

~~OF R 392~~



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

THE EFFECT OF OXIDATION ON THE PROPERTIES OF DEVCO 26 COAL

K. BELINKO AND B.N. NANDI

MARCH 1979

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 78-44 (TR)

CANMET LIBRARY

ERP/ERL 78-44 (TR)
~~OF R 392~~

THE EFFECT OF OXIDATION ON THE PHYSICAL
AND CHEMICAL PROPERTIES OF COKING COALS

by

K. Belinko * and B.N. Nandi **

ABSTRACT

The effect of low temperature oxidation on the coking characteristics of an eastern Canadian high volatile bituminous coal was investigated. The changes in oxygen content and in thermal rheological properties resulting from oxidation of the coal were examined in terms of their influence on coke structure. Optical micrographs of the semi-cokes produced from oxidized coals revealed a transformation to progressively finer grain mosaic structures with increasing degree of oxidation experienced by the coal. Severely oxidized coals produced predominately isotropic coke structures. The significance of these finds in relation to the development of the anisotropic mesophase during carbonization of oxidized coals was discussed.

Toluene extractions of fresh and oxidized coal samples revealed decreasing extraction yields with increasing severity of oxidation. Extraction yields with toluene/methanol mixtures were found to remain approximately constant regardless of the extent of oxidation of the coal.

* Research Scientist, Bitumen Processing Section and ** Head, Coal and Constitution Section, Coal Resource and Processing Laboratory, Canada Centre for Mineral and Energy Technology, Energy Research Laboratories, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

The mechanism of coal oxidation has been extensively investigated both from an academic and from a practical point of view. Many workers have studied the reaction of oxygen with coal as a means of elucidating the chemical structure of coal, while others have investigated the effect of oxidation on the use of coal as an energy source. For instance, in coal gasification processes, a mild oxidation of a strongly caking bituminous coal is desirable to prevent operational problems associated with agglomeration of the coal (1). Coal oxidation has also been suggested as a pretreatment of strongly caking coals in carbonization processes (2). In general oxidation has been found to have an adverse effect on the use of coal as fuel (3, 4).

If a coal is oxidized under moderate conditions, e.g. at temperatures below 200°C in air, the incorporation of oxygen into the coal structure is thought to generate primarily carbonyls and carboxylic groups (5). These functional groups may be expected to induce various types of polymerization reactions during pyrolysis of the coal, including the formation of oxygen cross-linkages between structural units of the coal. Such polymerization reactions would significantly alter the thermal rheological properties of the coal.

A coking coal which has been subjected to various degrees of oxidation progressively loses its coking character (3, 6). It has been proposed that the process of oxidation results in polymerization reactions which interfere with the natural progression of carbonization (6). During pyrolysis of a coking coal, structural units known as liquid crystals are formed and align themselves, thereby giving rise to what is commonly referred to as an anisotropic mesophase. The development of the mesophase constitutes the reinforcing network within the coke structure which is responsible for the strength of the coke. The formation of cross-linkages between structural units of the coal, resulting from oxidation, may inhibit the growth mechanism of the liquid crystals and interfere with the development of the anisotropic mesophase. When this happens, the coal loses its coking properties.

A high volatile bituminous coking coal from Nova Scotia (Devco 26) was selected for this investigation. Samples of this coal were subjected to various degrees of oxidation under controlled conditions and the thermal rheological properties of the fresh and oxidized coal were examined and correlated to changes in the coke structure of the carbonization products. Solvent extraction of the fresh and oxidized coal were also carried out using foluene and toluene/methanol mixtures.

EXPERIMENTAL PROCEDURE

Devco 26 coal, crushed to minus 100 mesh U.S. standard sieve was spread on trays to a thickness of about 2mm and oxidized in air at 105°C in a thermostatically controlled oven. Representative samples of the oxidized coal were collected at specified time intervals and immediately sealed in plastic bags for storage under refrigeration until used. This method of storage has been found to be satisfactory for arresting oxidation of coals (7). The oxygen content of the fresh and oxidized coals were determined by neutron activation and by elemental analysis with a Perkin-Elmer 240 analyzer.

