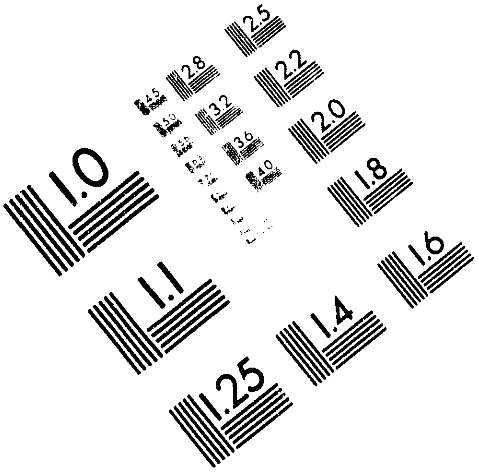
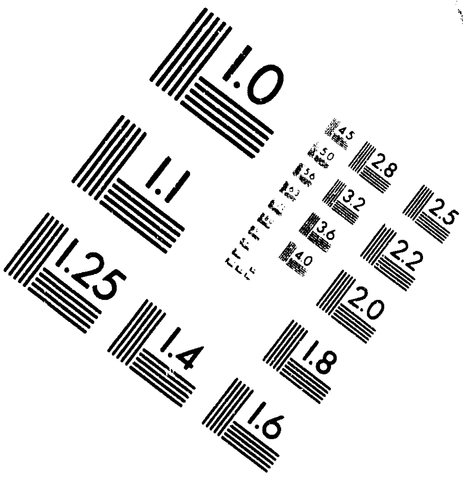
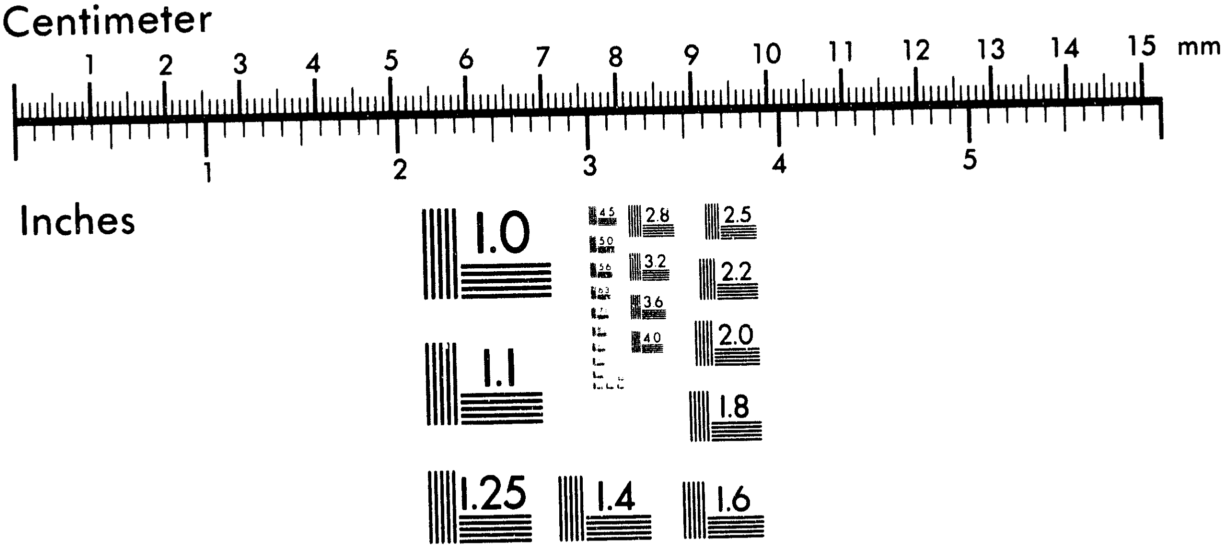
AIIM

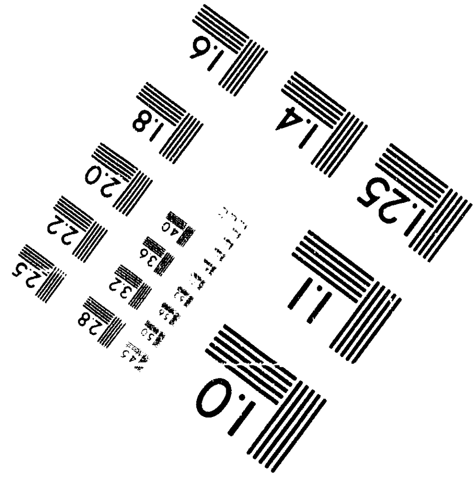
Association for Information and Image Management

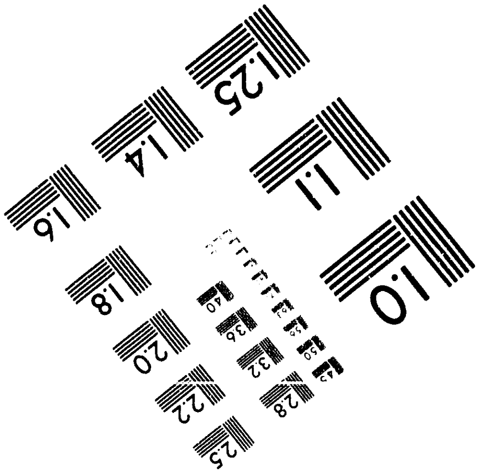
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202











MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

N-2
3

QUARTERLY REPORT
ADVANCED DIRECT COAL LIQUEFACTION CONCEPTS

Contract No: DE-AC22-92PC91050
Report No. QR 93/02

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

Canadian Energy Development Inc.
#12, 4290 - 12A Street
Edmonton, Alberta, Canada
T6E 5V2
and
Alberta Research Council
250 Karl Clark Road
P.O. Box 8330, Station F
Edmonton, Alberta, Canada
T6H 5X2

January 1, 1993 - March 31, 1993

SUMMARY

Five barrels of a Wilsonville process derived solvent (V-1074) from Black Thunder coal were obtained. This material boils within the preferred gas oil range, is more aromatic than previous solvents, and will therefore be used for the bench unit studies.

Several repeat runs were performed in the autoclave to confirm the results of the matrix study. In addition, runs were carried out with different catalysts, with agglomerates and with the V-1074 solvent. The results of the autoclave runs were analyzed with respect to coal conversion, CO conversion, oil yield, hydrogen consumption and oxygen removal. It was concluded that the best operating conditions for the first stage operation was a temperature of at least 390°C, residence time of at least 30 minutes, cold CO pressure of at least 600 psig and potassium carbonate catalyst (2% wt on total feed). The data also indicated however, that the coal conversion goes through a maximum, and too high a severity leads to retrograde reaction and lower coal solubilization. The scope for increasing temperature and time is therefore limited.

Petrographic examination of the THF insoluble resids from the autoclave program indicated a maximum coal conversion of about 90% for Black Thunder coal.

The bench unit construction was also essentially completed and the bench unit program to be carried out in the next twelve months was defined.

INTRODUCTION

The previous quarterly report detailed the background to the current project and defined the objectives. At the end of the last quarter (December 31, 1992) the following progress had been achieved:-

1. Representative bituminous and subbituminous coals were procured from two mine sites in Illinois and Wyoming, respectively. These two coals (Illinois #6 and Black Thunder) will be the major coal feedstocks for the project. Characterization of the Black Thunder coal was completed. Efforts had been made to obtain suitable coal derived solvents. Two samples of Black Thunder derived solvents were obtained, but were judged to be too light to be suitable for the autoclave and bench unit programs. A bottom fraction was therefore prepared by distilling off the lighter components from one of the solvents (V-178) and was then characterized and used in the autoclave tests. At the end of the quarter, the issues of what solvent to use for the bench unit tests on Black Thunder coal, and the solvent to be used for work on Illinois #6 remained unresolved.

2. Agglomeration tests with Black Thunder coal were completed. Ash removal was quite low (about 10%) under all conditions, not surprising in view of the low ash content of the original coal.

3. The first series of autoclave tests with Black Thunder coal was completed, indicating that almost complete solubilization (close to 90%) of coal can be achieved in a CO/H_2O environment under anticipated process conditions.

4. The design of the bench unit was completed, equipment moved from Nisku to Devon, and prefabrication started.

During this quarter, work has concentrated on resolving the issues described below:-

1. Establishing the solvent to be used in the bench unit program with Black Thunder coal.

2. Defining the conditions to be used in the first stage of the bench unit, from the results obtained in the autoclave and agglomeration studies.

3. Completing the erection of the bench unit and determining the bench unit test program.

Five barrels of a Wilsonville V-1074 process derived solvent produced from Black Thunder coal were obtained. One barrel contained a substantial amount of water, so it was set aside, and the other four barrels were blended and the blend characterized. This solvent is more aromatic than V-178 and boiled within the preferred gas oil range and on that basis was judged to be a better solvent than V-178 for the bench unit studies.

Several repeat runs were performed to confirm the results of the autoclave matrix study. In addition, runs were carried out with different catalysts, agglomerates, and the V-1074 solvent. These results were analyzed carefully to select the initial conditions for the first stage of the bench scale unit program. Petrographic examination of the THF insoluble resids from the autoclave program also provided some insight into the relationship between conversion and structure.

Bench unit construction was essentially completed, preparing the way for commissioning and operation during the next quarter.

The details of all these activities are described in the subsequent sections.

EXPERIMENTAL PROGRAM

Task 2 Feedstocks

2.1 Procurement

Black Thunder and Illinois #6 coals in sufficient quantity have been obtained to carry out the autoclave and bench unit programs defined by the project (see previous quarterly report). On the other hand, there has been difficulty in obtaining appropriate solvents. It was considered desirable that the solvents to be used be derived from the coals being processed, since ultimately in a commercial operation the solvent would have to be a recycle stream. To date we have not been able to obtain an appropriate Illinois #6 derived oil, although there is indication that some will be available by the time the bench unit program on Illinois #6 proceeds later in the year. Samples of Black Thunder derived oil were obtained but did not have the preferred boiling range and had to be distilled for use in the autoclave programs.

In this quarter, five barrels of a Black Thunder derived oil from Wilsonville V-1074 were obtained from a DOE sample bank. This material met the boiling range criteria for the preferred solvent, and this oil will be used for the bench unit program.

2.2 Analysis of V-1074 Solvent

The simulated distillation analyses of each of the five barrels was completed and are shown in Table 1. The first barrel was found to have free water on the top of the oil and also appeared to be somewhat emulsified. The simulated distillation also shows the material in this barrel to be quite a bit lighter up to the 25% point than the material from the other barrels. The first barrel was therefore set aside and an equi-volume blend made from the other barrels (2-5). The simulated distillation of the blend was performed as well as proximate and NMR analysis. The results are also given in Table 1.

TABLE 1: PROPERTIES OF V-1074 SOLVENT

Barrel	**1**	**2**	**3**	**4**	**5**	**Blend**
D2887 % off @ °C						
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
Carbon (wt%)						87.8
Hydrogen (wt%)						8.5
Nitrogen (wt%)						0.85
Sulphur (wt%)						0.05
H^1 aromatics						23
C^{13} aromatics						54

A blend of barrels (2-5) will be used for the bench unit program. V-1074 is more aromatic than the solvent used in the autoclave studies (V-178, + 320°C) and boils within the preferred gas oil range. On this basis, it is expected that V-1074 would be a slightly better coal liquefaction solvent than V-178, + 320°C.

