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DURING THERMAL HYDROCRACKING OF ATHABASCA BITUMEN

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THE DISTRIBUTION OF COKE PRECURSORS IN THE REACTOR  
DURING THERMAL HYDROCRACKING OF ATHABASCA BITUMEN

by

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ABSTRACT

Liquid samples from five levels along the length of the reactor were collected during thermal hydrocracking of Athabasca bitumen. Analysis of these samples revealed that asphaltenes were undergoing conversion to coke-precursors or benzene-insoluble organic matter. A decrease in the concentration of this benzene-insoluble organic material was generally observed in the reactor as a function of operating time.

Optical microscopic investigations of the benzene-insoluble residue at the bottom level of the reactor revealed a laminar stacking of asphaltene molecules on an inert particle present in the feed. These agglomerated particles were not present at the top levels of the reactor. The coke formed in the liquid phase of the reactor appeared to be derived solely from the asphaltenes. There was no coke originating from the heavy oils in any of the samples analysed.

## INTRODUCTION

Predictions of impending shortages of crude oil have generated a strong stimulus to the search for sources of clean fuel. An area of investigation which has received considerable attention at the Energy Research Laboratories has been the hydrogenation of residual oils and tars.

Thermal hydrocracking has proven to be an efficient first-stage refining process for Athabasca bitumen (1). In the development of this technology, a major effort has been made to investigate conditions favouring reduction in reactor fouling (2). In a recent publication (3), the carbonaceous deposits collected from within the reactor were reported to originate from the asphaltenes and the heavy aromatic oils of the bitumen. Spherical agglomerates of asphaltene-coke were also present in the coke layer collected from the reactor. This paper deals with the distribution of coke and coke-precursors in the liquid phase of the thermal hydrocracking reactor. The run considered was chosen to exemplify a successful run, during which little coke was formed during the three weeks of operation. Data for samples collected at five reactor levels will be presented. These studies will be complemented by optical microscopic investigations of the benzene-insoluble matter present in the reactor during the thermal hydrocracking process.

## EXPERIMENTAL

The operational aspects pertaining to the thermal hydrocracking pilot plant have been reviewed elsewhere (1,2). The data presented here correspond to a reactor run lasting three weeks. Experimental conditions for this run are summarized in Table 1.

Samples were collected daily at five levels of the 3.95-m long reactor. Levels 1 to 5 (bottom to top of the reactor) were equally spaced along the height of the reactor. Experimental details regarding the removal of samples from the reactor during the run are given in a previous publication (4).

The weight per cent concentrations of asphaltenes, benzene-insolubles and ash were determined by standard ASTM procedures (5). The data for asphaltenes and benzene-insolubles are reported on an ash-free basis. Samples for petrographic examinations were embedded in Lucite and polished by standard methods. Microscopic investigations were performed with a Leitz reflected-light microscope.

## RESULTS

Representative sample data compiled for the run are tabulated in Table 2. To facilitate interpretation of the results, level 1 (bottom of the reactor) will be considered separately from the rest of the reactor. The results for level 1 reflect the early stages of the hydrocracking process, where extensive thermal cracking of the various components of the bitumen has not yet occurred. Furthermore, the temperature at the bottom level of the reactor was found to gradually decrease as a function of operating time presumably because of accumulation of coke in the preheater.

The variation in concentration of asphaltenes and benzene-insoluble organic matter (BIOM) as a function of operating time during the run is shown in Figure 1. The concentration of BIOM was found to increase as a function of operating time, with a commensurate decrease in the concentration of asphaltenes. The sum of these two fractions, at the first level, remained approximately constant during the entire run.

Figures 2 and 3 are optical micrographs of the benzene-insoluble residue present in samples at the bottom of the reactor, collected on the 3rd and 16th day of operation, respectively. These micrographs revealed the presence of agglomerated particles in the form of spheres, generally containing a fragment of coal acting as a nucleus. Areas in the periphery of some of these particles appeared to be undergoing transformation to coke, and were found to have anisotropic character. The structure of the coke formed was found to be similar to that obtained from carbonization of asphaltenes (3). In general, the number and size of the agglomerated particles were significantly greater for reactor samples taken on the 16th day when compared with those taken on the 3rd day.

The results corresponding to reactor samples at levels 2 to 5 are given in Table 2. Certain trends are readily apparent from the data. For instance, the concentration of BIOM increased from bottom to top of the reactor. Furthermore, for every level of the reactor (levels 2 to 5, inclusive) a decrease in the concentration of BIOM was observed as a function of operating time during the run (Figure 4). There appeared to be no distinctive variation in the distribution of asphaltenes at levels 2 to 5 in the reactor.

Optical micrographs of the benzene-insoluble residue from reactor samples at levels 2 to 5 showed little evidence of the agglomerated particles detected at the first level. Representative micrographs of samples taken on the 3rd and 16th days of operation are shown in Figures 5 and 6, respectively.

