPHALTENE
▤ PREASPHALTENE
▨ IOM

FIGURE 4.3.28



ILLINOIS #6 COAL LIQUEFACTION

MOLYBDATE CATALYST, 430 C, 17.24 MPa

FIGURE 4.3.29

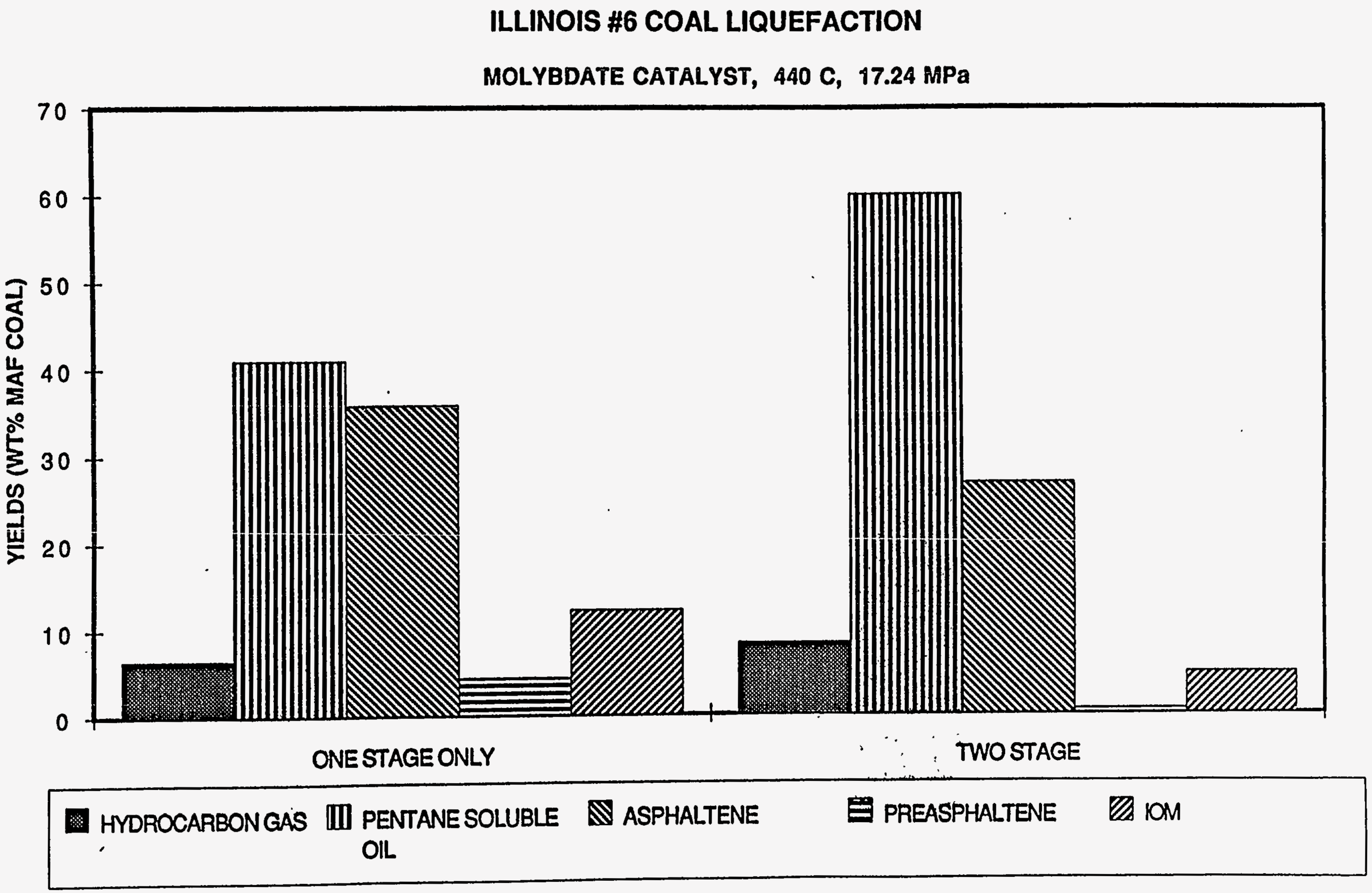

ILLINOIS #6 COAL LIQUEFACTION
MOLYBDATE CATALYST, 440 C, 17.24 MPa
YIELDS (WT% MAF COAL)
70
60
50
40
30
20
10
0
ONE STAGE ONLY
TWO STAGE
HYDROCARBON GAS
PENTANE SOLUBLE OIL
ASPHALTENE
PREASPHALTENE
IOM

FIGURE 4.3.30

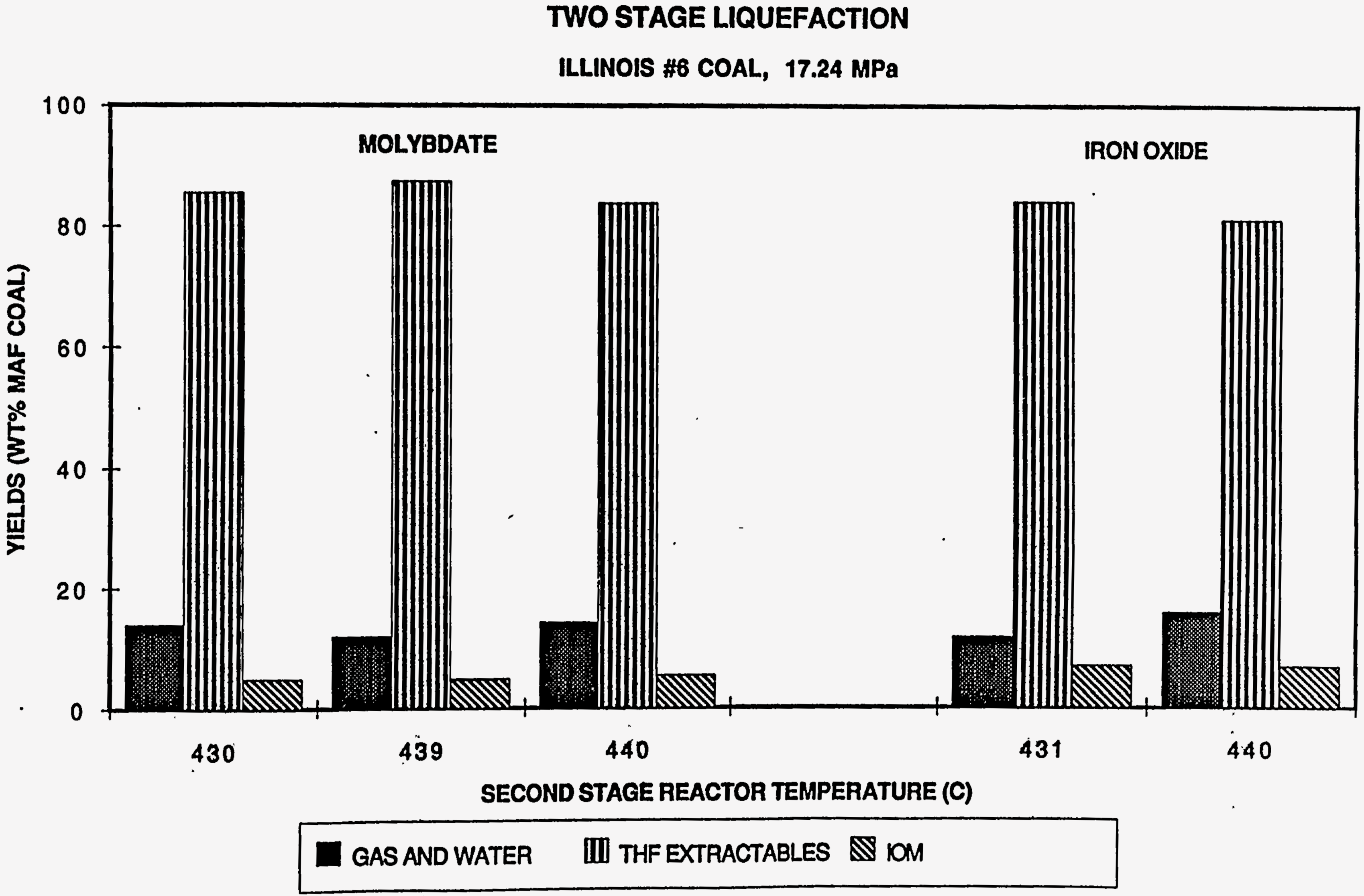
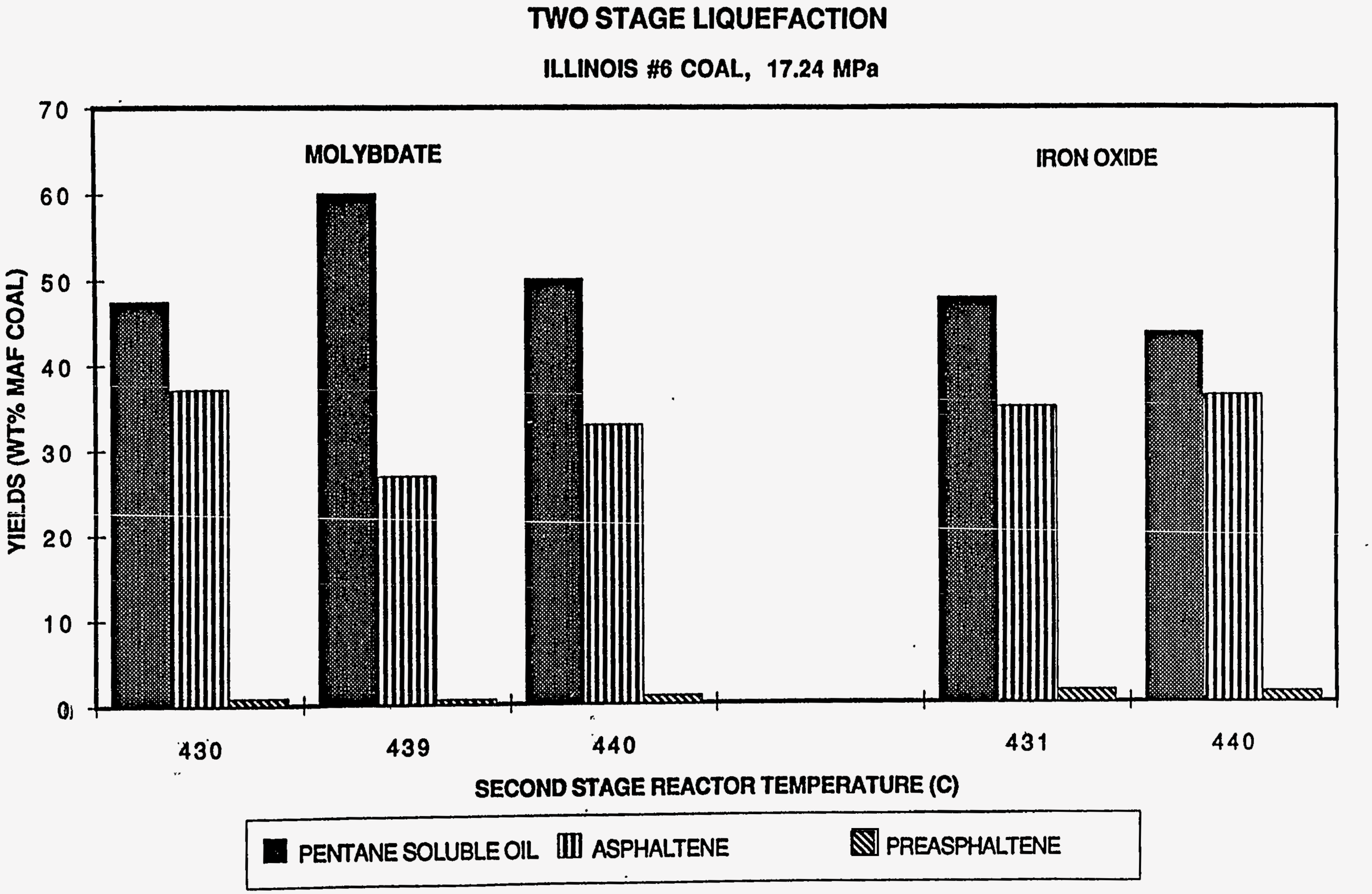

TWO STAGE LIQUEFACTION
ILLINOIS #6 COAL, 17.24 MPa
YIELDS (WT% MAF COAL)
0
20
40
60
80
100
MOLYBDATE
IRON OXIDE
430
439
440
431
440
SECOND STAGE REACTOR TEMPERATURE (C)
GAS AND WATER
THF EXTRACTABLES
IOM

FIGURE 4.3.31


TWO STAGE LIQUEFACTION
ILLINOIS #6 COAL, 17.24 MPa
MOLYBDATE
IRON OXIDE
YIELDS (WT% MAF COAL)
70
60
50
40
30
20
10
0
430
439
440
431
440
SECOND STAGE REACTOR TEMPERATURE (C)
PENTANE SOLUBLE OIL
ASPHALTENE
PREASPHALTENE

indicate that ammonium molybdate gave somewhat better performance, slightly higher coal conversion, and higher pentane soluble oil yields. Gas and water yields were similar for both catalysts.

As in the case of Black Thunder coal, there was a fairly close correlation between pentane soluble oil yield and distillable oil yield (524°C-) based on simulated distillation results (Figure 4.3.32). In this case distillable oil yields in the range of 50 - 55% wt on MAF coal were achieved on a once through basis. Higher distillable oil yields should be achievable on solvent recycle and/or more optimized operation.

4.3.3.3 Severity Index

A severity index is a simple kinetic model, normally based on first order kinetics to describe process severity as a function of reactor temperature and residence time. A severity index has been used by Hydrocarbon Research Inc. (HRI) and others for operations in coal liquefaction, coprocessing and resid upgrading. This index is defined by the following formula:

Severity Index

$$SI = t * EXP\left(\frac{53200}{R}\left(\frac{1}{721.7} - \frac{1}{T_r}\right)\right)$$

where t = residence time in minutes

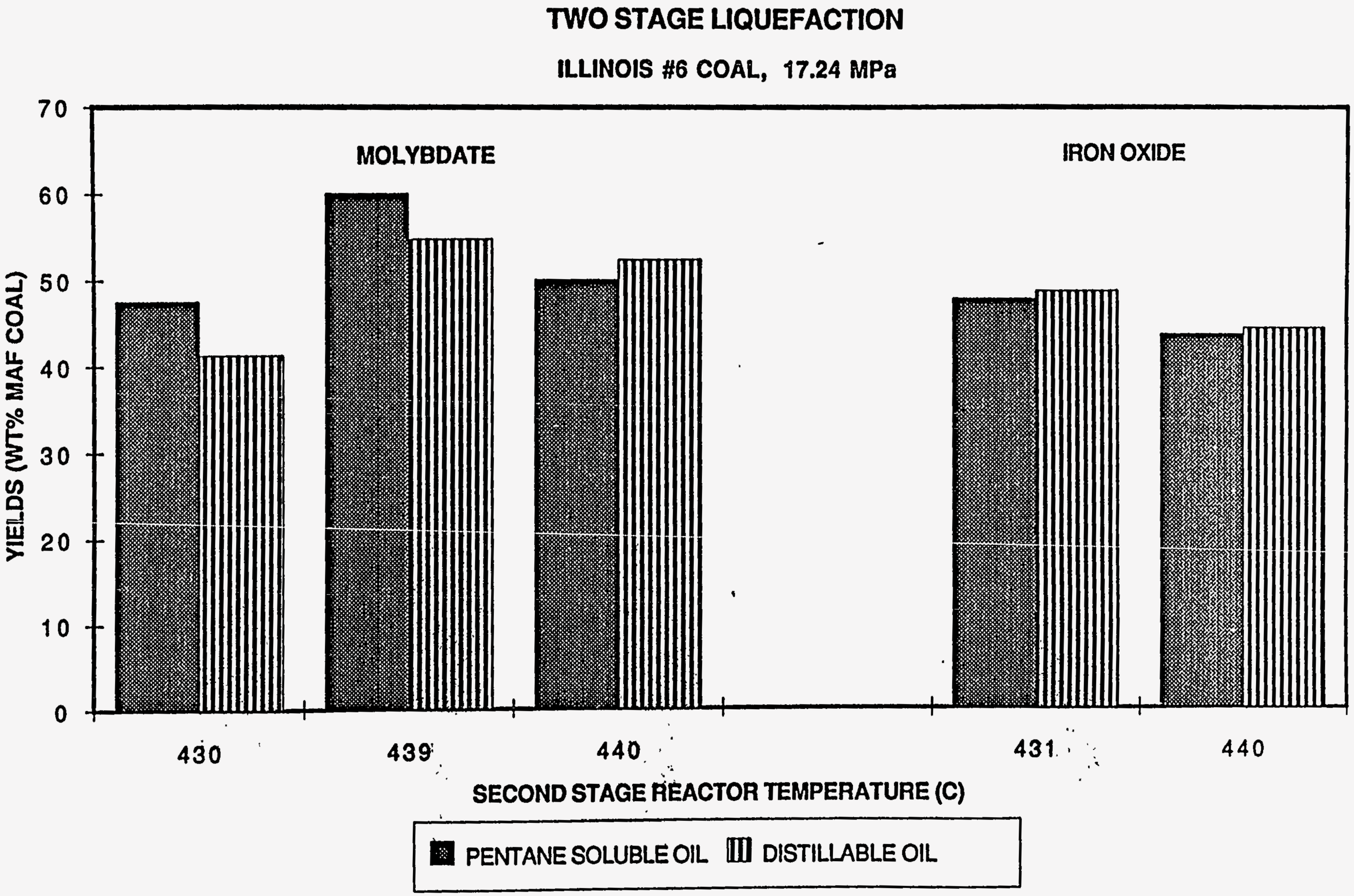
T_r = reactor temperature in deg. K

R = Gas constant, 1.987 cals/deg.mole.

We have used this index for define process severity in both one and two stage processing. An empirical overall severity index for two stage operations was defined as the sum of the severity indices of the two individual stages.

A number of variables were plotted against severity index to determine if any

FIGURE 4.3.32


TWO STAGE LIQUEFACTION
ILLINOIS #6 COAL, 17.24 MPa
MOLYBDATE
IRON OXIDE
YIELDS (WT% MAF COAL)
70
60
50
40
30
20
10
0
430
439
440
431
440
SECOND STAGE REACTOR TEMPERATURE (C)
▩ PENTANE SOLUBLE OIL
▥ DISTILLABLE OIL

significant relationships could be identified. Scatter in the data might be expected since the severity index does not account for other process variables e.g. catalysts, pressures, gas flow rates, etc.

Coal conversions for Black Thunder coal were plotted against severity index for all the bench unit runs, both one stage only and two stage (Figure 4.3.33). Coal conversions increase with severity index as expected, to a maximum at a severity index of about 30. There is an indication that conversion drops off at higher severities perhaps due to retrograde reactions. The data points listed as no catalyst refer to the first stage only, and indicate again the importance of having a catalyst to promote the shift reaction in the solubilization step to achieve the required coal conversion in the two stage process.

Hydrocarbon gas yields (Figure 4.3.34) follow a more linear relationship, with gas yields tending to be higher where no catalyst is used in the first stage. The reduced scatter on the other points suggests other variables do not have a very significant impact on hydrocarbon gas yield.

Pentane soluble oil, asphaltene and preasphaltene yields were also plotted against severity index (Figures 4.3.35 - 4.3.37). Pentane soluble oil yields follow a similar trend as coal conversion, but here there is more scatter, suggesting other variables play a significant role in pentane soluble oil yield. Asphaltene yields follow the reverse trend to pentane soluble oils and coal conversion, reaching a minimum at a severity index of about 30, and then possibly tending to increase at higher severities. Preasphaltene yields also reach a minimum at a severity index of about 30, and do not appear to be eliminated completely even at high severity.

The corresponding data for Illinois #6 coal is shown in Figures 4.3.38 to 4.3.42. Here the number of mass balance periods is limited and no runs were carried out at severity indices less than about 20. The data shows both one stage and two stage operation.

