DOE/PC/91050--T1

QUARTERLY REPORT
ADVANCED DIRECT COAL LIQUEFACTION CONCEPTS

Contract No: DE-AC22-92PC91050

Report No. QR 93/01

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

October 1, 1992 - December 31, 1992

SUMMARY

During the first quarter of FY1993, the Project proceeded close to the Project Plan.

The analysis of the feed material has been completed as far as possible. Some unplanned distillation was needed to correct the boiling range of the Black Thunder solvent used during the autoclave tests. Additional distillation will be required if the same solvent is to be used for the bench unit tests. A decision on this is still outstanding. The solvent to be used with Illinois #6 coal has not yet been defined. As a result, the procurement of the feed and the feed analysis is somewhat behind schedule.

Agglomeration tests with Black Thunder coal indicates that small agglomerates can be formed. However, the ash removal is quite low (about 10%), which is not surprising in view of the low ash content of the coal.

The first series of autoclave tests with Black Thunder coal was completed as planned. Also, additional runs are in progress as repeats of previous runs or at different operating conditions based on the data obtained so far. The results are promising indicating that almost complete solubilization (close to 90%) of Black Thunder coal can be achieved in a CO/H_2O environment at our anticipated process conditions.

The design of the bench unit has been completed. In contrast to the originally planned modifications, the bench unit is now designed based on a computerized control and data acquisition system. All major items of equipment have been received, and prefabrication of assemblies and control panels is proceeding on schedule. Despite a slight delay in the erection of the structural steel, it is anticipated that the bench unit will be operational at the beginning of April, 1993.

Despite the slight delays mentioned above, no change in the completion date of the Project is anticipated.

BACKGROUND

Conventional crude oil reserves in North America are 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 soon to be commissioned Husky Lloydminster plants. The continent, however, also possesses vast quantities of coal which have the potential to be converted to liquid fuels to replace those from conventional crudes. With world conventional crude oil prices at less than $20/barrel, the production of liquid fuels from heavy oil and coal cannot be currently justified 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.

In coal liquefaction, there has been steady progress in this regard. Using recently developed two-stage liquefaction technology it is estimated that liquid fuels produced from coal would be competitive with crude oil at $33/barrel. Integration of innovative process steps into new advanced processes have the potential to reduce costs even further. It is with this objective in mind that Canadian Energy Development Inc. and the Alberta Research Council, supported by the U.S. Department of Energy, are engaged in the current project.

For this project, two key technologies are to be coupled: carbon monoxide/steam will be used to solubilize and remove some heteroatoms from the coal, and the liquid product from this unit will be further hydrogenated using a counter-flow reactor system developed by Canadian Energy Developments Inc. Alberta Research Council agglomeration technology may be used initially to deash the coal if it is established that this would be economically beneficial.

A one kilogram per hour integrated continuous flow bench scale unit will be constructed at the Alberta Research Council site in Devon, Alberta based on modifications to a unit located at Nisku, Alberta. This unit has been used for both coal liquefaction and coal/oil coprocessing work. This modified unit, which will integrate the carbon monoxide/steam unit with the counter-flow hydrogenation reactor system, will generate data which will allow a preliminary economic evaluation to be made. The features of this process which are expected to lead to improved economics are:

1. lower gas, higher liquid yields.
2. lower operating costs through more efficient heat utilization.
3. minimal catalyst costs.

Laboratory and autoclave studies done prior to, and in support of the bench scale unit operation will provide basic information to determine the optimum operating parameters for the continuous unit.

Much work has been done on agglomeration and carbon monoxide/steam technologies over the years at Alberta Research Council and elsewhere. Recent work at the University of Kentucky has provided an excellent review of the status of the carbon monoxide/steam technology. The work in this project is aimed at defining the effects of key parameters on coal solubility, carbon monoxide conversion, heteroatom removal and product quality using the feedstocks that will be used in the continuous unit. It is not certain at this point that maximum coal solubility is required in the first stage to provide the best operating scenario. Obtaining the correct balance of conversion between the first and second stages for optimum economic benefit will be a key objective for the bench scale study. A detailed knowledge of the effects of various parameters on the product slate from the first stage is therefore required. This information will be provided by the autoclave study.

The work completed in this quarter is discussed in detail in the following sections.

EXPERIMENTAL PROGRAM

Task 2 Feedstocks

2.1 Procurement

Representative bituminous and subbituminous coals were procured from two mine sites in Illinois and Wyoming, respectively, (Table 1). The bituminous coal had been washed prior to shipment. Two processed derived oils from coal liquefaction operations were also obtained (see also Table 1). The properties of these oils did not match the preferred solvent characteristics; therefore, enquiries were made for alternative sources of solvent. NEDO (Japan) did not have any oils available for this purpose. British Coal had processed derived oils but these proved prohibitively expensive. They also offered to provide anthracene oil, but previous work at ARC has showed that unhydrotreated anthracene oil is an inferior coal liquefaction solvent because of its low hydrogen donating capability. Ultimately the search for a suitable solvent ended when DOE released several barrels of Wilsonville oil derived from Black Thunder coal (this oil had not arrived during this quarter). The solvent to be used with the Illinois #6 coal has yet to be determined.

Table 1: Source of Coal and Oil Feedstocks

	DOE-BT	DOE-Ill#6	DOE-V178	DOE-LO-6050
Source	ARCO Black Thunder mine	Consol, Inc.	Wilsonville	HRI
Nature	Subbituminous Coal	Bituminous washed Coal	process derived oil ex Black Thunder Run #263	process derived oil ex Black Thunder
Quantity	2 x 5 gallon pails 4 barrels	4 barrels	3 barrels	2 x 5 gallons
Characterization	Complete	None	Complete	Complete

2.2 Analysis and Preparation

2.2.1 Coals

During this quarter the program concentrated exclusively on the Black Thunder coal; hence, the Illinois #6 coal was stored as received. Standard laboratory inspections were performed on the Black Thunder coal following crushing, pulverizing and partial drying.

Properties of the Black Thunder coal are given in Table 2. The ash content, sulphur and oxygen are typical of the values reported by Wilsonville[1]. The thermal gravimetric analyzer plots are also recorded in Appendix A. Petrographic and infrared analyses will be described in a later report.

2.2.2 Oils

A profile of the properties which best represented the ideal solvent for use in the ARC/CED Direct Coal Liquefaction concept was drawn up. This profile included boiling range (350-525°C), hydrogen donor activity, aromaticity and origin. Hydrogen donor properties (hydroaromatics) and aromaticity have been studied by many authors including Burke[2], Sato[3] and Awadalla[4], as well as the Alberta Research Council[5]. In the absence of hydrogen, the aromaticity of the solvent should be within the range, fa 0.3 - 0.8 for 3 ring structures and fa 0.4 - 0.8 for 4 ring structures. ARC has found that 50 - 60% of hydrocarbons should be aromatic and at least 45% hydroaromatic to prevent coke formation during donor solvent resid upgrading. Finally, from a compatibility and representative view point, it is preferable to utilize a process derived solvent from the same (or at least a similar) coal to the one used in the process. In a commercial process, the derived oil would have to be a recycle stream.

The Wilsonville solvent (DOE-V178) had some of the desired properties. However,

Table 2: Properties of Coal and Oil Feedstock

	DOE-BT	DOE-V178	DOE-V178 (+320)	DOE-LO-6050
Proximate[1] (weight, %)				
moisture	15.5			
ash	5.2			
volatiles	35.8			
fixed carbon	43.4			
Elemental (daf, weight %)				
carbon	75.7	87.7	88.3	87.6
hydrogen	5.6	10.2	9.5	11.3
nitrogen	1.03	0.71	0.96	0.21
sulphur	0.43	0.027	0.036	0.031
oxygen[2]	17.2			
H/C ratio	0.88	1.40	1.29	1.55
molybdenum[3]		2.2	1.1	
Density (g/mL)		.9826	.9954	.9421
Distillation (D2887) (%distilled by °C)				
IBP		200	262	183
5		244	284	239
10		261	297	262
25		289	320	300
50		326	344	339
75		355	363	374
90		375	381	409
95		386	397	431
EP		414	459	487
Aromaticity (weight %)				
^{1H}		9	8	4
^{13C}			33	15
Cyclic ^{1}H, hydroaromatic, solvent quality		16	24	18
Base Number (g/100g)				2.3

1. Partially dried
2. By difference
3. mg/L

its boiling range of 200 - 414°C was somewhat low (Figure 1). The HRI LO-6050 solvent had a better boiling range, but it was very poor in aromatic character, which would limit its coal solubilization properties. It was decided therefore, to prepare a more suitable solvent from the V-178 by removing the lower boiling components by distillation.