Analysis of the heavy-oil product collected from the reactor was conducted on a daily basis during the run. Some analytical data are presented in Table 3. The concentration of asphaltenes and benzene-insolubles was found to vary only very slightly as a function of operating time. Microscopic investigations of the benzene-insoluble residue present in the heavy-oil product again showed no evidence of any agglomerated spheres detected at the bottom level of the reactor.

## DISCUSSION

Based on the analytical data collected for level 1 of the reactor, Figure 1, there appears to be a conversion of asphaltenes to benzene-insoluble organic matter during thermal hydrocracking of Athabasca bitumen. The total concentration of asphaltenes and BIOM at the bottom of the reactor was found to approximate the concentration of asphaltenes present in the feed, corrected for vaporization of liquid products at this first level of the reactor (see Figure 8). The microscopic observation that the spherical agglomerated particles of BIOM increased in size and number during the run (Figures 2 and 3) is consistent with the analytical results.

The gradual increase in concentration of BIOM at the bottom of the reactor, as a function of operating time (Figure 1) is somewhat difficult to interpret. If this effect was simply the result of an accumulation of BIOM

in the reactor during the run, the rate of increase in concentration of BIOM would have been much greater than the rate of decrease in asphaltene concentration. However, this is inconsistent with the analytical results. An alternative explanation could be that the increase in concentration of BIOM is partly related to the temperature effect at the pre-heater outlet and at the bottom level of the reactor (Table 1). The decrease in temperature, along with thermal hydrocracking of some of the constituents of the bitumen which help keep the asphaltenes soluble, may have caused the latter to precipitate out of the bitumen. The precipitated asphaltenes would have then deposited on some nucleation site (e.g., a fragment of coal), thus explaining the presence of agglomerated spheres at the bottom level of the reactor. The precipitated asphaltenes would probably undergo polymerization reactions, and the polymer products would be benzene-insoluble. Dehydrogenation of these asphaltene polymers or coke-precursors would ultimately result in coking, and this is observed in some of the agglomerated particles in Figure 2.

The absence of agglomerated spheres at the higher levels of the reactor may again be interpreted in terms of a temperature effect. The higher temperature at these levels ( $460^{\circ}\text{C}$ ) would have caused extensive thermal hydrocracking of the precipitated asphaltenes. The generation of volatile matter by this process probably resulted in the breaking up of the agglomerate of particles. Any coke formed would remain in a dispersed form as observed in micrographs of samples collected at levels two to five (e.g., Figures 5 and 6).

The optical micrographs shown in Figures 2 and 3 revealed that a small fragment of carbonaceous material, generally coal, acted as a nucleus for the precipitating asphaltenes. Microscopic examination of the benzene-insoluble residue in the feed stock (Figure 7) showed that particles of coal were inherently present in the bitumen. A similar effect was recently reported during hydrogenation of bituminous coals (6).

The decrease in concentration of BIOM at reactor levels 2 to 5 as a function of operating time, Figure 4, may be reflecting the role of mineral matter in inhibiting coke formation (7,8). The data for ash content in Table 2 shows that there is an accumulation of mineral matter in the reactor during the run. It is possible that this mineral matter has some activity towards catalyzing hydrogenation reactions, thereby minimizing the need for H-donors which invariably turn out to be the coke-precursors.

The variation in concentration of BIOM at levels 2 to 5, Figure 4, may be largely due to differences in the extent of vaporization at these levels. The amount of vaporized product in the reactor will vary with residence time, and consequently, samples at the higher levels of the reactor will show a greater apparent concentration of BIOM. This can be demonstrated for instance by comparing data corresponding to the heavy-oil product (Table 3), with those of samples collected at the very top of the reactor (level 5). Differences in these concentrations arise primarily from the presence of vaporized product at level 5 of the reactor and, therefore, approximately 75% of the product must exist in the vapour state at level 5. If it is assumed that the variation in concentration of BIOM at levels 2 to 5 (Figure 4) is due to differences in the extent of vaporization, a profile showing the per cent product vaporized along the length of the reactor can be plotted (figure 8).

If a correction is made for the asphaltene concentration in the reactor based on the vaporization profile shown in Figure 8, a plot of asphaltene concentration versus residence time in the reactor can be determined, Figure 9. This plot then shows the extent of thermal hydrocracking undergone by the asphaltenes in the reactor.

Finally, some mention should be made regarding the coke structure observed in the benzene-insoluble material present in reactor samples. Generally, for runs carried out under similar conditions but at lower hydrogen pressures than in this particular case (e.g., 13.4 MPa), there was evidence of coke originating from both the asphaltenes and the heavy aromatic oils (3). In this run, the only coke observed appeared to originate from the asphaltenes, with no evidence of any coke from the heavy aromatic oils of the bitumen. Furthermore, the total amount of coke formed in this run was negligible as compared with runs carried out at lower hydrogen pressures. It therefore appears that hydrogen pressure is a very important factor in preventing coke formation and that the formation of coke from the heavy aromatic oils of the bitumen is inhibited at high hydrogen pressures.