FIGURE 4.3.33

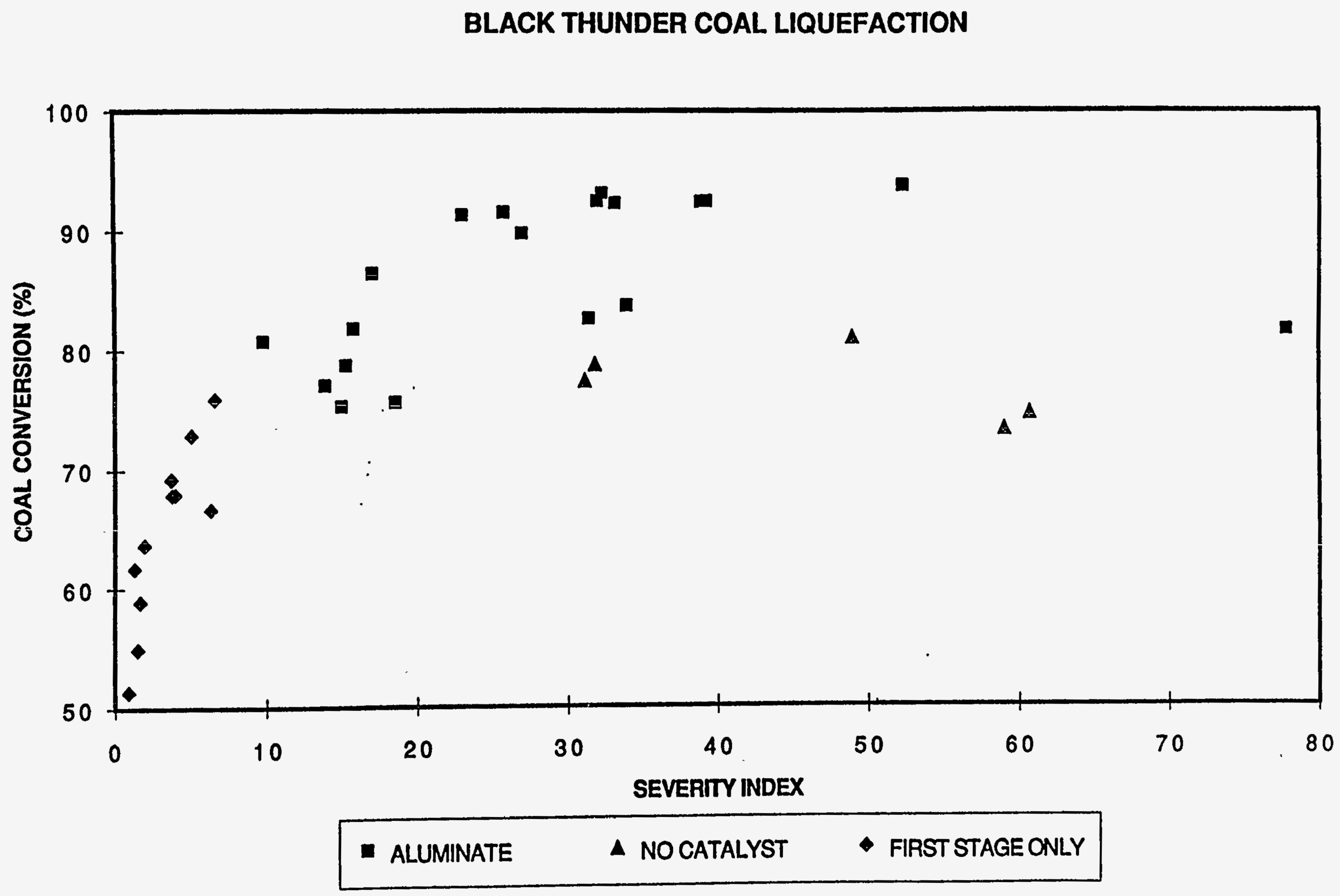

BLACK THUNDER COAL LIQUEFACTION
COAL CONVERSION (%)
100
90
80
70
60
50
0
10
20
30
40
50
60
70
80
SEVERITY INDEX
■ ALUMINATE
▲ NO CATALYST
◆ FIRST STAGE ONLY

FIGURE 4.3.34

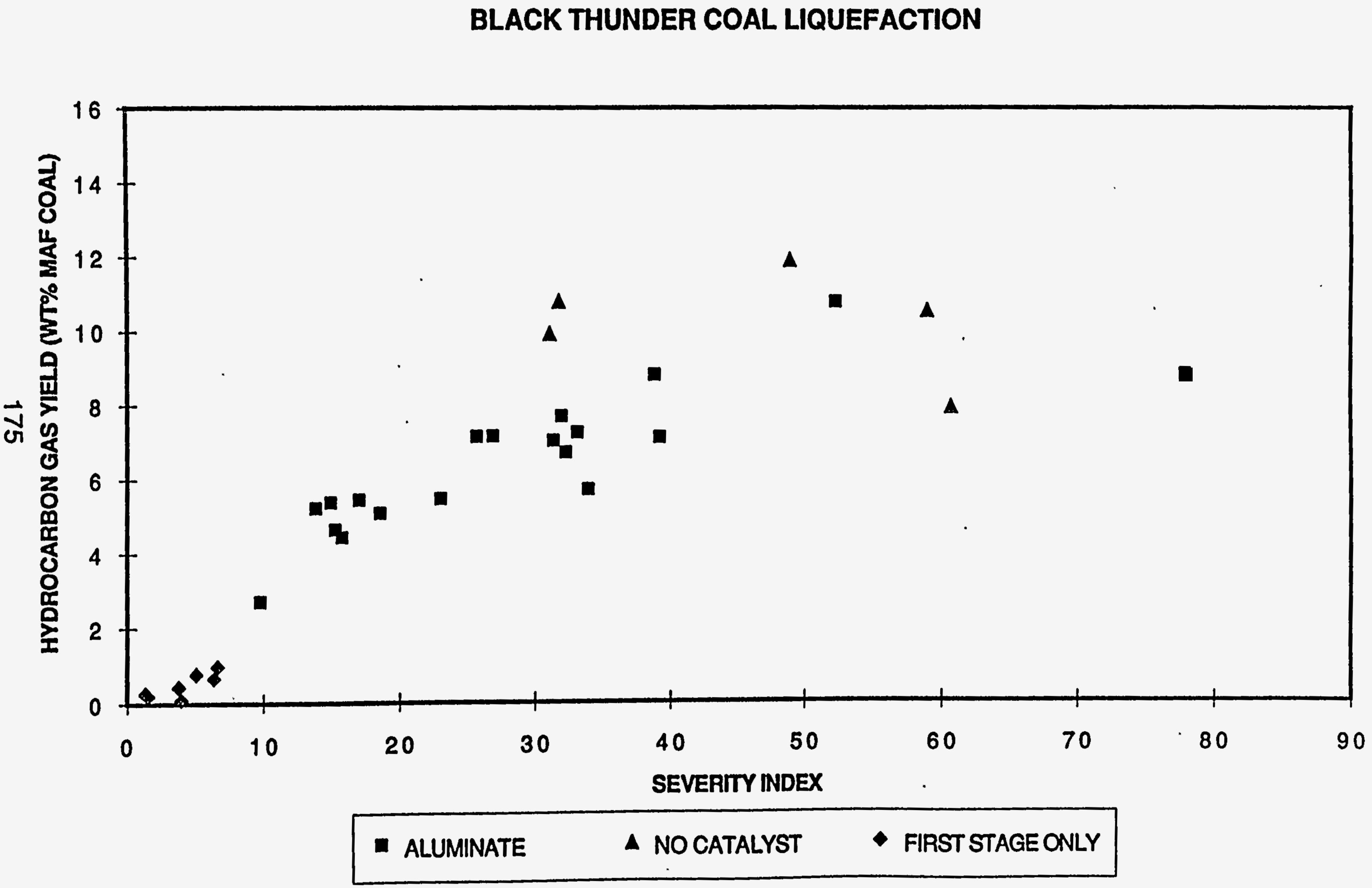

BLACK THUNDER COAL LIQUEFACTION
HYDROCARBON GAS YIELD (WT% MAF COAL)
0
2
4
6
8
10
12
14
16
SEVERITY INDEX
0
10
20
30
40
50
60
70
80
90
■ ALUMINATE
▲ NO CATALYST
◆ FIRST STAGE ONLY

FIGURE 4.3.35

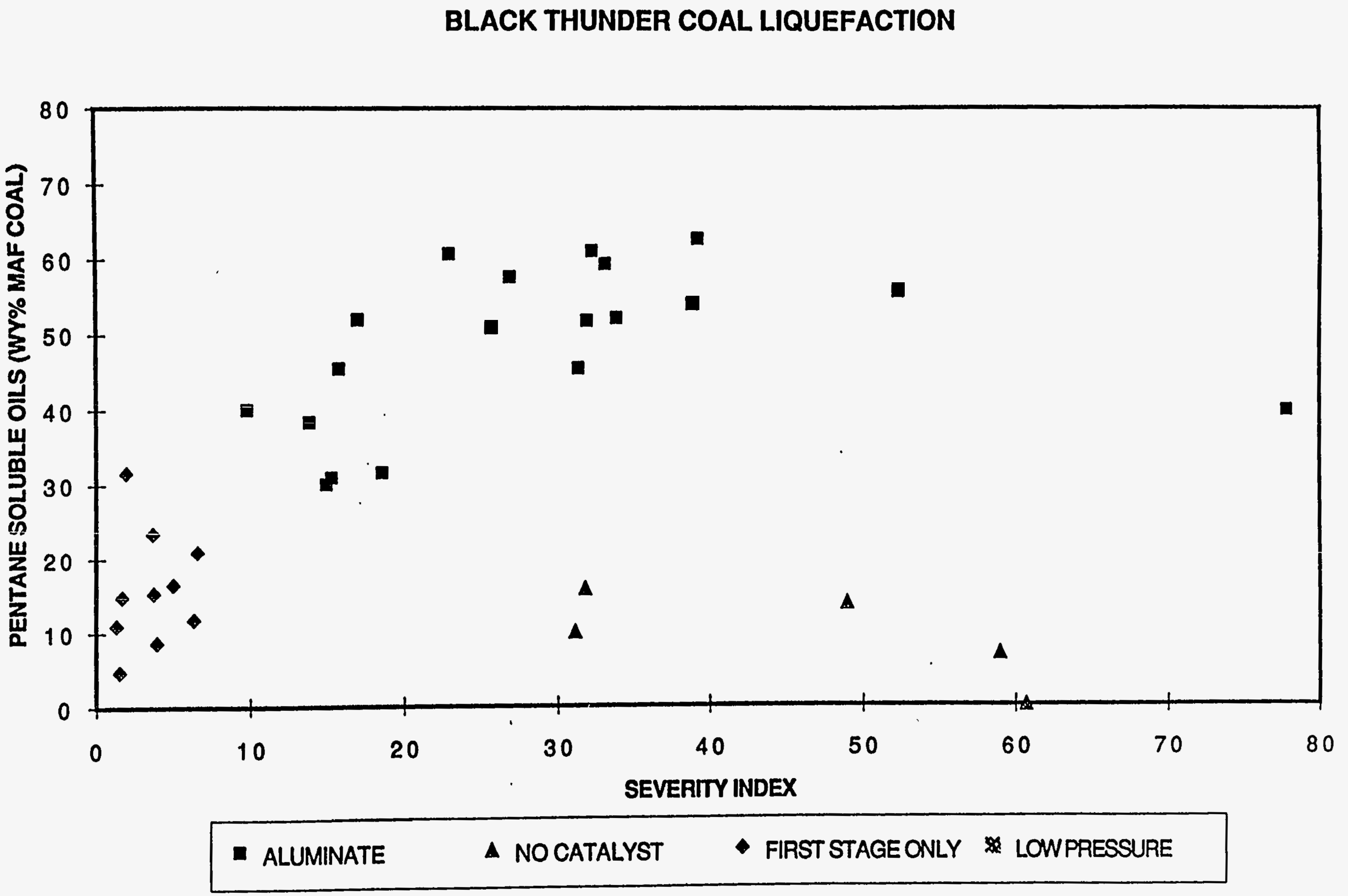

BLACK THUNDER COAL LIQUEFACTION
PENTANE SOLUBLE OILS (WT% MAF COAL)
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
SEVERITY INDEX
■ ALUMINATE
▲ NO CATALYST
◆ FIRST STAGE ONLY
※ LOW PRESSURE

FIGURE 4.3.36

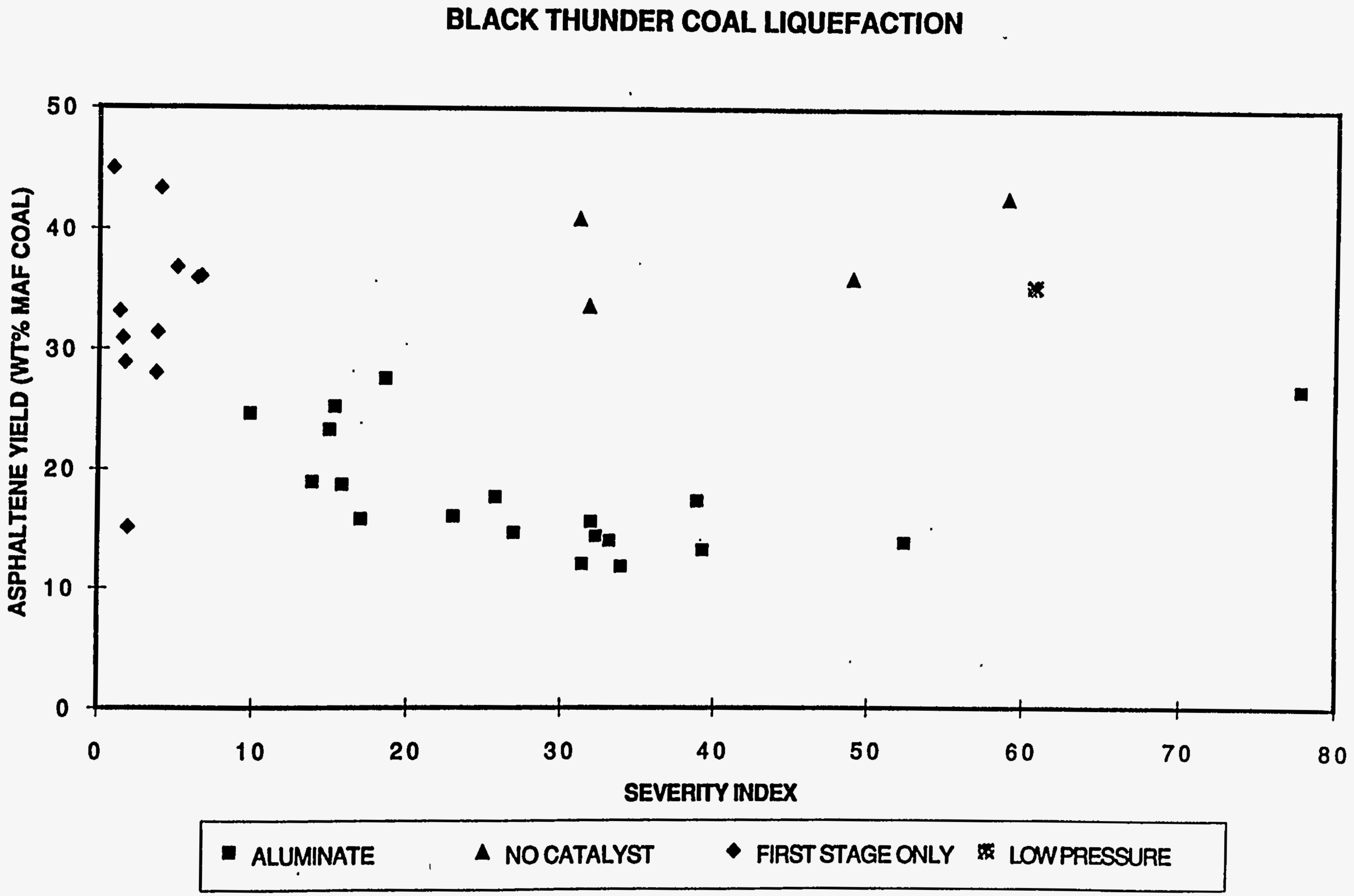

BLACK THUNDER COAL LIQUEFACTION
ASPHALTENE YIELD (WT% MAF COAL)
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
SEVERITY INDEX
■ ALUMINATE
▲ NO CATALYST
◆ FIRST STAGE ONLY
※ LOW PRESSURE

FIGURE 4.3.37

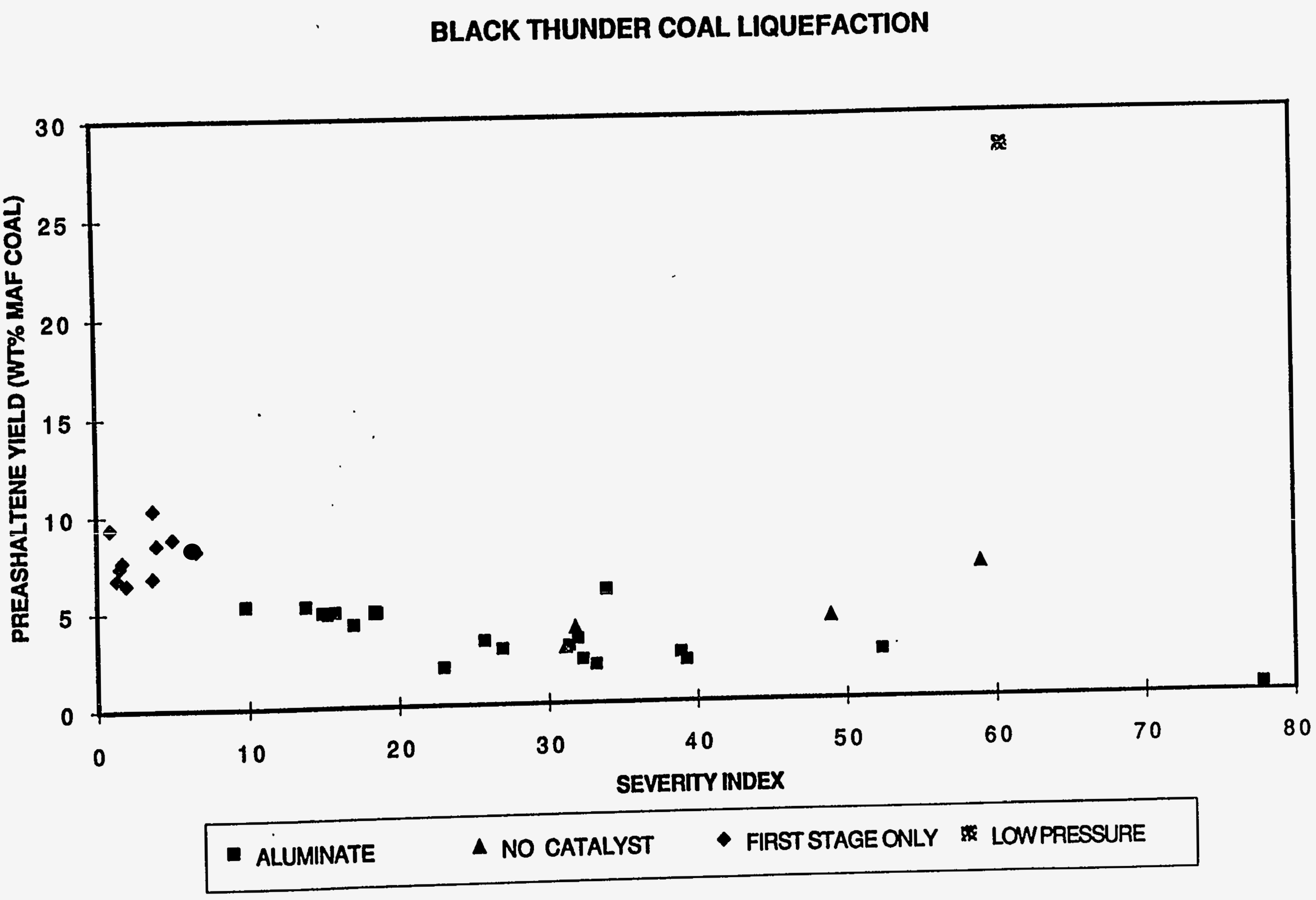

BLACK THUNDER COAL LIQUEFACTION
PREASHALTENE YIELD (WT% MAF COAL)
0
5
10
15
20
25
30
SEVERITY INDEX
0
10
20
30
40
50
60
70
80
■ ALUMINATE
▲ NO CATALYST
◆ FIRST STAGE ONLY
※ LOW PRESSURE

FIGURE 4.3.38

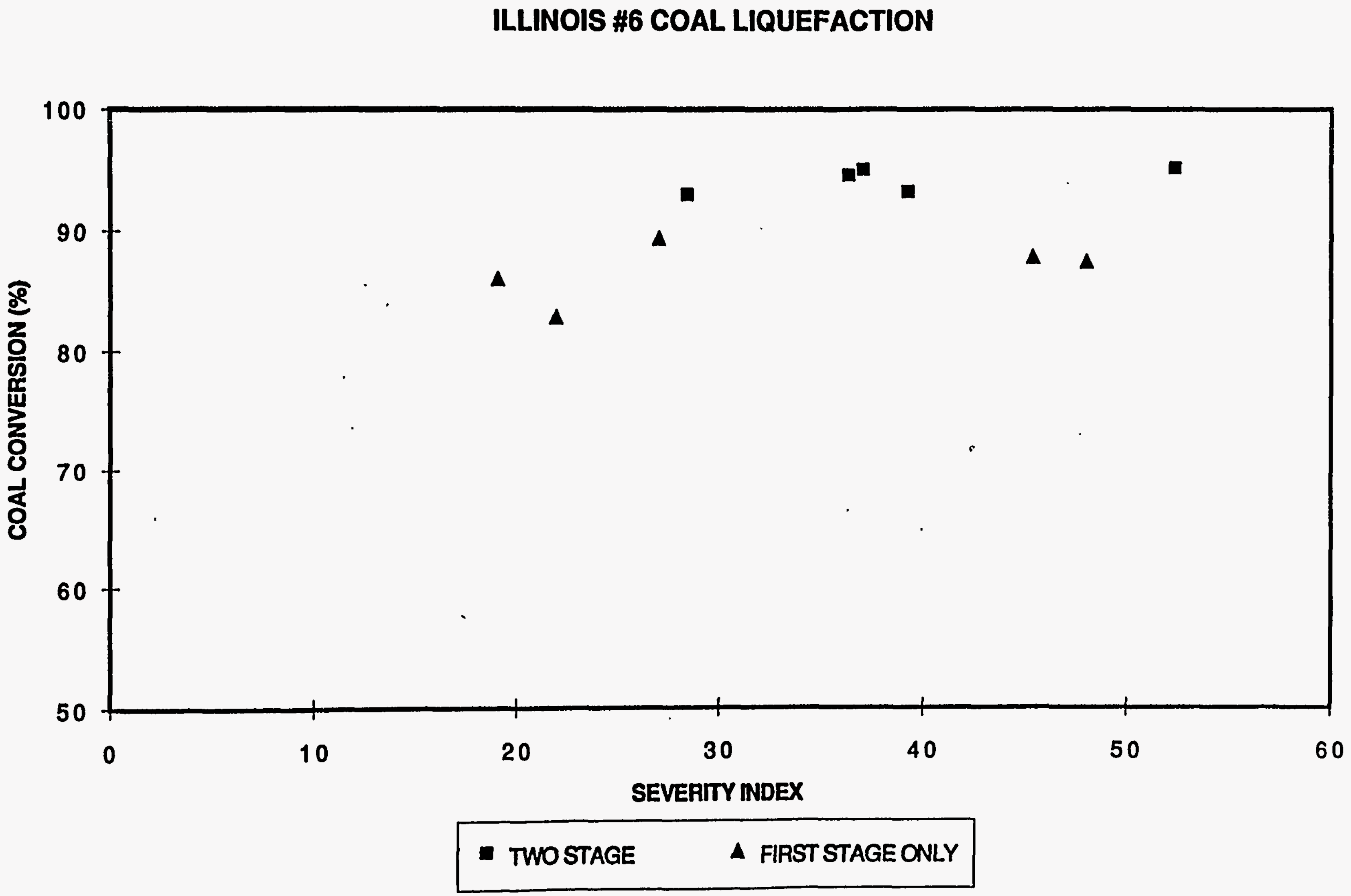

ILLINOIS #6 COAL LIQUEFACTION
COAL CONVERSION (%)
100
90
80
70
60
50
0
10
20
30
40
50
60
SEVERITY INDEX
■ TWO STAGE
▲ FIRST STAGE ONLY

