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by

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ABSTRACT

In this study, pilot plant experiments are described in which topped Cold Lake bitumen was thermally hydrocracked. The experiments consisted of a short run series at different temperatures and a long run to provide hydrocracked product and to assess longer term operation with Cold Lake feedstock.

The results indicate that topped Cold Lake bitumen can be thermally hydrocracked for pitch conversions up to 50% and that the topping operation seemed to have eliminated many of the operational problems associated with water in the Cold Lake heavy oil.

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INTRODUCTION

The refining of Canada's low grade petroleum resources to clean liquid fuels is complicated by the presence of unwanted minerals, metals and sulphur. In addition, because the heavy oils or bitumens are hydrogen poor, the material must be coked to remove carbon or hydrogenated and cracked to produce distillate liquid fuels. In keeping with the Department of Energy, Mines and Resources (EMR) policy of maximum utilization of non-renewable resources, CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch) has supported research on thermal and catalytic hydrocracking (1,2). Thermal hydrocracking has been evaluated in a 1 bbl/day pilot plant for several feedstocks like Athabasca bitumen, Cold Lake heavy oil, Lloydminster heavy oil, topped feedstocks, etc.

Cold Lake heavy oil is a material which has been recovered from deep tar sands deposits using an in-situ technique in which high pressure steam serves to fracture the formation, heat the oil and provide a driving force for production (3). Cold Lake and Athabasca bitumen feedstocks are similar in many respects with significant differences in only the ash, benzene insolubles, carbon disulphide insolubles, the acid number and asphaltene molecular weight. These feedstocks were found to behave differently in a thermal hydrocracking process. Cold Lake heavy oil was more difficult to hydrocrack and had a strong coking tendency compared to Athabasca bitumen (4). The Athabasca bitumen used in all experiments was obtained from GCOS (Great Canadian Oil Sands Co.). It was already topped to 500°F and did not contain any water. The Cold Lake feedstock used in the early work was not topped and contained about 2 wt % water.

This report describes a series of thermal hydrocracking runs carried out using topped (650°F+) Cold Lake heavy oil. A portion of this research was done for Imperial Oil Ltd., Sarnia, on contract basis. Results and operating conditions for a short series of runs at different temperatures and a long run for 150 hrs at 430°C are given in this report.

EXPERIMENTAL

Feedstocks

Properties of the feedstocks used for the short series of runs and the long run are listed in Tables 1 and 2. The feedstock 7-CL-77 (Table 1) was supplied by Imperial Oil Ltd., Sarnia. The feedstock 1-CL-77 (Table 2) was prepared at the Energy Research Laboratories using a continuous vacuum distillation column. Since Cold Lake bitumen contained about 2% water, it had to be "dewatered" for 24 hours before distillation. For both the feedstocks the pitch content and other properties were similar.

Apparatus

A schematic of the thermal hydrocracking pilot plant is shown in Figure 1. Feed oil from a weighed tank is pumped under pressure through preheaters to the bottom of a liquid phase reactor. The reactor was 0.038 m in diameter and 3.96 m long and has been described in earlier reports (1,2).

Short Runs (77-7-67 to 77-T-70)

For start-up, the reactor and hot separator were heated to 350°C with hydrogen circulation. The reactor was then heated to reaction temperature while bitumen was fed at a rate of 6.75 kg/h. The recycle gas rate was 8.53 m^3 API/h (6700 scf/bbl) for all runs. The reaction conditions are given in Table 3. Each run was conducted for 4 hours. After 430°C, the run at 425°C was repeated for a period of 22 hours. The heavy-oil and light-oil products were collected for each run. The off-gases from heavy oil, light oil and scrubber and recycle gases were measured. The hydrogen fed was measured for each run. The procedures for analysis of products are described in earlier reports (1,2). Preheater details are given in Fig. 2.

Long Run (77-T-84)

The start-up procedure for this run was the same as above. Initially the reactor was operated at 425°C for 12 hours before the reactor temperature was increased to 430°C. After two hours of operation at 430°C, the heavy-oil and light-oil products were collected in new drums. The thermal hydrocracking at 430°C was carried out for 150 hours. The reaction conditions used for run 77-T-84 are given in Table 4.