## CONCLUSIONS

The analytical results and microscopic investigations indicate that, during thermal hydrocracking of bitumen, asphaltenes are converted to benzene-insoluble matter, possibly by a series of steps involving precipitation and polymerization (or condensation) reactions. This benzene-insoluble matter constitutes a coke-precursor which can ultimately transform to coke by undergoing further condensation and dehydrogenation reactions.

There appears to be a decreasing tendency for formation of benzene-insoluble organic matter in the reactor as a function of operating time. This result may be related to the accumulation of mineral matter in the reactor during the run, suggesting that this mineral matter has some catalytic activity towards hydrogenation reactions.

The absence of coke from the heavy aromatic oils of the bitumen is presumed to be due to the high hydrogen pressure in the system. The availability of molecular hydrogen precludes the necessity of the heavy oils to act as H-donors, and dehydrogenation of these oils is not extensive; consequently, they do not undergo coking.



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TABLE 1

Thermal Hydrocracking Conditions

Pressure (MPa)	24.23
LHSV	2
Recycle gas flow (l/h at 24.23 MPa, 25°C)	9147
H <sub>2</sub> purity	85%
Temperatures:	
Reactor (2nd and subsequent levels)	460°C
Reactor (1st level)	
Day 1	440°C
Day 21	414°C
Preheater outlet	
Day 1	415°C
Day 21	360°C

TABLE 2

Distribution of Asphaltenes, Benzene Insolubles  
and Ash in the Reactor During Thermal Hydrocracking of Athabasca Bitumen

Sample		Asphaltenes %	Benzene - Insolubles %	Ash %	Sample		Asphaltenes %	Benzene - Insolubles %	Ash %
Day	Level				Day	Level			
1	1	18.00	1.41	3.59	13	1	16.42	2.26	8.42
	2	18.49	2.91	4.10		2	20.82	2.35	3.93
	3	19.02	4.08	4.10		3	18.45	3.60	3.55
	4	20.80	4.79	3.71		4	20.40	4.70	3.70
	5	17.74	4.68	3.48		5	17.49	4.56	2.55
3	1	19.19	1.41	4.30	16	1	15.22	3.83	10.85
	2	20.48	2.81	4.11		2	19.34	2.34	4.82
	3	19.40	4.17	3.73		3	18.16	3.01	4.43
	4	22.73	5.08	3.79		4	19.92	3.42	4.46
	5	15.93	5.61	3.96		5	18.74	4.31	2.85
7	1	17.49	2.38	7.83	18	1	14.43	4.15	13.02
	2	20.72	3.06	4.12		2	18.34	1.73	5.53
	3	20.90	4.29	3.61		3	15.99	2.99	4.92
	4	21.64	5.34	3.42		4	15.81	3.25	3.14
	5	18.37	5.32	3.01		5	17.00	3.66	2.64
10	1	16.80	2.11	8.19	21	1	13.60	5.52	18.28
	2	18.73	2.36	3.71		2	14.76	2.28	7.36
	3	21.41	3.70	3.59		3	15.60	2.46	5.94
	4	21.74	4.64	3.61		4	15.77	3.13	5.40
	5	20.44	4.73	4.43		5	16.74	3.68	2.98

TABLE 3

Sample Analysis of the Heavy-Oil Product

Sample Day	Asphaltenes %	Benzene-Insolubles %	Ash %
1	7.04	1.97	0.96
3	7.12	2.26	0.98
5	7.17	2.40	1.05
7	7.70	2.36	0.96
9	7.71	2.36	0.98
11	7.13	2.21	0.95
13	7.40	2.26	0.99
15	6.50	2.10	1.08
17	7.15	1.69	0.91
19	6.50	1.52	0.85
21	6.73	1.95	0.77
Average over total sample (light oil + heavy oil)	4.6	1.4	0.62