2.3 Characterization of Illinois #6 Coal

The characterization of the Illinois #6 coal was also completed. The results are shown in Table 2. It should be noted that this coal also has a rather low ash content at 12.6%.

Table 2: Properties of Illinois #6 Coal

Moisture	%	8.9
Ash (MF)	%	12.6
Elemental (MAF)%		
carbon		77.7
hydrogen		5.4
nitrogen		1.4
sulphur		4.2
oxygen (difference)		12.9
Forms of Sulphur (MF) %		
Total		3.6
sulphatic		0.3
pyritic		1.3
organic		2.0

Task 3 Experimental Work

3.1 Ash Removal - Selective Oil Agglomeration

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 ≈ 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 the previous quarterly report for agglomeration of Black Thunder coal.

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 3). 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.

3.2 Autoclave Test Program

The experimental procedure used in the autoclave program was described fully in the previous quarterly report. This procedure was also used during this quarter.

TABLE 3 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	9.0
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

3.2.1 Matrix Program Results

The matrix program, shown graphically in Figure 1, was completed last quarter, but only a preliminary review of the results was carried out. The data for coal conversion, CO conversion, gas yield and hydrogen consumption are shown in Table 4. The results for coal conversion are shown graphically in Figure 2. Excellent repeatability was obtained on coal conversion at the centre point. The coal conversion data appeared to be consistent in following expected trends, except that the conversions for Runs DOE-9 and DOE-14 seemed low. It was therefore decided to repeat these runs and also Run DOE-5, where the maximum conversion was obtained. In addition, three other runs were carried out; one with agglomerates and one with the new Wilsonville solvent both at centre point conditions, and one at conditions which from the matrix program was felt to represent the best to obtain maximum conversion i.e: 400°C, 30 mins at 900 psi initial CO pressure. The results of these additional runs are given in Table 5.

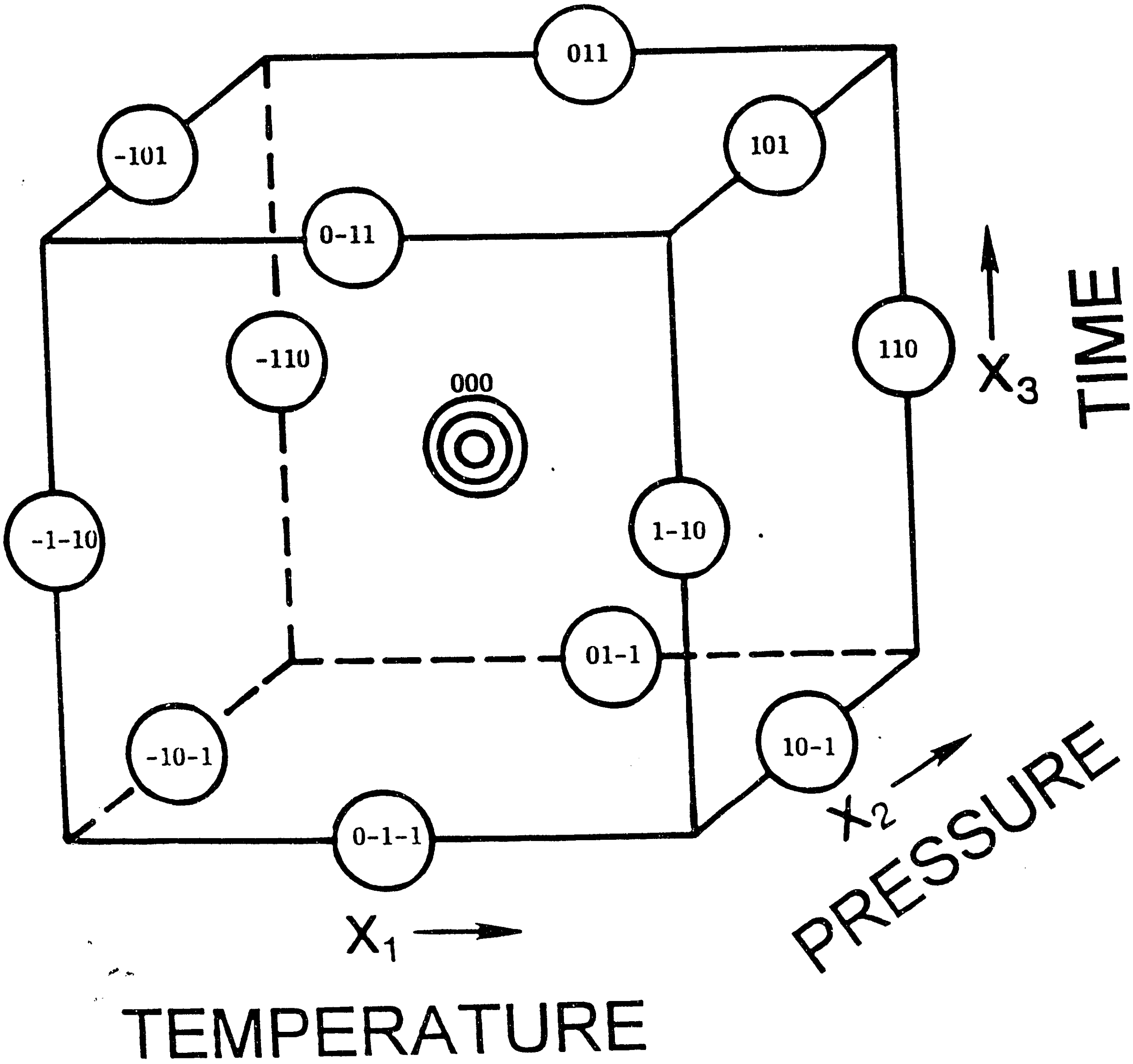
The repeat of Run DOE-5 (Run DOE-19) confirmed the maximum coal conversion of 89% under those conditions. The repeat of Run DOE-9 (Run DOE-20) gave a much higher coal conversion (80% vs 44%) confirming our belief that the coal conversion obtained originally was in error. An additional run done under these conditions (Run DOE-23) confirmed the higher coal conversion. It should be noted that the CO conversion, gas yield and hydrogen consumptions of all three Runs (DOE- 9, 20 and 23) are comparable indicating no errors in the gas sampling or analysis.

Run DOE-21 was a repeat of Run DOE-14, at the highest process severity, and showed a higher coal conversion (83% vs 73%), more in line with the expected results. Again it should be noted that the CO conversion, gas yields and hydrogen consumption are in close agreement between Runs DOE-14 and DOE-21. Petrographic analysis indicated that there was a possible mixing problem during Run DOE-14 resulting in poorer coal conversion than expected.

Agglomerates were prepared from Black Thunder coal and run in the

Figure 1:

EXPERIMENTAL MATRIX



LEGEND			
	T	Temperature	-1 = 370, 0 = 390, +1 = 410 oC
	P	Pressure	-1 = 400, 0 = 600, +1 = 800 psi CO initial
	t	Time	-1 = 0 , 0 = 30 , +1 = 60 minutes

Figure 2:

COAL CONVERSION

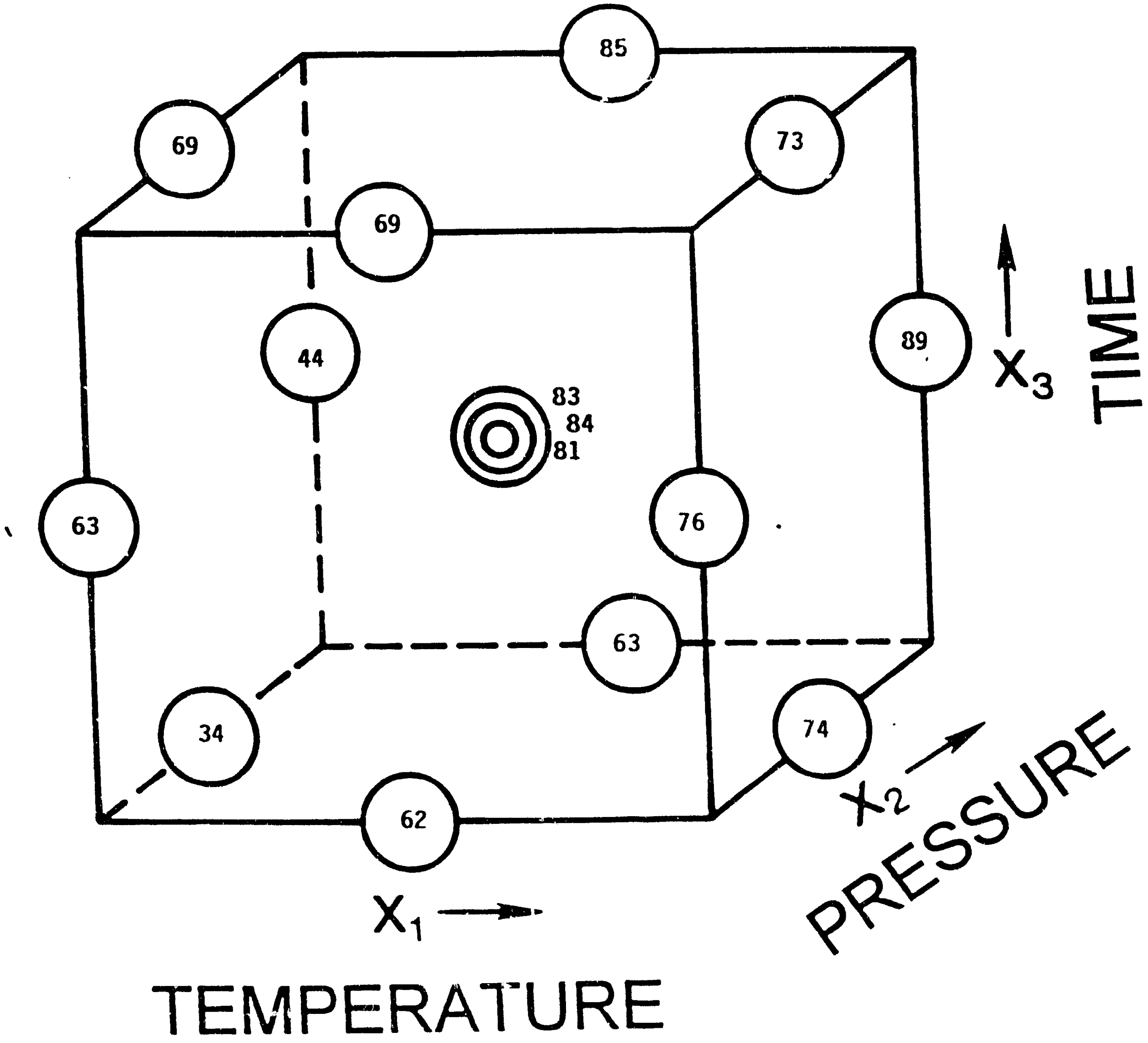


TABLE 4 AUTOCLAVE MATRIX PROGRAM

RUN #	RUN CONDITIONS			COAL CONV	CO CONV	GAS YIELD	H2 CONS
	T	P	t	%	%	g/100g	g/100g
DOE-04	1	-1	0	76	84	2.9	1.3
DOE-05	1	1	0	89	83	2.8	2.1
DOE-06	0	0	0	83	79	1.3	1.6
DOE-07	0	1	1	85	84	1.7	2.1
DOE-08	-1	0	-1	34	33	0.2	0.9
DOE-09	-1	1	0	44	70	0.5	1.4
DOE-10	0	-1	1	76	74	1.4	1.3
DOE-11	0	-1	-1	62	42	0.4	0.6
DOE-12	0	0	0	84	73	2.4	0.1
DOE-13	1	0	-1	74	64	1.0	1.1
DOE-14	1	0	1	73	87	4.7	1.7
DOE-15	-1	-1	0	63	71	0.8	1.2
DOE-16	-1	0	1	69	65	0.9	1.2
DOE-17	0	0	0	81	79	1.7	2.1
DOE-18-1	0	1	-1	63	51	0.3	1.3