A modified D1160 apparatus was employed for the distillation. Approximately 1200g of DOE-V178 was loaded into a 2 litre pot and vacuum distillation was initiated. Distillation was continued to 320°C, atmospheric equivalent temperature. Sufficient solvent (+320°C) was prepared to ensure that the initial autoclave program could be completed. Therefore, a total of distillations were performed yielding 6.0 kg of nominally +320°C DOE-V178 (+320°C)) material and 3.5 kg of overheads (-320°C).

Properties of the DOE-V178 (+320) solvent are also included in Table 2. Since the D1160 apparatus is close to a one plate unit the cut points of the products show considerable overlap. Also, a high proportion of the original V-178 solvent was concentrated within the 310 - 330°C range. Ultimately, the distillation profile (262 - 459°C) of the DOE-V178 (+320) solvent more closely matched that of the ideal solvent, however, a fairly substantial -320°C component remained.

The remaining properties of the DOE-V178 (+320) reflected a concentration effect for the heteroatoms and aromatic components. The ^{13}C aromatics were within the acceptable range, fa = 0.33 while the hydroaromatics increased by 50%. The change in the H/C ratio from 1.40 to 1.29 indicated that many of the aliphatic components were contained in the -320°C fraction.

The DOE-V178 had been prepared from a Wilsonville run (#263), which utilized a soluble molybdenum complex as a catalyst. There was some concern that if molybdenum was present in the solvent it would invoke a catalytic effect. Both DOE-V178 and DOE-V178 (+320) were, therefore, tested for the presence of molybdenum by direct injection into plasma. The molybdenum content of both solvents proved to be minimal.

Task 3 Experimental Work

3.1 Ash Removal - Selective Oil Agglomeration

3.1.1 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 (~ 20g) was put onto a set of 8 cm (3 1/2") screens. The screens were vibrated for 5 minutes and subsequently the contents of each screen were weighed. Results for the two samples (BT-1A, BT-1B) prepared for the agglomeration matrix program are shown in Table 3.

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 paint can. A proximate analysis is performed immediately and then samples are withdrawn for testing purposes.

3.1.2 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 (150g MAF) are blended at a stirring speed of 1200 rpm. The binding oil (15 - 75g) 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 agglomerates has started. At this time the stirring rate is increased to 1800 - 2000 rpm.

Table 3: 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

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 2. 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.

3.1.3 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.

Results of the screening tests are given in Table 4. In all cases the inversion time was extremely short, less than 2 minutes. Agglomerate growth was quite limited with the

Table 4: 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.

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 a 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 or oil content and stirring speed for the following matrix tests.

3.1.4 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 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 5). 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 there were no correlations which could be drawn between operating parameters and ash rejection.

Again to summarize, agglomeration of Black Thunder coal by Wilsonville V-178 oil produced small, but 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.

3.2 Autoclave Test Program

3.2.1 Procedure

ARC employed a 1L autoclave fitted with a magnadrive stirrer (Figure 3) to screen conditions for the first stage coal liquefaction step. Coal (80 g); water (13-27 g), solvent (120 g) and potassium carbonate (4 g) were loaded into the autoclave. Air was removed by purging six times with carbon monoxide. The autoclave was then pressurized with 400 - 800 psi of carbon monoxide.

The temperature was raised at an average rate of 4.3°C/minute which resulted in

Table 5: 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	.160	.125	.090
oil, g	60	45	30
rpm	1200	1600	2000

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

a typical heat up time of 90 minutes, at a run temperature of 410°C. Temperature was controlled by maintaining the furnace at 50-75°C above the run temperature and by injecting small volumes of water into the cooling coil. At the end of the prescribed run time, heating was discontinued, and the autoclave contents were rapidly cooled by the continuous passage of water through the internal coil. The work up procedure is summarized in Figure 4.

Product gas was discharged at 130-140°C. This temperature permitted recovery of the carbon dioxide, part of which would otherwise stay in aqueous solution at lower temperatures. [During the subsequent opening of the autoclave the carbon dioxide tends to be released from solution and causes frothing and overflow of liquid products.] Liquids were trapped from the gas stream by an ice water condenser. In this program, total liquid product from the gas stream rarely exceeded 2 g and consisted almost entirely of water. The product gas was then quantified through a dry gas meter and the total gas was collected in a gas bag. The autoclave and collection system was then flushed with nitrogen. Flushed gas was collected sequentially in 75 litre and 40 litre gas bags. The product gas plus the 2 flushed gas samples were all characterized by gas chromatography.

The autoclave was then cooled to room temperature and the liquid slurry was transferred to a 500 mL single neck flask. The slurry was carefully distilled at atmospheric pressure to remove water and light hydrocarbons. After cooling, the slurry was diluted with THF and filtered by gravity through a Whatman #1 filter paper. The filter paper and remaining solids were folded and placed in a cellulose thimble. The thimble was extracted with THF in a Soxhlet extractor for a minimum of 15 hours. The remaining solids were dried at 70°C and weighed. A proximate analysis was then performed to determine ash and insoluble organic matter.

The filtrate and THF extracted material were combined and THF was removed first by rotary evaporation, then by atmospheric distillation. The remaining oils were then

separated by a D1160 distillation. Initially no heat was applied to remove the final traces of THF. This was discernable since the column temperature dipped below zero degrees. Heating was then started and two distillable oil cuts were collected: a distillate (200 - 343°C) and gas oil (343-504°C). In practice the maximum atmospheric equivalent temperature rarely exceeded 450°C. A resid or non-distillable oil fraction, nominally 504+°C remained.

This experimental procedure was refined during the initial series of runs. The refinement led to improved mass balances usually exceeding 97 weight %. In the earlier runs the quantification of gases, especially carbon dioxide, was low. This problem was largely rectified when the flushing procedure was adopted. Two samples of flushed gas were collected, but the product gas was all contained in the discharge and first flushed gas samples.

3.2.2 Experimental Program

3.2.2.1 Solvent Stability

Three tests were conducted to determine the stability of the solvents and to establish instrument/heating settings. Operating conditions and results are presented in Table 6.

The conditions represented the maximum severities which might be expected in single stage (CO/H_2O) and two stage (FeS_2/H_2) operations. The two solvents (LO-6050 and V-178 (+320)) were stable at single stage temperatures although there was a small increase in pressure during the run indicating gas production. However, the hydrocarbon gas production was under 1% and no detectable amount of naphtha was collected in the condenser or during distillation. The simulated distillation for LO-6050 (Figure 5) showed a small shift to lighter products, 56% distilled at 343°C verses 53% in the feed.

Table 6: Autoclave Program - Solvent Stability

	DOE-1	DOE-2	DOE-3
Operating Conditions			
Charge			
Solvent, 200 g	LO-6050	LO-6050	V-178 (+320)
Initial pressure, MPa	1100 H_2	750 CO	800 CO
Catalyst, 4 g	pyrite	K_2 CO_3	K_2 CO_3
Water, g	-	25	25
Temperature, °C	460	410	410
Time, minutes	60	30	60
Run pressure, t_o t final	2330 2800	2590 2708	2760 2850
Product distribution[1], g/100g			
Hydrocarbon gases, C_1 - C_5	1.2	0.6	0.2
Naphtha	21.8	0	0
Distillate	40.4	61.5	48.9
Gas Oil	30.0	38.0	51.6
[1] liquid products characterized by D1160 distillation			
CO conversion, wt%	-	58	59

The D1160 gave comparable distillate cut, (61%). For the V-178 (+320°C) solvent the D1160 distillation yielded 49% distillate, which was identical to the simulated distillation of the feed.

At 460°C, the LO-6050 showed considerable instability. Run pressure continued to increase during the run as volatile components were formed. Approximately one third of the gas oil fraction was upgraded to lighter products. The solvent, which originally was virtually naphtha free, now contained 22%. (This probably explains the poor mass balance for this run, i.e. evaporation losses during transfer.) Gas production was surprisingly low, at 1.2%.

The carbon monoxide conversion was almost the same for the two runs at first stage conditions. Both runs showed a very small surplus of hydrogen, <0.1%. In contrast, the higher severity run consumed hydrogen during the upgrading process. This run also generated H_2S. However, there was an analytical problem which resulted in a failure to quantify this gas.

As both solvents were equally suited for the first stage testing program from a stability view point, other characteristics formed the basis for the selection of the preferred solvent. For the initial runs, the V-178 (+320) solvent was chosen, based on its greater aromaticity and hydroaromaticity, and higher boiling range.

3.2.2.2 Matrix Program

The rational for this program was described in the August - September 1992 Quarterly Report. Briefly, preferred conditions for the solubilization of coal in the bench scale unit will be selected based on experiments which vary the process temperature, carbon monoxide pressure and process time.

