PITCH RESIDUES FROM UPGRADING OF BITUMEN AND HEAVY OILS AS ADDITIVES IN COKEMAKING: INFLUENCE OF PITCH PROPERTIES

K. Belinko, L.A. Ciavaglia, B.N. Nandi and J.M. Denis,

Energy Research Laboratories
Canada Centre for Mineral and Energy Technology,
Department of Energy, Mines and Resources,
c/o 555 Booth Street, Ottawa, Ontario K1A 0G1

INTRODUCTION

Impending shortages of good coking coals throughout the world have prompted a series of investigations at CANMET (Canada Centre for Mineral and Energy Technology) into the utilization of western Canadian marginal coking coals in the production of metallurgical grade coke. One possible way to do this is to add residual pitch from thermal hydrocracking of bitumen and heavy oils to such coals (1). This pitch has been found to be an excellent additive for up-grading low fluid, low volatile, inert-maceral rich coals. The pitch acts as a fluidity-enhancing agent, and by interacting with the vitrinite of the coal, augments the supply of reactive carbon necessary for bonding together of inert macerals.

The purpose of this publication is to add further insight into the role of pitch in carbonization of coal/pitch blends. Pitches derived from thermal hydrocracking of bitumen at different degrees of severities were utilized for this purpose. This provided a means of assessing the properties of the pitches in the carbonization process without changing the basic chemical nature of the parent material.

EXPERIMENTAL

The properties of the pitches derived from thermal hydrocracking of Athabasca bitumen under various operating conditions are given in Table 1. These four pitches were produced under different degrees of severity during the process A being characteristic of pitch obtained under relatively mild conditions and D, of pitch obtained at high severities. A relation was found to exist between the degree of severity during hydrocracking and the various properties listed in Table 1 (e.g. CCR, aromaticity, softening point).

TABLE 1

Physical and Chemical Properties of Pitches

		Pitch			
		A	B	C	D
Volatile matter	%	73.1	64.8	53.5	44.6
Ash	%	1.8	2.3	3.2	5.8
Softening temperature	°C	50	95	105	135
Conradson carbon residue	%	34.7	42.2	50.7	64.6
Specific gravity		1.10	1.13	1.16	1.24
Benzene-insolubles*		2.6	4.2	11.6	20.6
Asphaltenes	%	37.2	44.6	48.1	55.2
H/C		1.32	1.19	1.09	0.94
Sulphur	%	5.58	5.63	6.33	4.85
Aromaticity**	%	38.2	49.4	56.3	69.8

* Ash-free basis, ** ^{13}C NMR analysis

The coal used was a western Canadian, low fluid, high rank bituminous coal having a relatively high concentration of inert macerals. Proximate, ultimate and petrographic analyses of this coal are given in Table 2.

TABLE 2

Properties of the Coal

Proximate Analysis		(dry basis)
Ash	%	9.8
Volatile matter	%	21.2
Fixed Carbon	%	69.0
Ultimate Analysis		
Carbon	%	78.9
Hydrogen	%	4.3
Sulphur	%	0.8
Nitrogen	%	1.3
Oxygen (by diff.)	%	4.9
Ash	%	9.8
Petrographic Analysis		
Vitrinite	vol. %	51.8
Semi-fusinite	vol. %	34.2
Fusinite	vol. %	11.2
Micrinite	vol. %	2.6
Exinite	vol. %	0.2
Mean reflectance in oil, R_o		1.17

Coal/pitch blends with varying pitch concentrations were prepared and their fluidities determined by means of a Gieseler plastometer. The fluidities of the various blends are reported in Table 3. A value representing the concentration of pitch which can potentially interact with the coal during carbonization, C_p, is also given in Table 3. C_p was calculated on the following basis:

$$C_p = \begin{pmatrix}\text{Concentration of pitch}\\ \text{in the coal-pitch blend}\end{pmatrix} \times \begin{pmatrix}\text{wt.\% CCR in}\\ \text{the pitch}\end{pmatrix} \qquad 1)$$

where CCR is the Conradson carbon residue (2) and approximates the contribution of carbonaceous material made by the pitch to the blend during carbonization.

The various coal/pitch blends were carbonized using a canister coking technique developed at CANMET (3). The blends were packed to a bulk density of 801 kg/m^3 into perforated tin plate canisters 29.3 cm long and 7.6 cm in diameter. Twenty cans, each containing a different blend were side-charged into CANMET's 250-kg moveable wall coke oven.

The relative strengths of the cokes produced from the canister test were determined by a small sample tumbler test developed by Bituminous Coal Research (BCR) (4) and are reported in Table 3. These strength indices are a measure of size reduction in tumbled coke particles and therefore a large index corresponds to a weak coke.