RESULTS AND DISCUSSION

Short Runs (77-T-67 to 77-T-70)

The results of the short runs are given in Tables 5 and 6. It is seen from the results of run 77-T-68 and 77-T-70 at 425°C, that the results are reproducible. Increasing the reaction temperature increased the pitch conversion, sulphur conversion and distillate yield, whereas the total liquid yield decreased slightly. The short run series indicated that the topped Cold Lake bitumen can easily be thermally hydrocracked at the reaction conditions in Table 3.

Long Run (77-T-84)

This long run was carried out to obtain more product for Imperial Oil Ltd., and to assess the coking tendencies of the topped Cold Lake bitumen. The results in Table 7 for the long run are comparable to the results for the short run at 430°C (Table 5). The pitch conversion* is slightly lower probably because of lower reactor temperature at the inlet (TRI).

The total pressure drop in the system during the run is shown in Figure 3. The system pressure drop increased initially and slowly dropped to a final steady state value. This pattern is typical for a thermal hydrocracking run (5). Also, the pressure drop is within the range of pressure drop data obtained for topped feedstocks. As was generally observed, the major portion of the pressure drop was in the cross-over line between the reactor and the hot separator.

At the end of the run, the shutdown was successful and normal. The pilot plant was dismantled and the solids in the system were collected and weighed. The results in Table 8 show that there were only about 100 g of solids in the system. This was only about 0.01% of feedstock pumped through the system. It is important to note that the solid deposits include insoluble inorganic material, mineral matter, metals, sulphur, quinoline and benzene soluble organic material and some heavy oil. Comparison with previous data (4,5) indicates that this run is highly successful. The "coke" deposition is a slow process and the pressure drop curve (Figure 3) seems to suggest that it has reached a steady state.

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* Mean value for 3 samples.

The photographs (Figures 4 to 6) indicate very little solids deposits on the hot separator down tube. The bottom cap of the hot separator (Figure 7) and top cap of the reactor (Figure 8) contain some solids. It should be noted that these caps are of "conical" shape, leading to a 1/8" ID high pressure line. The solids seemed to have deposited on the conical slope whereas the opening to the outlet was free from deposits. The bottom cap of the reactor (Figure 9) showed some heavy oil with the solids obtained. The inside walls of the reactor and hot separator were clean.

CONCLUSIONS

The results reported indicate that topped Cold Lake bitumen can be thermally hydrocracked for pitch conversions up to 50%. A long run for 150 hours at 46% pitch conversion showed that only about 100 g of solids had accumulated in the system.

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TABLE I

Properties of Feed: 7-CL-77* (650°F)

Details

Specific gravity, 60/60°F	1.022
Sulphur, wt %	5.01
Ash, wt %	0.07
Conradson carbon residue, wt %	16.9
Pentane insolubles, wt %	20.0
Benzene insolubles, wt %	0.15
Vanadium, as V, wt ppm	141
Carbon, wt %	83.75
Hydrogen, wt %	10.23
Nitrogen, wt %	0.48
Viscosity at 100°C, Kin, cSt	609
Pitch (524°C+), wt %	63.84
Pitch Sp Gr, 60/60°F	1.05
Distillate (524°C), wt %	36.16

Distillate Hempel Distillation:

Cut, °C	Volume %	Sp Gr 60/60°F	Sulphur wt %	Nitrogen wt %
Total Distillate	–	0.955	3.23	0.145
(1) IBP to 200	1.9	0.787	3.07	0.005
(2) 200 to 250	3.6	0.836	2.79	0.010
(3) 250 to 333	6.6	0.916	3.08	0.038
(4) 333 to 418	46.3	0.948	3.11	0.093
(5) 418 to 524	40.4	0.978	3.38	0.241
Loss	1.2			
TOTAL	100.0			

* Supplied by Imperial Oil Limited

TABLE 2

Properties of Feed: 1-CL-77 (650°F)

Details

Specific gravity	60/60°F	1.020
Sulphur	wt %	4.84
Ash	wt %	0.05
Conradson carbon residue	wt %	12.7
Pentane insolubles	wt %	18.8
Benzene insolubles	wt %	nil
Vanadium, as V	wt ppm	
Carbon	wt %	83.65
Hydrogen	wt %	10.27
Nitrogen	wt %	0.44
Viscosity at 100°C	Kin cSt	413.0
Pitch (524°C+)	wt %	63.33
Pitch specific gravity	60/60°F	1.092
Distillate (524°C-)	wt %	36.67