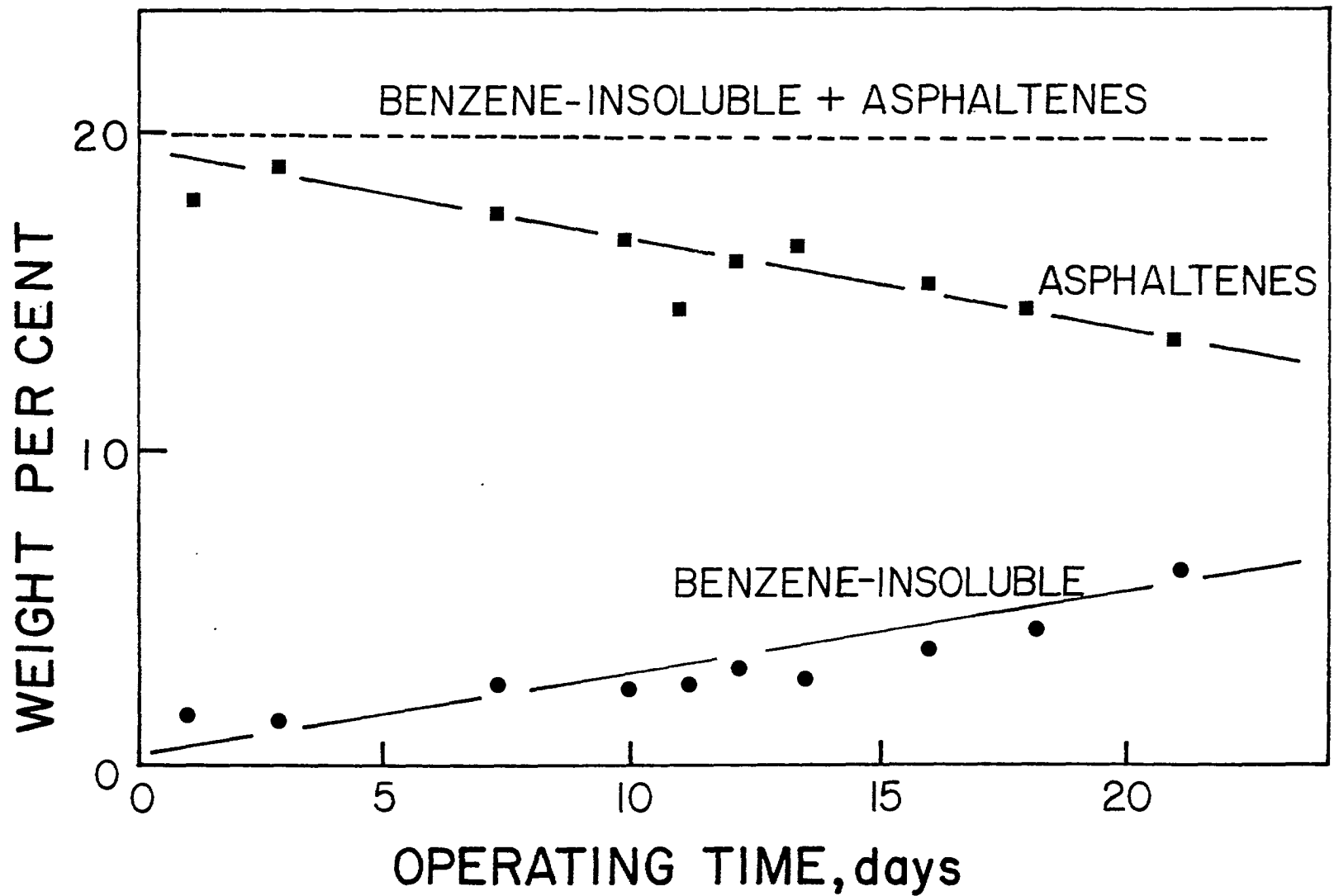


FIGURE 1 - Concentration of asphaltenes and benzene-insolubles at the bottom level of the reactor as a function of operating time

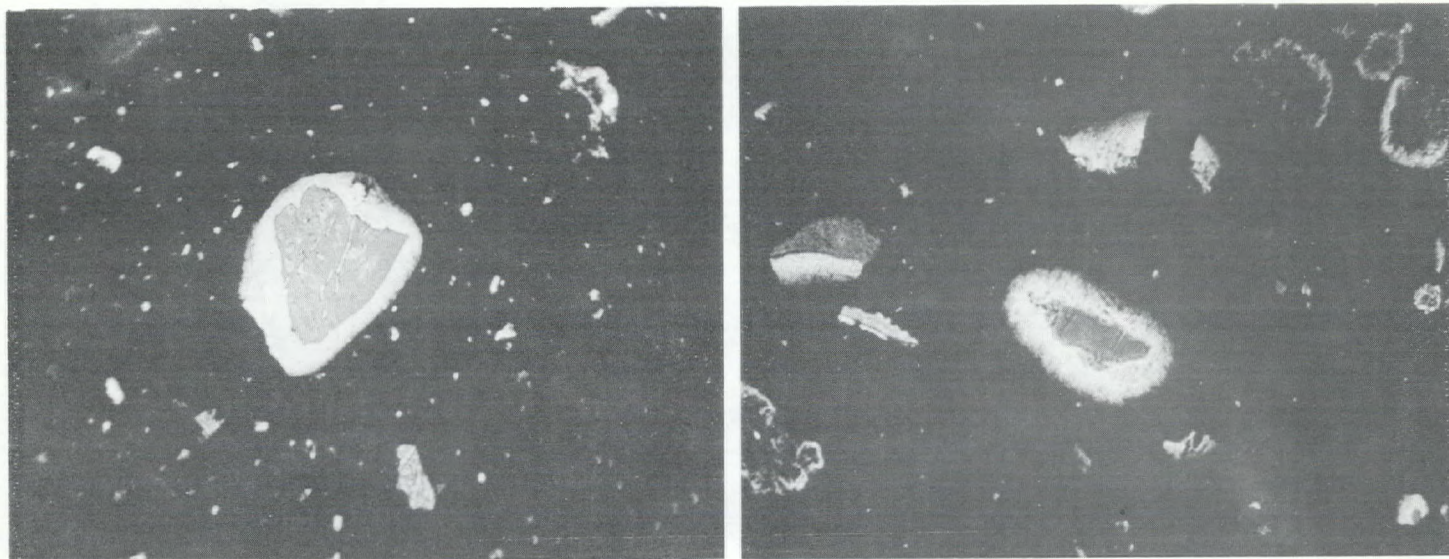


FIGURE 2 - Benzene-insoluble residue collected from the bottom level of the reactor on the 3rd day of operation (x 600)