The data collection for each run was assembled in a tabular form as illustrated by

Table 7. The carbon monoxide conversion was the most reliable information derived from the WGSR stoichiometry, especially after the flushing procedure was introduced. Carbon dioxide production then exceeded the stoichiometric value indicating that coal derived CO_2 was produced (a small quantity could also be attributable to the potassium carbonate). CO conversion for the most part averaged over 80% (Table 8), when the temperature was over 390°C and the time greater than 30 minutes. The maximum quantity of CO converted was 0.71 moles at 400 psi, 1.05 moles at 600 psi and 1.43 moles at 800 psi. That is equivalent to the moles of hydrogen produced. The average (net) consumption of hydrogen was 1 - 1.5 g/100g coal (daf), or 0.2 - 0.3 moles per charge.

The total pressure in the autoclave could be predicted by a simple linear mathematical function using temperature, CO pressure and water input as variables (Table 9). This model subsequently showed that a leak in a fitting had started to form during Run DOE-17, and subsequently led to a premature shut down in DOE-18. DOE-17 had an unusually low pressure illustrated by the graph (Figure 6) of residuals (fitted values vs actual values). DOE-18 developed a leak at about 360°C and was repeated, DOE-18-1.

Table 7: Data Collection and Treatment

Run #DOE-16 **Conditions: 370°C/600 psi/60 min** **Code: -1 0 +1**

Inputs				
coal g	80	61.4 HC	13.8 H_2O	4.8 Ash
solvent g	120.4	58.9 -343	61.4 +343	
catalyst g	4.0			
H_2O g	20.0			
CO g	34.4	594 psi	1.23 moles	
Total	258.8			
Outputs				
water g	8.2			
slurry g	159.6	44.6 -343	60.5 +343	54.5 +524
solids g	24.1	6.2 ash	19.0 IOM	
condenser g	2.5	assign to water		
towels g	1.1	assign to solids		
product gas g	45.4	34.7 L at STP		
flushed gas g	15.5	65.1 L at STP		
Total g	256.4			
Gas Composition g		Product	Flush	Total
carbon monoxide		10.1	1.5	11.6
carbon dioxide		34.2	13.7	47.9
hydrogen		0.64	0.18	0.82
methane		0.10	-	0.10
ethane		0.10	0.04	0.14
ethylene		-	-	-
propane		0.11	0.06	0.17
propylene		0.02	0.01	0.03
butane		0.01	0.02	0.03
i-butane		0.03	-	0.03
butenes		0.02	-	0.02
pentane		0.01	-	0.01
i-pentane		-	-	-
Total Hydrocarbons		0.43	0.13	0.56

Gas Stoichiometry/ Conversion				
	CO +	H_2O →	CO_2 +	H_2
in moles	1.23	1.91		
out moles	0.42	0.59	1.09	0.40
change moles	0.81	1.32	1.09	0.40

CO conversion = (0.81/1.23) x 100 = 66%

H_2 consumption = (0.81 - 0.40) x 2.02 = 0.82 g

Mass Balance = (256.4 / 258.8) x 100 = 99.0%

Ash Balance = (6.2 / (4.8 + 4.0)) x 100 = 70.5%

Coal conversion = ((61.4 - 19.0) / 61.4) x 100 = 69%

Product Yield Distribution	g	g/100g		
HC gas	0.56	0.91		
distillate (net)	-14.3	-23.3		
gas oil (net)	-0.9	-1.5		
non-distillable oils	54.3	88.4		
IOM	19.0	30.9		
hydrogen consumption	0.82	1.34		

Table 8: Gas Conversion/Production

Run No.	Run Pressure psi	CO Conversion %	Moles CO converted	H_2 Cons. g/100g
4	1910	83	0.71	1.4
5	3120	85	1.35	2.2
6	2420	79	0.99	1.6
7	3010	85	1.43	1.8
8	2300	36	0.45	1.1
9	2920	68	1.14	1.6
10	1870	74	0.65	1.3
11	1770	44	0.40	0.4
12	2370	73	0.88	0.1
13	2460	68	0.79	1.0
14	2410	87	1.05	1.1
15	1660	76	0.63	1.1
16	2250	66	0.81	0.7
17	2310	79	1.00	1.6
18	2940	51	0.83	0.6

[1] suspect gas analysis

Table 9: Run Pressure as a Function of Temperature, CO and Water Inputs

Run No.	Temperature	Moles CO	Moles H_2O	Press	Fitted	Residual
3	410	0.85	1.51	1910	1888	22
4	410	1.63	2.29	3120	3079	41
5	390	1.25	1.92	2420	2402	18
6	390	1.67	2.29	3010	3018	-8
7	370	1.24	1.91	2300	2286	14
8	370	1.63	2.30	2920	2881	39
9	390	0.86	1.52	1870	1802	68
10	390	0.85	1.54	1780	1802	-22
11	390	1.21	1.90	2370	2351	19
12	410	1.22	1.91	2460	2468	-8
13	410	1.20	1.91	2410	2448	-38
14	370	0.83	1.52	1660	1670	-10
15	370	1.23	1.91	2250	2276	-26
16	390	1.26	1.91	2310	2408	-98
17	390	1.64	2.22	2940	2952	-12

Run Pressure, Y fitted = 5.07 (X1) + 1022 (X2) + 505 (X3) - 1821

Partial product work-up was performed in DOE-18 and will be reported in the next quarterly report. The correlation was also used to identify the maximum initial CO pressure which could be utilized before the safety rating for the autoclave was reached.

Coal conversion and product distribution data is given in Table 10. The centre point (Runs 6, 12, 17) gave good reproducibility confirming the experimental technique. Coal conversion data was initially interpretated by a linear regression (Table 11), but a poor fit was obtained (R^2 = 0.58). However, the following qualitative and quantitative conclusions could be made: the CO pressure function did not contribute significantly, and the curvature indicated interaction between X terms. A second order least squares regression gave a much improved fit (R_2 = 0.98) but again without major contributions from pressure functions, except the (temperature * pressure) interaction. A random distribution of residuals was obtained indicating the data was statistically valid. However, some inconsistencies are apparent which might be explained by process chemistry. DOE-14 coal conversion was lower than many other runs despite the process conditions which were the most severe. This could be explained by the formation of coke or other insolubles due to the occurrence of regressive reactions. The lowest severity conditions DOE-8 and 9 suggest that a threshold (temperature/time) severity is required to achieve the targeted coal conversion. (In continuous operation this might be in the 70%+ range instead of the maximum where regressive reactions may occur). The maximum coal conversion achieved was 89%, this result was confirmed by a repeat DOE-19 (complete results given in next quarterly report).

Hydrocarbon gas production was a function of temperature and time (Figure 7). The yield could be kept below 2 g/100g feed by keeping temperature below 390°C or restricting time to less than 20 minutes at 410°C. Hydrogen sulphide production was minimal throughout the program and rarely gave values greater than 0.1 g/100g. Total input of sulphur from feed and solvent was less than 0.4 g/100g.

TABLE 10 AUTOCLAVE MATRIX PROGRAM SUMMARY

RUN #	T	P	t	COAL CONV	CO CONV	GAS YIELD	DO YIELD	NDO YIELD	H2 CONS
				%	%	g/100g	g/100g	g/100g	g/100g
DOE-04	1	-1	0	76	83	3.0	-29.3	84.3	1.4
DOE-05	1	1	0	89	85	2.9	20.1	52.7	2.2
DOE-06	0	0	0	83	79	1.3	-2.5	74.5	1.6
DOE-07	0	1	1	85	85	1.6	14.3	67.6	1.8
DOE-08	-1	0	-1	34	36	0.2	-22.1	53.8	1.1
DOE-09	-1	1	0	44	68	0.5	-0.5	44.2	1.6
DOE-10	0	-1	1	76	74	1.4	-11.4	74.3	1.3
DOE-11	0	-1	-1	62	44	0.4	4.2	60.9	0.4
DOE-12	0	0	0	84	73	2.4	-9.7	92.6	0.1
DOE-13	1	0	-1	74	68	1.0	-9.1	79.2	1.0
DOE-14	1	0	1	73	87	4.0	-30.0	82.8	1.1
DOE-15	-1	-1	0	63	76	0.6	-38.6	83.6	1.1
DOE-16	-1	0	1	69	66	0.9	-25.2	89.9	0.7
DOE-17	0	0	0	81	79	1.7	-29.4	97.3	1.6
DOE-18-1	0	1	-1	63	51	0.3	-31.8	81.6	0.6