Hempel Distillation of Distillate

Cut, °C	Volume %	Specific Gravity 60/60°F	Sulphur wt %	Nitrogen ppm
Total Distillate	-	0.959	3.25	1126
(1) IBP-200	-	-	-	-
(2) 200-250	-	-	-	-
(3) 250-333	8.1	0.911	2.78	156
(4) 333-418	47.5	0.946	3.05	759
(5) 418-524	43.1	0.975	3.35	1726
Loss	1.3			

TABLE 3

Reaction Conditions for the Short Runs

		Run Numbers			
		77-T-67	77-T-68	77-T-69	77-T-70
Feed tank temperature	°C	135	135	135	135
Preheater temperatures:*	°C				
TP1		162-165	162-164	163-166	161-164
TP2		335-339	335	334	331
TP3		351	350	350	347-354
TP4		410-414	414-421	420-424	414-422
Reactor temperatures:*	°C				
TR1		420	424	429	424
TR2		420	425	430	425
TR3		420	425	430	425
TR4		420	425	430	425
TR5		420	425	430	425
Hot Separator temp.	°C	365-375	365-375	365-375	365-375
Reactor pressure	MPa	13.89	13.89	13.89	13.89
Recycle gas purity (hydrogen)	vol %	85	85	85	85
Recycle gas rate	m^3 API/h	8.53	8.53	8.53	8.53
Feed rate	g/h	6750	6750	6750	6750
LHSV		1.5	1.5	1.5	1.5
Operating time	h	4	4	4	22

* See Figure 2

TABLE 4

Reaction Conditions for the Long Run

Run Number 77-T-84

Feed tank temperature	°C	120
Preheater temperatures:*	°C	
TP1		120-158
TP2		285-290
TP3		333-340
TP4		363-374
Reactor temperatures:*	°C	
TR1		405-410
TR2		430
TR3		430
TR4		430
TR5		430
Hot Separator temperature	°C	370-410
Reactor pressure	MPa	13.89
Recycle gas purity (hydrogen)	vol %	85
Recycle gas rate	m^3 API/h	8.53
Feed rate	g/h	6750
LHSV		1.5
Operating time	h	150

* See Figure 2

TABLE 5

Results of Short Run Series (77-T-67 to 70)

	Run No.	77-T-67	77-T-68	77-T-69	77-T-70
Reactor Temp,	°C	420	425	430	425
Reactor pressure,	MPa	13.89	13.89	13.89	13.89
LHSV		1.5	1.5	1.5	1.5
Gas Flow,	m^3 API/h	8.53	8.53	8.53	8.53
Total liquid yield,	wt %	97.4	96.9	95.6	98.3
	vol %	100.3	100.0	99.4	101.5
Total liquid gravity,	60/60°F	0.993	0.991	0.983	0.990
Total liquid sulphur,	wt %	4.40	4.28	4.01	4.26
Total liquid nitrogen,	wt %				
Pitch (524°C) conversion,	wt %	38.7	44.4	50.6	41.4
Sulphur conversion,	wt %	14.4	17.2	23.5	16.4
Nitrogen conversion,	wt %				
Distillate yield,	wt %	57.5	60.1	63.2	60.7
Distillate yield,	vol %	63.5	66.5	70.3	67.1
Hydrocarbon gas C_4 +	wt %	0.23	0.43	0.47	0.47
Hydrocarbon gas, C_3^-	wt %	1.00	1.22	1.18	1.20
H_2 consumption	m^3 API/t	19.94	27.32	35.90	27.03

TABLE 6

Properties of Distillate and Fractions

Run No.			Total Distillate	IBP-200	200-250	250-333	333-418	418-524	Loss
77-T-67	Volume	%	-	10.3	6.1	13.7	35.5	33.1	1.3
	Sp gr	60/60°F	0.928	0.765	0.844	0.902	0.947	0.984	
	Sulphur	wt %	3.73	2.27	3.18	3.82	3.58	3.91	
	Nitrogen	ppm	1974	117	374	779	1477	3714	
77-T-68	Volume	%	-	11.6	6.6	13.8	35.3	31.2	1.5
	Sp gr	60/60°F	0.925	0.760	0.843	0.900	0.946	0.990	
	Sulphur	wt %	3.47	2.08	3.10	3.62	3.59	3.95	
	Nitrogen	ppm	1788	71	321	653	1389	3510	
77-T-69	Volume	%	-	13.9	7.2	17.6	33.8	26.2	1.3
	Sp gr	60/60°F	0.920	0.762	0.846	0.902	0.949	0.995	
	Sulphur	wt %	3.38	1.83	2.83	3.41	3.43	3.90	
	Nitrogen	ppm	1772	115	360	747	1488	3832	
77-T-70	Volume	%	-	10.8	6.0	15.2	35.3	31.8	0.9
	Sp gr	60/60°F	0.927	0.743	0.846	0.903	0.946	0.984	
	Sulphur	wt %	3.52	2.04	3.09	3.53	3.42	3.65	
	Nitrogen	ppm	1811	131	383	722	1391	3465	