FIGURE 4.3.39

ILLINOIS #6 COAL LIQUEFACTION

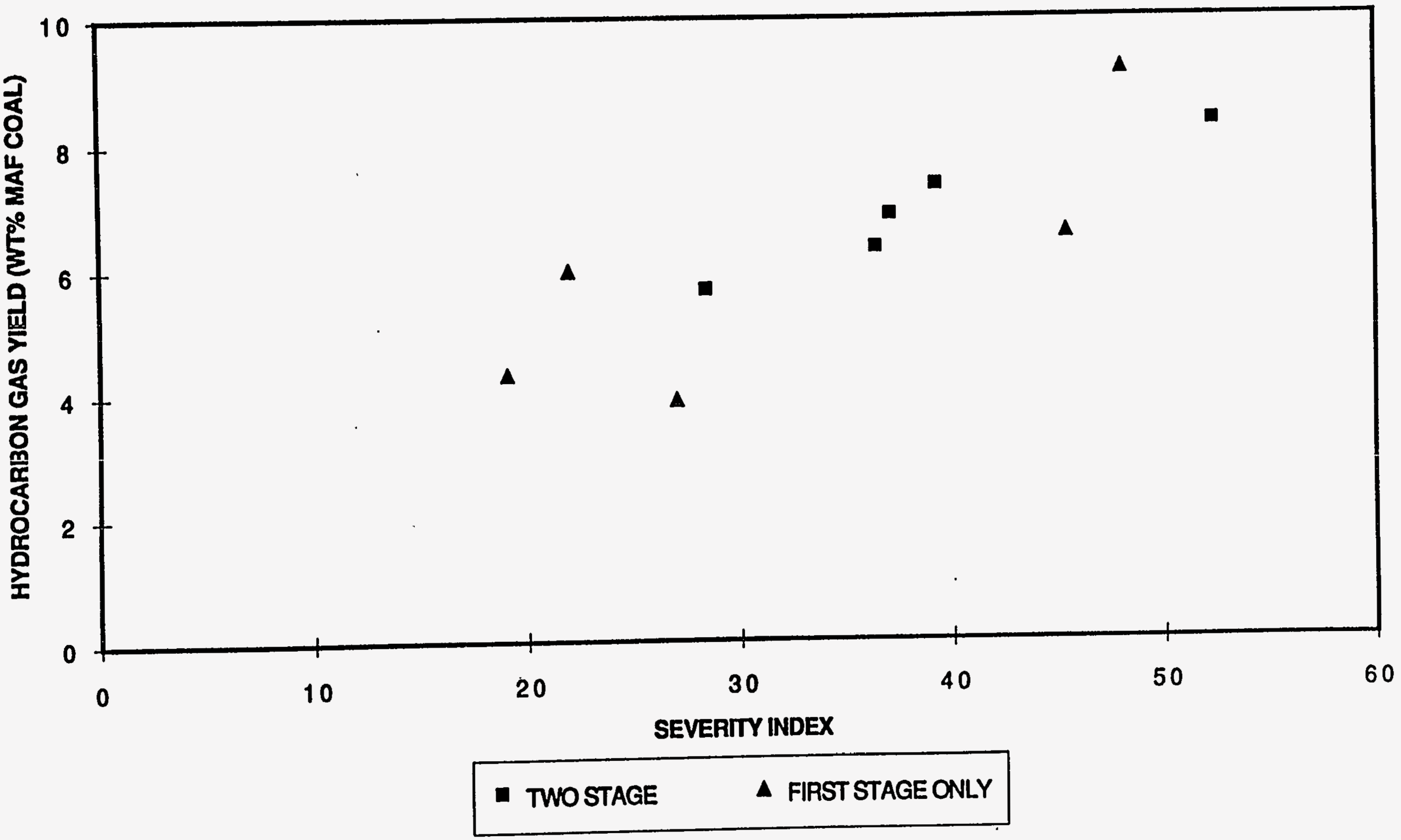


FIGURE 4.3.40

ILLINOIS #6 COAL LIQUEFACTION

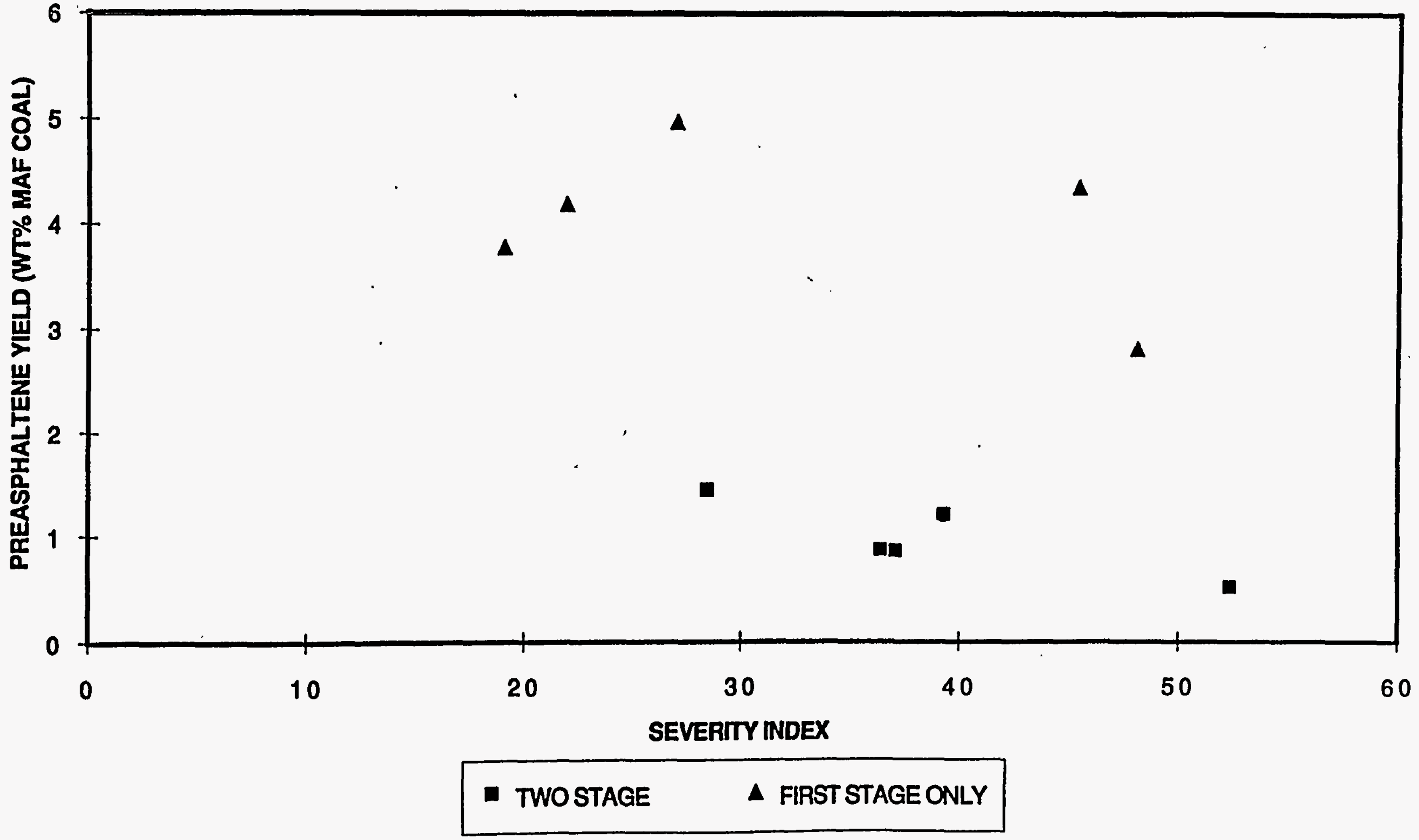


FIGURE 4.3.41

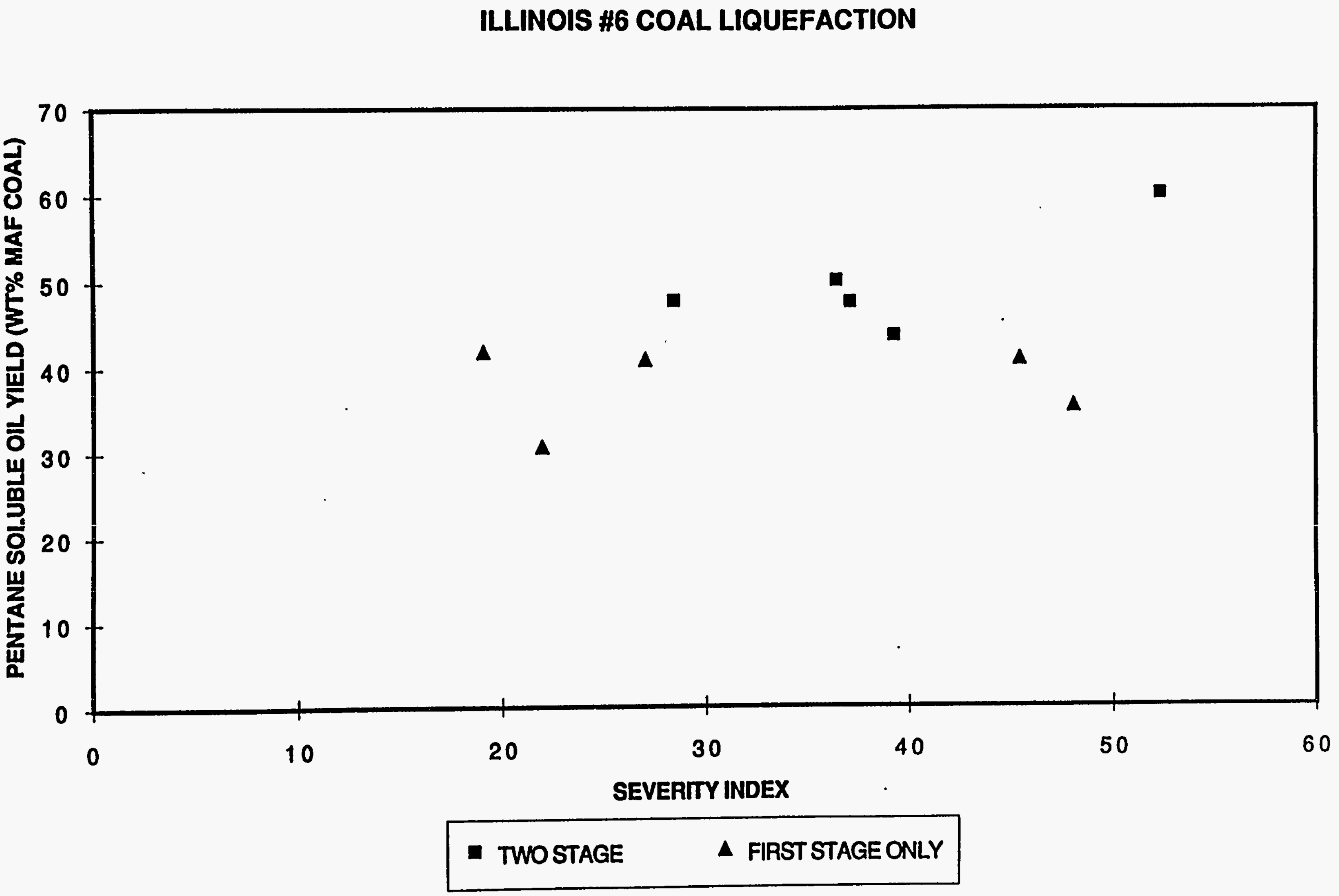
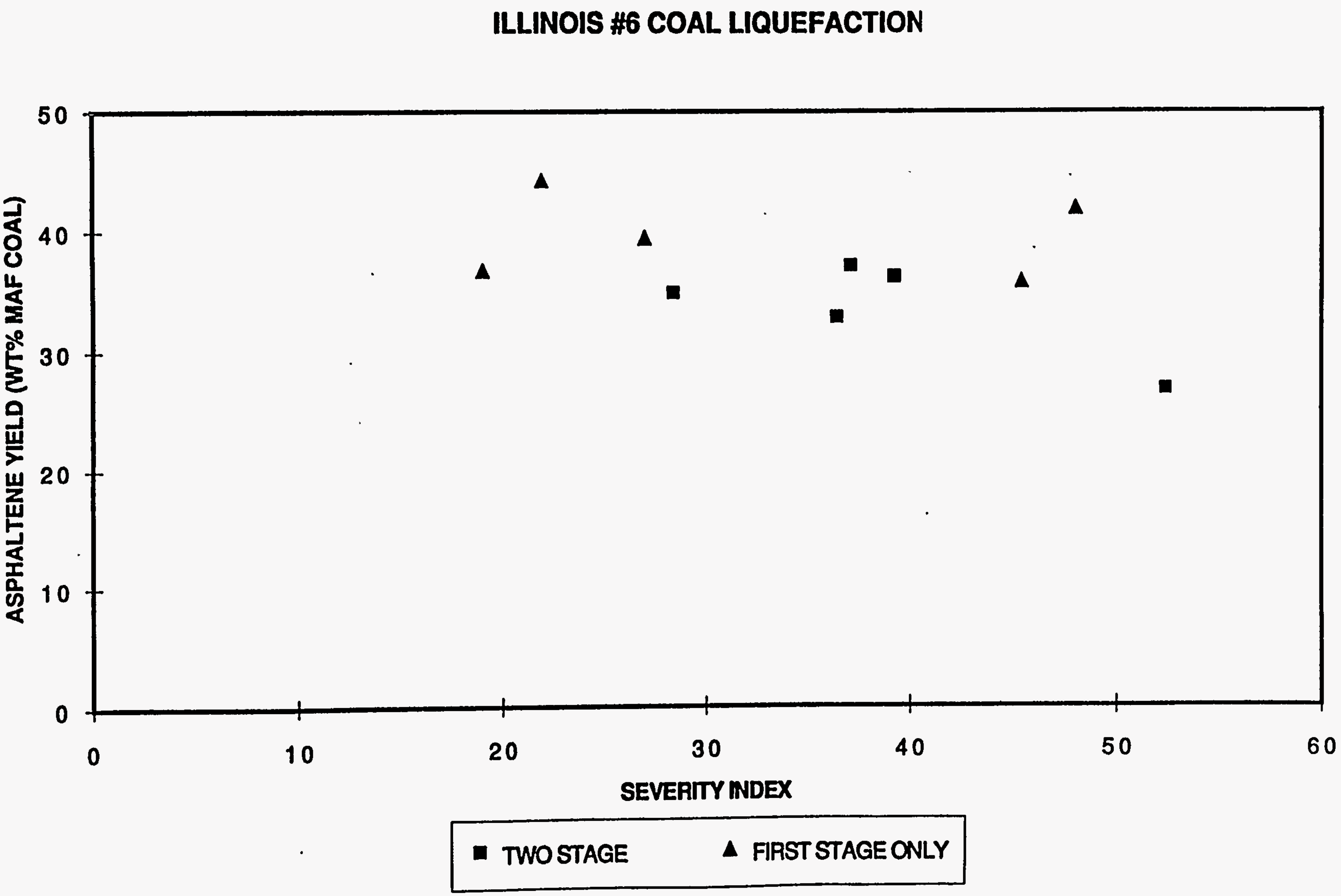

ILLINOIS #6 COAL LIQUEFACTION
PENTANE SOLUBLE OIL YIELD (WT% MAF COAL)
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
SEVERITY INDEX
■ TWO STAGE
▲ FIRST STAGE ONLY

FIGURE 4.3.42


ILLINOIS #6 COAL LIQUEFACTION
ASPHALTENE YIELD (WT% MAF COAL)
50
40
30
20
10
0
0
10
20
30
40
50
60
SEVERITY INDEX
■ TWO STAGE
▲ FIRST STAGE ONLY

Although there is considerable scatter in the data, the results show a similar trend to that observed with Black Thunder coal. Two stage operation appears to be more effective than one stage operation at equivalent seventies. Higher coal conversion and higher pentane soluble yields and in particular lower preasphaltene yields in two stage operation are evident.

4.3.3.4 Comparison of Product Slates from Black Thunder and Illinois #6 Coals

Under the best processing conditions, coal conversions of over 90% were obtained during two stage operations on the bench unit using Black Thunder and Illinois #6 coals. Processing conditions were different for the two coals. With Black Thunder coal, both stages were operated using a counterflow reactor, and carbon monoxide/steam was used to solubilize the coal in the first stage. In the case of Illinois #6 coal, a continuous flow autoclave system was used for the first stage, and a counterflow reactor used for the second stage. Hydrogen was used in both stages, for solubilization and further hydrocracking. At approximately the same conversion (90%+), the product slates were different. Figure 4.3.43 shows the comparison where iron oxide was used as second stage catalyst, at 440°C and 17.24 MPa in the second stage. Figure 4.3.44 shows a similar comparison where the second stage catalyst was ammonium molybdate. The following differences can be identified.

a. Black Thunder coal gives higher carbon oxide yields as expected.

b. Black Thunder coal gives higher pentane soluble oil yields and lower asphaltene yields. A higher hydrocracking severity may be needed to give equivalent pentane soluble oil yields for Illinois #6 coal.

c. Illinois #6 coal gave lower preasphaltene yields.

FIGURE 4.3.43

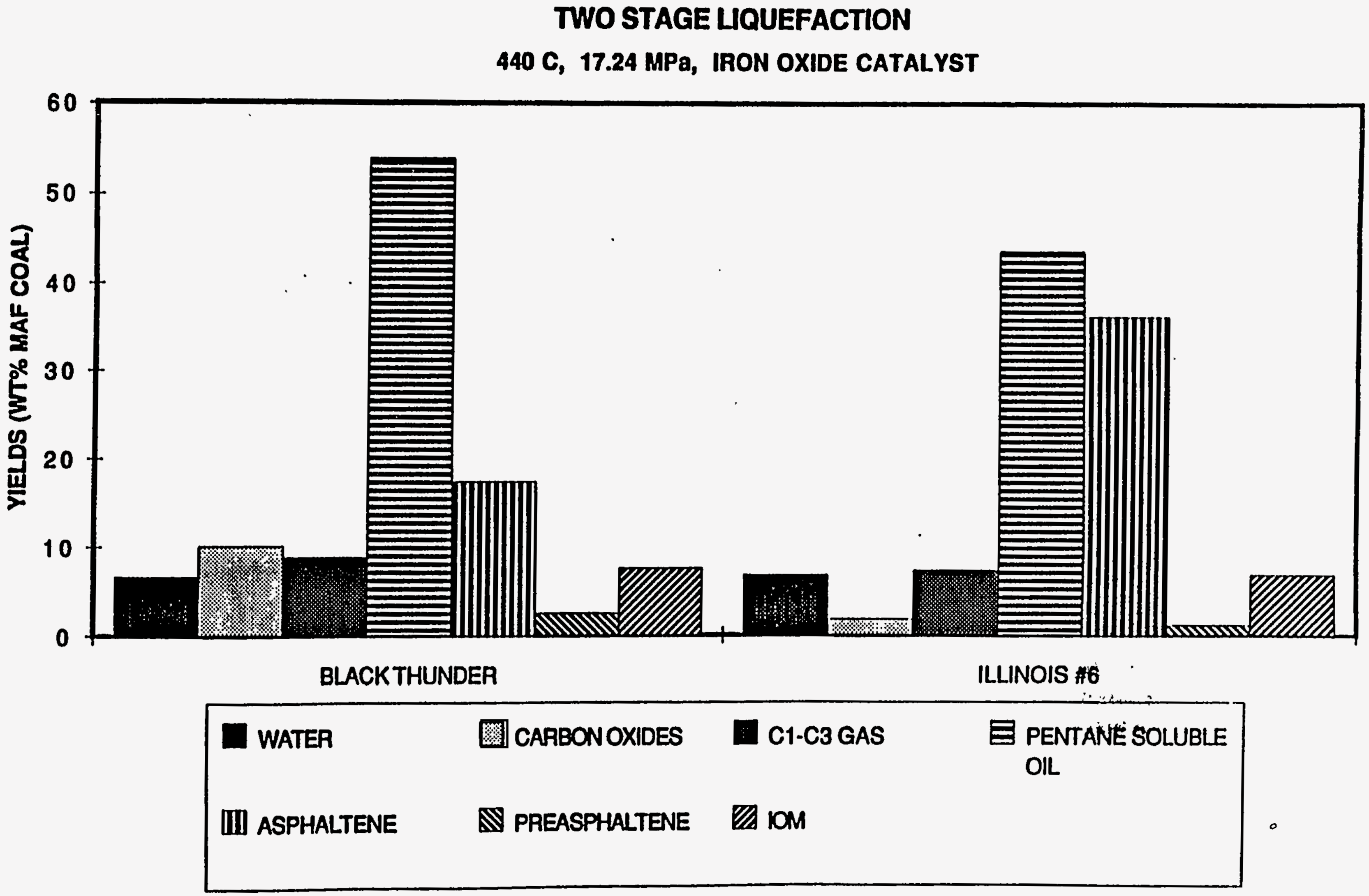
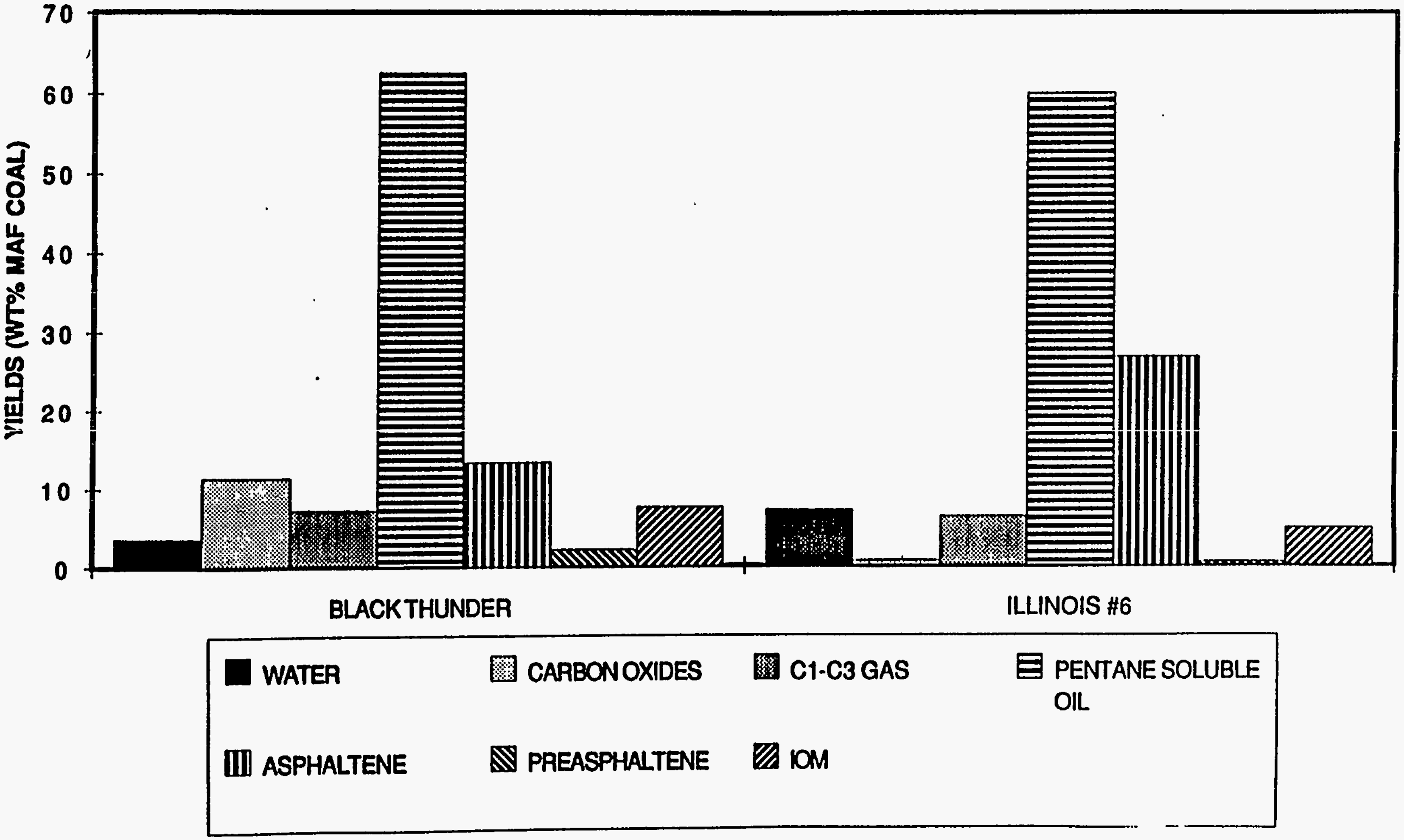

TWO STAGE LIQUEFACTION
440 C, 17.24 MPa, IRON OXIDE CATALYST
YIELDS (WT% MAF COAL)
0
10
20
30
40
50
60
BLACK THUNDER
ILLINOIS #6
WATER
CARBON OXIDES
C1-C3 GAS
PENTANE SOLUBLE OIL
ASPHALTENE
PREASPHALTENE
IOM

FIGURE 4.3.44



TWO STAGE LIQUEFACTION

440 C, 17.24 MPa, MOLYBDATE CATALYST

d. Water and hydrocarbon gas yields were comparable.

It is recognized that a operation with a recycle solvent as is proposed for Phase II may lead to a different product slate from the one above which represent once through operations.

A discussion of the results from all of the test program follows in Section 4.6.

4.3.4 Conclusions

The following conclusions were drawn as a result of operations on the bench unit:

1. Potassium carbonate added as a shift reaction catalyst caused operational problems for the bench unit on the scale used in this program (1 kg/hr). Replacement of this catalyst by an alternate, sodium aluminate, eliminated these operational problems.