The dilatation characteristics of the fresh and oxidized coals were determined by a Ruhr dilatometer at a heating rate of 3°C/min. to 550°C. Semi-cokes obtained from the dilatation tests were mounted in Lucite plastic and polished by standard methods. Microscopic examination of the semi-cokes were made with a Leitz reflected light microscope at a magnification of 600X using partially crossed nicols.

Samples of fresh and oxidized coal were extracted with boluene and with toluene/methanol mixtures (50:50 by volume) by soxhlet extraction methods for 24 hours. Coal extracts were concentrated to approximately 1 gm in a rotary evaporator. The concentration of the solutions therefore varied according to the extent of the extraction.

RESULTS AND DISCUSSION

Properties of the fresh Devco 26 coal are presented in Table 1. The changes in oxygen content and thermal rheological properties resulting from oxidation are summarized in Table 2. As the oxygen content of the coal increased, the dilatation, plasticity index, FSI and maximum fluidity of the coal were found to decrease.

Optical micrographs of polished sections of the semi-cokes produced from dilatation experiments of fresh and oxidized coal are shown in Figs.1-4. As the degree of oxidation of the coal increased, the anisotropic grain mosaic texture of the semi-coke was found to become progressively finer. Coal samples that had been oxidized for periods in excess of 100 hrs. at 105°C were found to produce semi-cokes having predominantly isotropic textures as shown for example in Fig.4. The absence of an anisotropic coke structure from coal samples that had been severely oxidized indicated that the presence of oxygen in the coal was interfering with the formation and growth of liquid crystal structures. This prevented the development of an anisotropic mesophase during carbonization. The mechanism of low temperature oxidation of coal has been suggested to involve the initial formation of an unstable peroxygen type carbon-oxygen complex which decomposes at temperatures above 70°C (8). The decomposition of the peroxygen complex is presumed to generate carbonyl and carboxyl groups in the coal. The presence of these oxygen functional groups during carbonization could induce various forms of polymerization and condensation reactions between structural units of the coal. This would then account for the deleterious effects on the thermal rheological properties of the coal. In addition, such polymerization reactions could inhibit the formation and growth of liquid crystals thereby preventing the development of an anisotropic mesophase during carbonization.

In a separate study, samples of a light volatile bituminous coal from Nova Scotia that had undergone extensive weathering thereby losing their coking properties were rendered coking again by thermal hydrogenation (9). Depending on the severity of the hydrogenation treatment, various

levels of deoxygenation were achieved and the coking properties of the deoxygenated coal were examined. Infra-red analysis of the original oxidized coal and its hydrogenated product revealed that the latter had a substantially lower concentration of $-H$, $C=O$ and $C-O-C$ and CH groups. As more oxygen was removed from the weathered coal, the thermal rheological properties were found to improve significantly and an anisotropic mesophase developed. A transformation from an isotropic coke structure to a grain mosaic and finally to a flow-type coke structure was achieved depending on the severity of the hydrogenation treatment. A similar study was undertaken by Wachowska et al (6) using various types of reducing agents as a means of restoring the coking properties of oxidized coals.

Results from toluene extraction of samples of the fresh and oxidized Devco 26 coal are shown in Fig.5. The extraction yield was found to decrease appreciably with increasing severity of oxidation. The optical density of the extracted solutions was found to decrease commensurately with extraction yield.

Extraction yields with toluene/methanol mixtures were not found to vary consistently with the degree of oxidation experienced by the coal as in the case of toluene extractions. Instead, the yield was found to be approximately $2.5 \pm 0.5\%$ irrespective of the severity of oxidation of the coal. The extract solutions were however found to become progressively darker as the degree of oxidation increased suggesting the presence of polar compounds. Some workers have reported increases in extraction yields of oxidized coals with benzene/alcohol mixtures (10).