TABLE 7

Results of Long Run (77-T-84)

Reactor temperature	^oC	430
Reactor pressure	MPa	13.89
LHSV		1.5
Gas flow	m^3API/h	8.528
Total liquid yield	wt %	95.9
Total liquid yield	vol %	99.5
Total liquid gravity	Kin cSt	0.983
Total liquid sulphur	wt %	4.04
Total liquid nitrogen	wt %	
Pitch (524^{o}C+) conv.	wt %	46.6
Sulphur conv.	wt %	20.0
Nitrogen conv.	wt %	
Distillate yield	wt %	62.2
Distillate yield	vol %	69.0
Hydrocarbon gas, C_4+	wt %	0.43
Hydrocarbon gas, C_3	wt %	1.35
H_2 consumption	m^3API/t	36.43

Hempel Distillation of Distillate:

Cut, ^oC	Volume %	Specific Gravity 60/60^{o}F	Sulphur wt %	Nitrogen ppm
Total Distillate	-	0.921	3.27	2017
(1) IBP-200	12.6	0.767	1.86	202
(2) 200-250	6.7	0.852	2.82	487
(3) 250-333	17.2	0.904	3.22	826
(4) 333-418	35.1	0.943	3.29	1465
(5) 418-524	26.8	0.991	3.71	4498
Loss	1.6			

TABLE 8

Solids in the System

	Weight, g
Reactor top cap	3.5
Reactor	36.2
Inlet Funnel	6.5
Hot separator walls	14.0
Hot separator down tube	7.0
Hot separator outlet funnel	35.5
TOTAL	102.7