2. Attempts to operate the bench unit where the reaction pressure in the first counterflow reactor was higher than in the second counterflow reactor, using control valves to transfer the material from the first reactor to the second, was unsuccessful. The installation of a transfer pump between the two reactors and operating the first reactor at a lower pressure than the second proved effective.

3. For Black Thunder coal, carbon monoxide conversion in the first stage was a function of the catalyst system used. Less than 5% conversion was obtained with no catalyst, 8 - 12% when aqueous sodium aluminate was used, 10 - 15% with aqueous potassium carbonate, and 18 - 40% was achieved using solid sodium aluminate added directly as a solid to the feed slurry. Hydrogen uptake in the first stage was linearly dependant on the carbon monoxide conversion.

4. Maximum coal conversions and pentane soluble oil yields were achieved under the best conditions at a severity index of about 30 (see Section 4.3.3.3.). There is evidence that coal conversion and pentane soluble oil yields decline at higher severity indices due to retrograde reactions.

5. Achieving an effective shift conversion in the first stage was found to be important for overall coal conversion and pentane soluble oil yield. Optimum operating conditions in the current bench unit for the first stage were 410°C, 10.34 MPa, WHSV 1.5 - 2.0, with solid sodium aluminate catalyst added to the feed slurry.

6. With the optimum first stage conditions, the best overall coal conversion and pentane soluble oil yields were obtained at the following second stage conditions: 440°C, 17.2 MPa, WHSV 1.0, with ammonium heptamolybdate and added dimethyldisulphide as second stage catalyst. These conditions provided a 62.3% wt. MAF coal distillable oil yield at a coal conversion of 92.4%. These conditions and yields were used as a basis for the preliminary economic feasibility study.

7. For Illinois #6 coal, the size of the first stage counterflow reactor was insufficient to achieve adequate solubilization of the coal. The coal was successfully solubilized (coal conversions in excess of 80%) using the larger second stage counterflow reactor. Future work on Illinois #6 coal will require two counterflow reactors of the same size as the current second stage reactor (1.6 litres) in series for successful operations. Using a flowthrough continuously stirred autoclave for first stage and the counterflow reactor as second stage, Illinois #6 coal was liquefied with coal conversions 93 - 95%, and pentane soluble and distillable oil yields of 50 - 53% wt. MAF coal. Further optimization of this operation is required to maximize yields.

4.4 RESIDUE PROCESSING

One option to be considered for handling the residue from this process scheme is coking. In this case the bottoms product from the second stage counterflow reactor represents an opportunity to recover additional liquid product. A small coking study was, therefore, carried out as part of this program. The feedstocks used were from the best bench unit runs with Black Thunder coal (DOE-BU-14.03 and DOE-BU-15.05) as well as bottoms from one and two stage operations with Illinois #6 coal (DOE-BU-16.02, DOE-BU-17.02, DOE-BU-18.02 and DOE-BU-18.04). Details of the feedstock properties, in particular asphaltene, ash and IOM content, plus Conradson Carbon are shown in Table 4.4.1. These feedstocks were subjected to coking according to the procedure described below.

4.4.1 Test Procedure

A tubular reactor was adapted for the batch coking tests. The system included nitrogen up-flow through the feed charge. Off gases and liquid products were passed through a condenser and a gas meter. The gases were collected in a gas bag and analyzed by GC. In a typical test approximately 100 g of V-340 residue from the bench unit was loaded into a reactor. Heating was initiated and nitrogen was introduced at a flow rate of 1 litre/minute. The reactor was raised either directly to 500°C or in 2 stages to 350°C and then 500°C. In the latter case it was anticipated that lighter boiling components would have an opportunity to be swept out by the nitrogen flow before the onset of coking. The temperature was held at 500°C for 30 minutes or until nitrogen flow was blocked by coke.

4.4.2 Results with Black Thunder Coal

The conditions used for the four runs with Black Thunder coal bench unit residues, and the product yields are shown in Table 4.4.2. It appeared that coke formation was

Table 4.4.1 Coker Feedstock Properties

Coker Feedstock

Origin	Bottoms from V-340					
Yield Period	14.03	15.05	16.02	17.02	18.02	18.04
Coal	Black Thunder	Black Thunder	Illinois # 6	Illinois # 6	Illinois # 6	Illinois # 6

Properties, g/100g

Distillable liquids, to 524° C	56.4	58.0	N/A	N/A	N/A	N/A
Residue, 524+	43.6	42.0	N/A	N/A	N/A	N/A
Asphaltenes	17.0	20.7	18.9	20.2	16.7	21.5
Ash + IOM	23.4	17.7	14.5	14.3	9.4	13.3
CCR	36.7	34.2	31.9	31.6	22.7	28.0

N/A Not Available

Table 4.4.2 Coking Performance -- Black Thunder Coal

Process Conditions

Run #	DOE-C-01	DOE-C-02	DOE-C-03	DOE-C-04
Feedstock	14-03	14-03	15-05	15-05
Temperature ° C	350/500	500	350/500	500
Time, minutes	30/30	35	30	20/30
N2 Flow, litre/min	1	1	1	1

Product Yields, g/100g

Gas	2.0	N/A	1.2	2.6
Liquids	53.5	65.4	60.4	60.4
Coke	41.5	28.5	29.9	33.9
Recovery	97.0	N/A	91.5	96.9

promoted by holding the temperature at an intermediate level. Coke levels were greater in runs DOE-C-01 and DOE-C-04 where there was a 350°C holding step. Raising the temperature directly to 500°C resulting in a lower coke yield and in the case of DOE-BU-14.03 residue higher liquid yield. In all cases more liquids were obtained by coking than by simple distillation (as determined by crude simulated distillation) of the V-340 bottoms product. The net increase varied between 4 and 1 wt% extra liquid yield based on MAF coal. The quality of the liquid product from coking would be expected to be lower than that from distillation, however. Recoveries were generally less than 100% (perhaps due to loss of naphtha) so the liquid yields determined can be considered conservative.

4.4.3 Results with Illinois #6 Coal

Since better results were obtained with Black Thunder coal when the temperature was raised directly to 500°C, this procedure was used for all the Illinois #6 coking runs. The condition and product yields are given in Table 4.4.3. Lower coke yields and higher liquid yields were obtained with the two stage residues from DOE-BU-18.02 and DOE-BU-18.04. This is consistent with the lower Conradson Carbon of these feedstocks. Again recoveries were less than 100% so the liquid yields determined are conservative. Although no distillation data were determined for the Illinois #6 feedstocks, it would appear that extra liquid yield could be obtained from coking based on the asphaltene, ash and IOM levels in the feedstocks, particularly from the two stage product where iron oxide was catalyst (DOE-BU-18.04). The implications of these results for the overall process scheme will be discussed briefly in Section 4.6.

Table 4.4.3 Coking Performance -- Illinois # 6 Coal

Process Conditions

Run #	DOE-C-05	DOE-C-06	DOE-C-07	DOE-C-08
Feedstock	16.02	17.02	18.02	18.04
Temperature ° C	500	500	500	500
Time, minutes	30	35	30	30
N2 Flow, litre/min	1.2	1.2	0.9	1

Product Yields, g/100g

Gas	3.8	2.4	6.0	N/A
Liquids	50.5	60.0	63.1	63.6
Coke	40.1	33.1	26.6	22.0
Recovery	94.4	95.5	95.3	N/A

N/A	Not available

4.5 OPTICAL CHARACTERIZATION OF LIQUEFACTION RESIDUES

4.5.1 Introduction

4.5.1.1 Coal Macerals

The term "maceral" refers to the partly coalified plant remains whose form and/or structure is still recognizable in the bituminous stage of coalification (Teichmuller, 1982). There are three main maceral groups, vitrinite (and its precursor huminite in low-rank coals), liptinite, and inertinite. Huminites and vitrinites originate from the lignin and cellulose of cell walls, and are coalification products of humic acids. Liptinites originate from the relatively hydrogen-rich plant remains, such as resins, waxes, sporopollenin, and fats, while inertinites are highly aromatized and condensed products, which have formed due to oxidation, charring, mouldering or fungal attack of the same precursors as the vitrinites.

4.5.1.2 Classification of Residue from Coal Liquefaction

The classification scheme used for the characterization of optical textures of components resulting from liquefaction of Black Thunder subbituminous and Illinois #6 bituminous coals is a modified version of those proposed by Mitchell *et al.* (1977) and Wakeley *et al.* (1979). The THF-insoluble residues are classified as follows:

1. Vitroplast, which is a plastic, pitch-like, isotropic phase, derived from the huminite and/or vitrinite component in the coal. Vitroplast is usually less than 100 microns in size, and may contain inertinite fragments. Depending on its reflectance under the optical microscope, vitroplast is subdivided into low-reflecting, and high-reflecting. Low-reflecting vitroplast often forms the matrix for coal- and process-derived inerts, and is capable of reacting fully to form liquid products or further condensing into high-reflecting material. Its low reflectance

indicates that hydrogenation reactions rather than retrogressive condensation reactions are responsible for its formation (Mitchell and Davis, 1991). High-reflecting vitroplast refers to process-derived material, produced through the condensation of liquid products formed during the liquefaction process.

2. Granular residue is an anisotropic matrix or an agglomerate, which binds fragments of unreacted vitrinite, angular inertinite, and mesophase, semicoke or coke.

3. Mesophase spheres, which are anisotropic spheres of 2-20 microns in diameter, and are formed out of pre-existing liquids by a homogeneous nucleation process (Marsh and Cornford, 1976). The formation of mesophase during hydroliquefaction is believed to occur under conditions where the hydrogen supply is less than the rate of breakage of bonds between the structural units of vitrinite and the rate of loss of side-chains. Adverse reaction conditions, where retrogressive carbonization is favoured, or mass transfer problems, are also responsible for the development of mesophase. When the spheres grow in size, they coalesce to form larger areas called domains.

4. Semi-coke and coke fragments, a minor constituent in the liquefaction residue, having high reflectance, anisotropy, and texture similar to metallurgical coke.

5. Unreacted fragments of inertinitic origin, mainly semifusinite, fusinite, and macrinite.

6. Mineral matter, consisting of clays, pyrite, and others.

The above residue components were selected because they can easily be identified as originating from either the coal maceral groups or from liquid products formed during liquefaction. Optical microscopy is a useful method for characterizing solid organic residues from coal liquefaction and provides valuable information into the process of coal conversion or retrogressive reactions during liquefaction.

4.5.2 Experimental

All samples, which include the original feed from Black Thunder and Illinois #6 coals, as well as their autoclave and bench unit liquefaction residues, were mixed with epoxy resin and molded into a polished block (pellet). The pellets were ground and polished to produce a surface suitable for microscopic examination at x640 combined magnification, under an oil immersion objective lens (N.A. x40). The microscope used for the residue characterization is a Zeiss MPM II, fitted with a photometer system and connected to an IBM PC. The relative concentrations of residue components were achieved using the point counting technique. The analysis was performed using a grid of 0.3 mm in traverses across the polished surface. Three hundred points were counted on each sample.

4.5.3 Results and Discussion

4.5.3.1 Petrographic Observations - Autoclave Tests

4.5.3.1.1 Black Thunder Coal

The Black Thunder feed coal is composed predominantly of huminite group macerals, and displays features typical of cell wall structures. Individual macerals include texto-ulminite, eu-ulminite, porigelinite, phlobaphinite, and humodetrinite. The liptinite group is represented by liptodetrinite, sporinite, and cutinite, seen under ultraviolet irradiation, whereas semifusinite, fusinite, sclerotinite, and inertodetrinite make up the majority of the inertinite group macerals. The maceral composition (Table 4.5.1) is: 68.3 vol.% huminite, 18.3% inertinite, 13.0% liptinite, and 0.3% mineral matter.

Table 4.5.1: Petrographic Composition of Feed and Residues

Sample ID	Experimental Conditions			Petrographic Composition, vol%			
	A	B	C	Vitroplast	Inertinite	Granular Residue	Mineral Matter
DOE 4	+	-	0	42.0	37.0	13.0	21.0
DOE 5	+	+	0	6.3	60.6		20.0
DOE 7	0	+	+	36.6	51.0		12.3
DOE 8	-	0	-	83.3	15.3		1.3
DOE 9	-	+	0	78.6	20.3		1.0
DOE 13	+	0	-	65.3	19.3	8.0	7.3
DOE 14	+	0	+	30.3	31.0		58.3
DOE 15	-	-	0	69.6	25.6	2.6	2.0
DOE 16	-	0	+	54.3	24.6		21.0
DOE 17	0	0	0	35.6	39.0		25.3
DOE 18A	0	+	-	64.0	29.0	13.0	4.0
Feed Coal				68.3[1]	18.3	13.0[2]	0.3

[1] Huminite macerals

[2] Liptinite macerals

LEGEND

A Temp.		B Pressure (psi)		C Time (mins.)	
+	410	+	800	+	60
0	390	0	600	0	30
-	370	-	400	-	0

A set of residues, produced under different conditions of temperature, time, and pressure was examined. The experimental conditions and corresponding component abundance are also shown in Table 4.5.1. In all cases, a K_2CO_3 catalyst was used. Even at temperatures of 370 °C, the botanical structure and microlayering seen in the feed coal are absent, instead, large, porous and agglomerated masses dominate. All eleven samples are characterized by the presence of vitroplast, granular residue, inertinite, and mineral matter, in varying proportions. Vitroplast content ranges from 6.3 vol.% (DOE 5) to 83.3% (DOE 8). Inertinite is the lowest in DOE 8 (15.3%) and the highest in DOE 5 (60.0%). Both low-, and high-reflecting vitroplast is observed; the former is evident by its "soft" nature and presence of numerous scratches due to polishing. It also acts as a binding matrix for inertinite and unreacted huminite fragments (Plate 1a-c). The boundary between the two types of vitroplast is mostly sharp, but it can also be graded. High-reflecting vitroplast is more homogeneous and occasionally forms large (200 microns in diameter), coherent, porous masses (Plate 1d-e). These areas show evidence of melting, and contain numerous devolatilization vacuoles (Plate 1f). Some of the pores are filled with homogeneous, low-reflecting and fluorescing, bitumen-like, tarry matter (Plate 1f), similar to that described by Lim *et al.* (1994). The tar originates from the liquid component of the coal, it is observed in residues treated at 370-410°C, 400-800 psi, and 30 minutes. The tar often fills the cell lumens of fusinite fragments (Plate 2a). Pyrolytic carbon, forming from the condensation of volatile matter, is seen in trace amounts in DOE 5 (410°C, 60 minutes, 600 psi). In sample DOE 14, which has the highest mineral matter content (58.3%), some of the vitroplast particles are completely rounded (Plate 2b), indicative of partial melting.

When the percent coal conversion is plotted against the percent vitroplast plus granular residue (Table 4.5.2), it becomes apparent that the sample with the highest conversion at 89% (DOE 5) contains the smallest amount of unconverted vitroplast (19.3 vol.%) and highest amount of inertinite (60.6%). Similarly, the sample with the lowest conversion at 34% (DOE 8) contains the highest percentage of unconverted vitroplast (83.3 vol.%) and the lowest amount of inertinite (15.3%). Therefore, the petrographic examination of this suite of samples clearly identified the order of increasing or decreasing severity during liquefaction. The presence of high concentrations of low-reflecting vitroplast (72.2% to 83.3%) in the THF insoluble residues of samples DOE 8, 9, 13, and 15 suggests some inefficiency in process conditions which has allowed vitroplast to escape conversion to liquid products. In other words, there is room for further conversion of the remaining unconverted vitroplast fraction in the above samples. With the exception of a few particles of pyrolytic carbon in sample DOE 5, no evidence of mesophase or coke formation exists. Pyrolytic carbon forms from the condensation of volatile matter of coal near 500°C, therefore, it is somewhat surprising that it formed at 410°C. Nonetheless, it appears that no retrogressive carbonization reactions to form mesophase and coke occurred in this set of samples.

Table 4.5.2: Composition vs Coal Conversion

Sample ID	8	9	13	15	18A	16	4	17	7	14	5
Conver. %	34	44	74	63	63	69	76	81	85	73	89
Vitroplast %	83.3	78.6	73.3	72.2	67.0	54.3	42.0	35.6	36.6	30.3	19.3
Inertinite %	15.3	20.3	19.3	25.6	29.0	24.6	37.0	39.0	51.0	31.0*	60.6

* High mineral matter content

Increasing severity during liquefaction ----------------------------->

A second suite of liquefaction residues of Black Thunder coal was examined. The experimental conditions are shown in Table 4.5.3. Based on the residue components and optical textures observed, the samples may be classified into three groups. The first group consists of samples DOE 25 and DOE 26, which have been treated at

Table 4.5.3: Petrographic Composition of Residues

Sample ID	Vitroplast	Cenospheres	Vacuoles	Gran. Residue	Semi-Fusinite	Fusinite	Pyrite	Clays	Exper.	Cond.	Conv. %
DOE-21	2.7	0.0	0.0	0.6	1.6	36.7	1.3	57.0	410*	K_2CO_3	83
DOE-23	27.0	0.0	6.7	11.0	0.3	35.0	0.7	17.0	370	K_2CO_3	76
DOE-24	26.3	0.0	0.0	0.0	9.3	36.3	1.0	27.0	390	agglom.	83
DOE-25	0.0	59.3	13.3	0.0	9.3	17.0	1.0	1.7	390	no catal.	78
DOE-26	0.0	52.3	14.0	0.0	9.0	7.7	14.6	2.3	390	FeS	81
DOE-27	5.0	0.0	4.0	40.6	10.3	33.6	2.0	4.3	390	$NaAlO_2$	82
DOE-28	2.7	0.0	0.0	7.3	5.7	42.0	1.0	41.3	390	K_2CO_3	88
DOE-29	60.7	0.0	3.7	0.0	4.0	19.3	1.3	11.0	390	CO,H_2	73
DOE-30	71.0	0.0	7.0	0.0	3.3	14.6	0.0	4.0	390	CO,N	66
DOE-31	75.7	0.0	10.3	0.0	1.0	7.3	0.7	5.0	390	N	48

* °C

390°C, and the conversion is 78% and 81%, respectively. No angular vitroplast is present, inertinite content is low (9.0-9.3 vol.%), and mineral matter consists of clays. Both samples are dominated by small (20 microns in diameter) to large (200 microns) rounded, porous particles, which show devolatilization vacuoles of varying size (Plate 2c-f). These spherical particles are similar in morphology to those developed in coal combustion, referred to as cenospheres. There is no evidence of any botanical structure or of any microlayering features, characteristic of the feed coal. No catalyst was used in sample DOE 25, but FeS was the catalyst in DOE 26, which is reflected in the high iron sulphide content (14.6%) of the latter. Sample DOE 25 shows little CO conversion (7%) and sample DOE 26 only a slightly higher conversion (9%) in the shift reaction.

The second group consists of samples DOE 29, DOE 30 and DOE 31, all showing the highest amount of unconverted vitroplast in the residues (Plate 3a-b). In all experiments involving samples DOE 21 to DOE 31, except for samples DOE 25, DOE 26 and DOE 27, a K_2CO_3 catalyst was used. Low- and high-reflecting vitroplast is present in the form of large, porous masses, showing evidence of dissolution and melting. Vitroplast content ranges from 60.6 vol.% to 75.7%, granular residue is absent in all three samples, inertinite is in the 8.3% to 23.3% range, and mineral matter is less than 12.3%, consisting mainly of clays. The liquefaction temperature is 390°C; however, there is a large variation in percent conversion, 73% in DOE 29, decreasing to 66% in DOE 30, and almost 48% in DOE 31 (Table 4.5.3). It appears that syngas (an admixture of CO and H_2, at a ratio of 3:1) used in DOE 29 contributed to the increased conversion. On the other hand, the mixture of CO and N (1:3 ratio) in DOE 30 and presence of pure N in DOE 31 have not contributed to an increase in conversion. Sample DOE 29 contained a few anisotropic areas (Plate 3c), formed following coalescence of mesophase. The areas are best observed under partially cross-polarized light, with the insertion of a gypsum interference plate. They form when the proportion of mesophase in the residue reaches a level where the individual spheres coalesce to form bulk mesophase and eventually a mosaic.

The third group consists of samples DOE 21, DOE 27, and DOE 28, which contain the lowest amount of unconverted vitroplast (2.7%-5.0%; Table 4.5.3). Conversion is the second highest at 83%. Sample DOE 21 has been subjected to the highest severity (410°C) and shows a large content of inertinite (38.3%) and insoluble mineral matter (57%) filling the fusinite cell lumens (Plate 3d). No mesophase spheres are observed, possibly indicating that the high mineral matter content has interfered with the mechanism of mesophase growth, an idea also shared by Mitchell and Davis (1991). The highest conversion in this suite is seen in sample DOE 28 (88%). Petrographic analysis shows the presence of large amounts of inertinite (47.5%), low vitroplast (2.7%), and the second largest mineral matter content (41.3%) (Plate 3e). On the other hand, sample DOE 27 is dominated by granular residue (40.6%), inertinite (43.9%), but little clay mineral matter (4.3%) (Plate 3f). Conversion is 83% and the catalyst used is a $NaAlO_2$. The fourth group consists of samples DOE 23 and DOE 24, both samples showing a moderate vitroplast content (36.3% and 27.0%; Plate 3g-h). Inertinite content is high (35.3% to 45.6%), and mineral matter is in the 17.0 to 27.0% range. Sample DOE 23 shows low conversion (73%) and has been treated under mild conditions (370°C). In the case of sample DOE 24, the feed is in the form of agglomerates, this being the only difference between this and the other samples. The high conversion of this sample (83%) is surprising when considering the moderate amount of vitroplast still remaining in the THF insoluble residue.

The following section describes the morphology of liquefaction residues of Black Thunder coal, produced under the experimental conditions shown in Table 4.5.4. The petrographic data is also shown in this table. The samples are: DOE 53, 54, 55, 57, 58 and 59, all treated at 390°C, except for DOE 57 (410°C). Coal conversion ranges from 55% in DOE 54, where no catalyst and no H_2O were used, and there was no CO conversion, to 86% in DOE 57, where CO/H_2O and a $NaAlO_2$ catalyst were used, and CO conversion was high (53%) (Table 4.5.4). The sample with no CO conversion but in H_2 stream (DOE 54) shows only minor changes in morphology. The majority of fragments retain their angularity, similar to that in the feed coal, and display certain

Table 4.5.4: Petrographic Composition of Residues

Sample ID	Vitroplast	Inertinite	Clays	Pyrite	Temp.	Exp. Conditions	Catalyst	Coal Conv. %	CO Conv.
DOE 53	49.0	49.6	1.3	0	390	H_2O/CO	ATM	73	6
DOE 54	79.0	18.3	2.6	0	390	H_2	no	55	0
DOE 55	76.3	23.3	0.3		390	CO	no	62	16
DOE 57	6.0	72.6	12.6	8.7	410	CO/steam	NaAlO	86	53
DOE 58	66.0	14.3	6.7	13.0	390	CO/steam	FeO_3/CS_2	80	20
DOE 59	47.0	44.7	7.0	1.3	390	CO/steam	ATM/CS_2	75	20

features such as woody cell structures and layering (Plate 4a). Some fragments also appear to have volatilized and disintegrated (Plate 4b). Vitroplast content is 79%, inertinite 18%, and mineral matter is 3%. A completely different situation exists in sample DOE 57, where the only coaly fragments seen are of inertinitic origin (73%), followed by a small amount of vitroplast (6%), clay mineral matter (13%) and pyrite (8%) (Plate 4c). Sample DOE 58 shows 80% coal conversion and 20% CO conversion, with the aid of an iron oxide and carbon disulphide catalysts. The residue is dominated by rounded, porous vitroplast, often exceeding 100 microns in diameter (Plate 4d). This indicates a more extensive reaction of the huminite group macerals, compared to DOE 54. No evidence of cell structure is seen, vitroplast is occasionally disintegrated and makes up 66% of total IOM, inertinite is 14%, clays at 7%, and iron sulphide 13%.