Low temperature extractions with solvents such as those used in this study are known to be non-representative of the constitution of the coal as a whole (11). The extracts are derived predominantly from resinous materials which make-up a relatively small fraction of the coal. In spite of this, it is noteworthy that the reduction in toluene extraction yield, as the degree of oxidation of the coal increased, complemented the corresponding changes in thermal rheological properties of the coal.

The results of Fig. 5 suggest that some of the toluene-soluble components of the fresh coal are converted to toluene-insoluble products during the course of oxidation. It seems likely that the toluene-insoluble products of oxidation make-up part of the toluene/methanol extract collected from oxidized coal samples. This may explain the relatively constant extraction yields obtained with toluene/methanol mixtures irrespective of the degree of oxidation experienced by the coal.

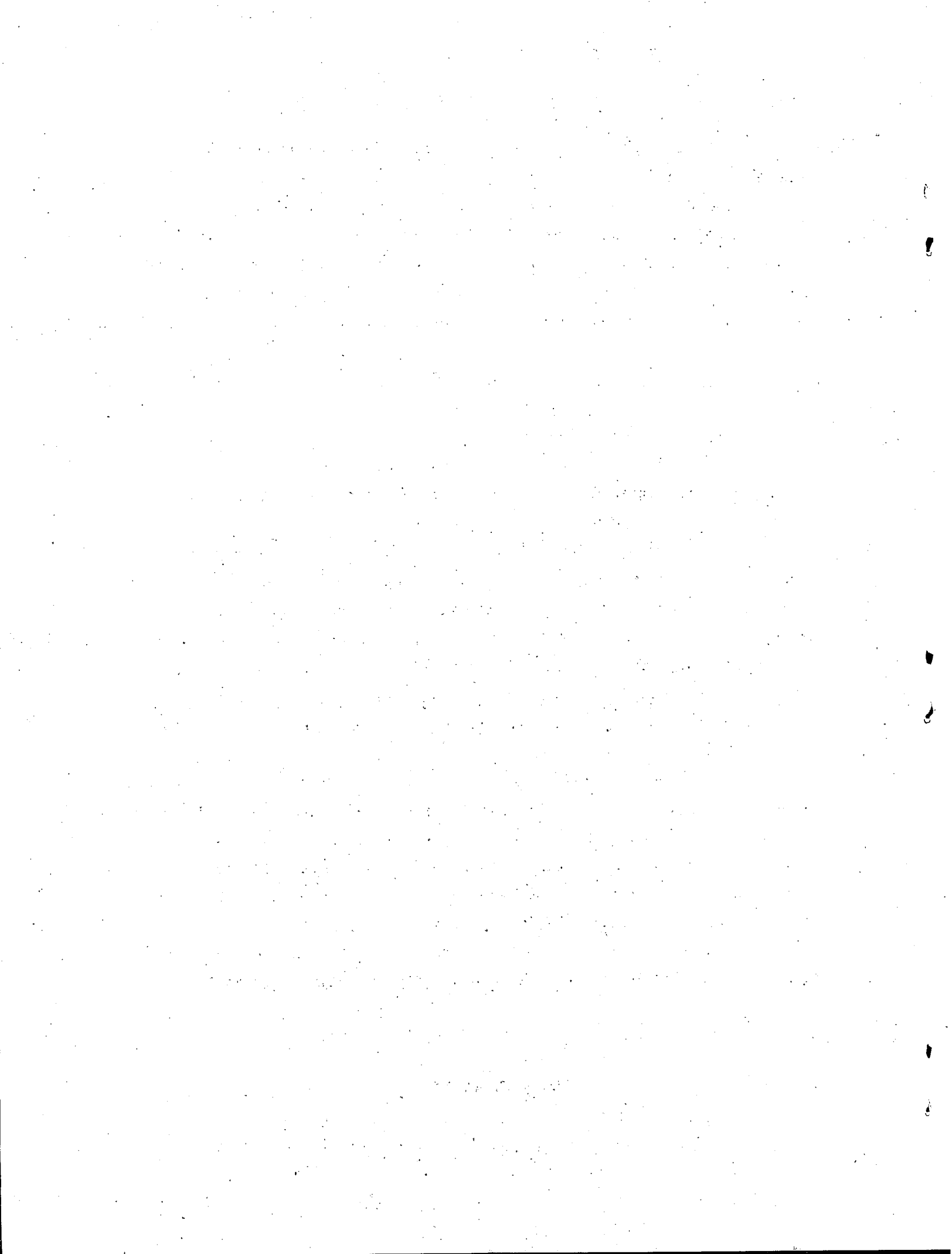
CONCLUSION

Oxidation of coking coals significantly alters their thermal rheological properties and consequently change their coking character. The incorporation of oxygen in the coal structure can result in a wide variety of polymerization reactions. These polymerization reactions account for the changes in thermal rheological properties of the oxidized coal and interfere with the development of the anisotropic mesophase during carbonization. As the degree of oxidation experienced by the coal increases, a progressively finer grain mosaic coke structure is formed on carbonization. When the coal has been severely oxidized, a predominantly isotropic coke structure is formed resulting in a non-agglomerated char product.

Solvent extraction of bituminous coking coals may serve as a means of detecting oxidation. If the coal is fresh, the extraction yield with toluene appears to be approximately equal to the yield obtained with a toluene/methanol mixture. As the coal undergoes oxidation, a greater extraction yield may be expected from a toluene/methanol mixture than from toluene alone. The incorporation of oxygen into the coal structure decreases the solubility of the coal in toluene, but appears to have a negligible effect on its solubility in toluene/methanol mixtures.