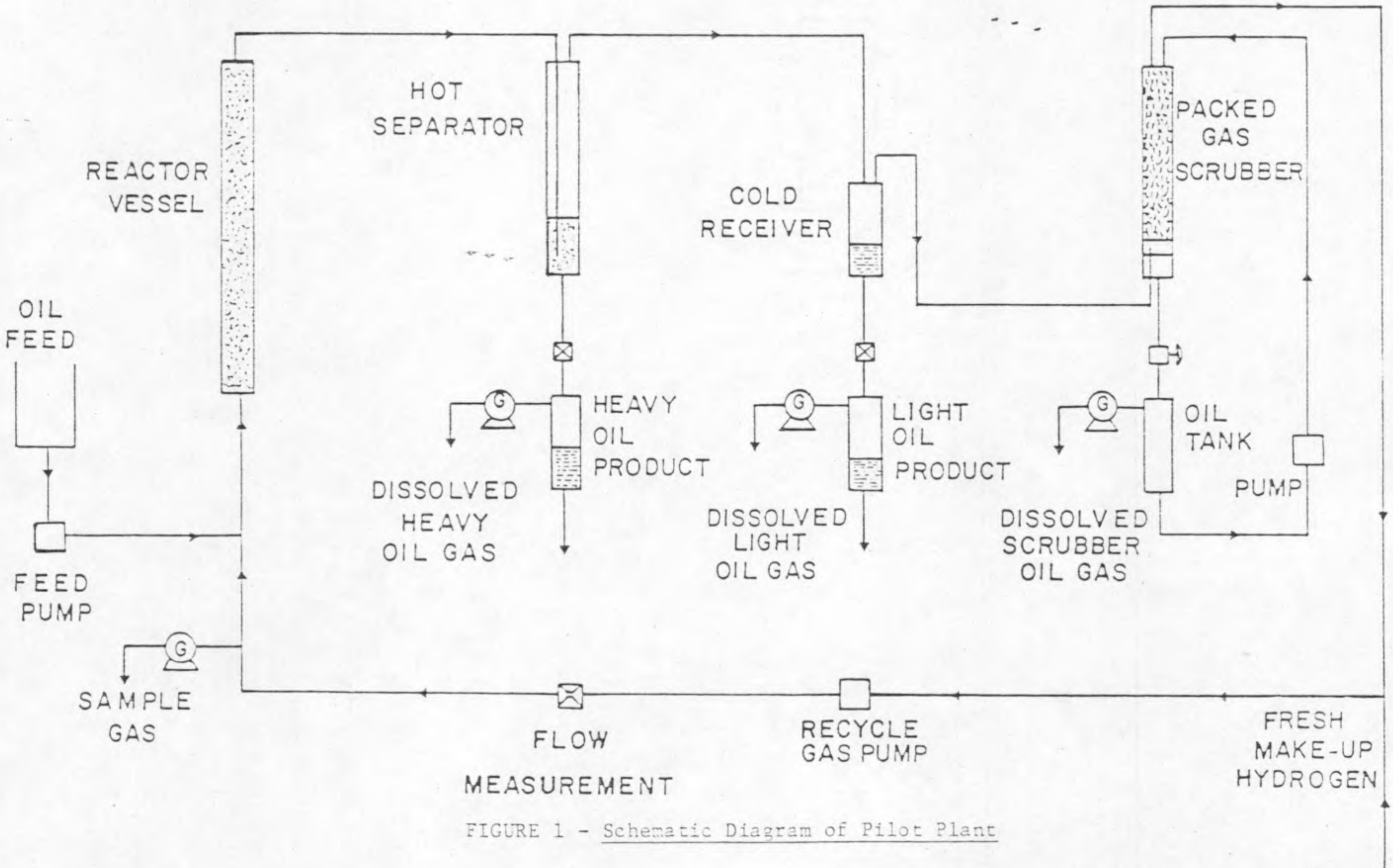


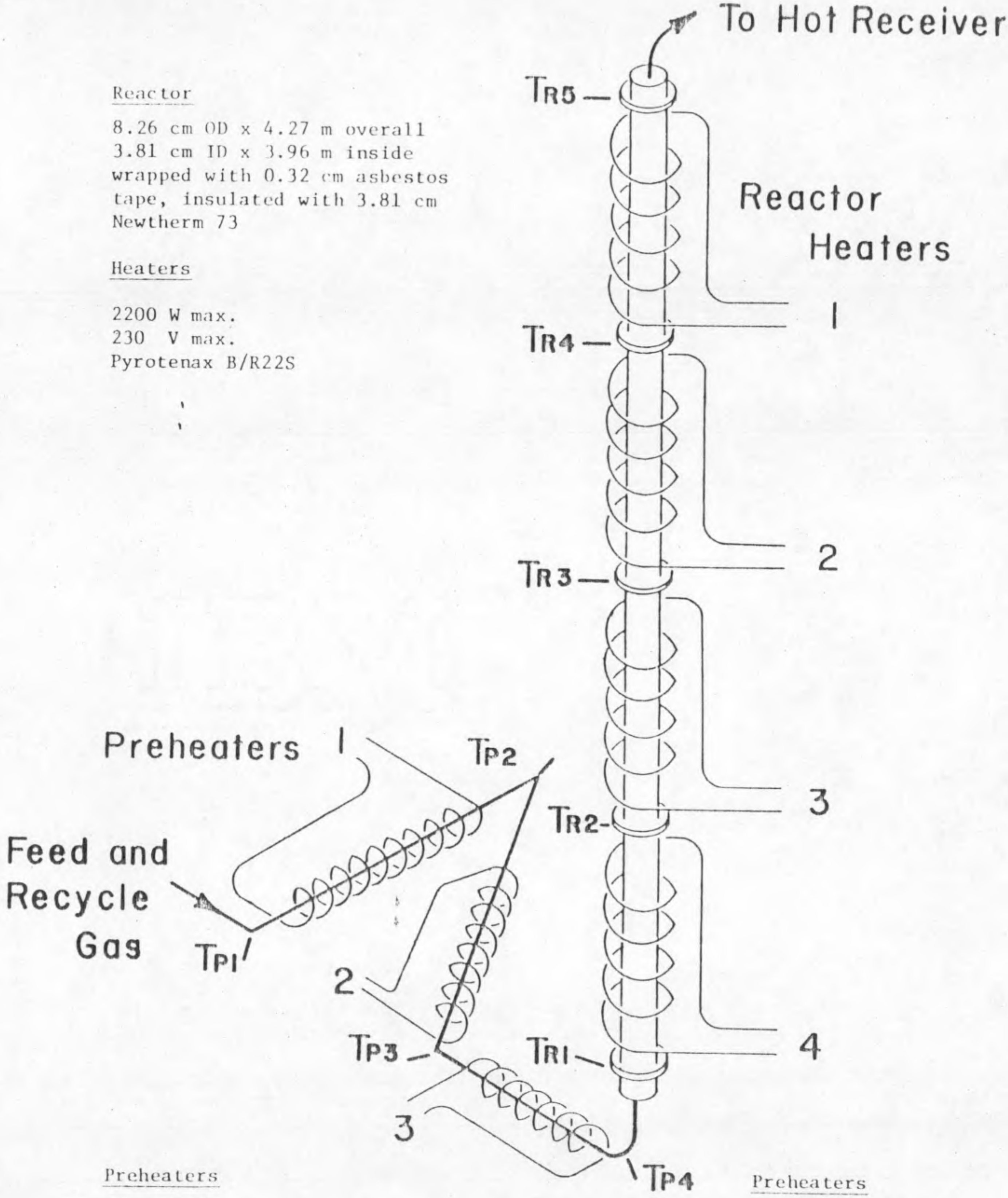
FIGURE 1 - Schematic Diagram of Pilot Plant