The coal conversion of samples DOE 53 and 59 is similar, 73% and 75%, respectively. The CO conversion is only 6% in DOE 53 and 20% in DOE 59. A tetrathiomolybdate catalyst was used in the former and a carbon disulphide catalyst was used in the latter (Table 4.5.4). The similarities in conversion are also reflected in their petrographic composition. Rounded, vacuolated vitroplast fragments are dominant in DOE 53 (49%), followed by inertinite (48%) (Plate 4e). Rounded, porous and agglomerated vitroplast is the dominant component in DOE 59 (Plate 4f). Here, vitroplast makes up 47%, inertinite 45%, and mineral matter 8%. Finally, sample DOE 55 is similar to DOE 54 in that it contains large amount of vitroplast (76%), the latter being semi-rounded to angular, showing botanical structure, and showing little morphological changes.

4.5.3.1.2 Illinois #6 Coal

The Illinois #6 feed coal is a humic coal, of high-volatile bituminous rank, with a high vitrinite content (mainly telocollinite, less desmocollinite), some inertinite, and liptinite (in the form of spores, cuticles and liptodetrinite). Three samples of liquefaction residues (DOE 60, DOE 62 and DOE 64) were examined. The petrographic composition and experimental conditions are shown in Table 4.5.5. Sample DOE 60 shows the lowest coal conversion (67%), which is reflected in the total amount of porous vitroplast (53%). Vitroplast acts as a binder for inertinite (17%) and mineral matter (2%) components. A considerably higher conversion is seen for sample DOE 64 (81%), most likely a reflection of the higher temperature of reaction (425°C) compared to 390°C for DOE 60. Vitroplast content is only 17%, total inertinite is 23%, and mineral matter is high (60%), mainly clay. In both samples the gas used is CO, and the catalysts are $NaAlO_2/FeS$ in DOE 60 and $NaAlO_2/Fe_2O_3$ in DOE 64. When H_2 is used with a Fe_2O_3 catalyst, coal conversion increases to 92% (Table 4.5.6). The amount of unconverted vitroplast in sample DOE 62 decreases drastically to only 3%, but mineral matter increases to 75%, the remainder being inertinite. It appears that coal conversion is higher when the amount of mineral matter in the residue is high, but the critical factors may be the nature of the gas (H_2) and the catalyst used.

4.5.4 Petrographic Observations - Bench Unit Tests

4.5.4.1 Black Thunder Coal

A set of three samples, all THF insoluble residues was examined. Sample DOE 008-01 consists of huminite (50%), inertinite (42%) and mineral matter (8%). Sample DOE 009-02 contains 31% huminite fragments still exhibiting botanical structure and cenospheric morphology (Plate 5a-b), inertinite (31%), clay mineral matter (34%), mesophase spheres (3%), and minor pyrite (1%). A different situation exists in sample DOE 009-03, where only 5% of the residue consists of rounded and porous particles originating from the huminite component, 40% is inertinite, 51% is clay mineral matter, 1% is pyrite, and 3% is mesophase. The walls of the rounded particles often show a granular mosaic texture.

Dissolution and partial melting of the huminite is evident in sample DOE 009-04 (Plate 5c). Here, coal particle outlines are rounded and form an interlocking network. The

Table 4.5.5: Petrographic Composition of Residues

Sample ID	Vitroplast	Semi-fusinite	Fusinite	Clays	Pyrite	Gas	Conditions	Catalyst	Conversion
DOE 60	53.3	10.3	7.0	15.3	14.0	CO	390/30	$NaAlO_2/FeS$	67
DOE 62	2.7	8.0	14.0	51.3	24.0	H_2	425/30	Fe_2O_3	92
DOE 64	16.7	8.3	15.0	52.3	7.7	CO	425/30	$NaAlO_2/Fe_2O_3$	81

Table 4.5.6: Experimental Conditions and Conversion, Bench Unit - Stage 1 and 2

	Stage	Gas	Conditions	Catalyst	Conversion
BU-8.02	2nd	H_2	435	ATM	79
BU-11.02	1st	CO	410	$NaAlO_2$	76
BU-12.02	2nd	H_2	435	Fe_2O_3	86
BU-15.02	2nd	H_2	435	Moly	87

same sample contains huminite which has been little altered and still shows cell structure (Plate 5d). Mesophase spheres are a significant component (Plate 5e-f), normally they are about 10 microns in diameter, but often they have coalesced to form a domain. Partially altered huminite and rounded vitroplast make up 41% of the residue, inertinite is 43%, and the remaining is mineral matter. A higher mesophase and coke content characterizes sample DOE 009-05 (39%), followed by vitroplast (40%), and inertinite (18%). Most huminite fragments are rounded and show evidence of partial dissolution and botanical layering (Plate 6a). Occasionally, they appear angular, disintegrated, and mixed with small to large mesophase spheres (Plate 6b). Large domains (>50 microns), formed from the coalescence of mesophase (Plate 6c-d), which are highly-reflecting and seen clearly with the insertion of a gypsum retardation plate.

Four THF-insoluble residues, three of which are from the second stage of liquefaction and one from the first stage, were also examined. All second stage samples have been treated with H_2 gas, at 435°C, but the catalyst is different (Table 4.5.6). Coal conversion ranges from 76% in the first stage sample DOE 11-02 ($NaAlO_2$ catalyst) to 87% in sample DOE 15-04 (molybdenum catalyst). The sample with the highest conversion is characterized by high mineral matter content (64%), a moderate vacuolated vitroplast component (19%), and a similar inertinite content (17%). Sample DOE 12-02 contains 19% vitroplast, 14% inertinite, 7% mineral matter, and 61% iron-bearing minerals, reflecting the Fe_2O_3 catalyst used. Sample DOE 008-02 shows 79% conversion with a ATM catalyst, vitroplast is 63% and inertinite is 76%. The vitroplast content increases to 39% in the sample with the lowest conversion (DOE 11-02), with inertinite being 37%, and clay mineral matter 23%.

4.5.4.2 Illinois #6 Coal

Two samples were examined to detect the potential formation of semicoke or coke, one was solids taken from the stirrer, the other was solids taken from the pumping system. No coke formation was detected, the solids consist of unconverted coal and mineral matter, an indication that there is insufficient solubilization of the coal.

4.5.5 References

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4.5.6 Description of Photographic Plates

All photomicrographs were taken in oil immersion, plane-polarized light, unless otherwise noted. Long axis of each photo is 180 microns.

4.5.6.1 Plate 1

a) Low-reflecting, granular vitroplast (VP) cementing fragments of inertinite (I) and sclerotinite (Sc).

b) Granular vitroplast having rounded edges and binding angular inertodetrinite (Id). Note the dissolution of vitroplast (upper part of photo) in the immersion oil.

c) Vacuolated vitroplast acting as binder for inertodetrinite fragments.

d) High-reflecting, massive vitroplast (VP-left side) and low-reflecting vitroplast (VP-right). The latter cements inertinite and tar (T) fragments.

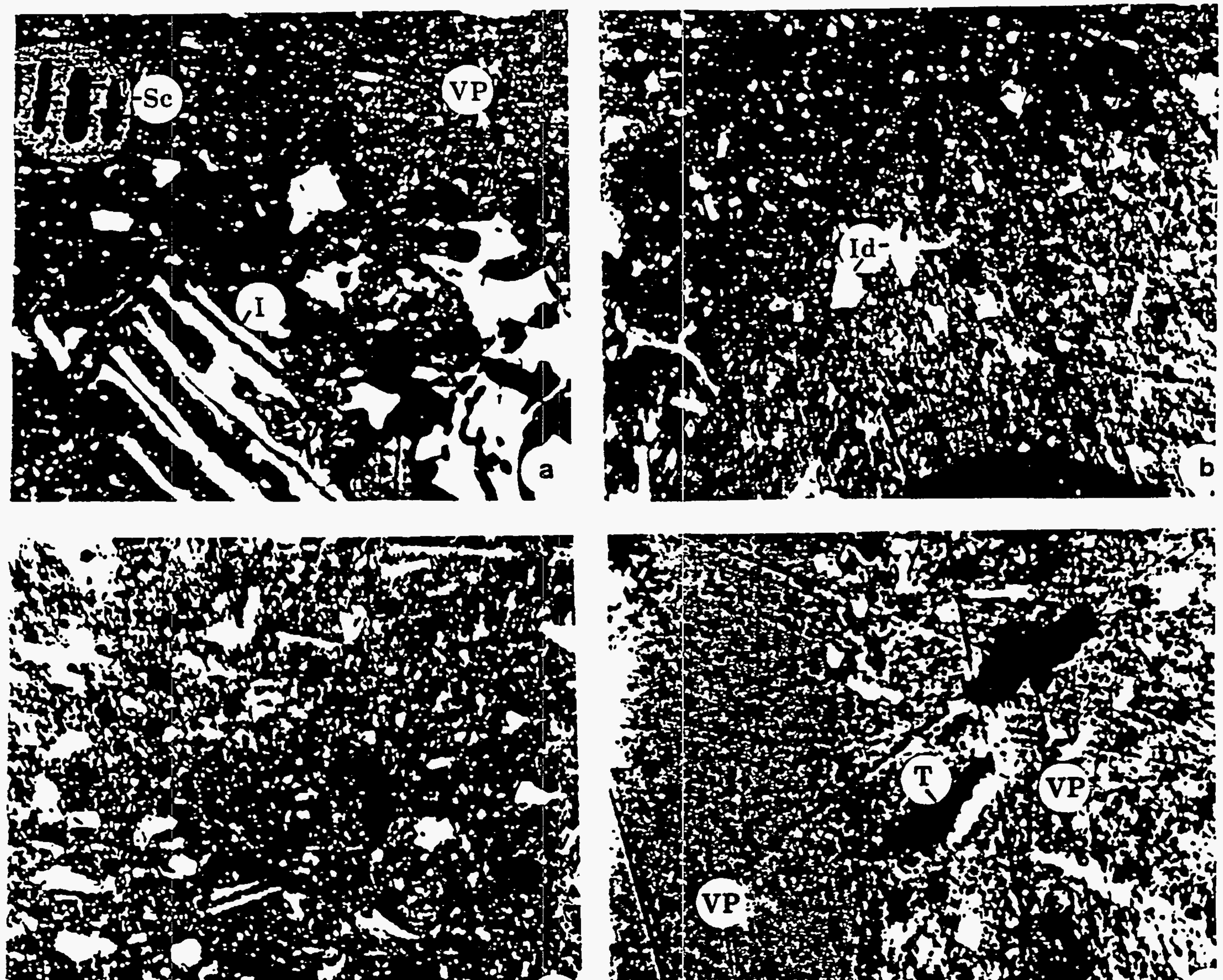
e) Transition between high-reflecting, homogeneous vitroplast (VP-right) and inhomogeneous vitroplast (VP-left) containing inertodetrinite (Id) fragments.

f) Highly-vacuolated vitroplast (V) with tar (T) infilling some vacuoles. Inertinite is present at the top of the photo.

4.5.6.2 Plate 2

a) Low-reflecting and soft vitroplast, inertinite (I) and tar (T).

b) Low-reflecting vitroplast (VP) showing numerous vacuoles, inertinite and mineral matter (MM). Partially crossed-polars, gypsum interference plate inserted.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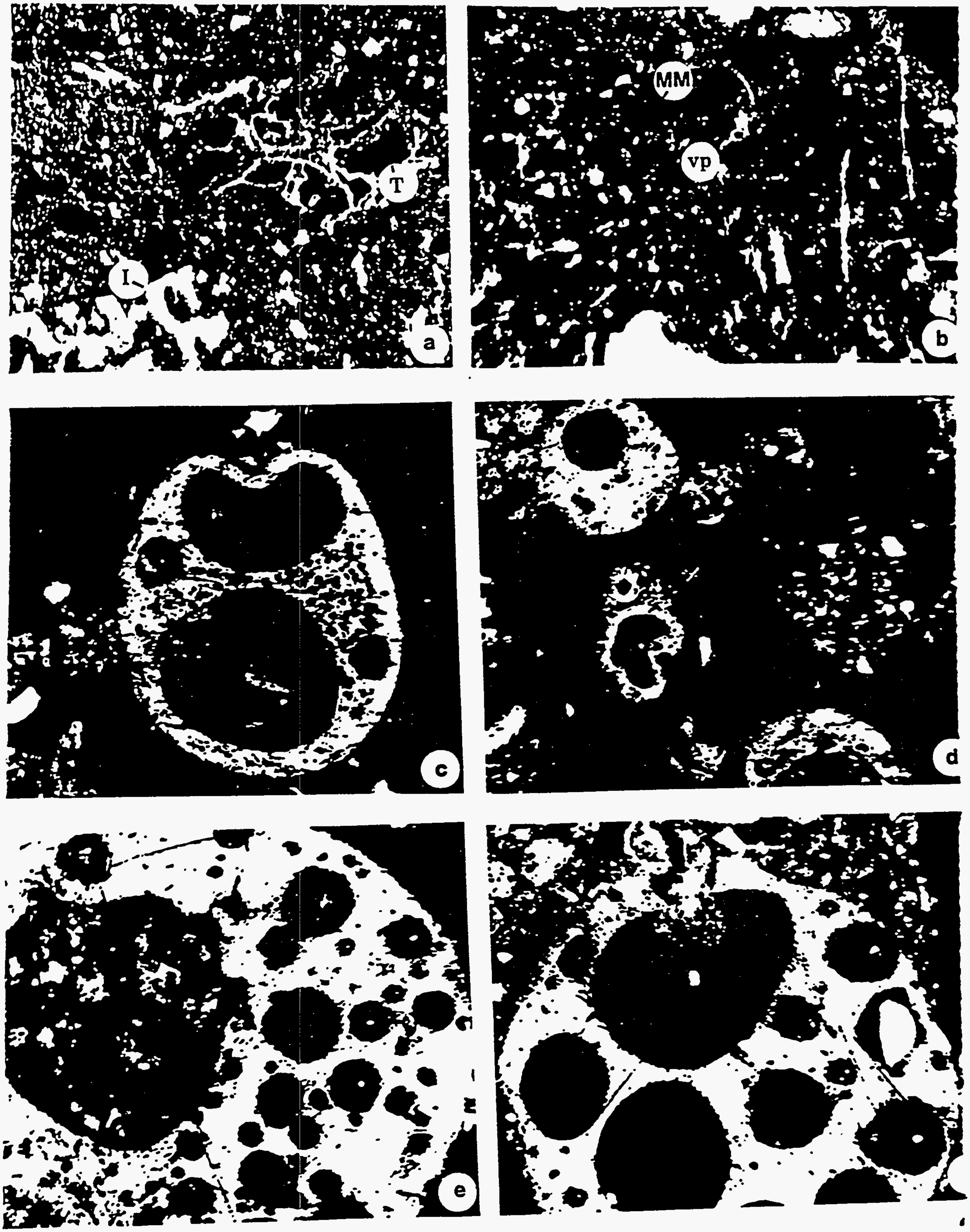

Plate 2

c-f) Rounded and highly-vesiculated vitroplast having a cenospheric morphology. Note melting in c) and d) and formation of agglomerates in f).

4.5.6.3 Plate 3

a) Highly-vesiculated and low-reflecting, unconverted vitroplast (VP).

b) High-reflecting, vesiculated vitroplast.

c) Large anisotropic domain formed from the coalescence of mesophase spheres. Adjacent are low-reflecting vitroplast (VP) and inertinite (I). Partially crossed-polars, gypsum interference plate inserted.

d) Fusinite showing cell lumens completely filled by clay mineral matter.
e) Fusinite with "bogen" structure surrounded by a ground mass of small, angular vitroplast, inertodetrinite and mineral matter.

f) Low-reflecting, granular vitroplast (VP) cementing angular inertodetrinite. Note dissolution of vitroplast in oil immersion.

g) Fragmented and vacuolated vitroplast (VP) containing inertodetrinite.

h) Fragment same as g) but containing more mineral matter and rounded to angular inertinite.

4.5.6.4 Plate 4

a) Rounded to angular vitroplast fragments, some showing cell structure and layering. Some of the fragments have volatilized, but generally appear similar to original feed.

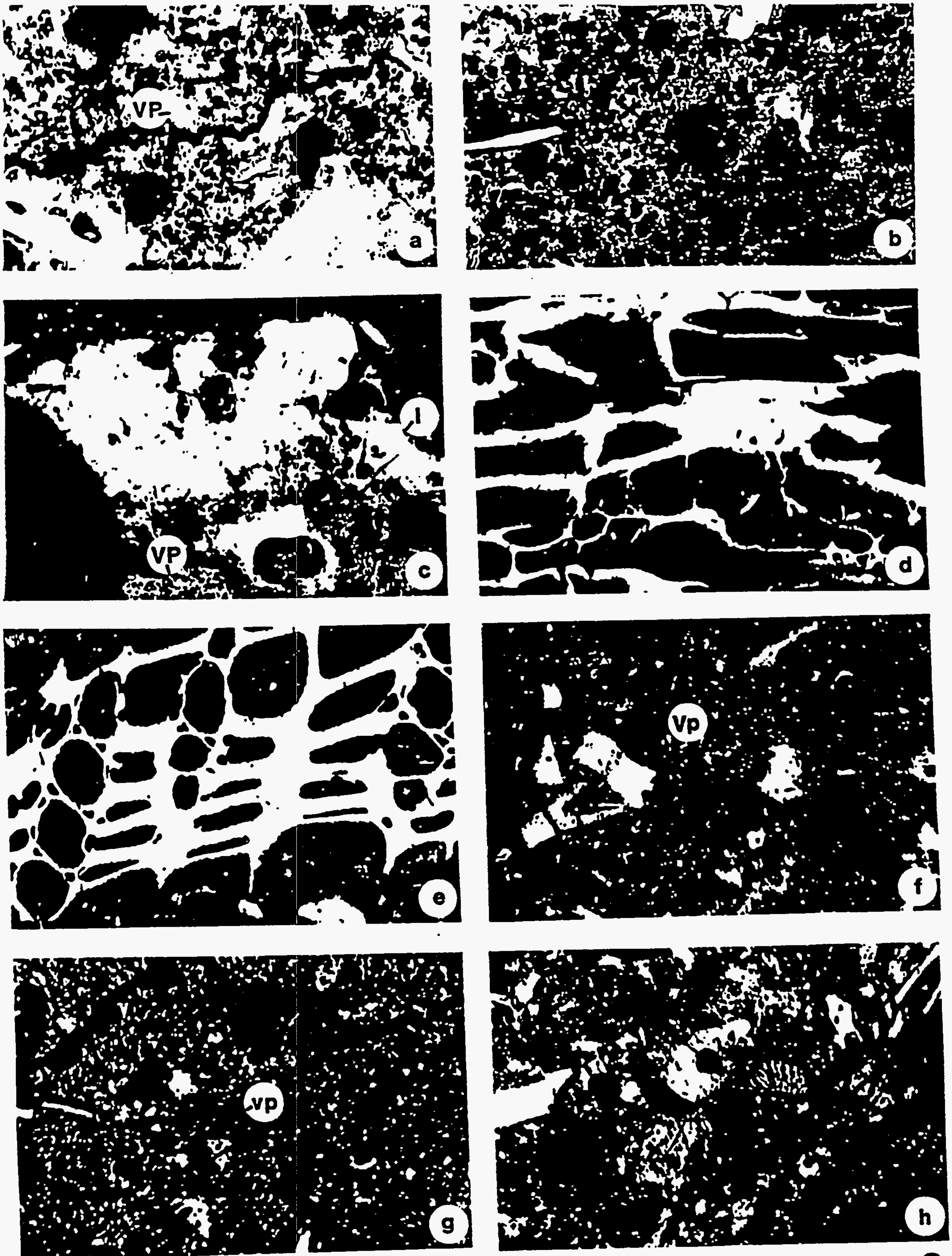

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Plate 3

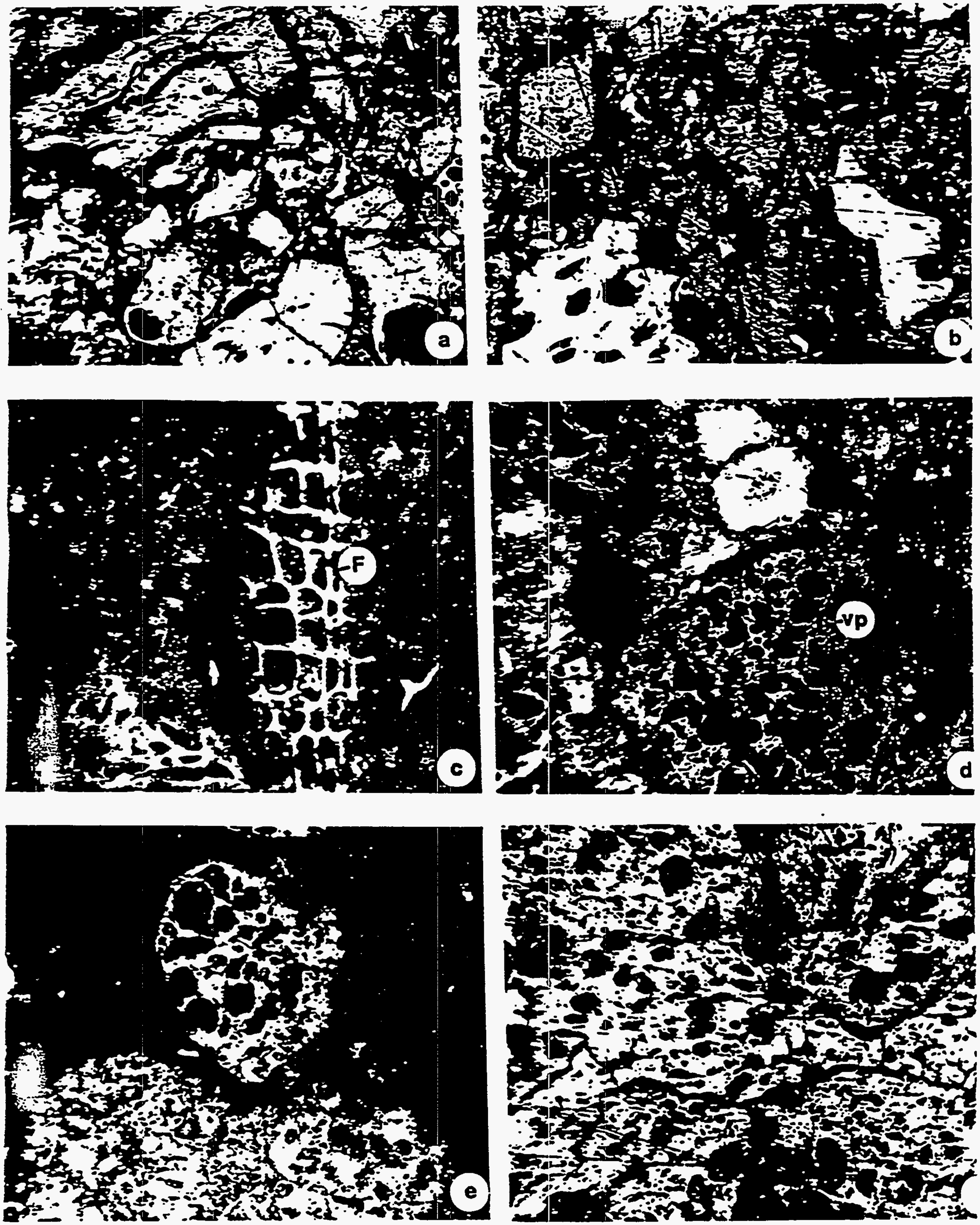


Plate 4

b) Disintegrated vitroplast and inertinite, similar to a).

c) Fusinite (F) showing open cell lumens and surrounded by clay mineral matter.

d) Highly-vesiculated, rounded vitroplast (VP) surrounded by clay mineral matter and inertinite.

e) Similar to d) but vitroplast has higher reflectance.

f) A large mass of porous, high-reflecting vitroplast.