Optical examinations of the various cokes were made with a Leitz reflected light microscope using an oil immersion lens. The micrographs were taken at 600X magnification using partially crossed nicols.

TABLE 3

Carbonization Data for Coal Pitch Blends

		Concentration of Pitch in Blend wt %					
		0	5	8	10	14	16
Pitch A							
Contribution of carbon from pitch, C_p	%	Nil	1.5	2.4	3.1	4.1	4.7
Fluidity of blend	dd/min	Nil	1.9	6.1	6.4	36	28
BCR* strength index		N/A**	49.0	36.4	38.2	37.4	38.1
Pitch B							
Contribution of carbon from pitch, C_p	%	Nil	2.1	3.3	4.1	5.7	6.6
Fluidity of blend	dd/min	Nil	1.5	5.7	7.1	120	530
BCR* strength index		N/A**	53.8	35.3	34.5	37.3	35.8
Pitch C							
Contribution of carbon from pitch, C_p	%	Nil	2.6	4.1	5.0	7.1	8.2
Fluidity of blend	dd/min	Nil	1.1	5.0	13.0	370	400
BCR* strength index		N/A**	52.7	36.7	36.9	39.0	40.3
Pitch D							
Contribution of carbon from pitch, Cp	%	Nil	3.3	5.2	6.5	9.1	10.4
Fluidity of blend	dd/min	Nil	1.0	4.0	6.8	260	1150
BCR* strength index		N/A**	57.8	43.1	35.1	41.3	45.1

* Bituminous Coal Research Inc., Pittsburgh, P.A.

** A non-agglomerated char was produced

RESULTS AND DISCUSSION

A photograph showing two representative cokes from the canister test is shown in Fig. 1. The coke shown at the top was produced from coal with no pitch additive and was poorly agglomerated. The coke at the bottom was agglomerated and hard and was typical of cokes produced from coal/pitch blends. The former coke could not be evaluated by the BCR tumbler test because of its non-agglomerated character. The strength indices of the cokes produced from coal/pitch blends are given in Table 3.

The strengths of the cokes produced from blends containing pitch A and pitch B were not found to vary significantly for pitch concentrations above 5%. On the other hand, additions of more than 10% pitch in coal/pitch C and coal/pitch D blends were found to be detrimental to coke strength. The influence of pitch concentration on coke strength was therefore more pronounced for pitch obtained from high severity thermal hydrocracking runs. It would be difficult to predict an exact optimum pitch concentration based solely on the results reported in Table 4 for coal/pitch D blends.

Coal/pitch blends having C_p values in excess of about 7% produced cokes of progressively weaker strengths. The Conradson carbon residue (CCR) contents of pitches A and B were sufficiently low to permit additions of up to 16% pitch to the coal without C_p values of the blend exceeding 7%. This would account for the lack of a minimum in BCR strength index for cokes produced from blends containing pitch

A and pitch B within the concentration range investigated.

Fluidity data for the various blends are summarized in Table 3. A marked increase in the fluidity of the blends was observed for pitch concentrations greater than 10%. The increase in fluidity was generally found to be more pronounced for pitch obtained from high severity thermal hydrocracking runs. This perhaps suggests that there is a better interaction between pitch and the vitrinite of the coal in cases where the pitch was treated under more severe conditions during thermal hydrocracking. It is evident from Table 1 that pitch aromaticity is directly related to the degree of severity during thermal hydrocracking. The interaction between the pitch and the vitrinite may therefore be related to the aromaticity of the pitch.

Based on some of the arguments presented above, the following relationship was found to be consistent with the data in Table 3:

$$\text{BCR strength index} = 26.47 + 1.75\ \text{Cp}\ \exp\frac{0.97}{A^{3/2}F}; \quad 1.5 \leq \text{Cp} \leq 10.4 \qquad 2)$$

Where Cp is defined according to Equation 1), A is the aromaticity of pitch determined by ^{13}C NMR and F is the fluidity of the coal/pitch blend. Equation 2) is plotted in Fig. 2 and was found to have a coefficient of correlation of 0.89.

According to Equation 2), the BCR strength index of a coke produced from a coal/pitch blend is not only dependent on the value of Cp, but also on the fluidity of the blend. Low values of Cp in the blend appear to be desirable in achieving good coke strength provided the fluidity of the blend is sufficiently high to make the exponential term in the equation approach unity. Once the exponential term has approached unity, additional increases in Cp may only contribute to a deterioration in coke strength. The inter-relationship between Cp and fluidity borne out by Equation 2) emphasizes the need for controlled fluidity in ensuring a uniform and efficient distribution of the binding material throughout the coal during carbonization. This is demonstrated, for instance, in the case of 5% addition of pitch D to the coal, Table 3. Although the Cp value was relatively high, low fluidity prevented proper distribution of the binding material in the coal during carbonization; consequently, a weak coke was produced.