Reactor

8.26 cm OD x 4.27 m overall
3.81 cm ID x 3.96 m inside
wrapped with 0.32 cm asbestos
tape, insulated with 3.81 cm
Newtherm 73

Heaters

2200 W max.
230 V max.
Pyrotenax B/R22S



Preheaters

#1 - 1.83 m
#2 - 1.22 m
#3 - 1.07 m
All 1.43 cm OD x 0.48 cm ID

Preheaters

Wrapped with 0.32 cm
thick asbestos,
insulated with 2.54 cm
thick Newtherm 73

FIGURE 2 - REACTOR AND PREHEATER DETAILS

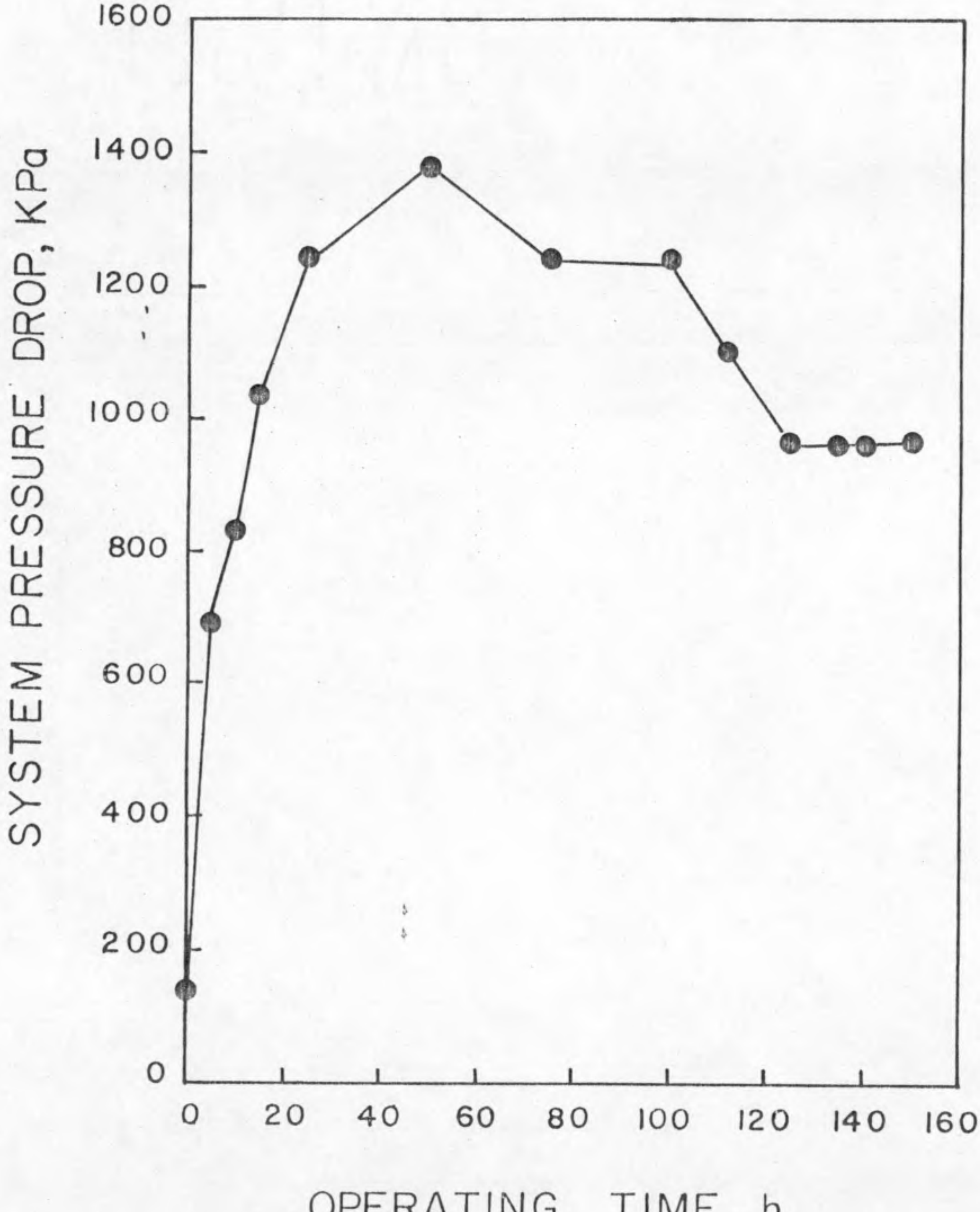


FIGURE 3 - Total System Pressure Drop for the Long Run, 77-T-84 (430°C)