PRELIMINARY DATA SUBJECT TO REVISION

Table 11: Statistical Analysis of Matrix Tests

Linear regression

$$Y \text{ fitted} = 70.4 + 12.75\,(X1) + 0.50\,(X2) + 8.75\,(X3)$$

Quadratic regression

$$Y \text{ fitted} = 82.7 = 12.75\,(X1) + 0.50\,(X2) + 8.75\,(X3) + 8.0\,(X1) * (X2) - 9.00\,(X1) * (X3) + 2.00\,(X2) * (X3) - 11.8\,(X1)^2 - 2.83\,(X2)^2 - 8.33\,(X3)^2$$

Coded variables +1, 0, -1

X1 = Temperature
X2 = CO pressure
X3 = Time

Run No.	Y Observed (coal conv.)	Y Fitted Linear	Residual	Y Fitted Quadratic	Residual
4	76	83	-6.7	72	3.75
5	89	84	5.4	89	-0.25
6	83	70	12.6	83	0.33
7	85	80	5.4	83	2.25
8	34	49	-14.9	32	2.00
9	44	58	-14.2	48	-3.75
10	76	79	-2.7	78	-1.75
11	62	61	0.9	64	-2.25
12	84	70	13.6	83	1.33
13	74	74	-0.4	76	-1.50
14	73	92	-18.9	75	-2.00
15	63	57	5.9	63	0.25
16	69	66	2.6	68	1.50
17	81	70	10.6	83	-1.67
18	63	62	0.9	61	1.75

Total oil yield was quite scattered, especially for the centre point repeats. The only conclusions that can be drawn are: 1. total liquid yield in the first stage process is likely to be in the 70 - 80 g/100g range, 2. some regressive reactions involving the solvent may occur. This observation is based on the fact that in many runs a net negative yield of distillable oils was obtained, the solvent was stable in the absence of coal, it appears, therefore, likely that coal fragments have been stabilized by the addition to solvent, rendering the latter part of the non-distillable oil fraction. (These adducts may rupture at the higher severity conditions of the second stage.)

Further comment on the process chemistry awaits the characterization of the non-distillable oils (TLC/FID and IR) and solid residue (petrography and IR). Repeats of several runs are also planned.

3.3 Bench Unit Program

3.3.1 Modifications

The design of the modifications of the bench unit (BU) has been completed. The P&ID's have been updated to the point that they are now used as construction blueprints. As erection of the BU proceeds, the P&ID's will be updated.

All major equipment items have been specified and procured. Available empty tube reactors are being modified for use as counter-flow reactors by installing additional feed and effluent nozzles as well as thermocouple connections. Electrical and instrumentation has been taken-off, and replacement or additional items have been specified and procurement is progressing as scheduled. The computerized control system has been received, and programming and configuration of the system has started.

The erection of the structural steel is about two to three weeks behind schedule due to a delay in the procurement cycle and some wrong dimensions on prefabricated

parts. Measures are being taken, such as additional prefabrication of equipment and other materials (heat tracing and insulation), to ensure that the BU will be ready for operation during April 1993.

FUTURE WORK

During the next quarter, it is planned to complete the following items:

1. Characterization of the new Wilsonville solvent.

2. Matrix tests on agglomeration using Illinois #6 coal and V178 +320 solvent.

3. Tests at selected conditions for agglomeration of Black Thunder and Illinois #6 coal with the new Wilsonville solvent.

4. Repeat Runs #5, #9, and #14 in autoclave test program.

5. Autoclave tests at matrix centre point conditions to study other parameters, namely agglomerate feedstock, no catalyst, FeS catalyst, Na aluminate catalyst.

6. Stability test on new solvent.

7. Erection and possibly the commissioning of the bench unit.

8. Definition and agreement on bench unit initial test program.

REFERENCES

1. S.V. Gollakota, P. Vimalchaud, O.L. Davies, J.M. Lee, M.C. Corser and C.E. Cantrell, Liquefaction Contractors' Review Meeting, Pittsburgh, Pennsylvania, September 1991.

2. F.P. Burke, R.A. Winschel and T.C. Pochapsky (1981) Fuel 60, 562-572 and (1987) 66, 654-660.

3. Y. Sato, Y. Yamanoto, T. Kamo, A. Inaba, K. Miki and T. Saito, Int. Conference on Coal Science (1989), Vol. 2, 831-834.