4.5.6.5 Plate 5

a) Altered huminite fragment showing cell structure and layering adjacent to a rounded and highly-porous vitroplast. Clay minerals infill the huminite cells.

b) Little altered huminite (H) showing layering, fusinite (F), inertodetrinite (Id) and mineral matter.

c) Highly-dissolved vitroplast having a rounded, melted appearance.

d) An agglomerate consisting of vitroplast (VP), inertinite, mineral matter and anisotropic mesophase (Me). Note the presence of almost isotropic vitroplast spheres in the upper right of the photo, evidence of melting.

e) Mesophase sphere (middle) adjacent to a coalesced mesophase fragment. Vitroplast and inertinite are also present.

f) An admixture of vitroplast, still showing cell structure, and anisotropic mesophase.

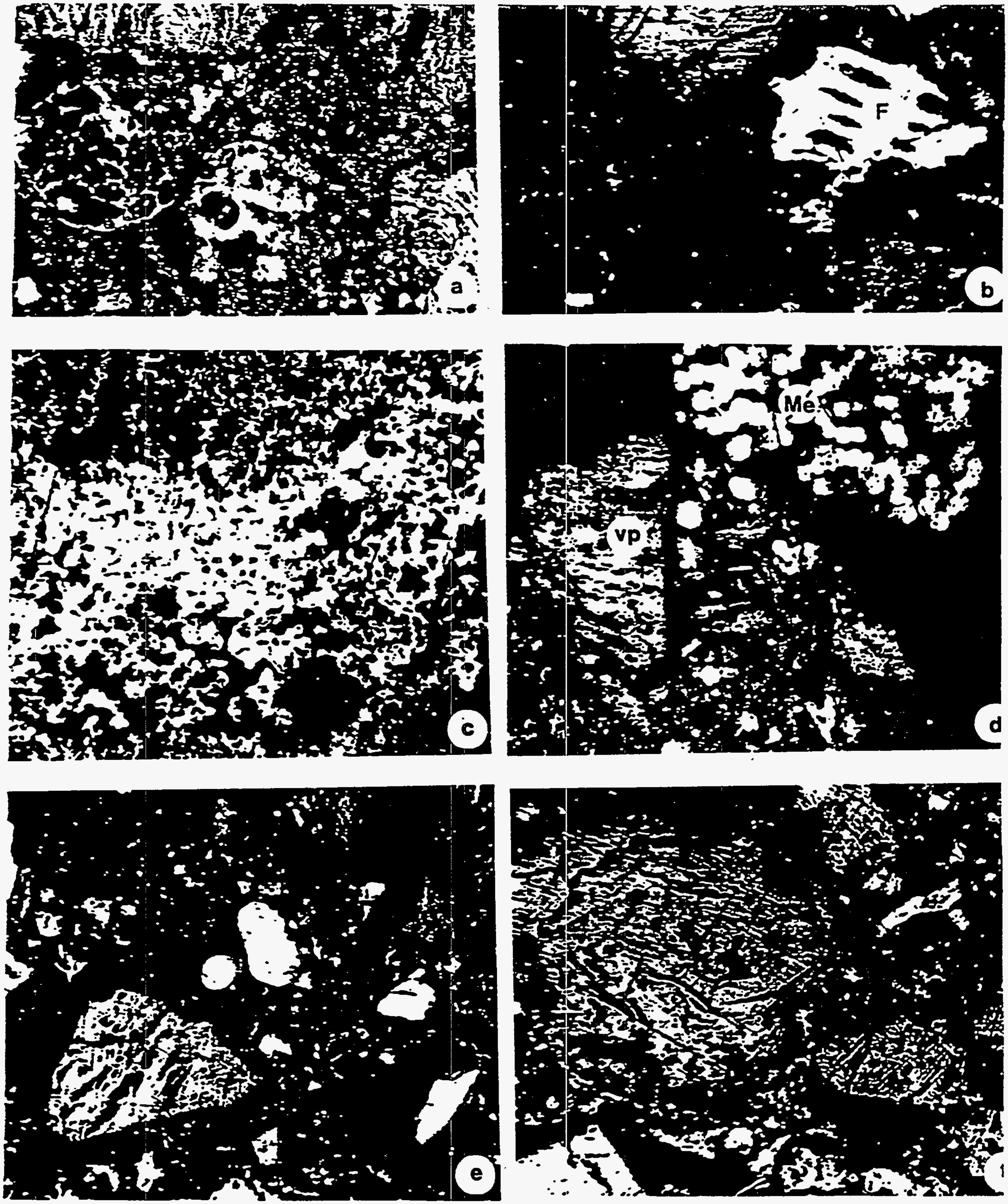


Plate 5

4.5.6.6 Plate 6

a) A large vitroplast fragment showing evidence of woody cell structure and rounded edges surrounded by small to large anisotropic mesophase spheres (Me).

b) Numerous mesophase spheres in a matrix of fragmented angular vitroplast.

c) Fusinite (F), vitroplast (VP), mesophase and coalesced mesophase. Partially crossed-polars, gypsum interference plate inserted.

d) Highly-anisotropic domain formed from the coalescence of mesophase spheres, along with melted vitroplast (VP). Partially crossed-polars, gypsum interference plate inserted.

6

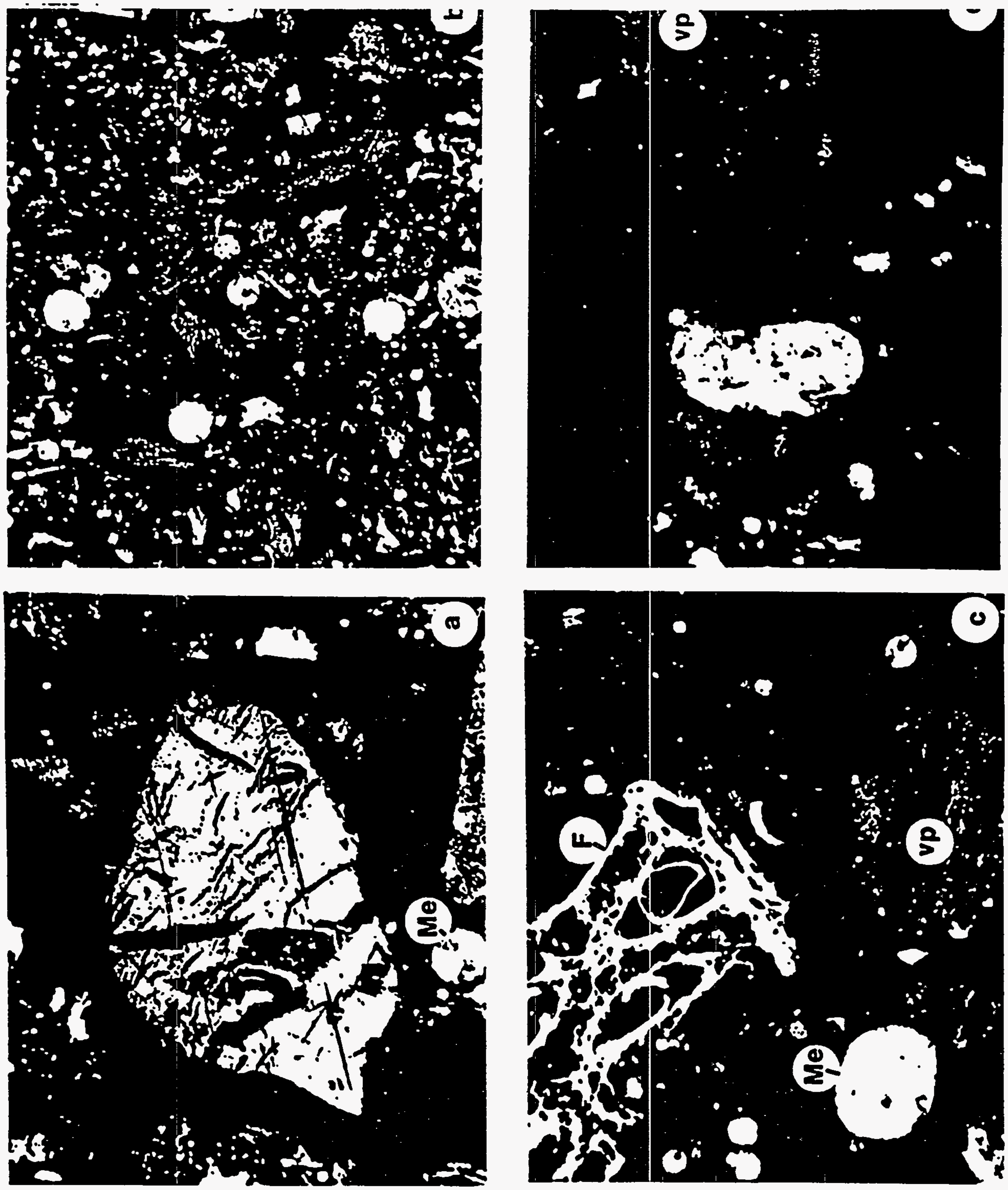


Plate 6

4.6 DISCUSSION

In this section the overall implications of the results of the experimental work on agglomeration, coal solubilization and hydroconversion, and coking on the process concept proposed by ARC and CED will be discussed.

Deashing coal prior to liquefaction can potentially be both beneficial or detrimental. On the one hand removal of inorganics, not a source of hydrocarbon product, reduces the amount of material to be processed and leads to increased coal throughput, but on the other hand any catalytic activity for liquefaction inherent in the ash is also lost. In this case, the two coals studied in this project, Black Thunder and Illinois #6, contained relatively low ash (5.2% and 11.5%, respectively). Agglomeration tests using ARC's technology and externally provided coal derived solvents did not lead in either case to very significant removal of ash. In addition, autoclave tests to compare the liquefaction behaviour of the agglomerates and the untreated coal did not show any advantage of one over the other. It was concluded, therefore, that for these coals at least an initial agglomeration step could not be justified. This position could be re-examined particularly if different coals were to be studied. Agglomeration of the coal feedstocks is not proposed for Phase II since it is intended to work with the same coals as in Phase I.

For coal solubilization, initial autoclave work with Black Thunder coal was carried out using potassium carbonate as shift catalyst for the conversion of carbon monoxide/steam. This was a logical choice since previous studies at ARC and elsewhere indicated that this was a preferred catalyst. Much of this autoclave work was completed while the modification to the bench unit was in progress. It was intended to use the potassium carbonate catalyst in the bench unit, but unfortunately operational problems (blockages) prevented its use in two stage operations. It is likely that in a bigger unit blockages due to potassium carbonate would not be an issue and it could be used. The autoclave studies did however indicate that sodium aluminate, although not as effective as potassium carbonate, was the best alternative shift catalyst of those tested, and in fact this was used in most of the bench unit runs. The autoclave study confirmed the following:

a. The externally provided coal derived solvents were quite stable at coal solubilization conditions.

b. The matrix study confirmed that temperature and residence time were key parameters for coal solubilization, pressure being less significant. This information was used as the basis for adjustment of conditions in the bench unit to achieve higher coal conversions and pressure reduction in the first stage reactor.

c. For Black Thunder coal, solubilization was best achieved using carbon monoxide/steam; Illinois #6 coal was best solubilized using hydrogen. This impacted the decision to use a continuous stirred tank reactor for the first stage of the process with Illinois #6 coal.

d. Syngas can replace carbon monoxide in the solubilization step up to a ratio of 40% hydrogen/60% carbon monoxide without significant reduction in coal solubilization.

e. About 60% of the oxygen is removed from Black Thunder coal during the solubilization step. The amount of pentane soluble oils produced is however low, most of the product from the coal is asphaltene or preasphaltene.

The results on coal solubilization from the bench unit generally paralleled those in the autoclave except for the coal and carbon monoxide conversions. In the counterflow reactor gas residence times are much lower than in the autoclave. The best carbon monoxide conversions in the CFR were about 30%, compared with 80% in the autoclave. Taken on a moles converted per given weight of MAF coal processed, however, the results were relatively comparable (1 - 1.5 moles/100g MAF coal). Coal solubilization was lower in the CFR than in the autoclave at the same settings of temperature and residence time. Figure 4.6.1 shows the comparison of coal conversion with severity index for the two reactors. Differences in yields and selectivities have been noted by others using different types of liquefaction reactors[1]. The differences may be due to gas/liquid contacting, heating and cooling times in the autoclave, heat transfer effect, etc. The impact of changes to key variables in both systems appears the same, however. For Illinois #6 coal, the lower coal conversions meant that sufficient solubilization could not be achieved in the smaller first stage CFR on the bench unit. Eighty percent conversion was achieved, however, using the larger second stage CFR. Therefore, for future work a larger CFR will be required for the first stage.

Most of the work combining solubilization and hydroconversion in a two stage process was done in the bench unit. In the two stage operation, the differences between the two reactor systems with regard to the relationship between coal conversion and severity index are less marked (Figure 4.6.2). In the hydroconversion step the key is the conversion of preasphaltenes to asphaltenes and then to pentane soluble oils. Since the main products on solubilization were found to be asphaltenes and preasphaltenes, and a fairly close correlation was found between pentane soluble oils and distillable oils, maximizing the conversion to pentane soluble oils becomes all important. The bottoms product from the second stage CFR will contain essentially all of the unconverted asphaltenes and preasphaltenes and therefore the recycle of this material is necessary to optimize distillable oil yields. This is a basis for our proposal in Phase II.

Bench unit runs DOE-BU-014 and DOE-BU-015 represent the best conditions for liquefaction of Black Thunder coal on this unit. The conditions may not be optimum, but are close to it for this scale of unit. Previous runs on Black Thunder coal were

FIGURE 4.6.1

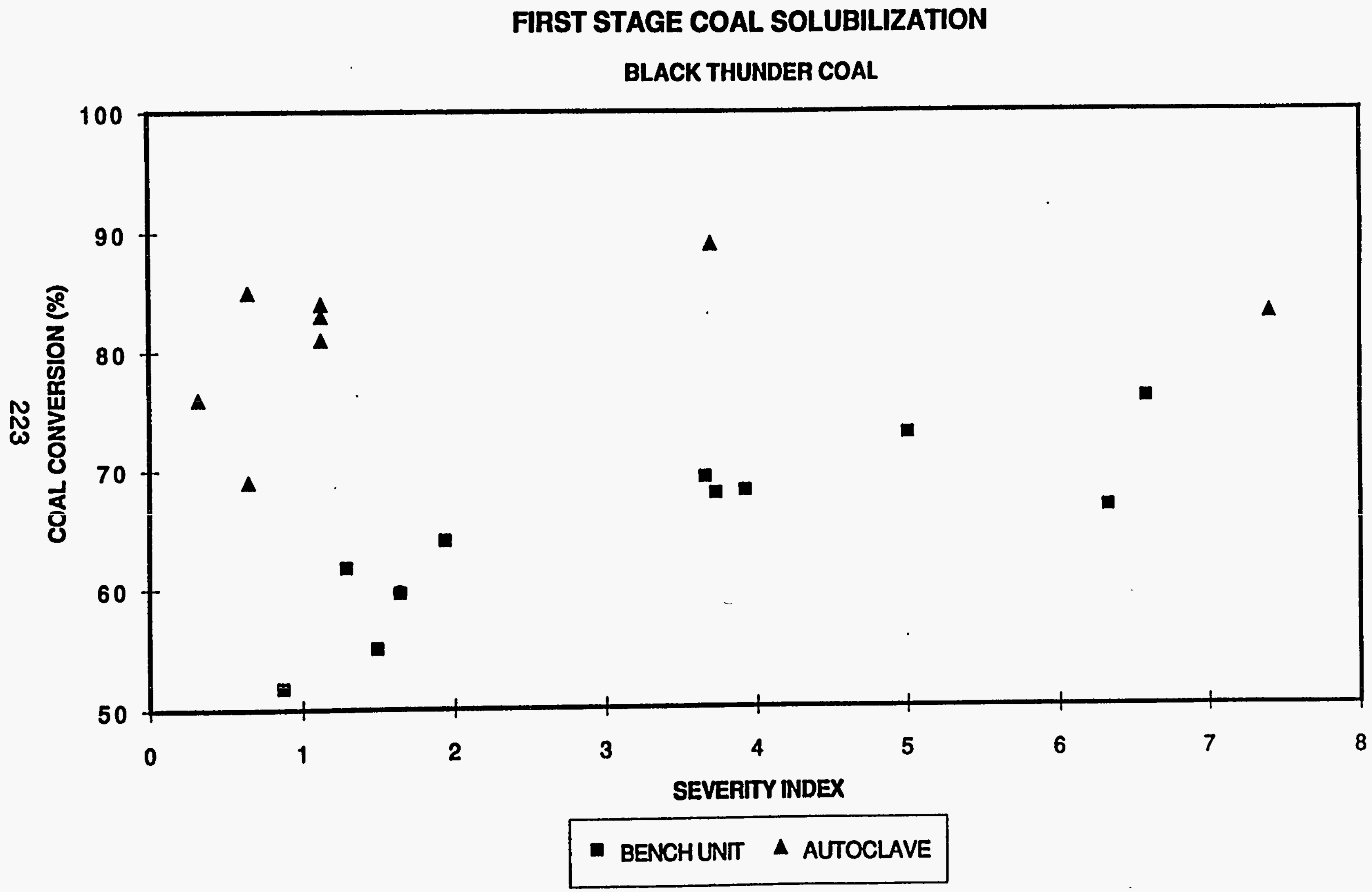
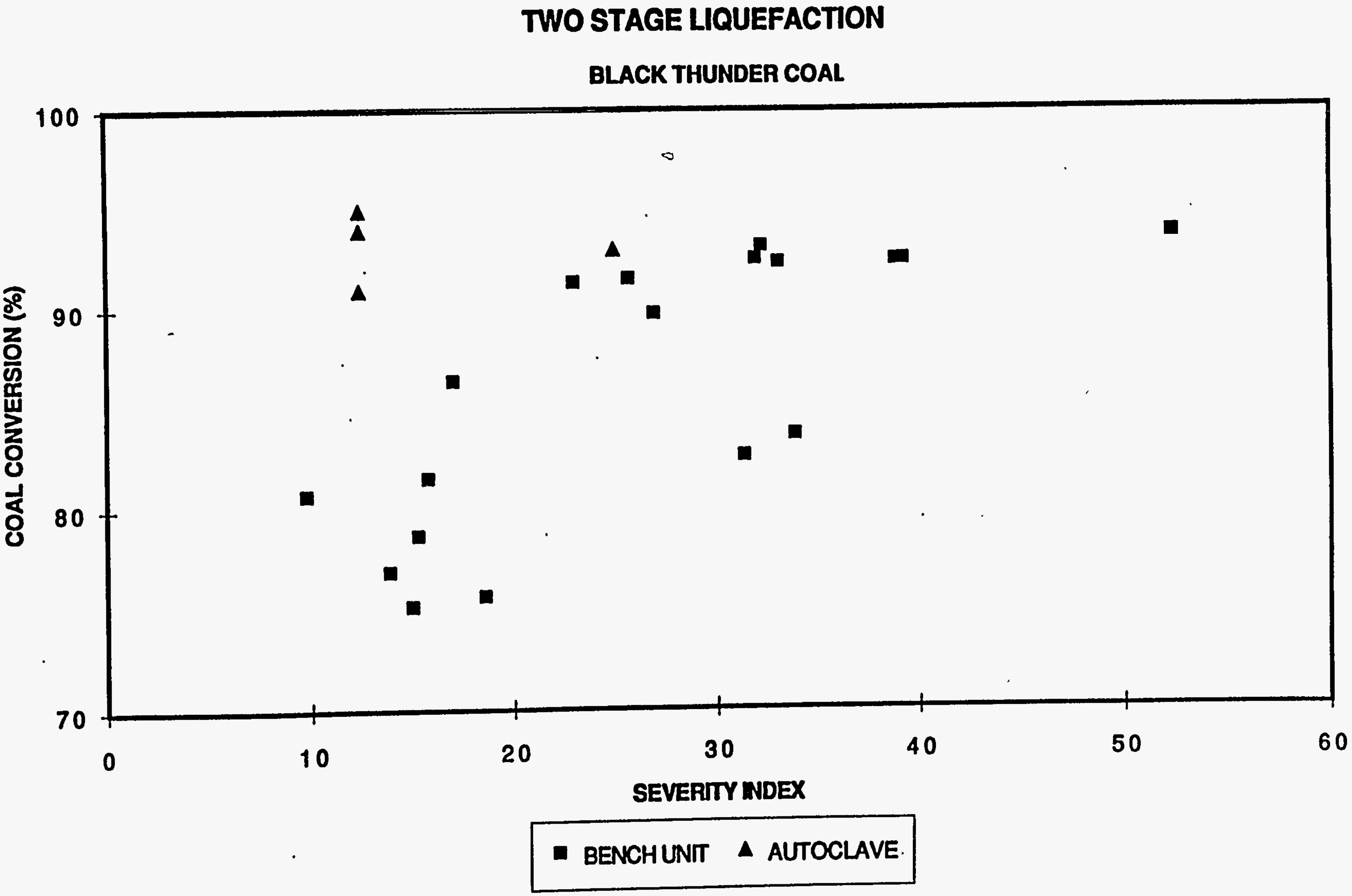

FIRST STAGE COAL SOLUBILIZATION
BLACK THUNDER COAL
COAL CONVERSION (%)
100
90
80
70
60
50
0
1
2
3
4
5
6
7
8
SEVERITY INDEX
■ BENCH UNIT
▲ AUTOCLAVE

FIGURE 4.6.2


TWO STAGE LIQUEFACTION
BLACK THUNDER COAL
COAL CONVERSION (%)
100
90
80
70
0
10
20
30
40
50
60
SEVERITY INDEX
■ BENCH UNIT
▲ AUTOCLAVE

important for narrowing down the best conditions. Coal conversions in the range of 82.6 - 93.7 wt% were obtained with pentane soluble oil yields between 45.6 wt% and 62.6 wt%, and distillable oil yields in the range of 49.9 - 62.8 wt% based on MAF coal. Iron oxide and ammonium molybdate were used as hydroconversion catalysts, the best results being obtained with ammonium molybdate. The results compare favourably with other technologies, particularly when it is considered that this is a once through operation.