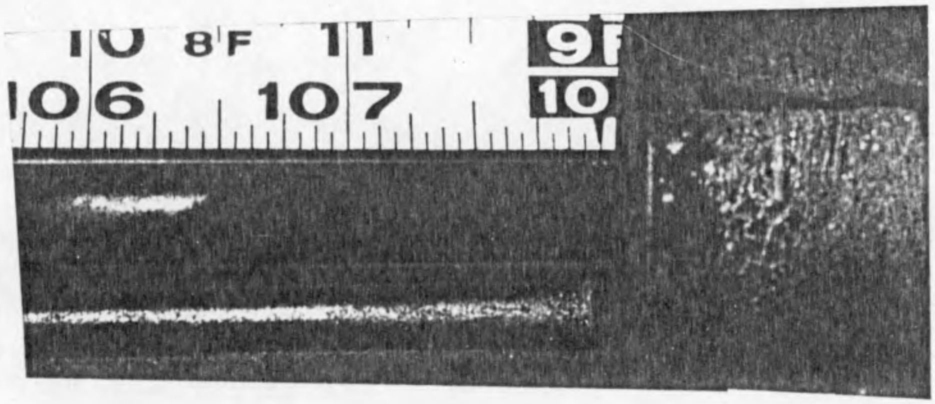


FIGURE 4

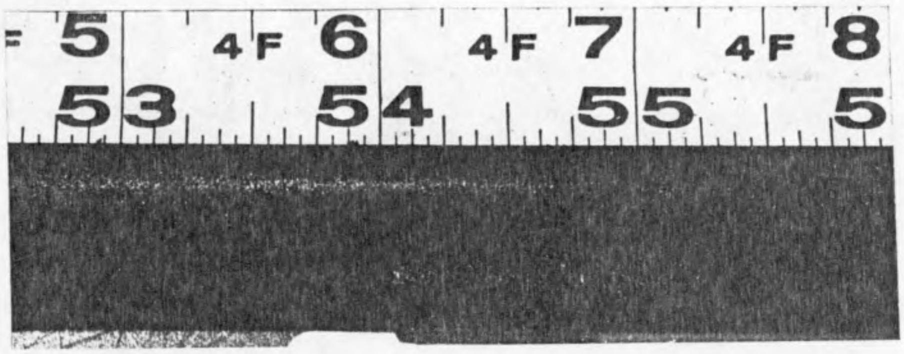


FIGURE 5

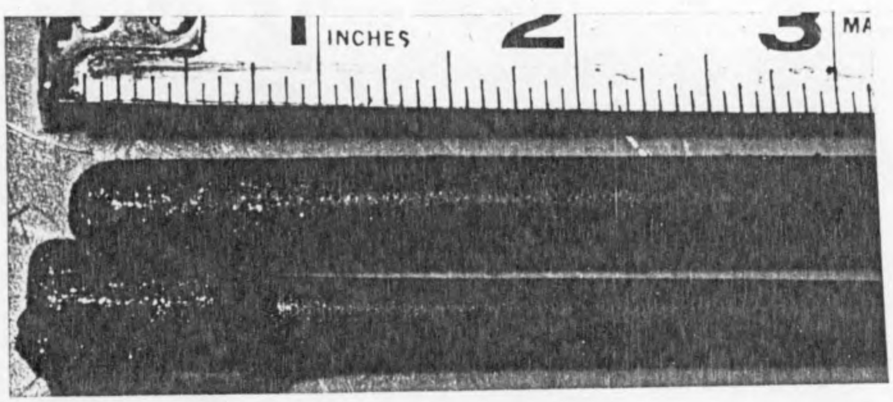


FIGURE 6

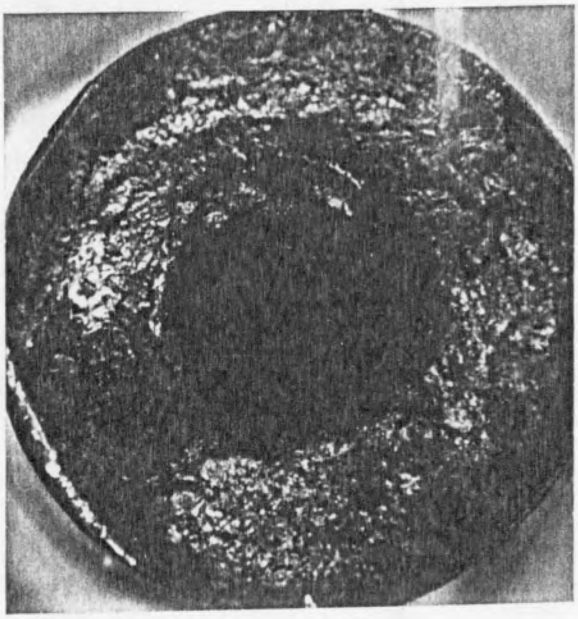
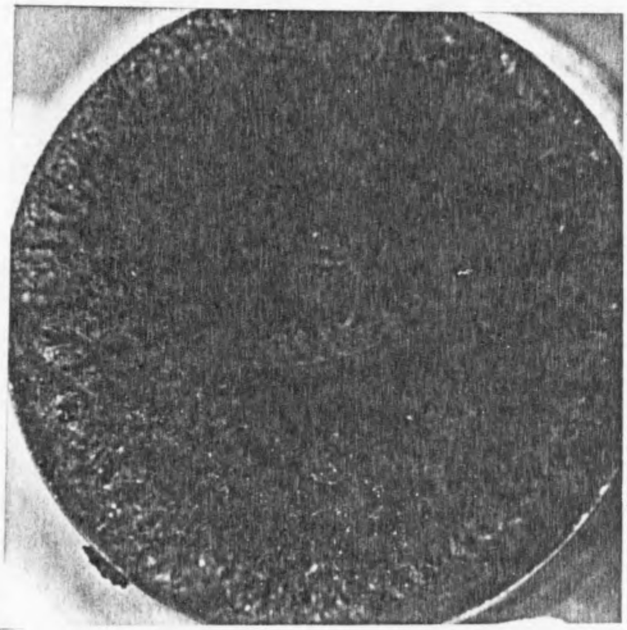


FIGURE 7

FIGURE 8 →



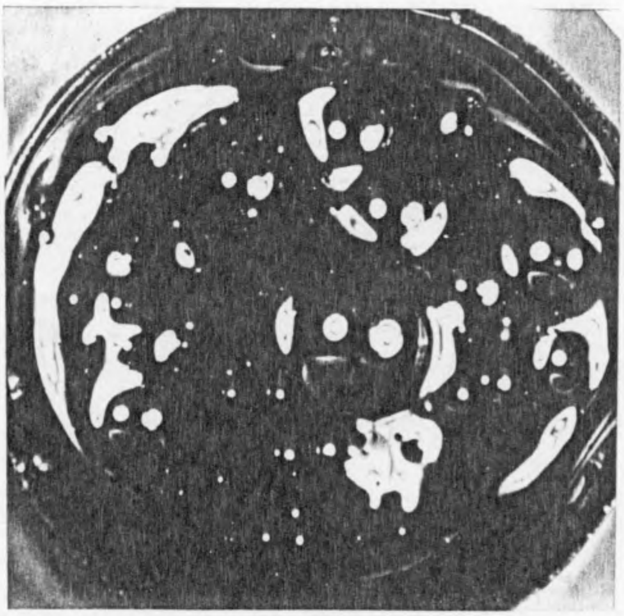


FIGURE 9