LEGEND

T Temperature -1 = 370, 0 = 390, +1 = 410 oC

P Pressure -1 = 400, 0 = 600, +1 = 800 psi CO initial

t Time -1 = 0, 0 = 30, +1 = 60 minutes

TABLE 5 AUTOCLAVE MATRIX PROGRAM

REPEATS

RUN #	RUN CONDITIONS			COAL CONV	CO CONV	GAS YIELD	H2 CONS	NOTES
	T	P	t	%	%	g/100g	g/100g	
DOE-19	1	1	0	89	82	2.2	1.6	Rep 5
DOE-20	-1	1	0	80	65	0.6	1.2	Rep 9
DOE-21	1	0	1	83	85	4.5	1.7	Rep 14
DOE-22	400	1.15	0	81	73	2.1	2.2	
DOE-23	-1	1	0	76	67	0.5	1.3	Rep 9
DOE-24	0	0	0	83	79	1.4	1.6	Agglom
DOE-28	0	0	0	88	78	1.4	1.4	V-1074

LEGEND
T Temperature -1 = 370, 0 = 390, +1 = 410 oC
P Pressure -1 = 400, 0 = 600, +1 = 800 psi CO initial
t Time -1 = 0 , 0 = 30 , +1 = 60 minutes

autoclave instead of coal at centre point conditions (Run DOE-24). The only difference here was the lower ash content of the agglomerates vs the coal (about 10% lower). This difference clearly had no effect on the process performance, coal conversion, CO conversion, gas yield and hydrogen consumption being very consistent with the data from Runs DOE-6 and DOE-17. The gas data from Run DOE-12 was known to be in error due to contamination, so cannot be compared.

Black Thunder coal was also run with the V-1074 blend Wilsonville solvent under centre point conditions (Run DOE-28). In this case the V-1074 blend appeared to give a slightly higher coal conversion, but the other data was again in close agreement with previous results at the same conditions. A more complete analysis of the behaviour of the new solvent is planned for the next quarter, prior to the start up of the bench scale unit. This initial result indicates that the solvent will, if anything, be better for coal solubilization than the V-178 solvent used for the autoclave matrix program. Therefore, conditions picked for the bench scale program for the first stage based on the autoclave matrix results should be on the conservative side.

Following the repeats of some of the runs in the matrix program the revised coal conversions are presented in graphical form in Figure 3. The statistical analysis presented in the last quarterly report was also revised and the comparisons are shown in Table 6. The analysis shows that a second order least squares regression gave a much better fit as in the initial case. However, the CO pressure term is much more significant in the revised fit than in the original data, although still less significant than temperature or time. The fit and residuals suggest that the low severity condition DOE-8 gave much lower coal conversion than expected. Also, since the centre points are also lower than the fitted values interaction between the variables may be occurring.

The CO conversions, gas and oil yields and hydrogen consumptions obtained from the matrix program are shown graphically in Figures 4-7. The data will be analyzed in more detail later.

TABLE 6 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

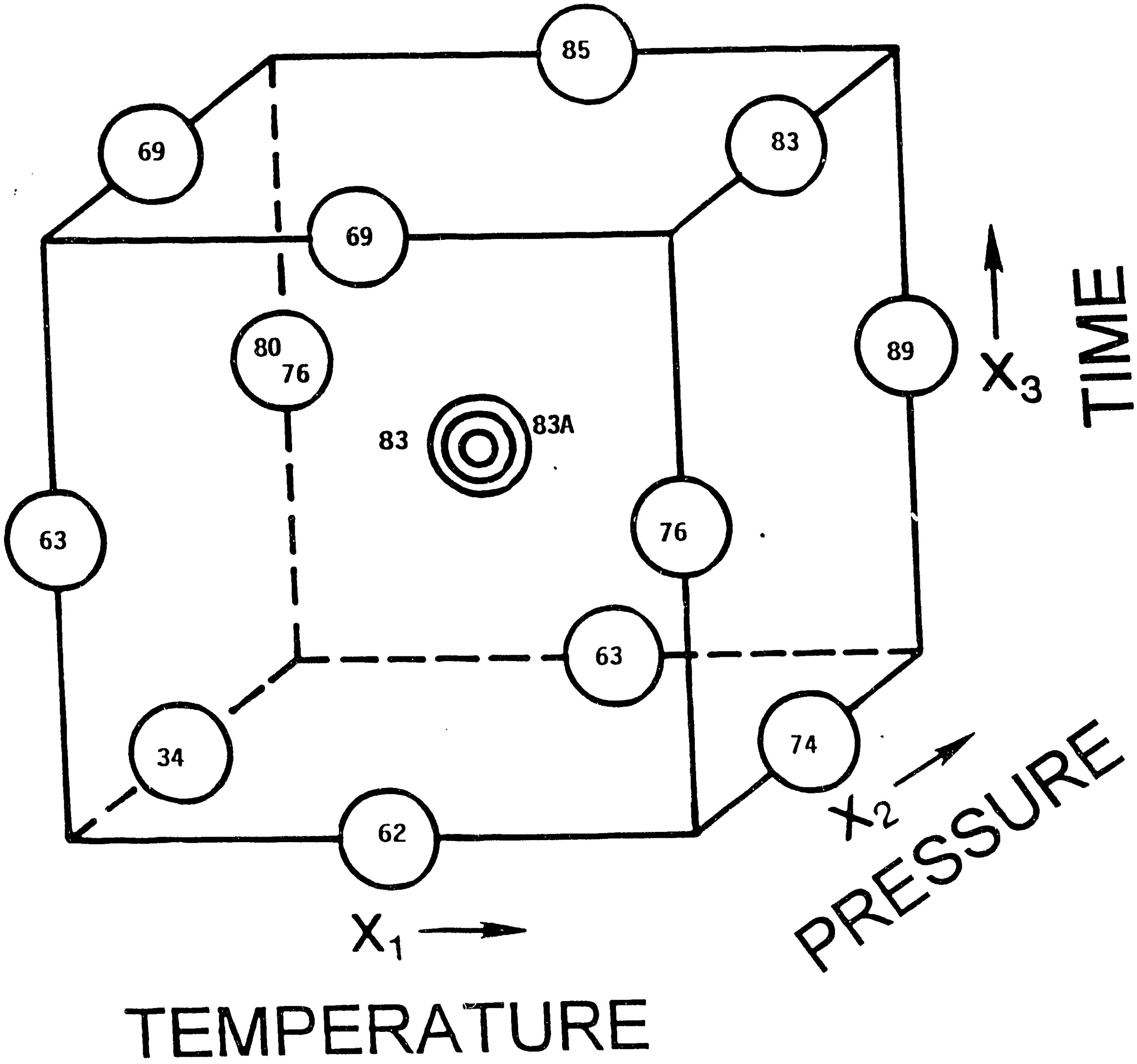
	INITIAL	REVISED
LINEAR	12.7T + 0.5P +8.7t + 70.4	10T +4.5P + 10t + 73.2
QUADRATIC	82.7 + 12.7T + 0.5P + 8.7t + 8T*P - 9T*t + 2P*t - 11T**2 - 2.8P**2 - 8.3t**2	82.6 + 10T + 4.5P + 10t - 6.5T*t + 2P*t - 6.6T**2 - 0.1P**2 - 11.1t**2

LEGEND

T	Temperature	-1 = 370, 0 = 390, +1 = 410 oC
P	Pressure	-1 = 400, 0 = 600, +1 = 800 psi CO initial
t	Time	-1 = 0 , 0 = 30 , +1 = 60 minutes

Figure 3:

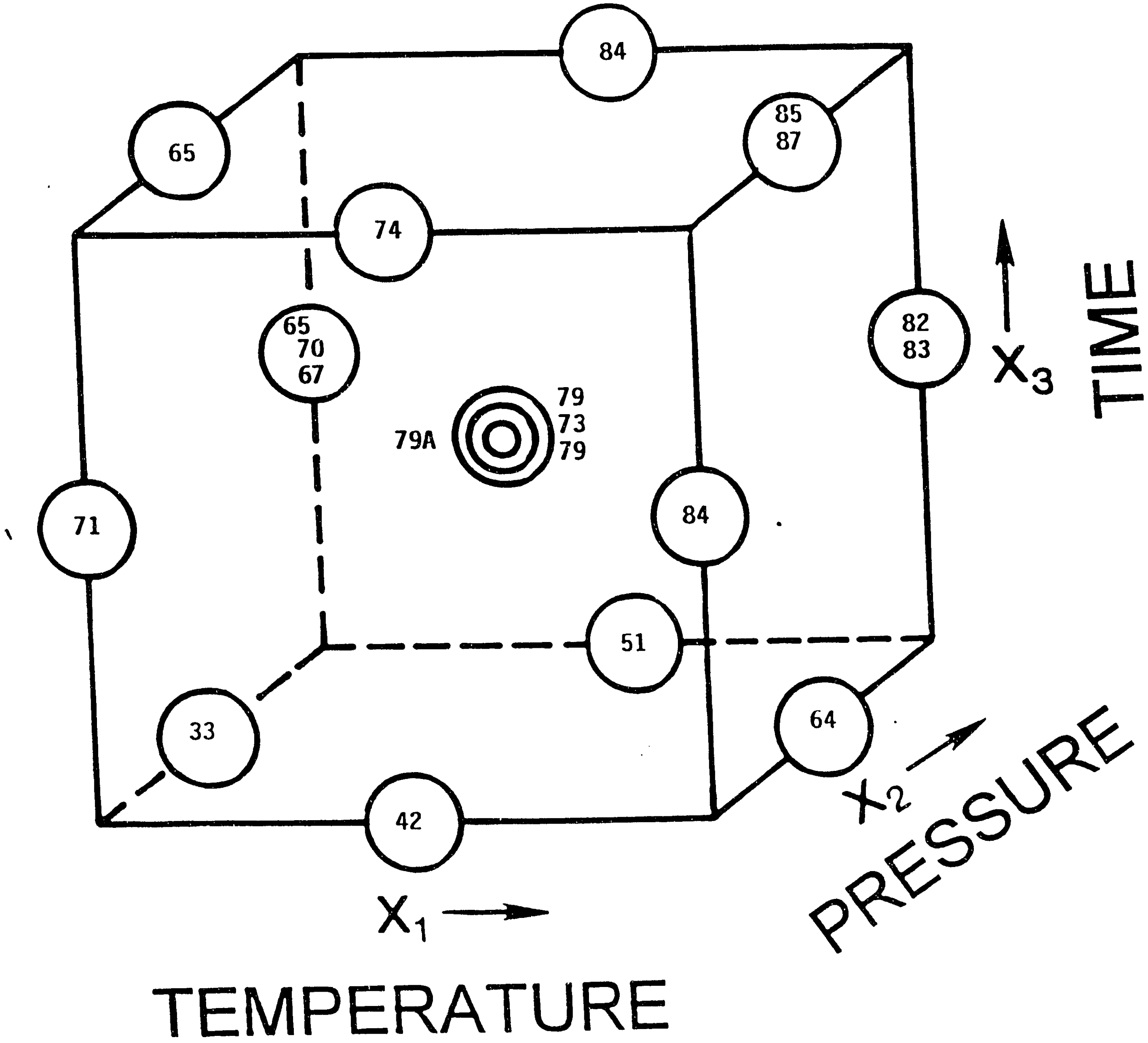
REVISED COAL CONVERSION



A = Run with agglomerates as feed

Figure 4:

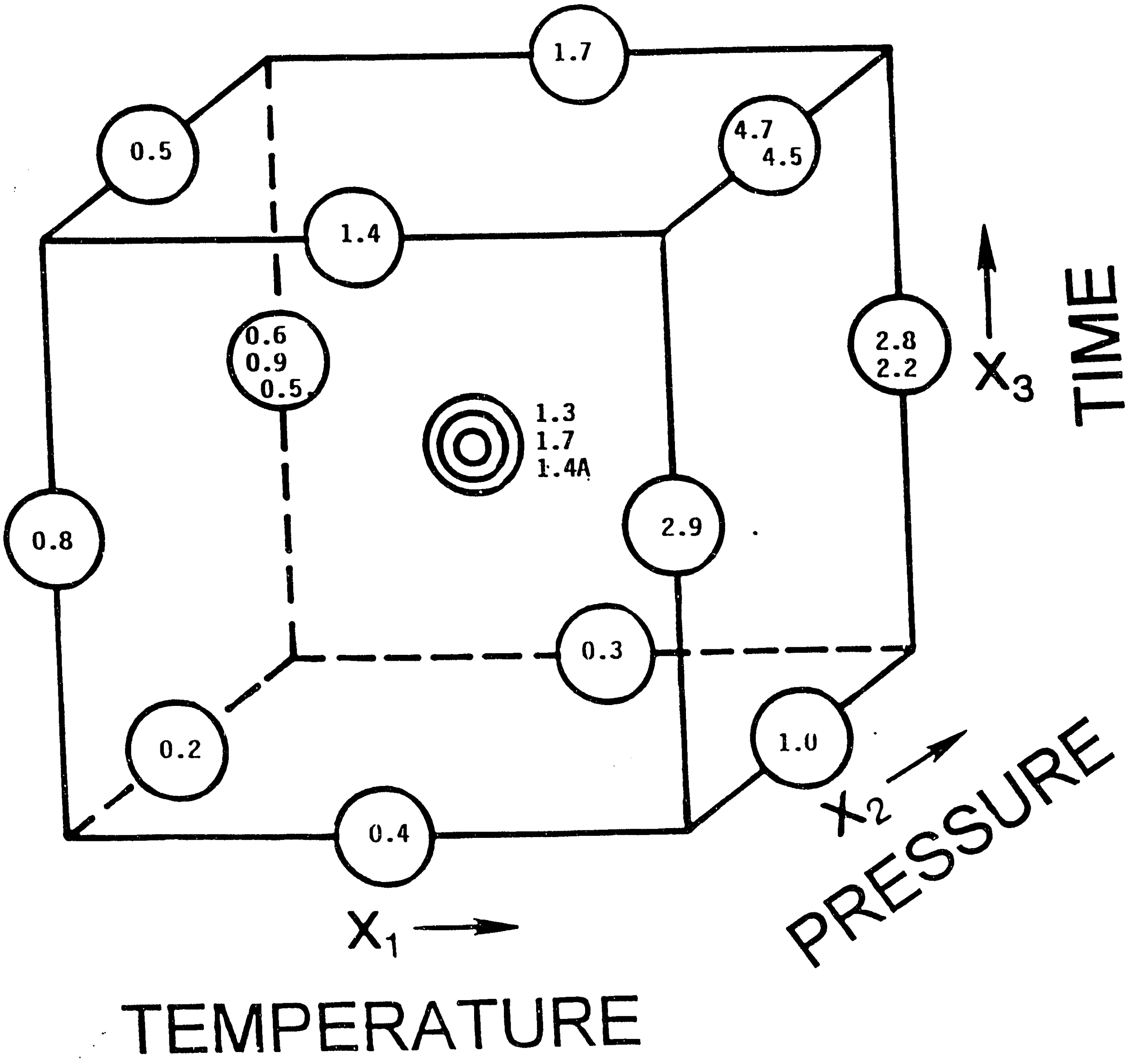
CO CONVERSION



A = Run with agglomerates as feed

Figure 5:

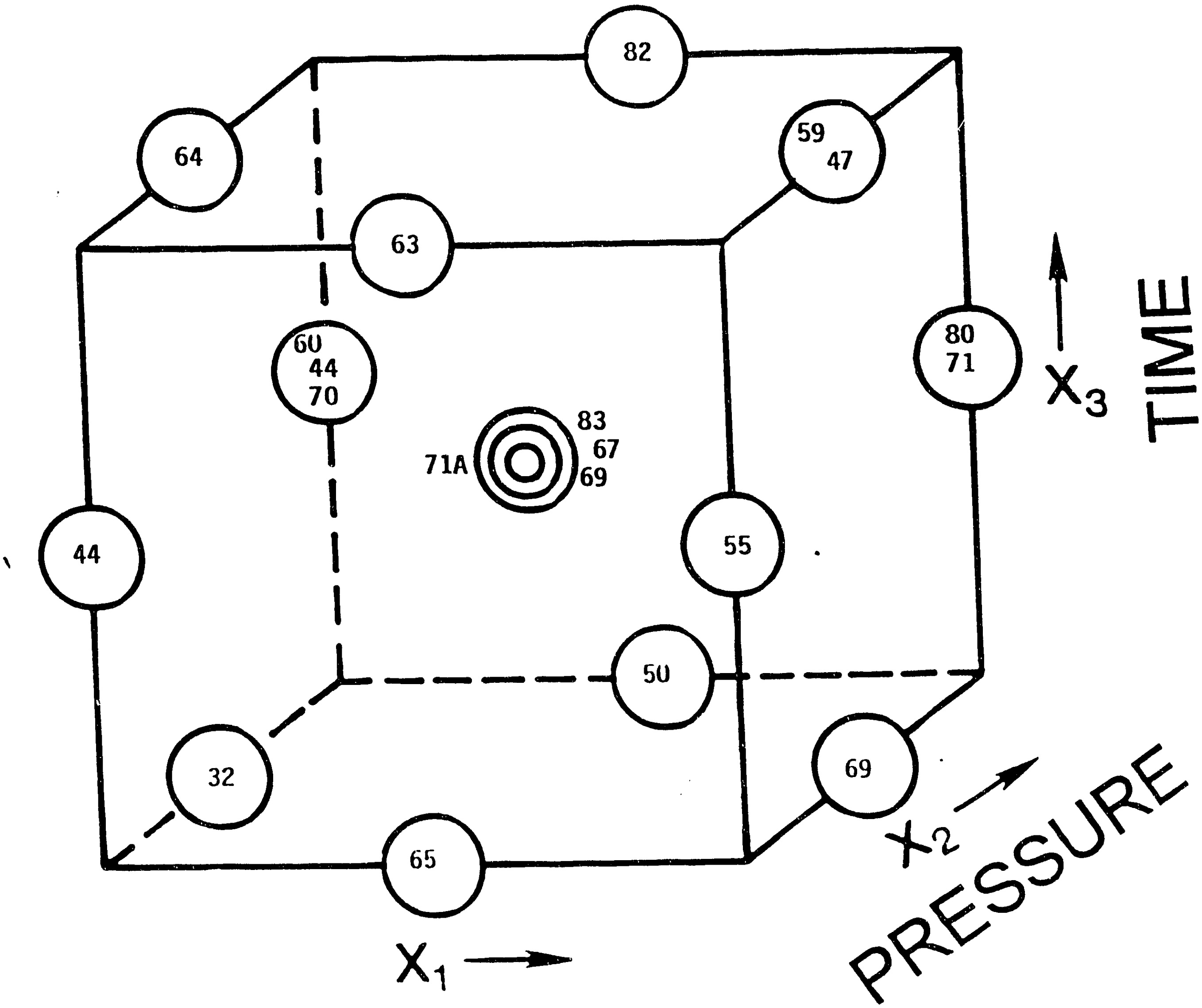
GAS YIELD



A = Run with agglomerates as feed

Figure 6:

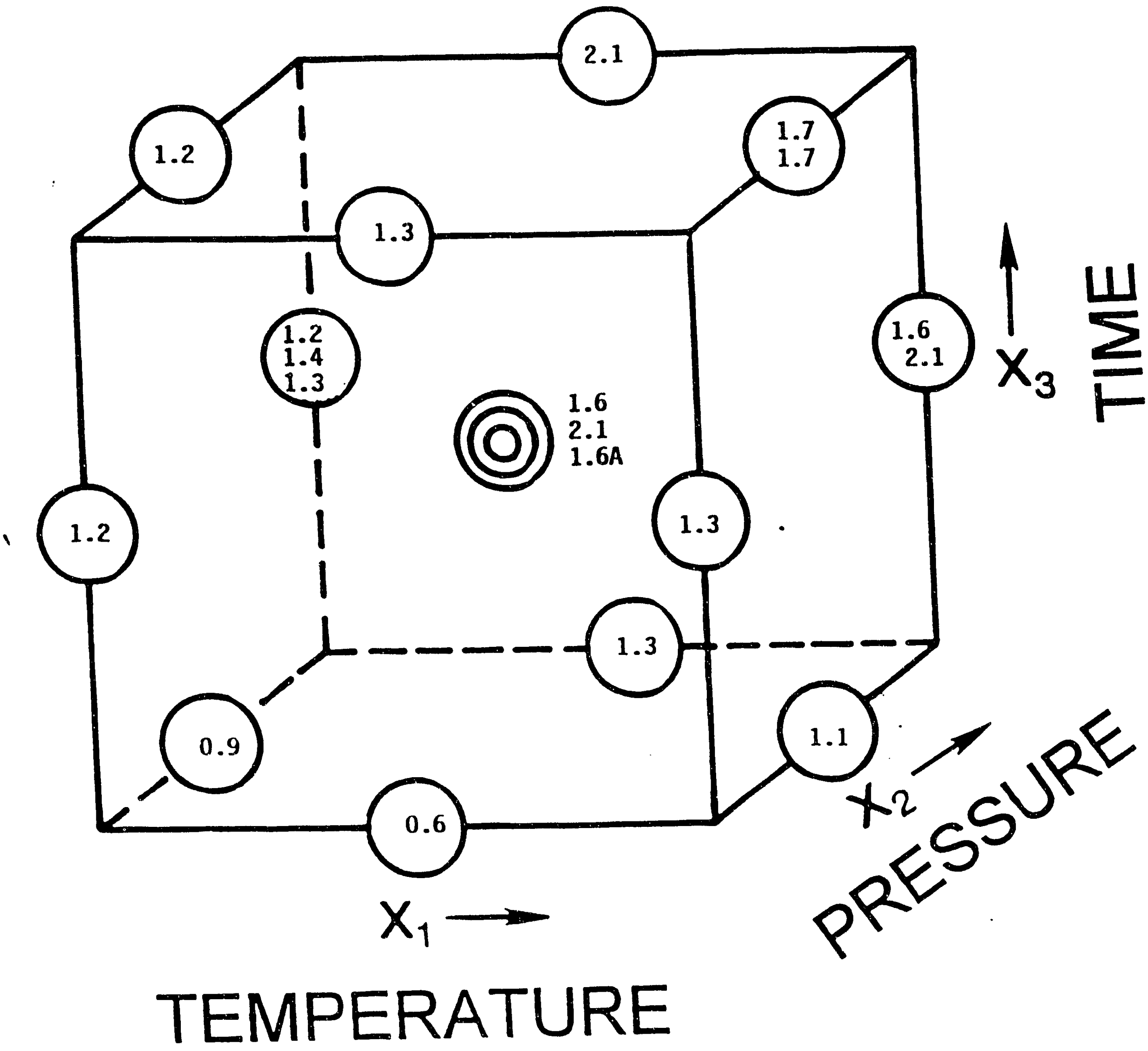
OIL YIELD



A = Run with agglomerates as feed

Figure 7:

HYDROGEN CONSUMPTION



A = Run with agglomerates as feed

One other variable was examined this quarter, the effect of catalyst. A series of autoclave runs were performed at centre point conditions using no catalyst, iron sulphide catalyst and sodium aluminate catalyst, Runs DOE-25, DOE-26 and DOE-27, respectively. The results, which should be compared with Runs DOE-6, DOE-12 and DOE-17 where the catalyst was potassium carbonate, are shown in Table 7. Clearly, coal conversion appeared to be unaffected by catalyst, however, the CO conversion and consequently hydrogen consumption was greatly reduced. Therefore, while the coal is solubilized, the quality of the produced oils is greatly reduced and presumably would require much more upgrading in the second stage. The viscosity of the oil from these runs, especially the one without catalyst, was noticeably higher than from corresponding potassium carbonate runs.

3.2.2 Hydrogen Consumption and Oxygen Removal

The question of the quality of the oil produced in the first stage is an important issue since it has a direct bearing on the process severity and hydrogen consumption required in the second stage. The hydrogen and oxygen contents of the first stage oil product is therefore important. These values particularly the oxygen content are difficult to determine accurately on the oils themselves due to the error factors involved in the analytical procedures. Therefore demonstrating differences due to processing poses a problem. Therefore, an effort was made to obtain a semi-quantitative estimate of hydrogen consumption and oxygen removal based on the observed gas analyses.

The consumption of carbon monoxide during an autoclave run was readily determined from a knowledge of the amount of gas loaded initially into the autoclave and analysis of the product gases. The amount of water present initially was also accurately known (from the water content of the coal and added water). From the water gas shift reaction stoichiometry, the amount of water consumed, and the amount of carbon dioxide and hydrogen produced based on the known consumption of carbon monoxide is readily calculated. The difference between the amount of hydrogen produced from carbon monoxide consumption and that observed in the product gas represents the hydrogen

TABLE 7 AUTOCLAVE PROGRAM

CATALYST EVALUATION

RUN #	RUN CONDITIONS				COAL CONV		CO CONV		GAS YIELD		H2 CONS	NOTES
	T	P	t		%		%		g/100g		g/100g	
DOE-06	0	0	0		83		79		1.3		1.6	K2CO3
DOE-25	0	0	0		78		9		1.3		0.08	No cat
DOE-26	0	0	0		81		7		1.4		0.04	FeS
DOE-27	0	0	0		82		44		1.4		1.1	NaAlO2

LEGEND
T Temperature -1 = 370, 0 = 390, +1 = 410 oC
P Pressure -1 = 400, 0 = 600, +1 = 800 psi CO initial
t Time -1 = 0, 0 = 30, +1 = 60 minutes

consumption. Some of this hydrogen is used to produce hydrocarbon gases (methane, ethane, propane and butanes). This amount can also be calculated from the product gas streams. The remaining hydrogen consumed, therefore, must be retained by the produced oils or THF insolubles. Similarly the difference between the amount of carbon dioxide observed in the produced gas and that produced from consumption of carbon monoxide must come from the coal (or possibly a small amount from the solvent or potassium carbonate). The amount of oxygen removed can therefore, be calculated. One other key item in the determination of oxygen removal, however, is water. The amount of water consumed by the water gas shift reaction is readily determined from the amount of carbon monoxide consumed. Having accounted for this consumption, if more water is found in the products than was initially fed to the autoclave, this indicates further oxygen removal from the coal. If on the other hand, a deficiency of water is observed, there exists the probability of reaction of coal fragments with water to produce phenols or other oxygenates which would appear in the non-gaseous products. Observed oxygen removal in this case would be lower.

Therefore, from an analysis of the gas data from the autoclave runs, a semi-quantitative estimate of hydrogen incorporation into and oxygen removal from the non-gaseous products can be made. The results showed that, when adjusted for overall mass balance, excess carbon dioxide was produced in all runs even those at the lowest severity. The amounts corresponded from 50% to 100% removal of the oxygen contained in the coal. However, in most cases, there was also loss in water indicating possible incorporation of oxygen into the product or from water. No consistent relationship to process conditions for these effects could be established.

Clearly in the first stage of this process, maximizing hydrogen incorporation and oxygen removal from the non-gaseous products is desirable both to achieve coal solubilization and to reduce the hydrogen requirement of the second stage.

An evaluation of the various autoclave runs was therefore carried out in which coal conversion, hydrogen uptake and oxygen removal were rated as high, medium and low.

	High	Medium	Low
Coal Conversion	>80% +	70 - 80%	<70% -
Hydrogen Uptake	>1.2% +	0.6 - 1.2%	<0.6%
Oxygen Removal	>75% +	40 - 75%	<40% -

Runs DOE-9 and DOE-12 were disregarded because of the known problem with coal conversion (Run DOE-9) and gas analysis (Run DOE-12). The results are shown in Table 8. It is interesting to note that the only runs meeting the criteria of high coal conversion and medium or high hydrogen uptake and oxygen removal were runs where the temperature was 390°C or above, the time was 30 minutes or above, the carbon monoxide initial pressure was 600 psig or above, and potassium carbonate was used as catalyst (Table 9).

This information, therefore, helps to set the conditions for the first stage of the process. One cautionary note, however, should be made on severity. A study of the time/temperature function on coal conversion shows that a maximum exists (Figure 8) and indicates that too high a severity in terms of temperature and time leads to retrograde reaction and a lower coal solubilization. The oil yield data (Figure 6) also confirm this observation. The window for optimum operation of the first stage would therefore appear to be quite small.

3.2.3 Analysis of Produced Oils

A few samples of produced oils were analyzed to try to determine the oxygen content of these products (by difference). The results (Table 10) indicate that the whole oil product has an oxygen content of about 5 wt%, the distilled oils range from 2.5 - 3.5 wt% and t non-distillable oils about 7 wt%. This compares with an estimated oxygen content of 1.2% wt in the original solvent.

TABLE 8

AUTOCLAVE DATA

RUN EVALUATION

RUN NO.	COAL CONVERSION	HYDROGEN UPTAKE	OXYGEN REMOVAL
DOE-4	M	M	M
DOE-5	H	H	M
DOE-6	H	H	H
DOE-7	H	H	M
DOE-8	L	M	L
DOE-10	M	M	M
DOE-11	L	L	L
DOE-13	M	L	L
DOE-14	M	M	H
DOE-15	L	M	H
DOE-16	L	M	L
DOE-17	H	H	M
DOE-18	L	H	M
DOE-19	H	M	H
DOE-20	M	M	M
DOE-21	H	M	H
DOE-22	H	H	M
DOE-23	M	M	M
DOE-24	H	H	M
DOE-25	M	L	M
DOE-26	H	L	L
DOE-27	H	M	L
DOE-28	H	M	M

CRITERIA:	HIGH	MEDIUM	LOW
COAL CONVERSION	80%+	70 -80%	70%-
HYDROGEN UPTAKE	1.2%+	0.6 -1.2%	0.6%-
OXYGEN REMOVAL	75%+	40 -75%	40%-

TABLE 9

AUTOCLAVE DATA

RUNS MEETING CRITERIA:

TEMPERATURE	390C+
PRESSURE	600 PSI (COLD)+
TIME	30 MINS.+
CATALYST	K2CO3 (2% ON COAL/SOLVENT)

RUN NO	TEMP (C)	PRESS (PSI)	TIME MINS	COAL CONVERSION	HYDROGEN UPTAKE	OXYGEN REMOVAL
DOE-5	410	800	30	89	H	M
DOE-19	410	800	30	89	M	H
DOE-21	410	600	60	83	M	H
DOE-14	410	600	60	73	M	H
DOE-22	400	930	30	81	H	M
DOE-7	390	800	60	85	H	M
DOE-6	390	600	30	83	H	H
DOE-17	390	600	30	81	H	M
DOE-24	390	600	30	83	H	M
DOE-28	390	600	30	88	M	M

ADDITIONAL RUN IF PRESSURE CRITERION IS REDUCED TO 400 PSI (COLD)+

DOE-10	390	400	60	76	M	M

Figure 8:

TEMPERATURE/TIME FUNCTION

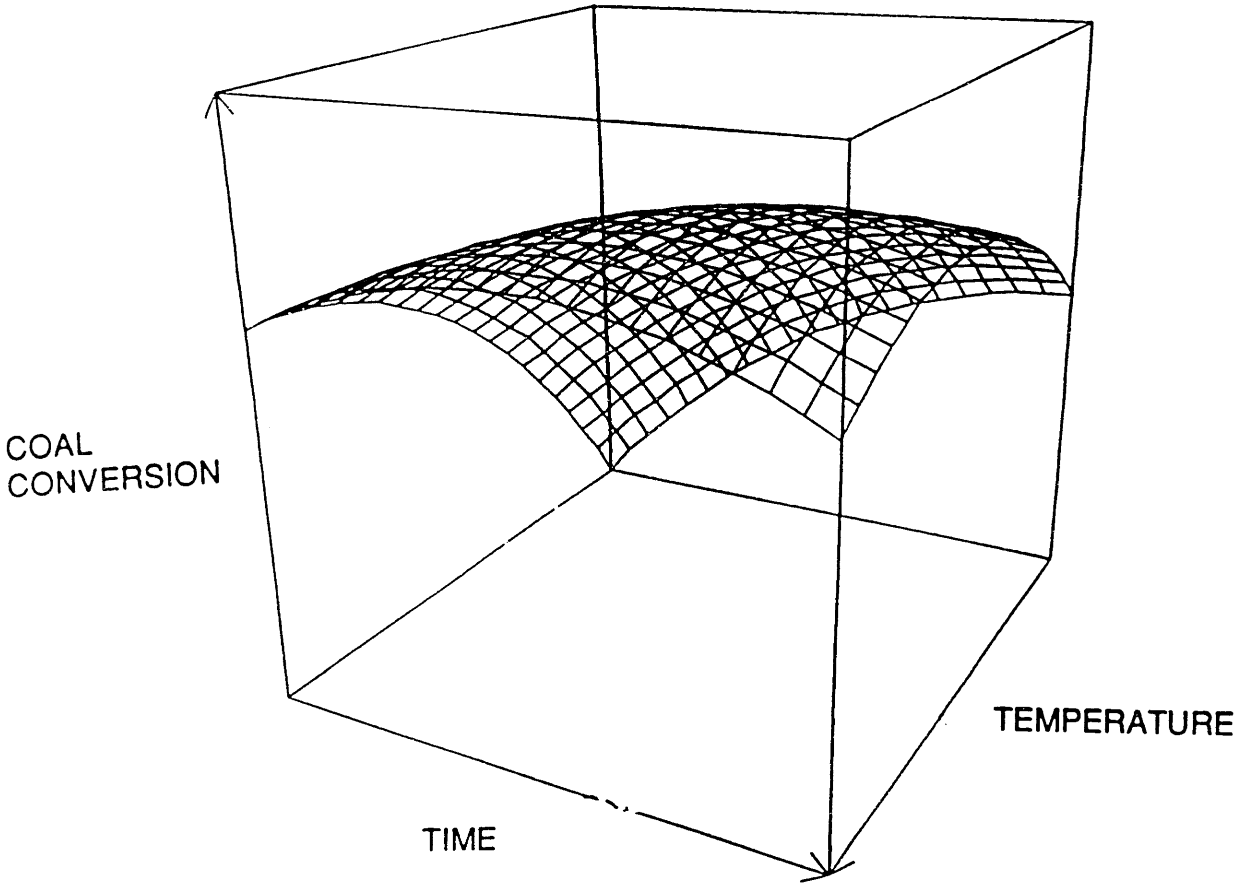


Table 10: Analysis of Produced Oils

Distilled Oils

	DOE-17	DOE-25	DOE-26	DOE-29
C	86.3	86.3	86.8	87.2
H	9.9	9.8	9.6	9.7
N	0.5	0.4	0.4	0.5
O (diff)	3.3	3.5	3.2	2.6

Residual Oils

	DOE-25	DOE-26	DOE-29
C	84.1	84.2	84.4
H	7.0	7.1	7.4
N	1.5	1.5	1.3
O (diff)	7.4	7.2	6.9

Whole Oil

	DOE-19
C	85.1
H	9.4
N	0.7
O (diff)	4.8

3.2.4 Characteristics of Solid Residues

The solid residues (THF insolubles) from the autoclave program are routinely characterized by proximate analysis to determine coal conversion. Petrographic analysis can also provide information on the process chemistry and efficiency of coal solubilization. Representative residues were characterized by petrography for the following purposes:

1. to indicate the occurrence of regressive reactions
2. to assist in the explanation of unusual results, and
3. to determine the maximum possible coal conversion

A full report of the petrographic analysis is given in the Appendix.

In Table 11 the raw data is listed in decreasing order of vitroplast content i.e. the reactive components of the coal. When these results are compared with the extent of coal conversion the following observation are apparent: the coal conversion achieved in Runs DOE-13 and DOE-14 are out of sequence, as can be seen by Figure 9. DOE-14 has previously been identified from statistical assessment as having a lower than expected coal conversion. The residue showed no sign of regressive reactions (presence of coke or mesophase) but the unusually high ash content suggests a mixing problem in the autoclave. DOE-13 fitted the statistical model and no suitable explanation can be given for its petrographic characteristics.

The results were also compared on the basis of quantity of component remaining in the unconverted coal i.e. g component * percentage of unconverted coal/100 g feed. This data is also included in Table 11 and plotted against coal conversion in Figure 10. The amount of inertinite remaining is essentially constant for all residues (except DOE-13 and DOE-14) at 10.1± 1.2 g/100g feed. Thus, the maximum coal conversion should be close to 90% for the Black Thunder coal. Part of the inertinite should be categorized as semi-inertinate since about 6% has been converted. The plot

TABLE 11 PETROGRAPHIC ANALYSIS

RUN #	COAL CONV %	INERTINITE	VITROPLAST	INERTINITE	VITROPLAST
		% in IOM , ash free		g/100g feed	
FEED	0	18.3	81	18.4	81.6
DOE-8	34	16	84	10.6	55.4
DOE-9	44	21	79	11.8	44.2
DOE-15	63	26	74	9.6	27.4
DOE-18-1	63	30	79	11.1	25.9
DOE-16	69	31	70	9.6	21.4
DOE-14	73	51	49	13.8	13.5
DOE-13	74	21	79	5.5	20.5
DOE-4	76	47	53	11.3	12.7
DOE-17	81	52	48	9.9	9.1
DOE-7	85	58	42	8.7	6.3
DOE-5	89	76	24	8.4	2.6

FIGURE 9 PETROGRAPHIC ANALYSIS

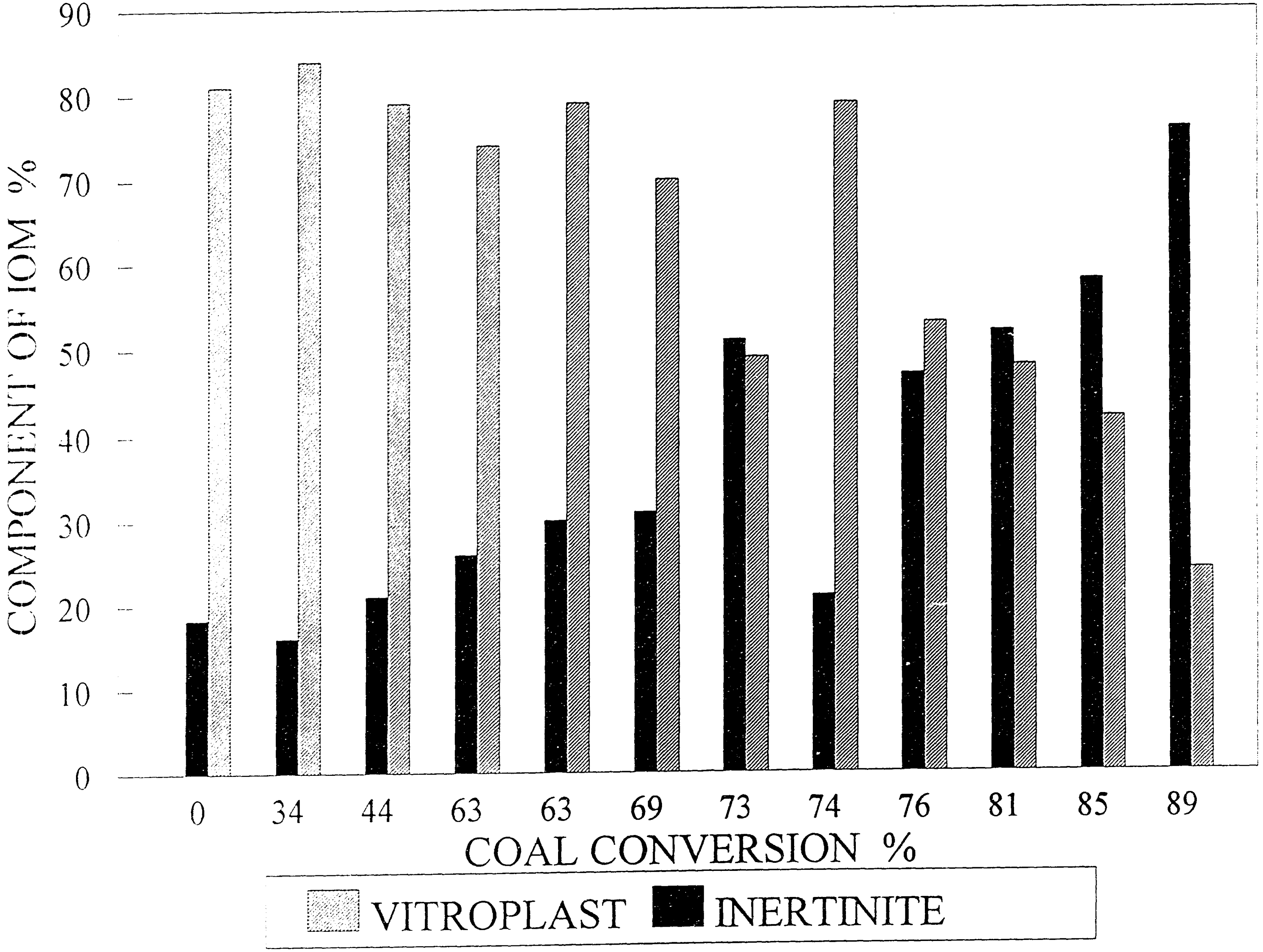
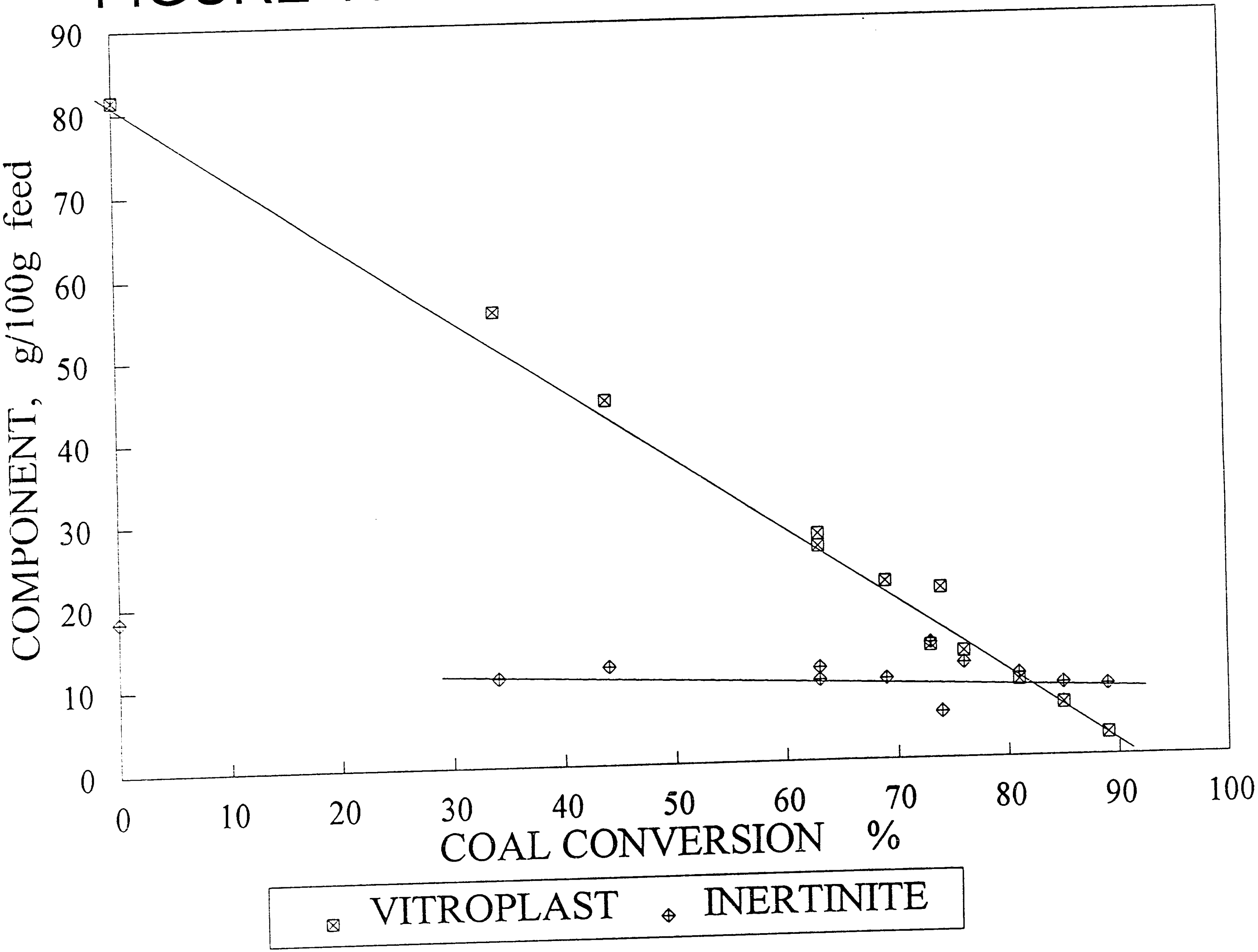