The number of bench unit runs on Illinois #6 coal were limited. DOE-BU-018 represents the only data on two stage operation. It is anticipated that considerable further optimization on this coal is still possible. As mentioned, due to the lower activity of this coal, a larger CFR unit is required for first stage solubilization. This improvement coupled with solvent recycle should produce higher yields. Nevertheless, in DOE-BU-018 coal conversions in the range of 93.0 - 95.2 wt% were achieved with pentane soluble oil yields between 47.6% and 60.0 wt% and distillable oil yields in the range of 37.5 - 51.5 wt% based on MAF coal. Again iron oxide and ammonium molybdate were the catalysts used and the latter gave the best results. In the case of Illinois #6 less conversion of asphaltenes to pentane soluble oils was achieved in the second stage which led to the lower distillable oil yields. Conditions to improve this conversion will be sought in Phase II.

The limited work on the coking of the bottoms fraction from the second stage CFR was designed to determine the potential for extra oil yield. This is one simple option for handling the residue. From the results it was clear that only marginal amounts of extra oils are obtained (1 - 5%). Consequently, it is believed that hot filtration of this bottoms fraction followed by recycle of the filtered oil supplemented by heavy distillate presents a more attractive option for increasing distillable oil yield.

4.6.1 Reference

1. Davis *et al*, Catalysis Today, 19 (1994) 421-436.

4.7 CONCLUSIONS

The following are the major conclusions resulting from the experimental program:

1. Counterflow reactor technology can be successfully applied to the solubilization and liquefaction of both Black Thunder and Illinois #6 coals.

2. Under the best tested conditions, in the continuous once-through bench scale unit, coal conversions up to 92.7 wt%, and distillable oil yields of 62.8% based on MAF coal were achieved with Black Thunder coal. The corresponding data for Illinois #6 coal were coal conversions up to 95.2 wt% and distillable oil yields of 51.5 wt%.

3. For Black Thunder coal solubilization was best achieved using carbon/monoxide steam. Potassium carbonate was a preferred catalyst, but due to operational difficulties with this catalyst in the bench unit, sodium aluminate, the best alternative, was used. Illinois #6 coal was best solubilized using hydrogen.

4. Iron oxide and ammonium molybdate (with added sulphur in the form of dimethyldisulphide in the case of Black Thunder coal) were effective catalysts for hydroconversion. Ammonium molybdate gave slightly higher distillable oil yields.

5. Agglomeration prior to liquefaction is not justifiable for the Black Thunder and Illinois #6 coals used in Phase I.

6. Coking of the bottoms fraction from the second stage counterflow reactor yielded only marginal amounts of extra oil. A more attractive option for increasing distillable oil yield is expected to be hot filtration of this bottoms fraction, followed by recycle of the filtered oil, supplemented by product heavy distillate.

5.0 PROCESS DEVELOPMENT

5.1 Process Concept

The process to be evaluated during this program originally combined four different concepts as outlined in Figure 5.1.1:

These concepts (described in some detail in Section 2) are summarized as follows:

1. In the coal slurry preparation, an ash removal step (coal agglomeration) is intended to remove most of the ash from the coal, and as a consequence reduce the solid loading in the reactors and other equipment.

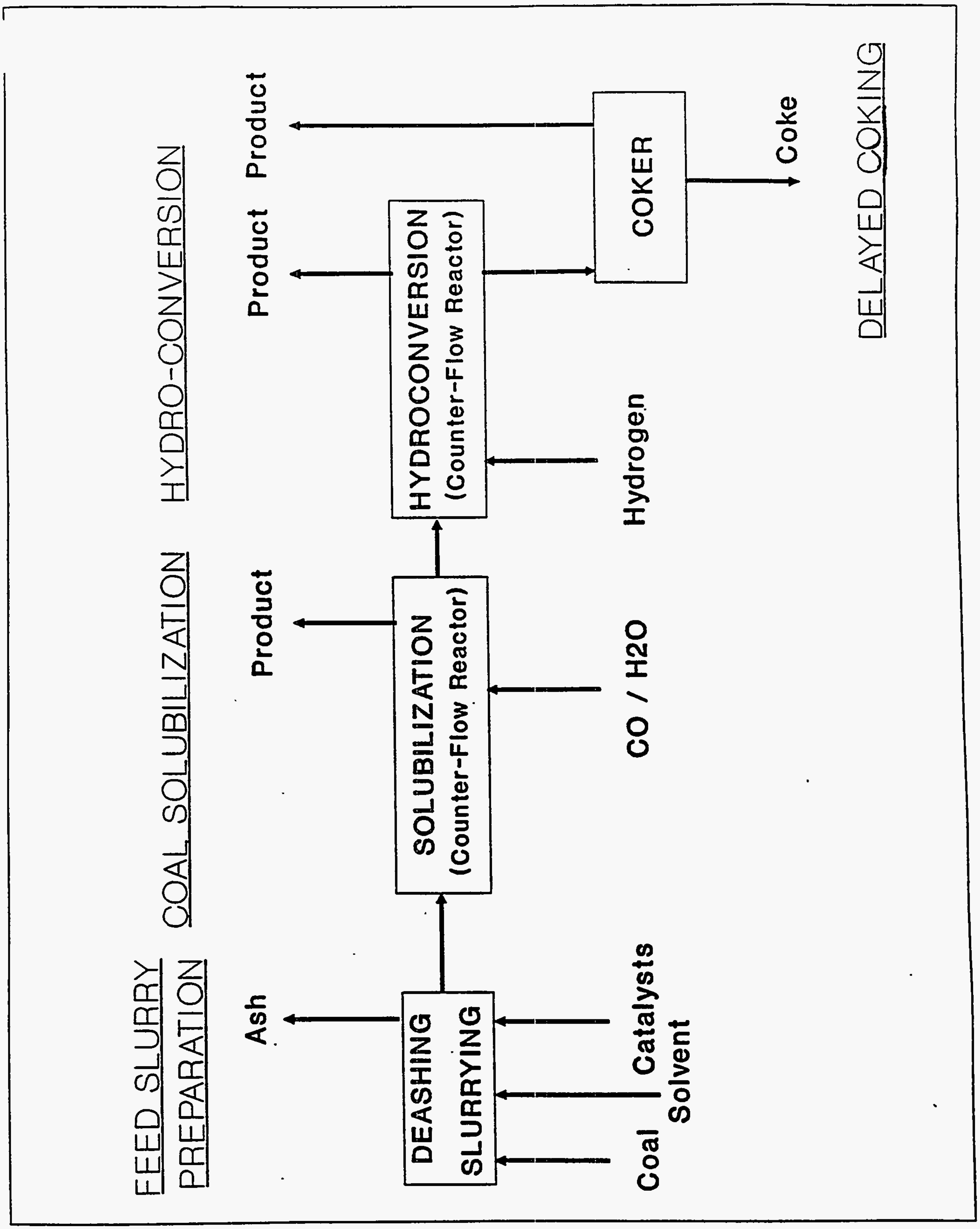
2. A two stage coal liquefaction step: The first, coal solubilization stage utilizes the shift reaction of CO and water to solubilize the coal. In the second, hydroconversion stage, hydrogen is added when converting the solubilized coal to lighter boiling fractions.

3. Both reactor stages employ the counterflow reactor (CFR) technology to realize the advantages of the CFR over conventional co-current upflow reactors.

4. For the "disposal" of the reactor bottoms stream from the hydroconversion stage, a delayed coking step is proposed to produce a coke product and a distillable oil product.

As results from the autoclave tests and particularly the bench unit tests became available, this initial process concept was continuously evaluated. At the conclusion of this phase of the project three major modifications characterize the CFR Advanced Coal Liquefaction process :

Figure 5.1.1: Process Concept



1. Deletion of Deashing Step

The ash levels in the as received coals were relatively low (5.2% and 11.5%, respectively). Coal agglomeration tests indicated that the ash removal was low for both Black Thunder and Illinois #6 coals (around 10% and 25%, respectively). Consequently, the ash removal step was deleted from the processing sequence.

2. Low Pressure Operation for First Stage

The initial concept used two counterflow reactor in series, with the first stage CFR operating at a slightly higher pressure than the second stage CFR. The idea being that the pressure differential between the two stages would be used in a control valve for the liquid level control in the first stage CFR. However, with this concept, continuous bench unit operation could not be maintained. Guided by results from autoclave tests, a new, improved concept was developed with the first stage CFR operating at a significantly lower pressure than the second stage CFR, and the liquid level in the first stage counterflow reactor is maintained by the variable speed drive of an interstage pump. This pump also increased the pressure of the first stage reactor bottoms stream to the operating pressure of the second stage CFR.

The next phase of the program should determine the lowest possible first stage operating pressure without significantly effecting coal solubilization.

3. Taller First Stage CFR

At the height of the liquid level possible in the first stage reactor of the bench unit, sufficient solubilization of Illinois #6 coal could not be achieved to maintain continuous operation of the bench unit. However, coal solubilization above 80% was achieved continuously using the second bench unit CFR only. This suggests that the settling time of coal particles rather than the WHSV based on the feed rate of the feed slurry is one of the determining operating parameters for the solubilization of the coal in the solubilization reactor. To achieve longer settling times, a tall, slim (large L/D ratios) first stage reactor must be used.

It is recommended that for the next phase of the program, a taller first stage reactor be installed in the bench unit.

5.2 Operating Parameters

The effect of most of the key operating parameters is discussed in detail in Section 4.3. Based on the bench unit tests, Table 5.2.1 summarizes the "best" operating conditions for the liquefaction of Black Thunder and Illinois #6 coal.

During most of the bench unit tests, the superficial gas velocity was kept constant at around 0.2 and 1.0 cm/sec in the first and second stage reactor, respectively. These velocities are very low and it is recommended to evaluate velocities up to about 3 cm/sec during the next phase of the program.

5.3 Yields of Product Streams

The yields and yield structure of the individual product fractions (boiling range fractions, components etc.) is presented and discussed in Section 4.3. From a process design point of view, however, it is equally important to provide information of the yields of total product streams. Figures 5.3.1 and 5.3.2 show the product stream yields for two individual mass balance periods, and Tables 5.3.1.and 5.3.2 summarize the stream yields for Black Thunder and Illinois #6 coal, respectively. In the case of the Illinois #6 coal, it must be realized that the first stage reactor for these bench unit tests was a flow-through stirred autoclave. Therefore, the yields of product streams do not reflect an integrated two stage CFR operation and will not be discussed below. The determination of these stream yields for Illinois #6 should be included as an objective for the next phase of the program.

Table 5.2.1: Summary of Key Operating Parameters

Operating Parameters		Black Thunder	Illinois #6
First Stage			
Feed Rate (WHSV)	(kg/hr)/litre	1.75	1.6
Pressure	MPa	10.3	17.2
Temperature	°C	410	425
Gas: Type Rate	 litre/kg (feed	CO 270	H_2 N/A
Catalyst		Aluminate	Molybdate
Second Stage			
Feed Rate (WHSV)	(kg/hr) litre	1.0	1.15
Pressure	MPa	17.2	17.2
Temperature	°C	440	440
Gas: Type Rate	 litre/kg (feed)	H_2 2,300	H_2 2,300
Catalyst	Type	Molybdate	Molybdate

N/A Not Available

Table 5.3.1

SUMMARY OF PRODUCT STREAM YIELDS
(In wt% maf coal plus solvent feed)

RUN No.:	DOE-BU-014				DOE-BU-015					
M.B.No.:	YP-01/ C1	YP-02/ C1	YP-03/ C1	YP-04/ C1	YP-01/ C1	YP-02/ C1	YP-03/ C1	YP-04/ C1	YP-05/C1	YP-06/C1
OPERATING CONDITIONS										
First Stage:										
Feed Rate (kg / hr) / IWHSV	1.77	1.79	1.76	1.73	1.62	2.29	1.74	1.86	1.83	1.85
Pressure Mpa	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34	10.34
Temperature deg C	411	411	411	410	411	412	412	409	411	411
Catalyst	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate	Aluminate
Second Stage:										
Feed Rate (kg / hr) / IWHSV	1.06	1.07	1.06	1.04	0.85	1.20	1.04	1.11	1.10	1.11
Pressure Mpa	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24	17.24
Temperature deg C	430	435	439	445	430	434	435	429	440	436
Catalyst	FeO+DMDS	FeO+DMDS	FeO+DMDS	FeO+DMDS	Molybdate	Molybdate	Molybdate	Molybdate	Molybdate	Molybdate
FEED STREAMS:										
Solvent	60.20%	58.02%	58.19%	58.19%	61.58%	59.39%	57.06%	55.30%	58.12%	58.38%
Coal	39.80%	41.98%	41.81%	41.81%	38.42%	40.61%	42.94%	44.70%	41.88%	41.62%
TOTAL SLURRY	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
CO (shift)	12.10%	11.60%	12.45%	12.72%	14.82%	11.30%	12.84%	12.07%	11.97%	11.73%
Water (shift)	7.78%	7.46%	8.01%	8.18%	9.54%	7.27%	8.32%	7.76%	7.70%	7.55%
Hydrogen (consumed)	2.30%	2.22%	2.35%	2.30%	1.00%	2.89%	2.63%	2.76%	2.68%	2.64%
TOTAL FEED	122.19%	121.28%	122.82%	123.20%	125.37%	121.47%	123.89%	122.69%	122.35%	121.91%
PRODUCT STREAMS										
First Stage:										
COx+H2	22.91%	22.98%	22.58%	23.04%	27.80%	20.11%	23.15%	21.52%	21.83%	21.41%
C1 - C4	0.33%	0.32%	0.31%	0.31%	0.04%	0.29%	0.31%	0.29%	0.03%	0.28%
Oil	8.37%	8.34%	3.43%	9.20%	12.30%	10.11%	14.87%	14.73%	13.29%	13.38%
Water										
TOTAL FIRST STAGE	31.61%	31.65%	26.32%	32.54%	40.14%	30.50%	38.33%	36.64%	35.15%	35.08%
Second Stage:										
OVERHEAD										
COx	1.81%	1.68%	1.52%	1.55%	2.39%	2.27%	2.93%	1.89%	2.07%	2.08%
C1 - C4	3.79%	4.08%	4.82%	5.92%	4.15%	3.87%	4.14%	3.35%	4.41%	3.83%
Oil	45.40%	44.54%	60.23%	58.19%	34.48%	53.57%	44.10%	46.39%	55.25%	59.02%
Water	2.46%	2.53%	2.79%	3.26%	0.92%	2.09%	1.99%	2.37%	1.52%	2.03%
Total Overhead	53.47%	52.82%	69.36%	68.92%	41.93%	61.79%	53.17%	54.01%	63.24%	66.96%
BOTTOMS										
Oil	33.74%	33.67%	23.97%	19.12%	36.62%	25.02%	29.10%	28.18%	20.80%	17.03%
Coal (maf)	3.37%	3.14%	3.16%	2.62%	6.67%	4.15%	3.29%	3.86%	3.16%	2.85%
Total Bottoms	37.11%	36.81%	27.13%	21.74%	43.29%	29.17%	32.39%	32.05%	23.96%	19.87%
TOTAL SECOND STAGE	90.58%	89.63%	96.49%	90.66%	85.22%	90.96%	85.56%	86.05%	87.20%	86.83%
TOTAL PRODUCT	122.19%	121.28%	122.82%	123.20%	125.37%	121.47%	123.89%	122.69%	122.35%	121.91%
Coal Conversion, wt.% maf coal	91.54%	92.51%	92.44%	93.74%	82.63%	89.78%	92.34%	91.36%	92.46%	93.16%
Net Dist. Oil Yield, Wt.% maf Coal	50.44%	55.28%	58.92%	52.41%	49.95%	59.01%	56.88%	62.79%	62.29%	55.66%

Table 5.3.2

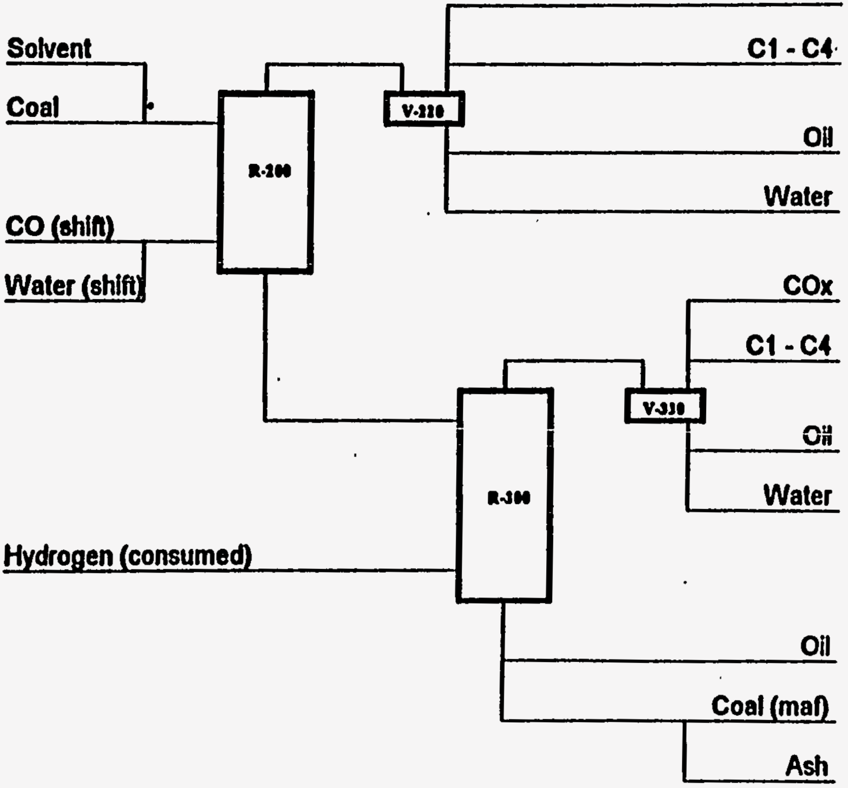
SUMMARY OF PRODUCT STREAM YIELDS (in wt% maf coal plus solvent feed)						
RUN No.: .		DOE-BU-018				
M.B.No.:		YP-01/ C1	YP-02/ C1	YP-03/ C1	YP-04/ C1	YP-05/ C1
OPERATING CONDITIONS						
First Stage:						
Feed Rate	(kg / hr) / I WHSV	1.48	1.40	1.55	1.79	1.64
Pressure	Mpa					
Temperature	deg C	428	425	422	417	415
Catalyst						
Second Stage:						
Feed Rate	(kg / hr) / I WHSV	0.96	0.91	1.42	1.16	1.06
Pressure	Mpa	17.24	17.24	17.24	17.24	17.24
Temperature	deg C	430	439	440	440	431
Catalyst		Moly	Moly	Moly	Iron Oxide	Iron Oxide
FEED STREAMS:						
Solvent		65.96%	62.92%	61.41%	62.12%	61.86%
Coal		34.04%	37.08%	38.59%	37.88%	38.14%
TOTAL SLURRY		100.00%	100.00%	100.00%	100.00%	100.00%
CO (shift)						
Water (shift)						
Hydrogen (consumed)		1.54%	1.56%	1.34%	1.48%	1.13%
TOTAL FEED		101.54%	101.56%	101.34%	101.48%	101.13%
PRODUCT STREAMS						
First Stage:						
COx+H2						
C1 - C4						
Oil						
Water						
TOTAL FIRST STAGE						
Second Stage:						
OVERHEAD						
COx		0.34%	0.33%	0.28%	0.70%	0.49%
C1 - C4		4.38%	5.63%	4.40%	4.89%	7.26%
Oil		30.53%	34.26%	30.88%	31.88%	29.13%
Water		2.09%	1.02%	2.78%	2.59%	1.87%
Total Overhead		37.34%	41.24%	38.35%	40.06%	38.74%
BOTTOMS						
Oil		62.51%	58.53%	60.90%	58.82%	59.71%
Coal (maf)		1.69%	1.79%	2.10%	2.59%	2.68%
Total Bottoms		64.20%	60.32%	62.99%	61.41%	62.38%
TOTAL SECOND STAGE		101.54%	101.56%	101.34%	101.48%	101.13%
TOTAL PRODUCT		101.54%	101.56%	101.34%	101.48%	101.13%
Coal Conversion, wt.% maf coal		95.03%	95.16%	94.57%	93.17%	92.99%
Net Dist. Oil Yield, Wt.% maf Coal		37.53%	48.05%	51.35%	44.36%	48.69%

PROCESS YIELD STRUCTURE

RUN No.: DOE-BU-015 M.B. No.: YP-05/C1

FEED

wt% (coal+solvent) as is	wt% (coal+solvent) maf	
53.0%	58.1%	Solvent
47.0%	41.9%	Coal
100.0%	100.0%	
10.9%	12.0%	CO (shift)
7.0%	7.7%	Water (shift)
2.4%	2.7%	Hydrogen (consumed)
120.4%	122.3%	



PRODUCT

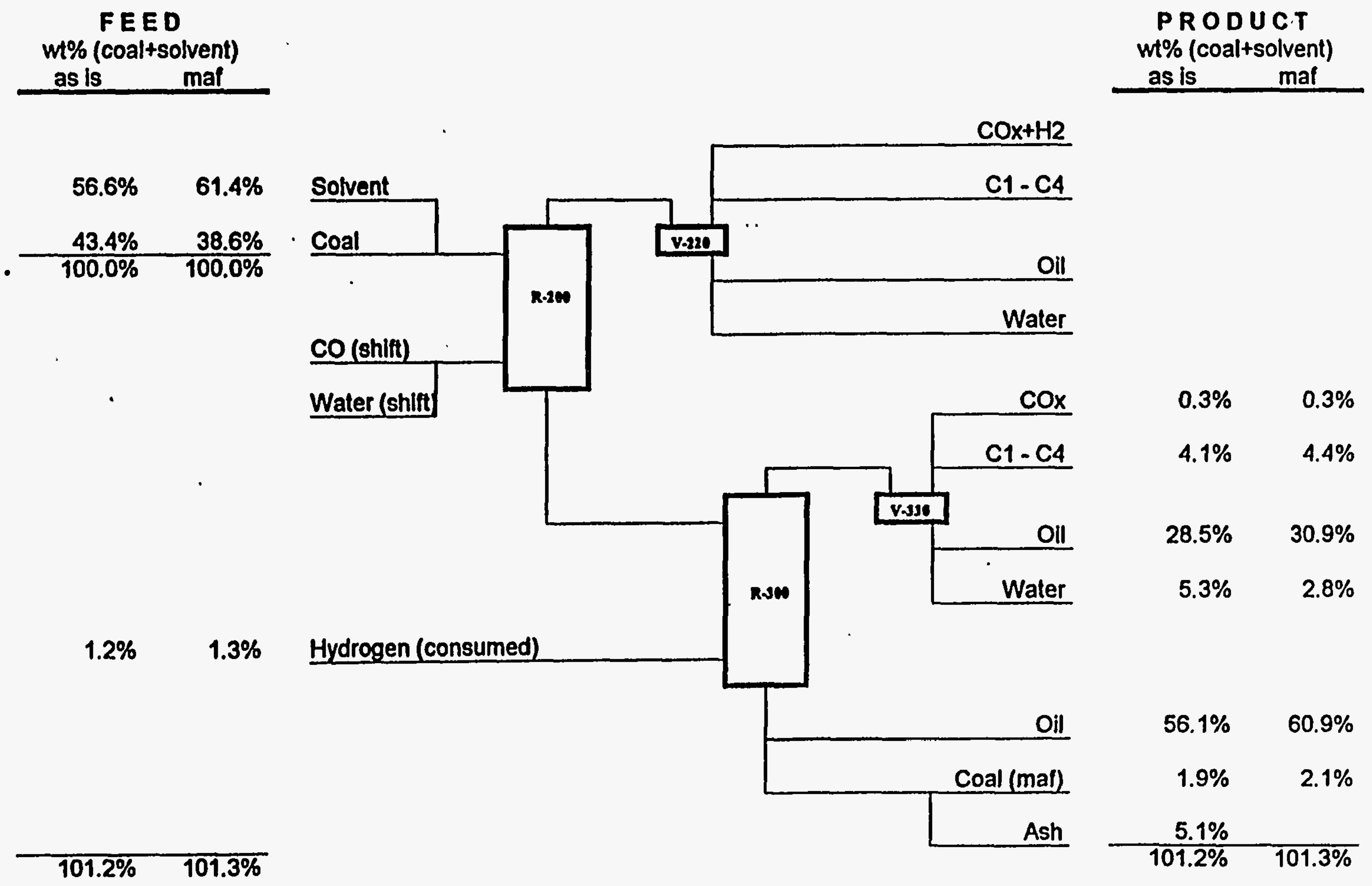
	wt% (coal+solvent) as is	wt% (coal+solvent) maf
COx+H2	19.9%	21.8%
C1 - C4	0.0%	0.0%
Oil	12.1%	13.3%
Water	4.7%	
COx	1.9%	2.1%
C1 - C4	4.0%	4.4%
Oil	50.4%	55.2%
Water	1.4%	1.5%
Oil	19.0%	20.8%
Coal (maf)	2.9%	3.2%
Ash	4.1%	
	120.4%	122.3%

Remarks:

Figure 5.3.1

PROCESS YIELD STRUCTURE

RUN No.: DOE-BU-018 M.B. No.: YP-03/ C1



Remarks:

Figure 5.3.2

For Black Thunder subbituminous coal, three observations are pointed out:

1. The overhead stream from the first stage CFR contains about 13.3 wt.% (maf feed) of oil. This corresponds to about 15 wt% of the total gross oil product.