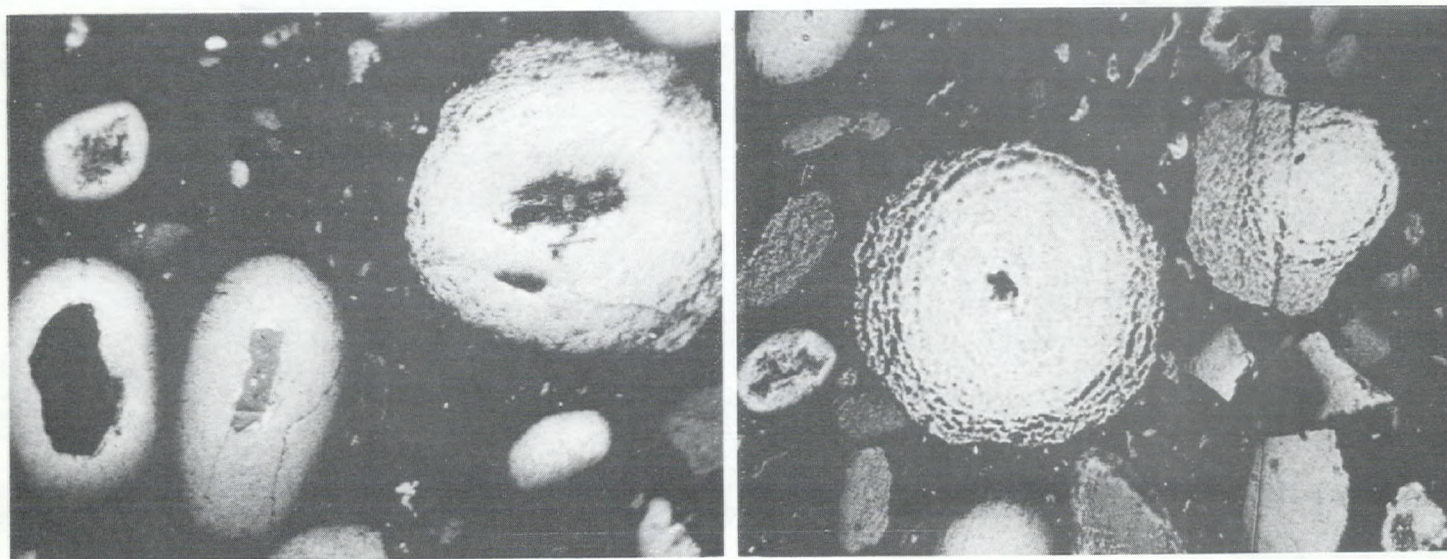


FIGURE 3 - Benzene-insoluble residue collected from the bottom level of the reactor on the 16th day of operation (x 600)