FIGURE 10 PETROGRAPHIC ANALYSIS



of the vitroplast versus coal conversion is quite linear and at the maximum conversion the vitroplast has virtually disappeared. Thus, increasing the process severity would do little to enhance coal solubilization or overall process performance.

3.3 Bench Unit

3.3.1 Modifications

As the modification of the bench unit proceeded, the P&ID's were updated. In the meantime, the safety review of the P&ID's has been completed and only very minor modifications on the flare system and the high pressure gas supply are required.

After the prefabricated structural steel had been installed, all major equipment items and the control panels for the high pressure gas supply and for the gas let down system have been installed. Installation of the main process piping is about 90% complete. The first, preliminary pressure test with nitrogen of the control panels for the high pressure gas supply and for the gas let down system has been completed successfully.

Installation of electrical and instrumentation is about 85% complete. Preliminary checking of instrument and control loops has started. The heating mantels for the counter-flow reactors had to be returned to the supplier as they were not supplied in an ex-prove design as specified. The mantels are scheduled to be returned by the supplier during the first two weeks of April 1993.

The modifications as result of the safety review of the P&ID's have been completed. Drafting of "Safe Operating Procedures" (SOP) has begun.

Completion and start-up of the bench unit is scheduled for the week of April 26, 1993.

3.3.2 Test Program

The planning of the test program for the coal liquefaction bench unit (CL-BU) has been initiated, and the following has been proposed to and discussed with DOE:

3.3.2.1 Commissioning and Start-Up

The commissioning of the coal liquefaction bench unit (CL-BU) is scheduled for the first two weeks of April 1993. During that time, all instrument and electrical connections, control loops, and gas and cooling water systems will be tested. Also, the unit as a whole will be pressure tested (cold and hot).

After the completion of the commissioning, the CL-BU will be started up with an oil-only feed.

3.3.2.2 Operation and Evaluation

The test program is scheduled to start during the week of April 26, 1993, and will continue through to the end of March 1994. Table 3.3.1 summarizes the scheduled test program.

The main objectives of the test program with the CL-BU area:

1. to establish optimum or near optimum operating conditions for maximum yield of distillable oil,
2. to establish the yield structure at these conditions,
3. to determine the most favourable processing sequence, and
4. to formulate the basis for the economic feasibility study.

Table 3.3.1: Summary of Scheduled Test Program

Feed Material		Coal Loading	Stage No.	Operating Parameters			No. of Op. Cond.	No. of Op. Days
Coal	Oil			Op. Temp	Gas Vel.	WHSV		
BT	CS1	1	1	2	2	2	5	10
BT	CS1	1	2	3	2	2	6	10
BT	CS1	1	1 + 2	3	3	3	9	15
III	CS2	1	1 + 2	3	3	3	9	15
AG	CS2/1	1	1 + 2	2	2	2	5	10

NOTES:

BT	Black Thunder Coal
III	Illinois #6 Coal
AG	Agglomerates of BT or III
CS1	Coal Solvent for BT
CS2	Coal Solvent for III (yet to be received)

It is proposed to operate the BU continuously for one week (5 days) at a time. During each week of operation, about 2 to 3 operating conditions will be investigated. This gives a total of about 60 operating days.

For each combination of operating conditions and feed compositions, on average two mass balances are performed. Each mass balance lasts for about eight (8) hours. During the scheduled test program, about 70 mass balances are anticipated.

As results from the tests become available, the proposed test program will be modified with the objective to gather the largest and most valuable data base within the project schedule and budget.

Based on the results obtained from the autoclave program, operating conditions for the first stage CO/H_2O system (coal solubilization) will cover the following range:

System Pressure (fixed)	MPa	20
Reactor Temperature	°C	360 to 400
WHSV	kg/(l*hr)	1.0 to 3.0
CO Flow Rate	l/min	7.5 - 15
Coal Loading (fixed)	wt%	max. (40)

From experience gained during previous coal liquefaction and coprocessing studies, the following range of operation conditions is anticipated for the second, CFR stage:

System Pressure (fixed)	MPa	20
Reactor Temperature	°C	420 to 460
WHSV	kg/(l*hr)	0.80 to 1.5
Recycle plus Make-up Gas	l/min	30 to 90
Coal Loading (fixed)	wt%	max. (40)

During the first two weeks of operation, it is proposed to run BT/CS1 in one stage operation (solubilization) only. This will provide some indication on how to use autoclave test conditions and results as guidance for selecting operating conditions for the CL-BU.

For the second test sequence, it is proposed to use the same feed, but operate the CL-BU in the two stage mode for one week (with fixed conditions in the first stage) to obtain first indication with regard to yields and conversions of the proposed coal liquefaction concept.

For the third test sequence, it is proposed to only operate the second stage of the CL-BU to evaluate the benefit of the CO/H_2O stage on the overall process.

3.3.2.3 Typical Test Sequence

The following is a brief description of a typical test sequence:

To bring the unit on line, an oil-only stream is fed to the CL-BU during the first 8 hours of each test week. After the system has reached the specified operating pressure, and the reactor temperature(s) are within 20 to 30°C of the value specified for the first mass balance, the oil-only feed is replaced by the proper coal/coal-solvent slurry. The reactor temperature(s) are then increased to the specified value(s). After about 4 hours of steady state operation (verified by computer trending and CH_4 content of the product gas stream), the first mass balance is performed. Mass balances are typically performed over 8 hour periods. For each operating condition, on average two mass balances are performed.

After a change in operating conditions, the CL-BU is allowed to reach equilibrium during a minimum of 4 hours of steady state operation. This provides sufficient time to 'flush' the unit, so that product samples truly correspond to the respective operating conditions and feed composition. This mode of operation is continued for one week. During the last 8 hours, the CL-BU is allowed to cool down while first 'flushing' with heavy oil and then with a 'light' solvent for cleaning.

After each test sequence, the CL-BU will be inspected to gather information about operating phenomena, such as corrosion, erosion, coking and/or fouling etc. which normally cannot be observed during the run.

3.3.2.4 Conditions for First Test Sequence

The first week of testing is scheduled for the week of April 26, 1993. The objectives for the run are:

1. Obtain guidelines on how to transfer test results obtained with the autoclave to the

bench unit, and

2. Select first stage operating conditions (to be kept fixed) for the next test run in the directly coupled two stage configurations.

The following conditions are scheduled for Run DOE-BU-001:

- Coal Feed: Black Thunder
- Coal Loading: 40 wt% (as received)
- Catalyst K_2CO_3
- Reactor Temperature: 390°C
- Reactor Pressure: 20 MPa
- Residence Time: 60, 45, 30 minutes
- CO Feed Rate: 2 to 3 times theoretical consumption based on autoclave results

If coal conversion appears low at the first condition (60 min residence time) instead of decreasing residence time, reactor temperature will be increased to 410°C.

FUTURE WORK

During the next quarter, the following items will be completed:

1. Solvent stability tests at first and second stage conditions for the blend of the new solvent (V-1074).
2. Autoclave runs with the new solvent (V-1074) for tie points to the previous matrix study.
3. Simulated two stage tests in the autoclave unit. Feed from the first stage operation of the bench unit will also be used in second stage autoclave tests.
4. Investigation in the autoclave of syngas and other gas mixtures for first stage operation.
5. Completion and commissioning of the bench unit. Completion of three bench unit runs, including initial first stage operation only and then first and second stage operation together.

APPENDIX

REPORT

on

Petrographic Characterization of Liquefaction Residues of Black Thunder Coal

by

Thomas Gentzis

March 1993

EXPERIMENTAL PROCEDURE AND TERMINOLOGY USED

A sample of Black Thunder coal from Wyoming, U.S.A., along with eleven (11) liquefaction residual solids were prepared for petrographic characterization. The liquefaction conditions provided were as follows:

Temperature:	370 - 410°C
Pressure CO:	400 - 800 psi
Time:	0 - 60 minutes

All tests were done in autoclave and the solids were extracted with THF

The feed coal and residues were mixed with epoxy resin and molded into a pellet. The pellets were then ground and polished to give a surface suitable for microscopic examination at 640 magnification, under oil immersion. The microscope used was a Zeiss MPM II, fitted with a photomultiplier and an IBM PC. The petrographic analysis (point counting) was performed with the aid of a Swift (Model F) automatic point counter on 300 points.

The classification used in this study is the one proposed by Mitchell *et al.*, (1977) for residue components derived from the liquefaction of bituminous coals. There are two main categories of residues and, briefly, they are the following:

(1) Relatively unaltered components, which consist of coal macerals having passed through the liquefaction process with little or no alteration. Identification is usually easy because the features are similar to those of the original coal macerals.

(2) Thermally-altered components, which includes residue components of organic origin having undergone a phase change. Nearly all of these materials have had vitrinite as their precursor and their morphological features are due to the thermoplastic behaviour of the macerals. The individual components are: 'Vitroplast', Cenospheres, and Semicoke. Vitroplast results from vitrinite or huminite having passed through a plastic phase and consists of individual spherical

droplets, coalesced droplets or broad (>100 µm) formless areas which may contain inclusions of other residue components. Cenospheres form due to rapid heating of coal, are believed to result from gas production by thermal cracking, and appear as vesiculated hollow spheres composed of ribs or 'honeycomb' texture. Semicoke, on the other hand, may originate from 1) vitroplast, ii) cenospheres, or iii) non-plastic components, such as semifusinite. It can be recognized easily because of its strongly anisotropic character and its mosaic texture. Finally, inorganic components, such as clay minerals, quartz and pyrite (or pyrrhotite) are present in the liquefaction residues, often in the granular residue.