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the technical assistance of B.H. Moffatt and S. Nixon during the course of this work.



References

1. Kam, A.Y., Hixson, A.N. and Perlmutter, D.D. "The oxidation of bituminous coal" Chem. Eng. Sc.; v.31, p.815; 1976
2. Ignasiak, B.S., Carson, D., Jadernik, P. and Berkowitz, N. "Metallurgical cokes from oxidized high caking coals" Am. Chem. Soc. Div. Fuel Chem.; V.23, no.1, p.252; March 1979
3. Gray, R.J., Rhoades, A.H. and King, D.T., "Detection of oxidized coal and the effect of oxidation on the technological properties"; Transactions of SME, V.260
4. Ignasiak, B.S., Nandi, B.N. and Montgomery, D.S. "Oxidation studies on coking coal related to weathering (1) Chromatographic analysis of pyrolysis gases as a method of studying coal weathering", Fuel; V.49, 1970
5. Mazumdar, B.K., Charkerabarty, S.K., Saha, M., Anand, K.S. and Lahiri, A. "Further studies on the mechanism of the oxidation of coal" Fuel, V.38, p.469, 1959
6. Wachowska, H.M., Nandi, B.N. and Montgomery, D.S. "Oxidation studies on coking coal related to weathering. (4). Oxygen linkages influencing the dilatometric properties and the effect of cleavage of ether linkages." Fuel; V:53, p.212; July 1974
7. Ciavaglia, L.A., Botham, J.C. and Nandi, B.N., "The effects of sample preparation and storage on the thermal rheological properties of coking coals"; CANMET Laboratory Report ERP/ERL 77-62 (R); 13 pp; July 1977
8. Lowry, H.H. "Chemistry of coal utilization" John Wiley and Sons, Inc., New York, p.281; 1963
9. Nandi, B.N., Belinko, K. and Ternan, M., "Conversion of non-coking coals to coking coals by thermal hydrogenation" Fuel (in preparation for submission)
10. Rusin, Aleksandra, "Effect of coal oxidation on the physical-chemical properties of benzene-alcohol extracts", Koks, Smola, Gas; V.17, p.193; 1972
11. Van Krevelen, D.W. "Coal", Elsevier Publishing Co. New York, p.185, 1961