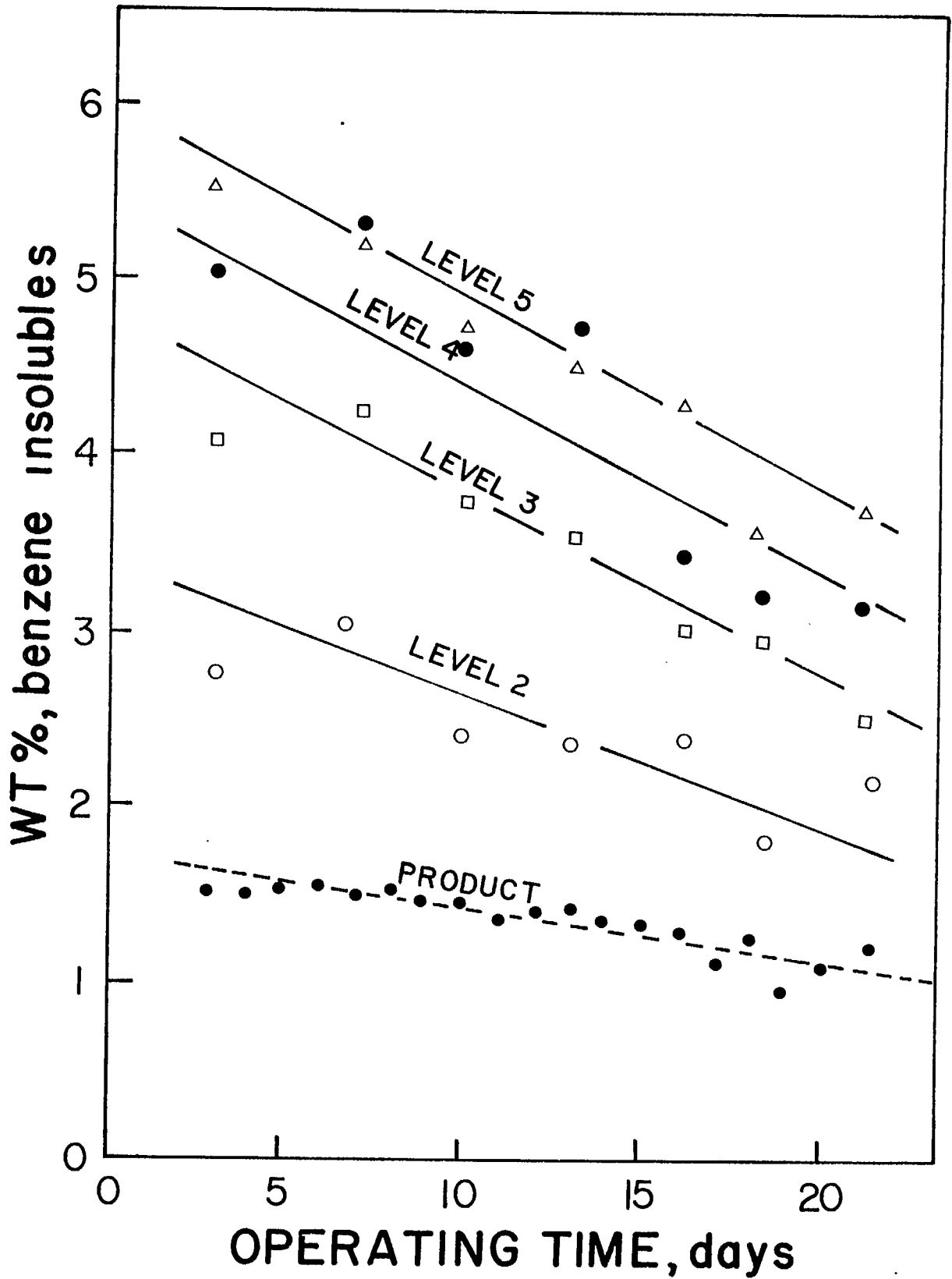


FIGURE 4 - Concentration of benzene-insolubles versus operating time for reactor levels 2 to 5 and product

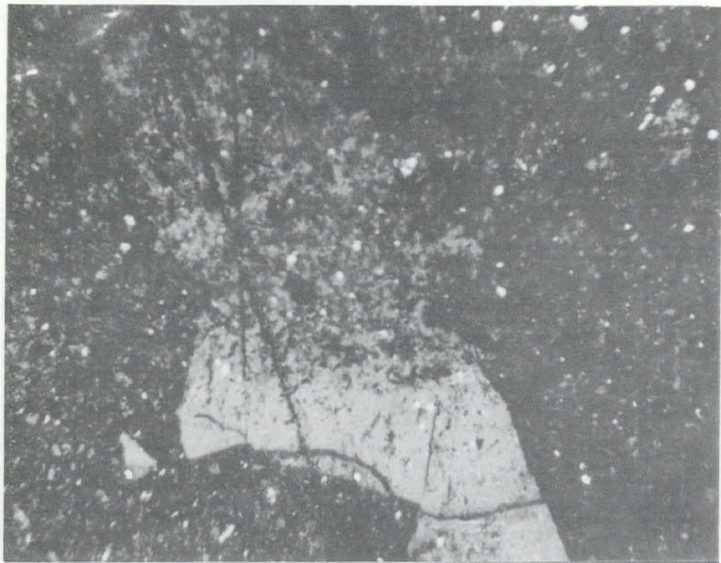


FIGURE 5 - Benzene-insoluble residue collected from level 5 of the reactor on the 3rd day of operation (x 600)

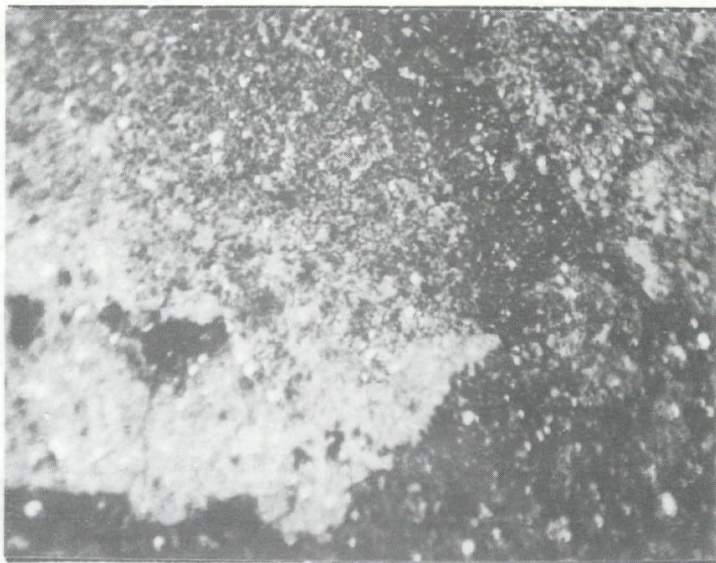


FIGURE 6 - Benzene-insoluble residue collected from level 5 of the reactor on the 16th day of operation (x 600)