RESULTS

Sample 12-93

Feed coal BT-1 (Black Thunder coal, Wyoming, U.S.A.).

The coal is a low-rank coal (subbituminous C) and contains large amounts of huminite group macerals. These macerals are texto-ulminite, eu-ulminite, porigelinite, phlobaphinite and humodetrinite. The liptinite group is represented by the macerals liptodetrinite, sporinite and cutinite, whereas the inertinite group is represented by semifusinite, fusinite, sclerotinite and inertodetrinite.

The maceral analysis shows that the feed coal contains 68.3% huminite, 13.0% liptinite, 18.3% inertinite, with the remainder (0.3%) being mineral matter.

Sample 1-93 (DOE-4-SD)

The sample contains 42.0% vitroplast, 37.0% inertinite and 21.0% mineral matter. The photomicrograph shows large fragments of inertinite being embedded in 'soft', low-reflecting vitroplast. Inertinite cell lumens are filled with tar.

Sample 2-93 (DOE-5-SD)

The sample contains 6.3% vitroplast, 13.0% granular residue, 60.6% inertinite and 20.0% mineral matter. The photomicrographs show the presence of large quantities of broken angular inertodetrinite surrounded by clay mineral matter. Pyrolytic carbon was observed in the sample indicating the severity of the experimental conditions.

Sample 3-93 (DOE-7-SD)

The sample contains 36.6% vitroplast, 51.0% inertinite and 12.3% mineral matter. Heterogeneous (granular) vitroplast cementing angular inertodetrinite is the main feature seen in the photomicrograph. Cell lumens of inertinite are filled with tarry material.

Sample 4-93 (DOE-8-SD)

The sample contains 83.3% vitroplast, 15.3% inertinite and 1.3% mineral matter. The photomicrographs show granular (heterogeneous) vitroplast cementing sclerotinite, inertinite (fusinite) and massive (homogeneous) vitroplast containing an abundance of devolatilization vacuoles, filled with mineral matter.

Sample 5-93 (DOE-9-SD)

The sample contains 78.6% vitroplast, 20.3% inertinite and 1.0% mineral matter. The vitroplast is slightly fluorescing, contains inertodetrinite, has concave boundaries and is soluble in immersion oil. The solubility is seen in the left-hand side of the photomicrograph (vitroplast appears 'dirty' and heterogeneous).

Sample 6-93 (DOE-13-SD)

This sample contains 65.3% vitroplast, 8.0% granular residue, 19.3% inertinite and 7.3% mineral matter. The photomicrograph shows heterogeneous vitroplast, containing angular to rounded inertinite fragment and exhibiting devolatilization vacuoles.

Sample 7-93 (DOE-14-SD)

This sample contains 30.3% vitroplast, 31.0% inertinite and 39.3% mineral matter. The photomicrographs show spheres of vitroplast (cenospheres) forming a network. Inertinite and granular vacuolated vitroplast are present.

Sample 8-93 (DOE-15-SD)

The sample contains 69.6% vitroplast, 2.6% granular residue, 25.6% inertinite and 2.0% mineral matter. The photomicrograph shows massive vitroplast (grey) and vitroplast cementing inertodetrinite. Tar is visible infilling cavities in vitroplast.

Sample 9-93 (DOE-16-SD)

The sample contains 54.3% vitroplast, 24.6% inertinite and 21.0% mineral matter. The photomicrograph shows 'soft' vitroplast (grey) cementing angular, high-reflecting inertinite. Tar is also present infilling cavities in vitroplast.

Sample 10-93 (DOE-17-SD)

This sample contains 35.6% vitroplast, 39.0% inertinite and 25.3% mineral matter. Fusinite, semifusinite, pyrite and clay minerals are present, along with heterogeneous vitroplast.

Sample 11-93 (DOE-18-1-SD)

The sample contains 64.0% vitroplast, 3.0% granular residue, 29.0% inertinite and 4.0% mineral matter. Massive, homogeneous vitroplast shows devolatilization vacuoles (rounded holes) and contains angular high-reflecting inertodetrinite. The contact between homogeneous and heterogeneous vitroplast ranges from sharp to transitional.

DISCUSSION

The severity of liquefaction may be predicted following petrographic characterization, which includes photomicrographs of the liquefaction residues.

Based on the results shown in Table 2, it becomes apparent that samples DOE 5 shows the lowest percentage of vitroplast (6.3%) and the highest percentage of inertinite (60.6%). Petrographic evidence shows that pyrolytic carbon, formed from the condensation of volatile matter and indicative of high temperatures (~500°C in natural systems), is present in trace amounts. The indication, therefore, is that sample DOE 5 represents the one with the highest severity conditions.

Sample DOE 8 contains the highest amount of vitroplast (83.3%) and the lowest amount of inertinite (15.3%). This sample is representative of the mildest liquefaction conditions. The remaining samples fall in between in the following predicted order based on the morphological and textural characteristics, as seen under the petrographic microscope (see Table 1):

Table 1

Sample ID DOE	8	9	13	15	18-1	16	4	17	7	14	5
Coal conversion (%)	34	44	74	63	63	69	76	81	85	73	89
Vitroplast % (includes granular residue)	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 percentage of mineral matter present in sample.

Increasing severity during liquefaction

--->

Decreasing severity during liquefaction

<---

Table 2

Sample ID	Pellet No.	Experimental Conditions	Petrographic Composition vol %			
			Vitroplast	Inertinite	Granular Residue	Mineral Matter
DOE 4	1-93	1 -1 0	42.0	37.0		21.0
DOE 5	2-93	1 1 0	6.3	60.6	13.0	20.0
DOE 7	3-93	0 1 1	36.6	51.0		12.3
DOE 8	4-93	-1 0 -1	83.3	15.3		1.3
DOE 9	5-93	-1 1 0	78.6	20.3		1.0
DOE 13	6-93	1 0 -1	65.3	19.3	8.0	7.3
DOE 14	7-93	1 0 1	30.3	31.0		39.3 *
DOE 15	8-93	-1 -1 0	69.6	25.6	2.6	2.0
DOE 16	9-93	-1 0 1	54.3	24.6		21.0
DOE 17	10-93	0 0 0	35.6	39.0		25.3
DOE 18-1	11-93	0 1 -1	64.0	29.0	3.0	4.0
Feed Coal BT-1	12-93		68.3 *	18.3	13.0 **	0.3
			* Huminite macerals		** Liptinite macerals	

	-1	0	1
Temperature, °C	370	390	410
Pressure, psi	400	600	800
Time, minutes	0	30	60

Photomicrographs

All photomicrographs taken in reflected, white light, under oil immersion. The long axis of each photo is 240 microns.

DOE-8-SD

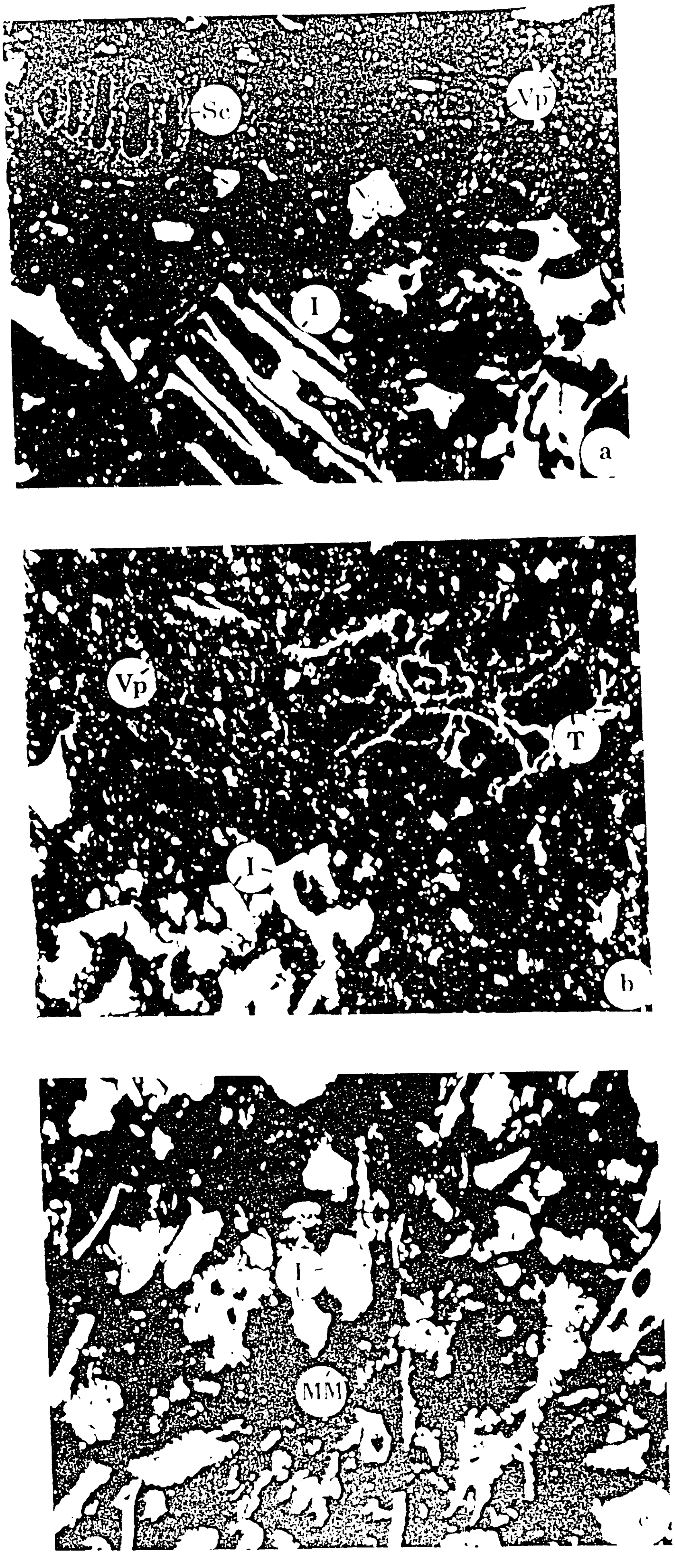
(a) The sample contains granular vitroplast (Vp), unreacted inertinite (I) and sclerotinite (Sc). This sample is of the lowest conversion.

DOE-16-SD

(b) The sample consists of broken fragments of inertinite (I), granular vitroplast (Vp) and tarry material (T) infilling inertinite cell lumens. This sample is of intermediate conversion.

DOE-5-SD

(c) The sample consists mainly of broken inertinite fragments (I) and mineral matter (MM). This sample shows the highest conversion.


Sc
Vp
I
a
Vp
T
I
b
I
MM
c

DATE

FILMED

8 / 19 / 93

END