TABLE 1
Properties of Devco 26 Coal

<u>Proximate analysis,</u>	wt %
Moisture	1.16
Ash	2.83
Volatile matter	33.95
Fixed carbon	62.06
 <u>Ultimate analysis,</u>	 wt. %
Carbon	84.09
Hydrogen	5.3
Sulphur	0.79
Nitrogen	1.74
Oxygen (by diff.)	4.09
(by neutron activation)	6.50
(by elemental analysis)	5.97
 <u>Maceral analysis,</u>	 vol. %
Vitrinite	73.6
Gxinite	6.0
Micrinite	4.8
Semi-fusinite	10.4
Fusinite	4.6
Pyrite	0.6

TABLE 2
Thermal Rheological Properties of Fresh
and Oxidized* Devco 26 Coal

		Oxidation time, hr.					
		0	24	48	72	96	144
<u>Oxygen content,</u>	wt %						
by neutron activation		6.50	8.07	8.50	-	-	9.53
by elemental analysis		5.88	6.15	6.47	6.51	6.67	7.92
<u>Free Swelling Index</u>		8	7½	7½	7	6½	4½
<u>Dilatation</u>							
Softening temperature	°C	344	350	355	356	359	371
Contraction	%	27	28	29	32	31	15
Dilatation	%	310	190	70	2	nil	nil
Plasticity index		0.50	0.40	0.40	0.37	0.27	0.12
<u>Gieseler Plasticity</u>							
Fusion temperature,	°C	405	414	422	430	435	-
Max. fluid temperature	°C	429	444	450	450	448	451
Final fluid temperature	°C	484	478	485	472	471	-
Solidification temperature	°C	484	482	485	480	478	473
Maximum fluidity	dd/m	26100	5900	1200	260	47	0.9

* at 105°C in air

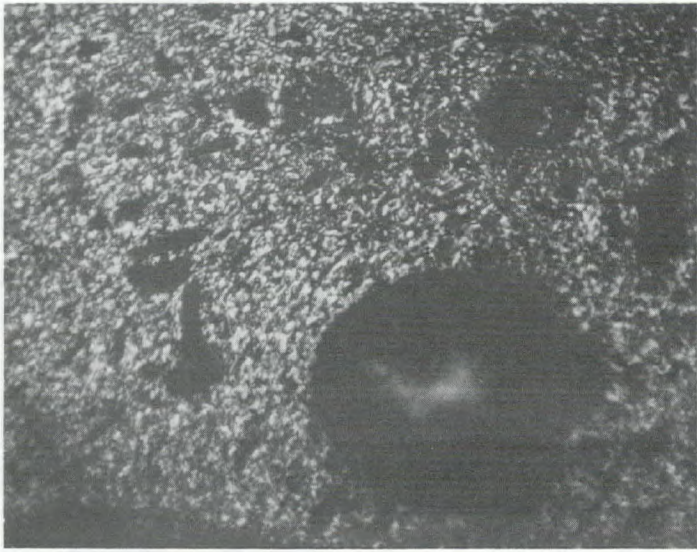


Figure 1 - Optical Micrograph
of Semi-coke of Fresh Devco 26
Coal Showing Medium-coarse Grain
Mosaic Structure (X600)