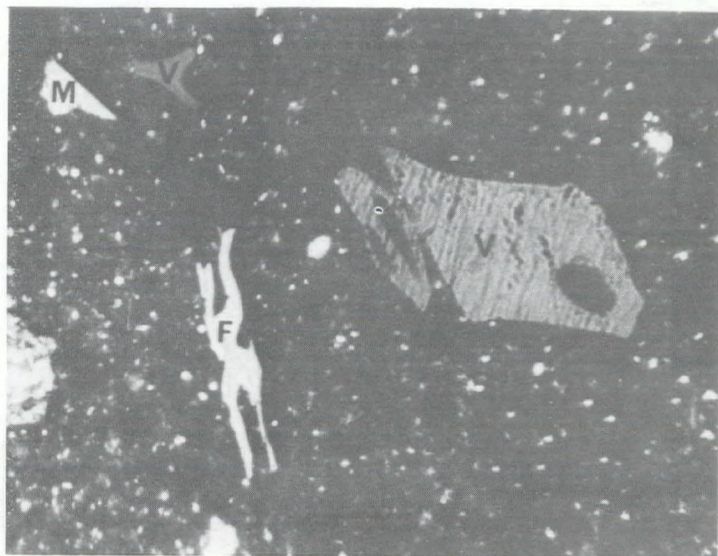


FIGURE 7 - Benzene-insoluble residue from the feed stock showing fragments of coal inherently present in the bitumen (x 600)  
 F - fusinite, M - micrinite,  
 V - vitrinite