4. A.A. Awadalla, D.J. Cookson, and B.E. Smith (1985), Fuel 64, 1097-1107.

5. P.L. Simpson, R.J. Parker, G.A. Beaulieu and L.A. Walker, AIChE Symposium Series, 282, Vol. 87, San Diego (1991).

FIGURE 1: DISTILLATION PROFILE

Process Derived Solvents

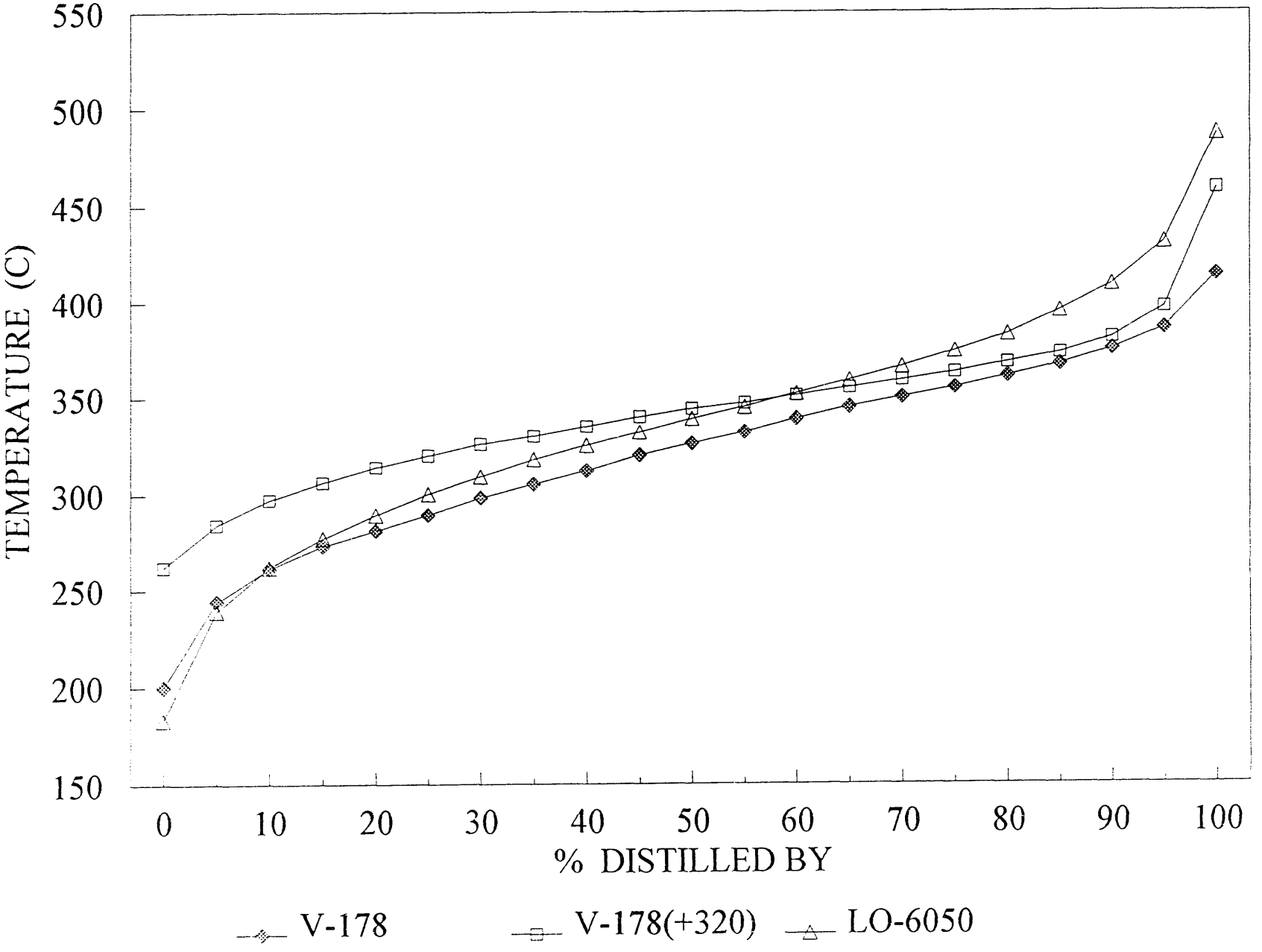


Figure 2: Laboratory Agglomeration Test Procedure Schematic

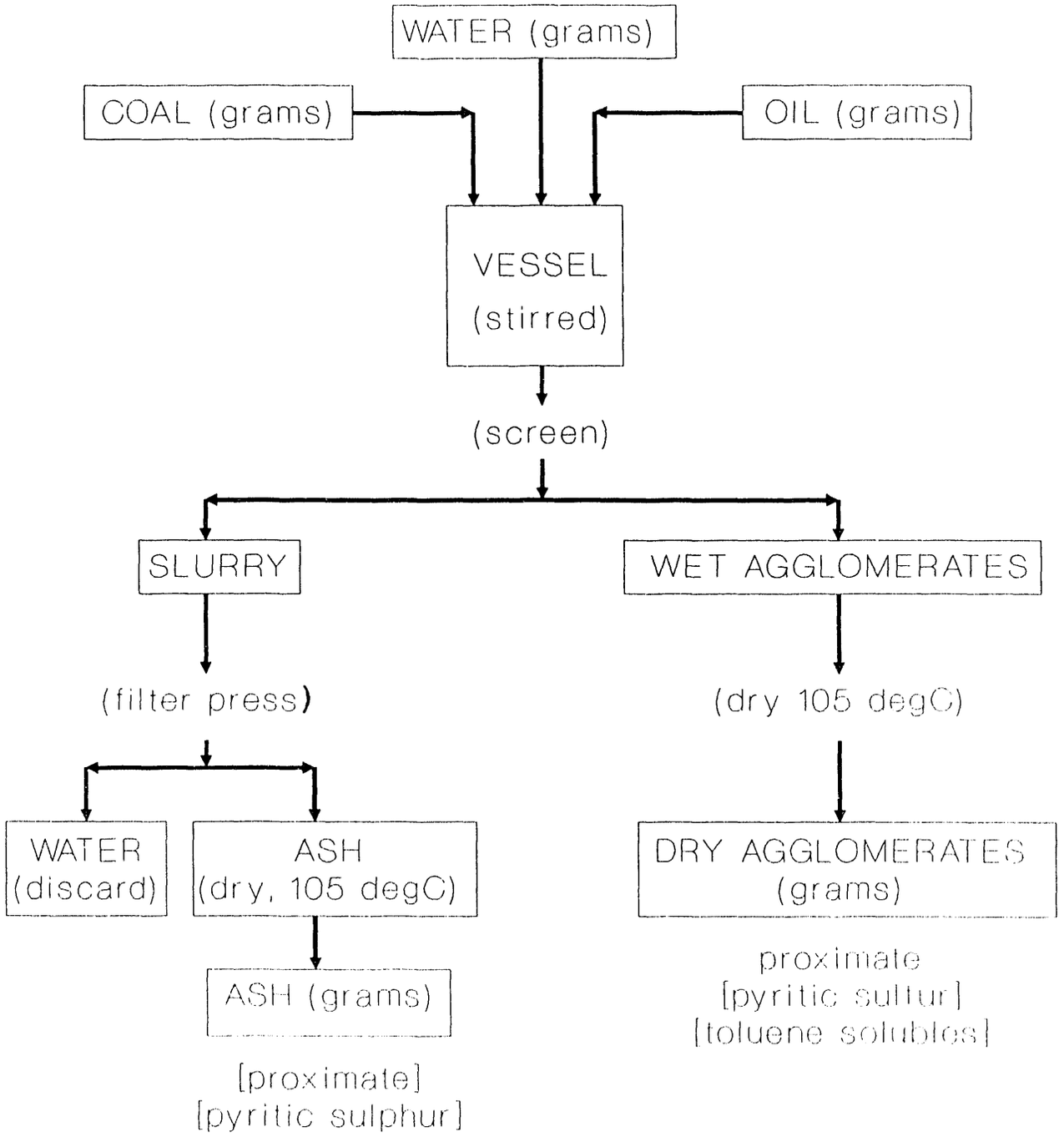


Figure 3: Simplified Set-Up of Batch Autoclave

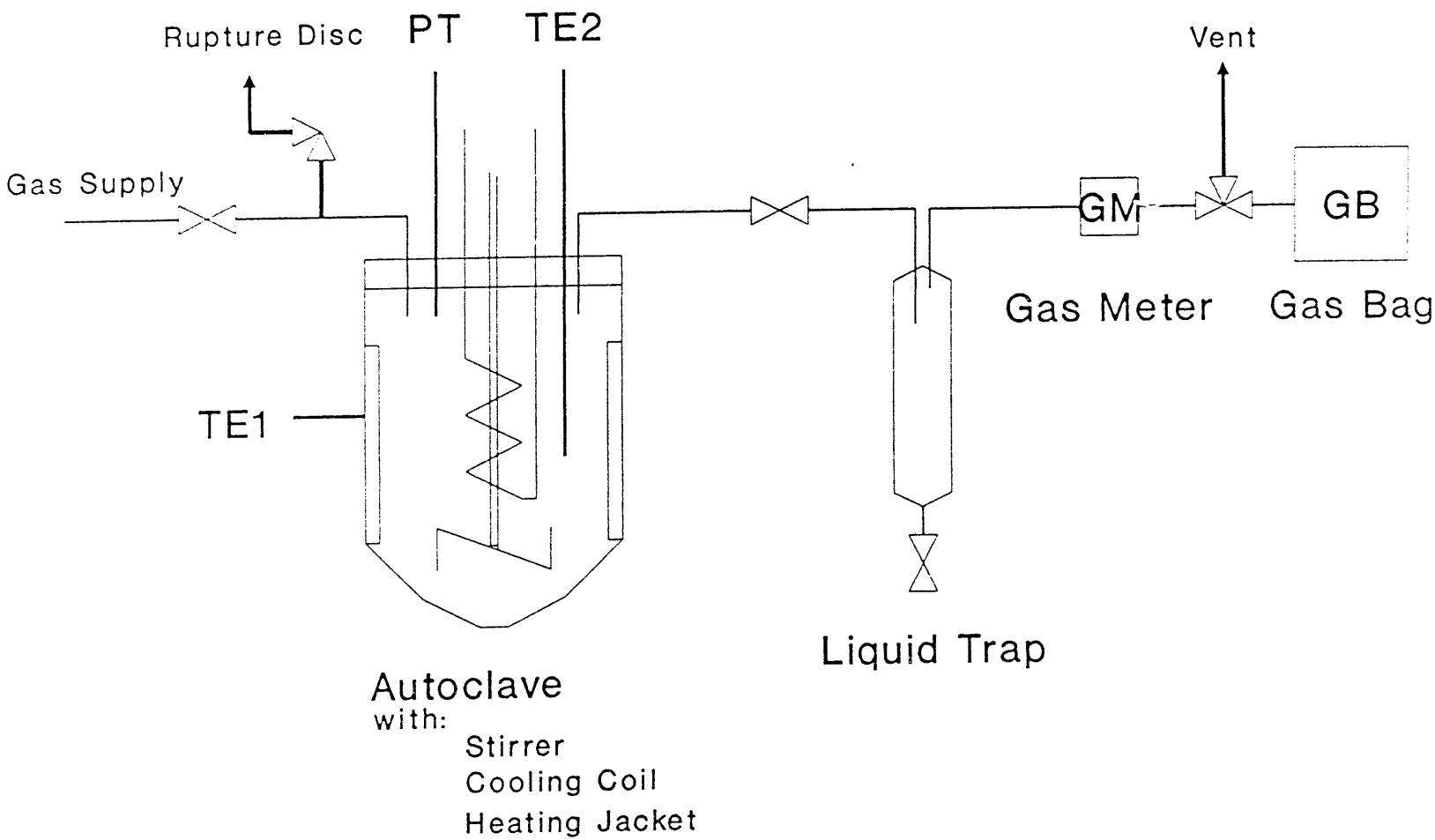


Figure 4: Autoclave Work-Up Procedure
(Updated Version)