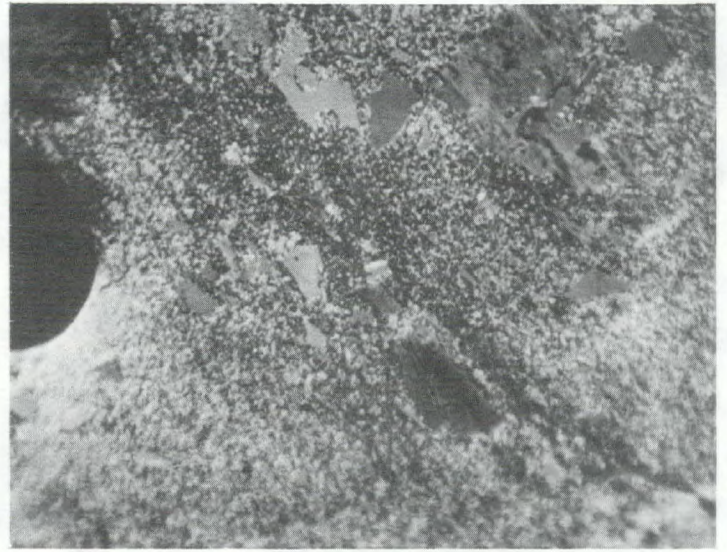


Figure 2 - Optical Micrograph
of Semi-coke of Oxidized Devco 26
Coal; 24 hr. at 105°C in air (X600)

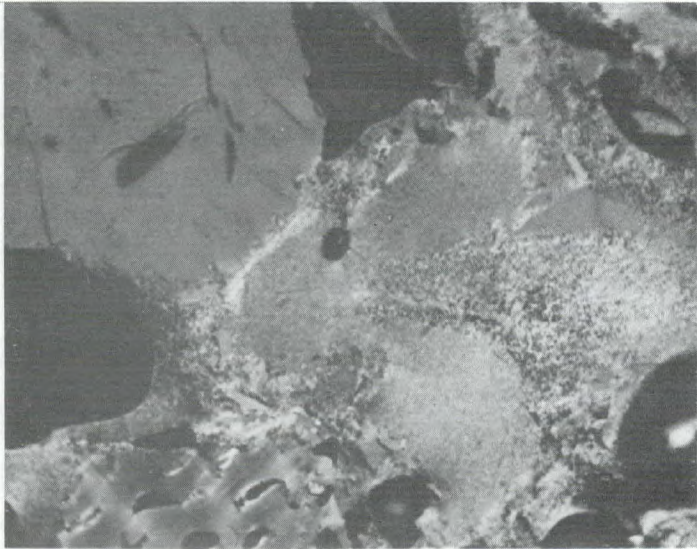


Figure 3 - Same as Fig.2;
Oxidized for 72 hr. at
105°C in air (X600)

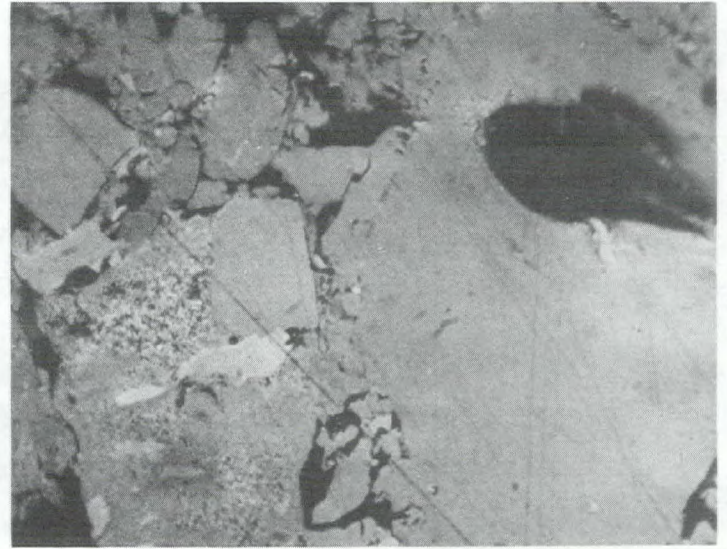


Figure 4 - Same as Fig.2;
Oxidized for 144 hr. at
105°C in air (X600)