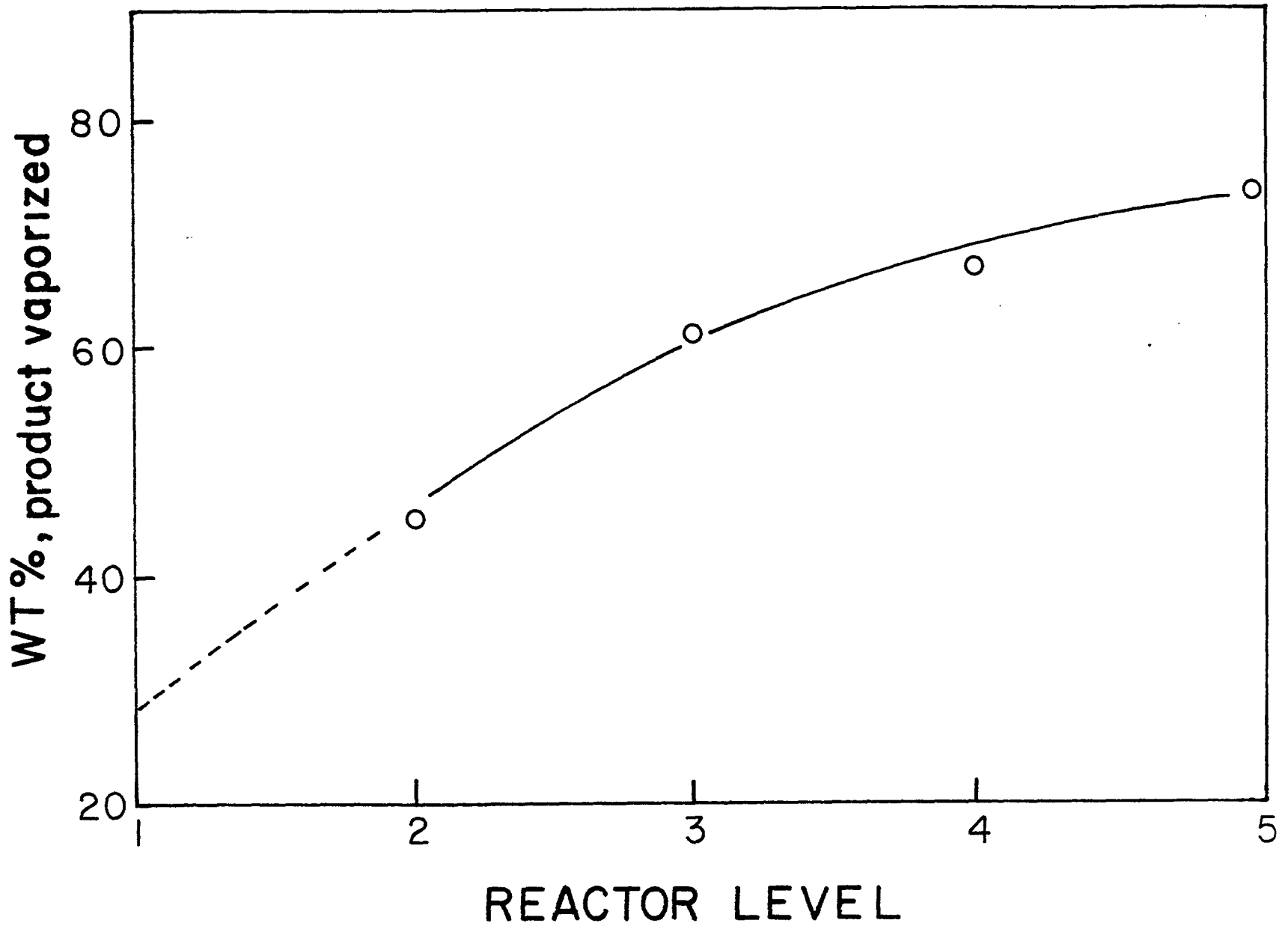


FIGURE 8 - Reactor profile showing the extent of product vaporization

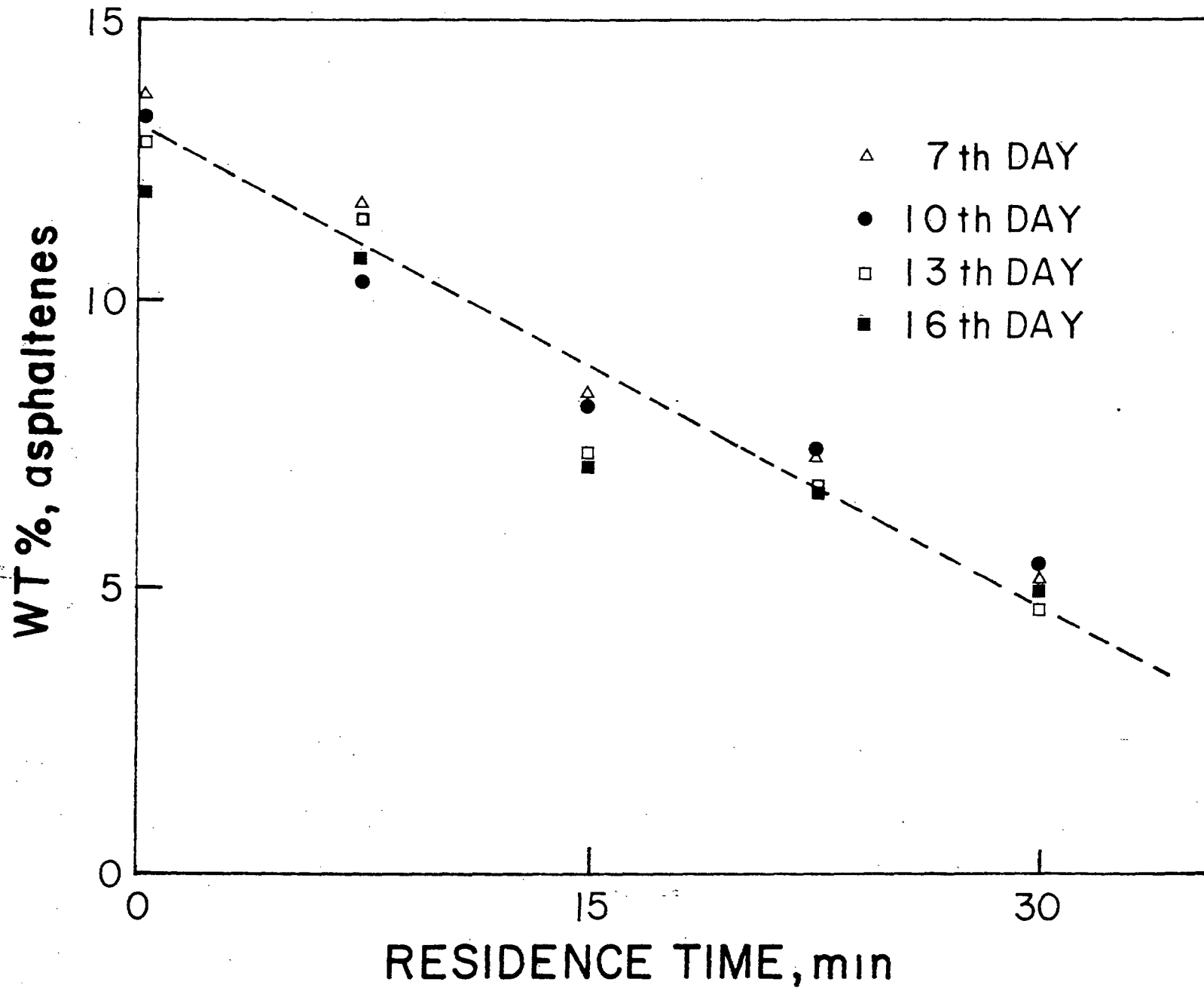


FIGURE 9 - Concentration of asphaltene corrected for product vaporization as a function of residence time in the reactor