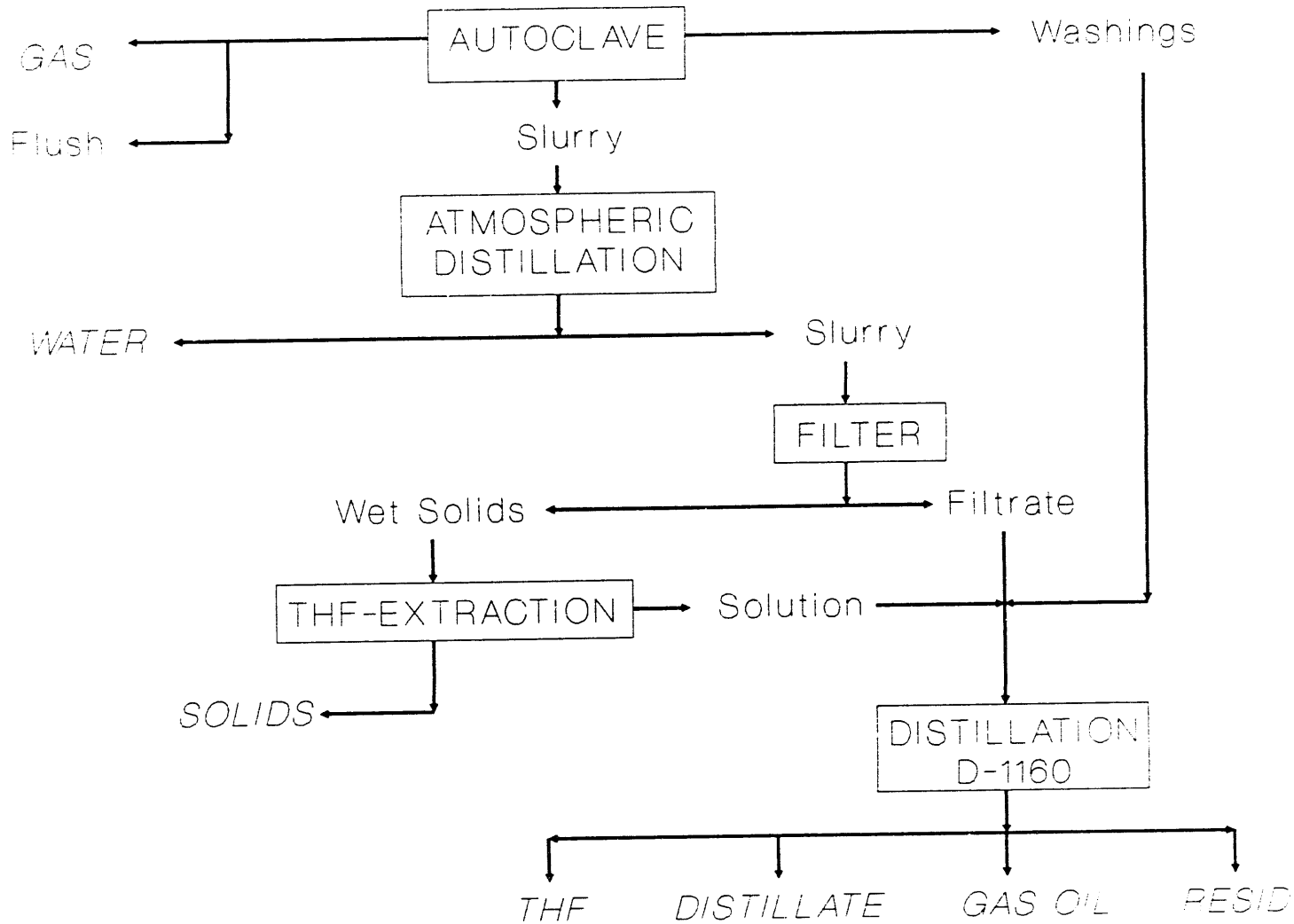


FIGURE 5: DISTILLATION PROFILE
PROCESS DERIVED LIQUIDS

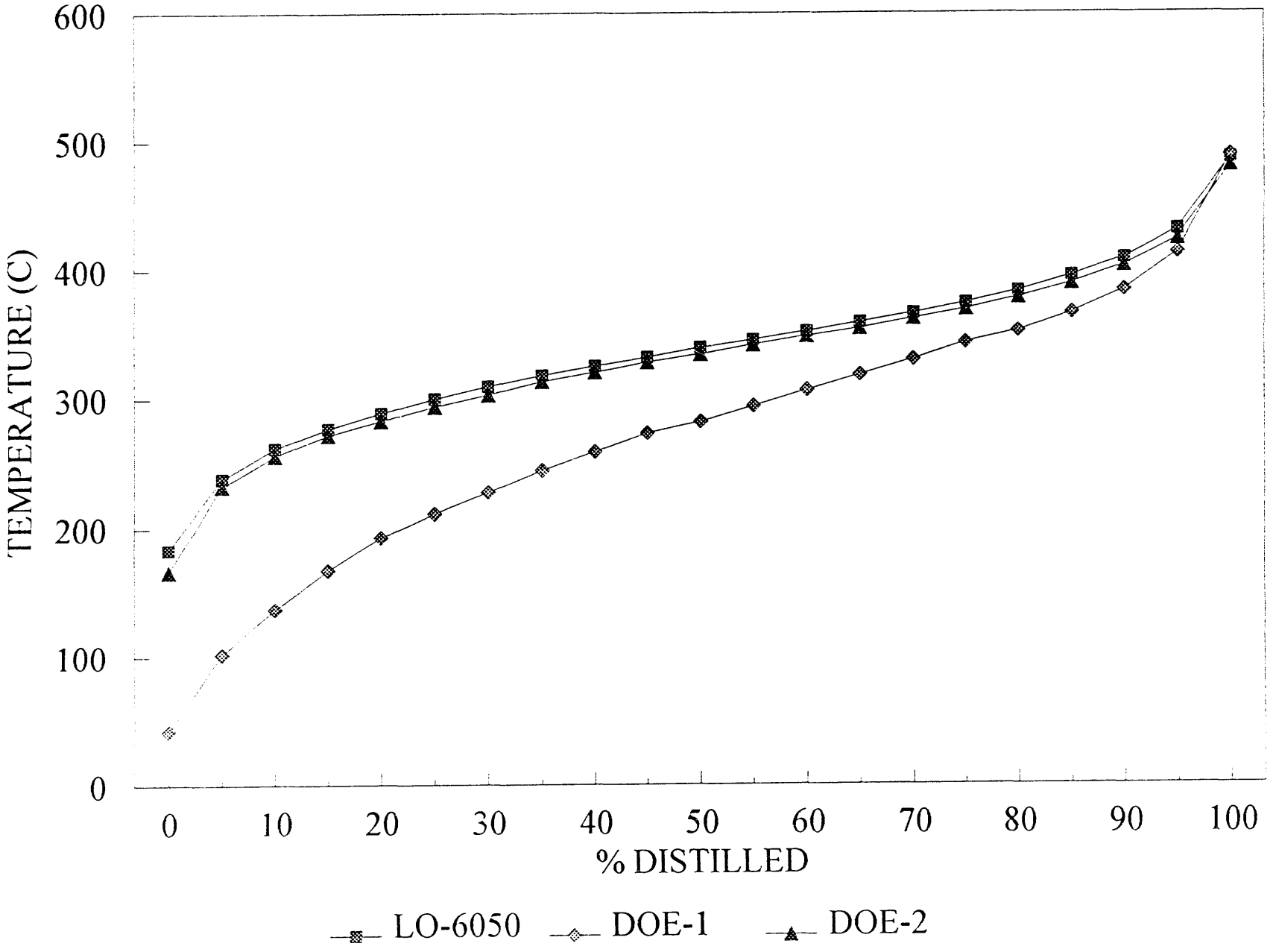


FIGURE 6 RESIDUALS vs PREDICTED VALUES