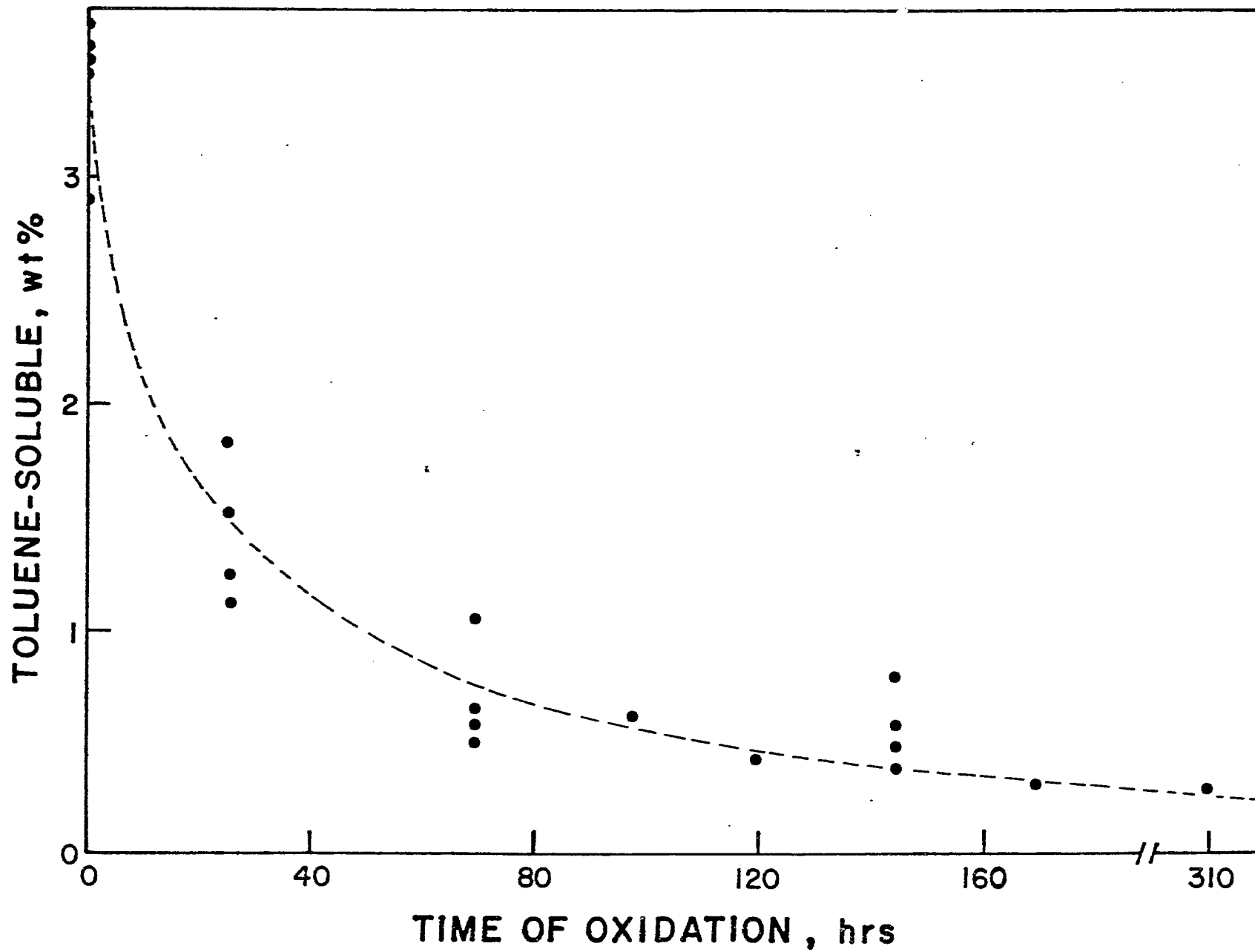


FIGURE 5 - Extraction Yields of Fresh and Oxidized Devco 26 Coal with Toluene