2. The overhead stream from the second stage CFR contains about 55.2 wt.% (maf feed) of oil. This corresponds to about 62 wt% of the total gross oil product.

3. The bottom stream from the second stage CFR represents about 26 wt% of the feed on an "as is" basis. The stream contains about 20.8 wt% (maf feed) of oil corresponding to about 23 wt% of the total gross oil product.

Although all the above data is based on operating the bench unit in a once through mode using a "foreign" solvent, it is important in evaluating the source of recycle oil generated by the CFR process in a fully integrated operation. First, the oil from the second stage CFR bottom stream can be recovered (hot filter, ROSE process, etc.). This would yield about half of the amount needed. To recover the remaining amount, the process design should include a hot and a cold second stage overhead separator. The operating temperature of the hot separator is selected so that sufficient oil is condensed to make up the amount of recycle solvent needed, plus an additional quantity to provide some margin for operation.

5.4 Improved CFR Advanced Coal Liquefaction Process

With the above outlined evaluation of the CFR process during this phase of the program, a block-flow diagram of the improved CFR Advanced Coal Liquefaction process is shown in Figure 5.4.1. This configuration forms the basis for the economic feasibility study (Section 6.0), and should be the concept for further investigation during Phase II of the program.

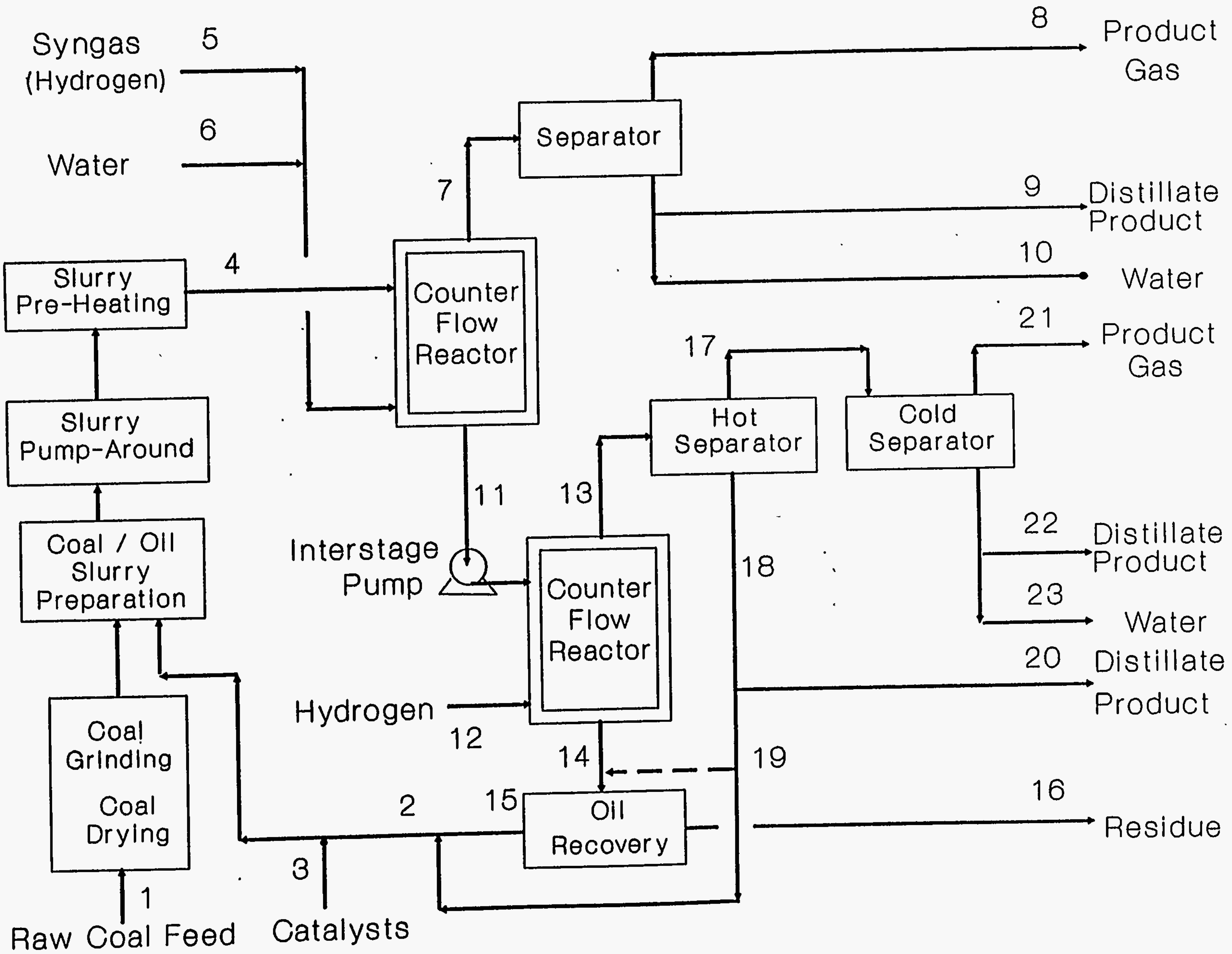

Syngas (Hydrogen)
5
Water
6
Slurry Pre-Heating
4
Slurry Pump-Around
Coal / Oil Slurry Preparation
Coal Grinding
Coal Drying
1
Raw Coal Feed
Counter Flow Reactor
7
Separator
8
Product Gas
9
Distillate Product
10
Water
11
Interstage Pump
Counter Flow Reactor
13
Hydrogen
12
14
Hot Separator
17
Cold Separator
21
Product Gas
22
Distillate Product
23
Water
18
20
Distillate Product
19
Oil Recovery
15
2
3
Catalysts
16
Residue

Figure 5.4.1

As received coal (1) is partially dried, ground and pulverized. Ground and partially dried coal is then slurried with recycle solvent (2) and catalyst (3) in the Coal/Oil Slurry Preparation area. Coal loading and catalyst content are adjusted. The Slurry Pump-Around circulates the prepared slurry to avoid settling of coal and/or catalyst and to ensure uniform composition.

After Slurry Pre-Heating, the slurry (4) is injected into the upper section of the first stage CFR. Syngas (5) and water (7) for subbituminous coal and hydrogen only (5) for bituminous coal are injected into the bottom of the CFR. Inside the CFR, the coal is solubilized as the coal/solvent slurry flows downwards against the upward flowing vaporized reaction products and gases.

The overhead stream (7) of the first stage CFR is routed to the Separator. Uncondensed material (8) leaves the top of the separator under back pressure control as first stage product gas which is sent to a gas recovery unit to recover a recycle stream and excess hydrogen. The condensate is withdrawn under level control as distillate product (9) and water (10).

The bottom stream (11) of the first stage CFR is withdrawn under level control via a variable speed drive Interstage Pump and injected into the upper section of the second stage CFR. Hydrogen (12) is injected into the bottom of the second stage CFR and flows upwards against the downward flowing first stage reactor bottoms stream. Vaporized reaction products and gases (13) are routed to the Hot Separator. The bottoms stream (14) is withdrawn under level control and injected into a Oil Recovery unit to recover a hydrocarbon oil stream (15) for recycle and a filter cake residue (16). This Oil Recovery Unit could be a hot filter, a ROSE-unit or similar.

The overhead stream (13) is partially condensed to recover a heavy distillate fraction (18). A sufficiently large portion (19) is combined with stream (15) to provide the required amount of recycle solvent (2). The remainder of stream (18) is withdrawn as distillate product (20).

The vapour stream from the Hot Separator (17) is cooled/condensed and routed to the Cold Separator. From there, the uncondensed material is withdrawn under back pressure control as second stage product gas (21) which is sent to a gas recovery unit to separate a recycle gas and a net product gas stream. The liquids are withdrawn under level control and separated into a lighter distillate product stream (22) and a product water stream (23).

Streams (2), (20) and (22) combine to give the total coal derived, all distillable oil yield.

6.0 ECONOMIC FEASIBILITY STUDY

As part of this phase of the program, a preliminary economic feasibility study has been prepared by Kilborn Inc. The following summarizes the results and conclusions from this technical and economic evaluation of the CFR Advance Coal Liquefaction process. A separate report from Kilborn is provided.

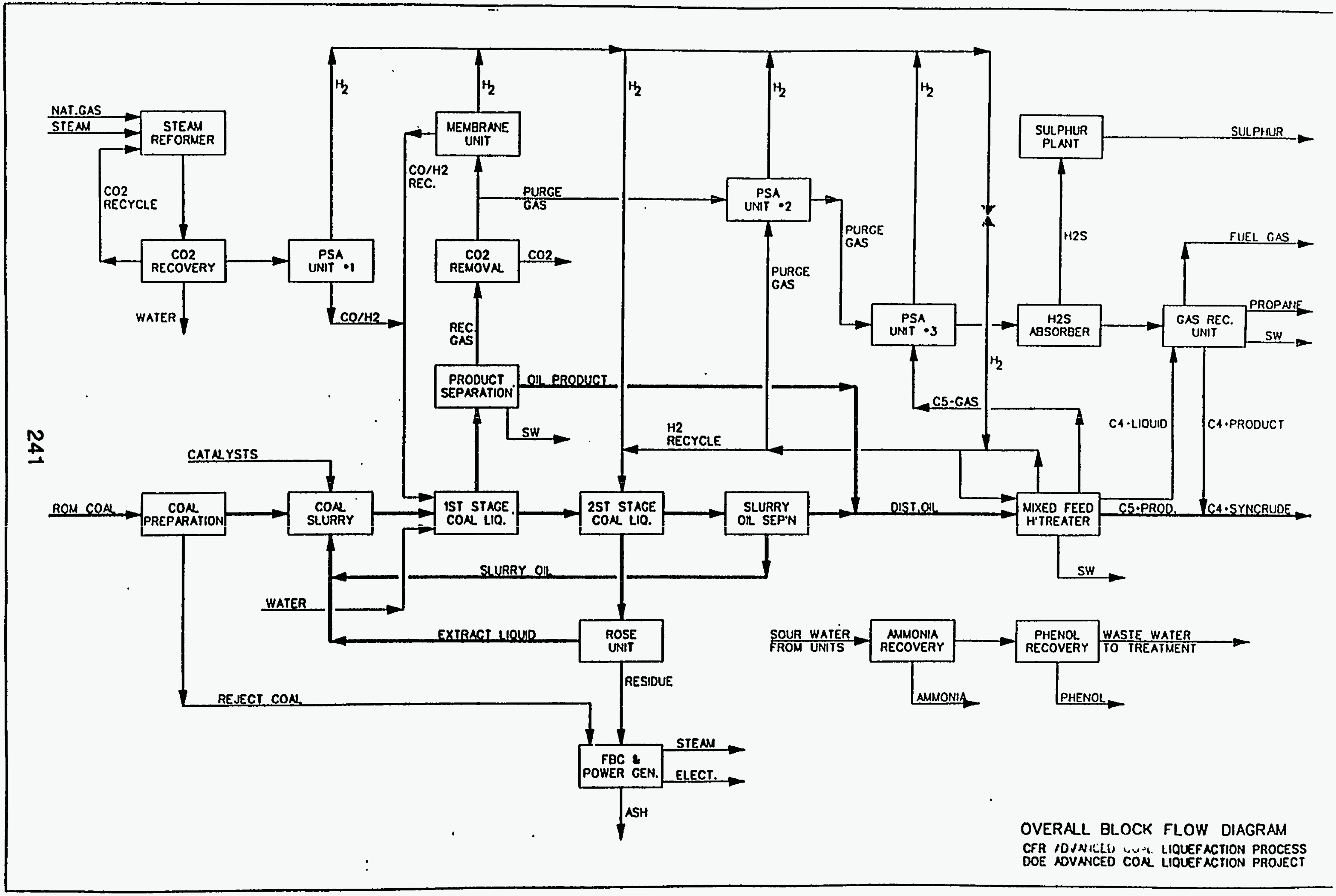
6.1 Technical Design

The conceptual CFR Advanced Coal Liquefaction project was configured similar to the Improved Baseline Design developed by Bechtel Corporation and AMOCO Oil Company under the DOE Advanced Coal Liquefaction Program using the HRI two stage coal liquefaction process. The study was based on the production of 75,000 BPD of C_4+ synthetic crude oil for subsequent processing in a conventional petroleum refinery from Black Thunder (Wyoming) subbituminous coal.

Figure 6.1 presents an overall block flow diagram of the conceptual coal liquefaction process. The coal is slurried in process derived recycle oils; solubilized in the first stage coal liquefaction reactors in the presence of carbon monoxide, hydrogen and an aluminate catalyst; hydrogenated in the second stage reactors in the presence of hydrogen and a molybdate catalyst; and hydrotreated for heteroatom removal and hydrogen addition in secondary hydrotreating facilities. Carbon monoxide and hydrogen required in the liquefaction process and hydrotreater are produced by steam reforming of natural gas followed by carbon dioxide removal and separation of the synthesis gas stream into high purity hydrogen and carbon monoxide-rich synthesis gas streams. By recycling the CO_2 to the reformer, the ratio of hydrogen to carbon monoxide in the synthesis gas can be controlled.

Unique features of the CFR Advanced Coal Liquefaction process are the use of carbon monoxide in the first stage liquefaction reactors, the use of counterflow reactors

Figure 6.1



OVERALL BLOCK FLOW DIAGRAM
CFR ADVANCED COAL LIQUEFACTION PROCESS
DOE ADVANCED COAL LIQUEFACTION PROJECT

in both stages and close coupling of the mixed feed hydrotreater and second stage liquefaction reactors, thereby avoiding a product recovery system on the second stage reactor system, a feed system on the hydrotreater and permitting a common hydrogen recycle system to be used.

Raw material requirements and product and by-product quantities for the conceptual plant are listed below:

Raw materials		
Coal	15,970	tonnes/day (MAF)
Natural Gas	161,370	MMBTU/day
Products		
Synthetic Crude Oil	75,000	BPD
Sulphur	107	tonnes/day
Ammonia	217	tonnes/day
Propane	6,030	BPD

Synthetic crude oil yield is 4.70 barrels per tonne of MAF coal (Black Thunder).

6.2 Financial

Capital and operating costs were developed for an Nth plant design, as given in Tables 6.1 and 6.2, respectively. The Nth plant design is defined as the Nth commercial plant built when the technology basis, plant design and operation are well established, resulting in the following characteristics:

- Lowest reasonable plant cost contingency
- No spare trains
- Lowest reasonable engineering cost

Table 6.1

CAPITAL COST INVESTMENT – COAL LIQUEFACTION PLANT

PLANT NO.	DESCRIPTION	BASIS	TOTAL RATE	NO. OF OPER UNITS	TOTAL NO. UNITS	ISBL FIELD COSTS ($1,000 US)	OSBL FIELD COSTS ($1,000 US)	INSTALLED COSTS ($1,000 US)
1	Coal Cleaning & Handling	MTPD (MF)	21,454	6	6	86,902	117,042	143,607
1.4	Coal Crushing & Drying	MTPD (MF)	17,879	12	12	100,644	135,550	166,316
2	Coal Liquefaction	MTPD (MF)	17,879	5	5	626,080	843,216	1,034,606
3	Gas Plant	Kg/h	125,471	1	1	46,123	62,119	76,219
5	Mixed Feed Hydrotreater	Kg/h	393,722	5	5	172,380	232,165	284,860
6	H2 Purification (PSA #2 & #3)	Kg/h	16,153	1	1	109,033	146,848	180,179
8	ROSE Unit	Kg/h	460,171	1	1	45,656	61,490	75,446
9-01	Methane Reforming	Kg/h	141,290	3	3	259,437	349,414	428,723
11	S Plant (Note 1)	Kg/h	4,470	1	1	13,053	17,580	21,570
38	NH3 Recovery (Note 2)	Kg/h	9,046	1	1	22,670	30,532	37,462
39	Phenol Recovery (Note 3)	Kg/h	1,357	1	1	8,531	11,490	14,097
	Total					1,490,509	2,007,445	2,463,086

NOTES:

1. S recovery based on 0.60 wt % organic sulphur in coal feed (MF).
2. N recovery based on 1.00 wt % organic nitrogen in coal feed (MF).
3. Phenol recovery based on 15 wt. % of the NH3 recovered.

Table 6.2

YEARLY OPERATING COSTS.

SCO PRODUCTION: 75,000 BPD

OPERATING FACTOR: 88.40 % YEARS OF OPERATION: 25.00

	UNIT RATE	QUANTITY	PRICE / UNIT ($)	OPER. COST ($/yr)
FEEDS:				
Coal (ROM)	MT/D	19,476	10.00	62,839,700
Natural Gas	MMBTU/D	161,371	2.00	104,135,800
Total Feeds				166,975,500
BY–PRODUCT CREDITS:				
Fuel Gas	MMBTU/D	75,481	2.00	48,709,400
Propane	BPD	6,029	7.50	14,589,900
Sulphur	MT/D	107	88.18	3,052,200
Ammonia	MT/D	217	132.28	9,265,700
Electricity	kWh	183,985	0.05	2,968,200
Total By–Products				78,585,400
NET FEED COST (Feeds minus By–products)				88,390,100
UTILITIES:				
Raw Water Makeup	MGAL/D	23,189	0.10	748,200
Fuel	MMBTU/D	155,634	2.00	100,434,000
Total Utilities				101,182,200
LABOUR:				
Operation				11,525,500
Management & Supervision				701,000
Laboratory				1,506,000
Engineering				1,953,700
Environ., Health, Safety & Security				2,773,600
Administration				2,691,200
Maintenance (@ 1.01 % of Capital Invest.)				24,958,000
Total Labour (@ 1.87 % of Capital Invest.)				46,109,000
SUPPLIES & MATERIALS DISPOSAL:				
Catalysts & Chemicals				28,574,300
Ash Disposal Cost	MT/D	1,909	5.51	3,394,100
Refuse Disposal Cost	MT/D	3,576	2.20	2,543,500
Total Supplies & Materials Disposal				34,511,900
TOTAL DIRECT COSTS:				270,193,200
INDIRECT COSTS:				
Operating & Office Supplies (0.05 % of Capital Invest.)				1,231,500
Maintenance Materials (@ 0.75 % of Capital Invest.)				18,473,100
Taxes & Insurance (@ 0.25 % of Capital Invest.)				6,157,700
Total Indirect Costs				25,862,300
MANUFACTURING COSTS:				296,055,500
REVENUE FROM SALES OF SCO (@ 29.75 $/BBL FOR BASE CASE)				719,853,500
NET PROFIT BEFORE TAXES				423,798,000
INTERNAL RATE OF RETURN BEFORE TAXES				16.75%

- Shortest possible project schedule to erect and start up
- Mature technology allowing the overall stream factor of the complex to be the same as that of the First plant (spare process trains, overcapacity).

The format of the capital cost estimate is similar to that used in the Bechtel report. The installed plant costs for the complex were developed by taking the estimated Inside Battery Limit (ISBL) plant cost for each ISBL plant, adding the respective portion of the total Outside Battery Limit (OSBL) costs and then adding the proportional amount of home office costs, engineering fee and contingency.

The annual operating cost estimate includes the cost of raw materials less by-product credits; the costs of utilities, operating, maintenance and management labour; supplies and materials disposal plus indirect operating costs, as shown in Table 6.2. By-product credits are shown in the operating cost table to facilitate the financial analysis which was based on a determination of the synthetic crude oil price required to achieve a 15% return on equity to the project owners.

The financial analysis for the Nth plant scenario was based on the following key assumptions:

Years of Construction	5
Year of Operation	25
Operating Factor, %	88.4
Depreciation, years	
Process Facilities	5
Buildings, Services	25
Working Capital, % of Revenue	10
Bank Interest Rate, %	8
Federal Income Tax, %	34
Percent Equity	25

Percent IRR on Equity	15
General Inflation, %	3
Raw Material Price Escalation	Same as Inflation
State Income Tax	0
Syncrude Premium	1.00 (multiplier)

The results of the financial and sensitivity analysis, given in Table 6.3, indicate that coal-derived synthetic crude oil can be produced by the CFR Advanced Coal Liquefaction process for a price that is only 25 - 70% above currrent crude oil price.

In order to further evaluate the future potential of the CFR Advance Coal Liquefaction process, it is recommended that the R&D program be continued so that assumptions made and questions raised during this study can be resolved. Key issues to be addressed in further work include:

- Operation in larger pilot scale equipment for improved reliability of data.
- Operation with slurry oil recycle rather than on a once-through basis with coal-derived solvent.
- Operation with a heavy solvent recovery unit for the recovery and recycle as slurry oil of heavy VGO, residual oil and asphaltenes from the second stage reactor bottoms outlet stream.
- Operation with CO-rich synthesis gas rather than high purity carbon monoxide in the first stage of the coal liquefaction process.
- Operation with lower hydrogen rates in the second stage reactor to evaluate the effect of superficial gas velocity and flow regime on product yield structure.

- Reduction of first and second stage catalyst requirements.
- Increased coal loading in the first and second stage reactors.
- Mixed feed hydrotreating tests to confirm final synthetic crude oil quality as a function of hydrotreating severity.

At the conclusion of the next phase of the R&D program, a new economic feasibility study should be commissioned to improve the accuracy of, and confidence in, the financial merits of the technology.

Table 6.3

Financial Results and Sensitivities

FINANCIAL CASES	CRUDE OIL EQUIVALENT PRICE ($/BBL)
Base Case	29.75
Capital + 10 %	31.43
Capital – 10 %	28.06
Capital + 25 %	33.97
Capital – 25 %	25.52
Coal Price + 25 %	31.06
Coal Price – 25 %	28.43
Natural Gas Price + 25 %	31.46
Natural Gas Price – 25 %	28.04
Owner's Equity 50 % (Double the Base)	31.59
SCO Yield + 10 %	27.04
SCO Yield – 5 %	31.31