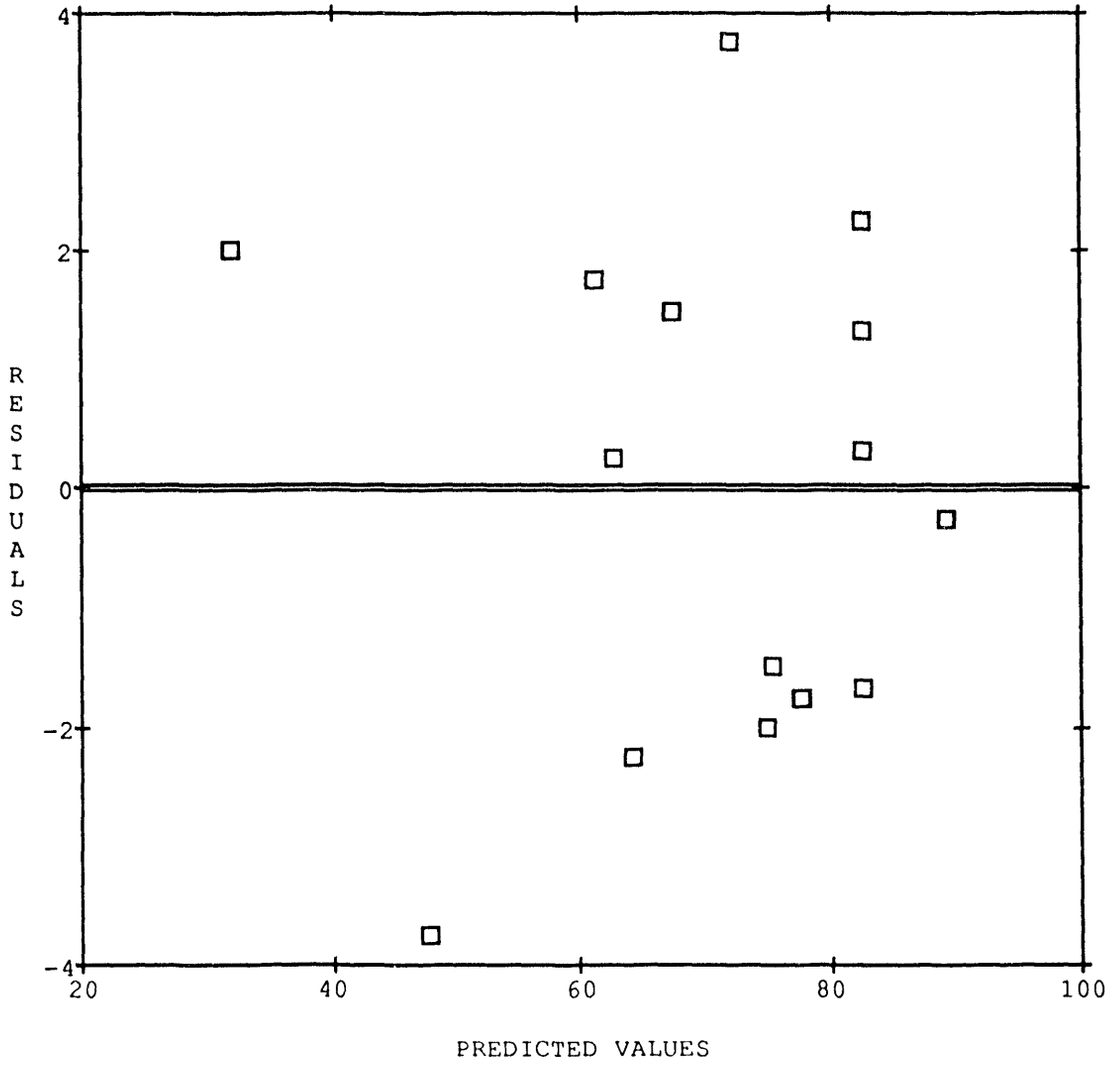
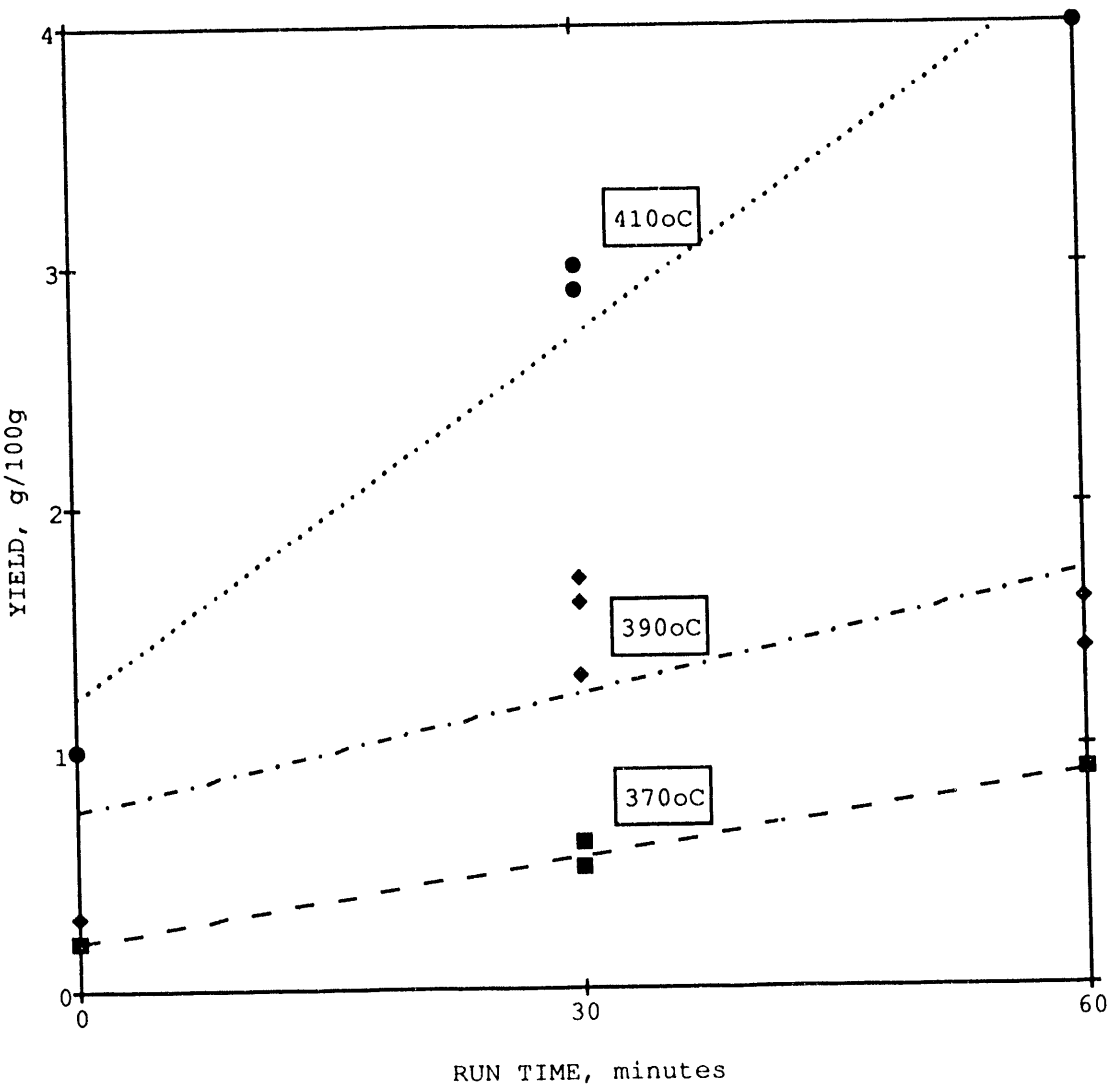
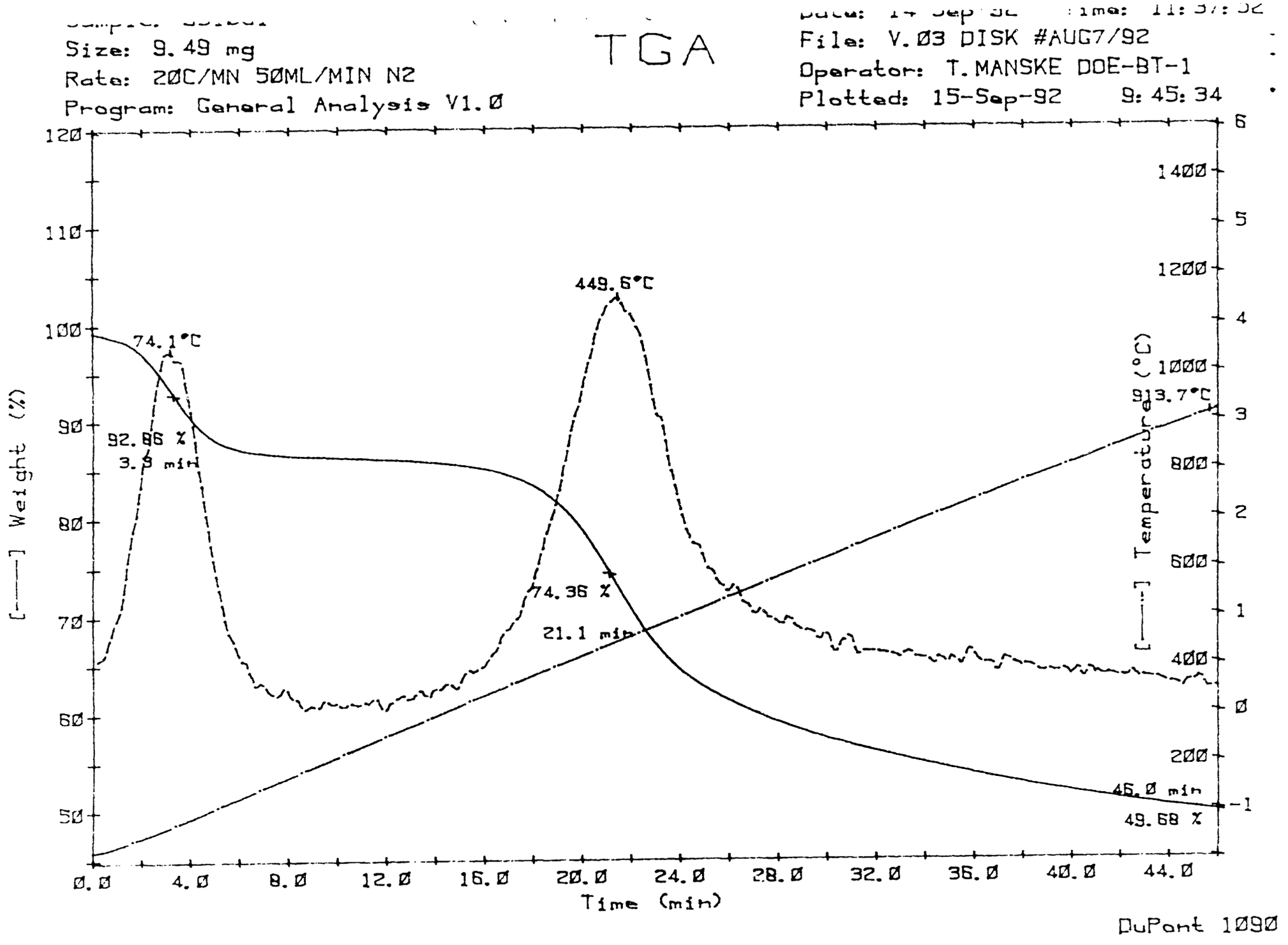
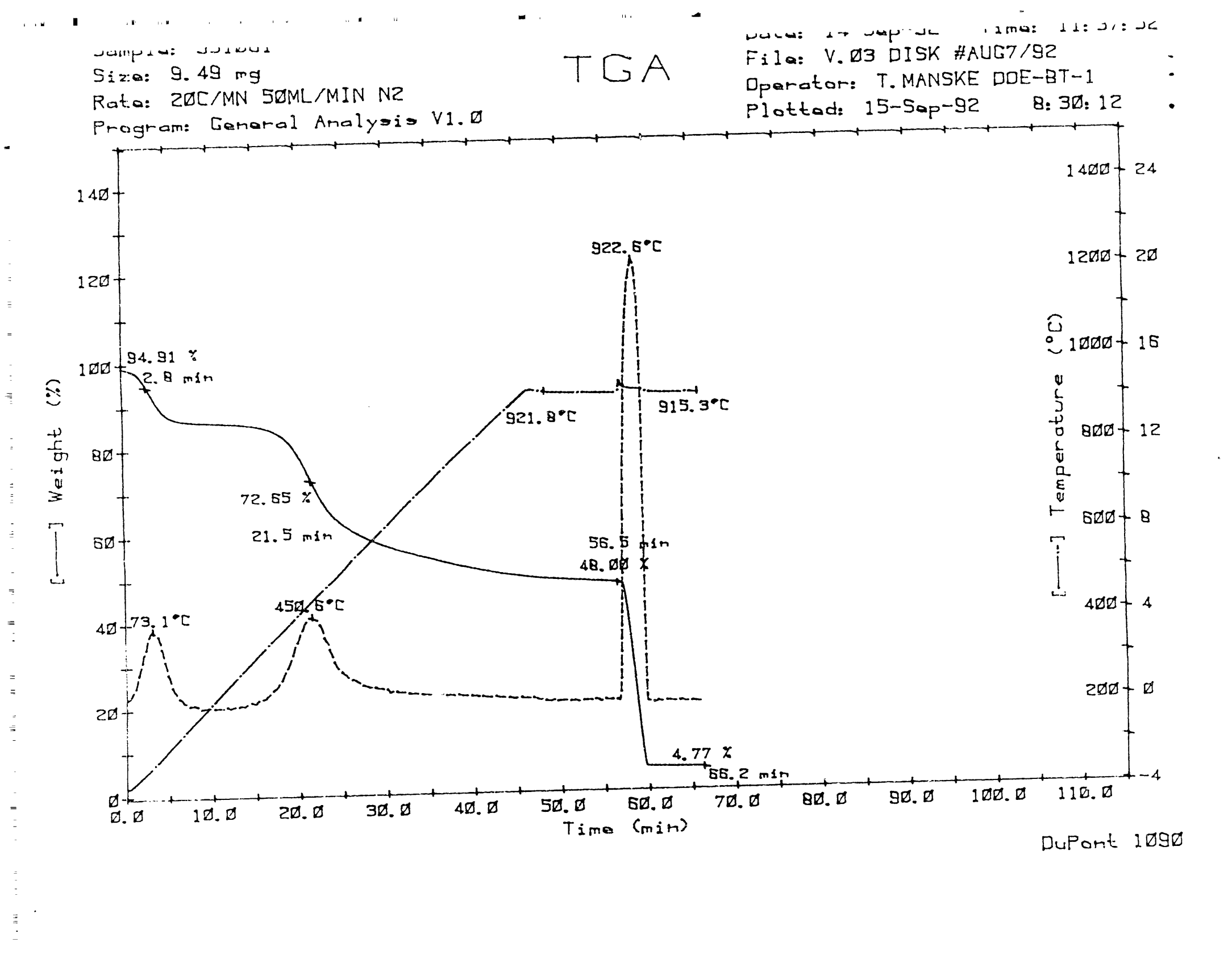


FIGURE 7 HYDROCARBON GAS YIELD



APPENDIX A


Size: 9.49 mg
Rate: 20C/MN 50ML/MIN N2
Program: General Analysis V1.0
TGA
File: V.03 DISK #AUG7/92
Operator: T.MANSKE DOE-BT-1
Plotted: 15-Sep-92 9:45:34
74.1°C
92.86 %
3.9 min
449.6°C
74.36 %
21.1 min
913.7°C
45.0 min
49.68 %
[——] Weight (%)
[——] Temperature (°C)
Time (min)
DuPont 1090


Sample: 551601
Size: 9.49 mg
Rate: 20C/MN 50ML/MIN N2
Program: General Analysis V1.0
TGA
Date: 14 Sep-92 Time: 11:37:52
File: V.03 DISK #AUG7/92
Operator: T.MANSKE DOE-BT-1
Plotted: 15-Sep-92 8:30:12
94.91 %
2.8 min
72.65 %
21.5 min
48.00 %
56.5 min
4.77 %
66.2 min
73.1°C
450.6°C
921.8°C
922.6°C
915.3°C
[ ] Weight (%)
[ ] Temperature (°C)
Time (min)
DuPont 1090

Sample: Soil
Size: 9.49 mg
Rate: 20C/MN 50ML/MIN N2
Program: General Analysis V1.0

Date: 14-Sep-92 Time: 11:37:32
File: V.03 DISK #AUG7/92
Operator: T.MANSKE DOE-BT-1
Plotted: 15-Sep-92 10:02:42

Time [min]	Sig-A [%]	Deriv-A [%/min]	Temp [deg]
0.00	99.494		20.6
1.30	98.462	1.31	38.2
2.60	95.407	3.34	62.4
3.90	90.718	3.23	88.2
5.20	87.863	1.25	115.1
6.50	86.936	0.39	142.5
7.80	86.589	0.28	169.7
9.10	86.399	0.08	196.9
10.40	86.262	0.11	224.0
11.70	86.094	0.11	251.1
13.00	85.925	0.16	278.2
14.30	85.630	0.28	305.1
15.60	85.177	0.45	332.0
16.90	84.376	0.86	358.4
18.20	82.912	1.53	384.8
19.50	80.152	2.84	410.9
20.80	75.611	4.07	436.7
22.10	70.175	4.02	462.6
23.40	65.718	2.76	488.3
24.70	63.011	1.72	514.2
26.00	61.146	1.27	541.1
27.30	59.650	1.07	567.0
28.60	58.397	0.93	592.9
29.90	57.322	0.83	618.1
31.20	56.384	0.59	643.5
32.50	55.573	0.61	668.9
33.80	54.815	0.55	695.3
35.10	54.119	0.58	719.6
36.40	53.403	0.51	744.6
37.70	52.739	0.49	769.2
39.00	52.149	0.46	793.5
40.30	51.591	0.44	817.4
41.60	51.075	0.39	841.7
42.90	50.579	0.36	865.4
44.20	50.158	0.31	887.9
45.50	49.758	0.25	911.1
46.80	49.431	0.33	928.3
48.10	49.157	0.16	922.8
49.40	48.968	0.08	920.5
50.70	48.778	0.17	919.9
52.00	48.609	0.10	918.9
53.30	48.430	0.20	918.5
54.60	48.272	0.08	917.8
55.90	48.093	0.19	917.5
57.20	46.597	8.64	930.9
58.50	24.600	20.29	922.7
59.80	4.930	0.20	917.5
61.10	4.920	0.12	917.0
62.40	4.857	0.04	916.4
63.70	4.836	0.04	915.6
65.00	4.783	0.00	915.4

SAMPLE #931061 DOE-BT-1

Start Method: 4

Method:	4	5
Initial Temp:	25.0	950.0
Program Rate:	20.0	10.0
Final Temp:	950.0	950.0
Iso Minutes:	10.0	10.0
Program Cool:	No	No
Program Gas:	1	2
Next Method:	5	0

FLOW 50 ML/MIN NITROGEN

END

DATE FILMED

7/13/93