In order to confirm this dependence on fluidity, a series of microscopic examinations was made on the cokes produced from the canister test. The coke produced from the coal with no pitch additive was found to be poorly bonded. Inert macerals were segregated within the coke structure with little or no binding material surrounding them (Fig. 3). Coal/pitch blends produced cokes of varying qualities depending on values of Cp and fluidity. Three specific cases were chosen to demonstrate this dependence: (i) coal + 5% pitch D, (ii) coal + 10% pitch D and (iii) coal + 16% pitch D.

In case (i), coal + 5% pitch D, some degree of bonding was observed between inert macerals, but the bonding was generally discontinuous and sporadic. This is exemplified for instance in Fig. 4. It is noteworthy that for blends having similar Cp values but higher fluidities, e.g. coal + 10% pitch A, bonding was found to be considerably more uniform than that shown in Fig. 4. The difference in bonding can therefore be attributed to the fluidity of the respective blends.

The coke produced from case (ii), coal + 10% pitch D, was found to exhibit excellent bonding. The binding material was uniformly and continuously distributed throughout the coke and the inert macerals were embedded within the coke matrix, Fig. 5. These observations were consistent with the relatively good BCR strength index obtained for this coke.

The deterioration in coke strength observed for case (iii), coal + 16% pitch D, was attributed to the development of micro-cracks within the coke structure, Fig. 6. The mechanism by which these cracks form is not well understood, but could perhaps result from an excess of binding material between the inert macerals of the coal, thereby weakening the overall structure.

From the three cases considered, it is evident that coke strength can be correlated to the micro-structure of the cokes. The coke quality appears to be a complex function of the amount of pitch added, the physico-chemical properties of the pitch and the fluidity of the coal/pitch blend.

It should be emphasized that the arguments presented in this paper apply specifically to inert-maceral rich, low fluid, high rank coals. Equation 2) has so far only been tested for this particular type of coal. It is possible that other coals may yield results that do not conform exactly to this equation. For instance, the coal used in this work had no inherent fluidity, and consequently a term for the fluidity of the coal itself does not appear in the equation. However Equation 2) does demonstrate the strong inter-relationship between the contribution of binding material made by the pitch and the fluidity of the blend.

CONCLUSIONS

High rank coals from western Canada which are rich in inert macerals, generally require a pitch additive to produce metallurgical grade coke. Pitch concentration in the coal/pitch blend dictates both the amount of binding material made available to the coal and the fluidity of the blend. Both these parameters depend on the physico-chemical properties of the pitch and on the extent of interaction between the pitch and the coal.

In order to produce good quality coke from a coal/pitch blend, the blend must possess sufficient fluidity to ensure a uniform and continuous distribution of binding material throughout the coal. Inert macerals of the coal must be adequately wetted and bonded together. Optimum coke strength is achieved when pitch is added in sufficient amount to generate a controlled fluidity with enough binding material to agglomerate the coke. If added in large amounts, the pitch can have deleterious effects on the resultant coke. The reason why too much pitch weakens the structure is not well understood, but appears to be related to the development of microcracks within the coke matrix.

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REFERENCES

1. Belinko, K., Ciavaglia, L.A. and Nandi, B.N. "Energy for industry", Ed. P.W. O'Callaghan; Pergamon Press (London); pp. 79-89 (1978).

2. American Society for Testing and Materials; Part 23, D-189 (1975).

3. Montgomery, D.S. and Nandi, B.N. Fuels Research Centre Divisional Report 73/11; Department of Energy, Mines and Resources, Ottawa, Canada (1973).

4. Moses, R.G. Bituminous Coal Research Inc., Monroeville, Pennsylvania; Personal Communication.

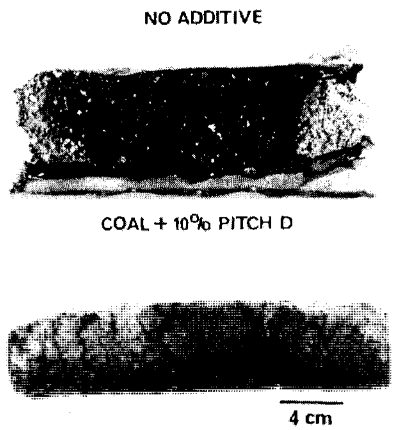

FIGURE 1: High Temperature Cokes Produced From Canister Tests

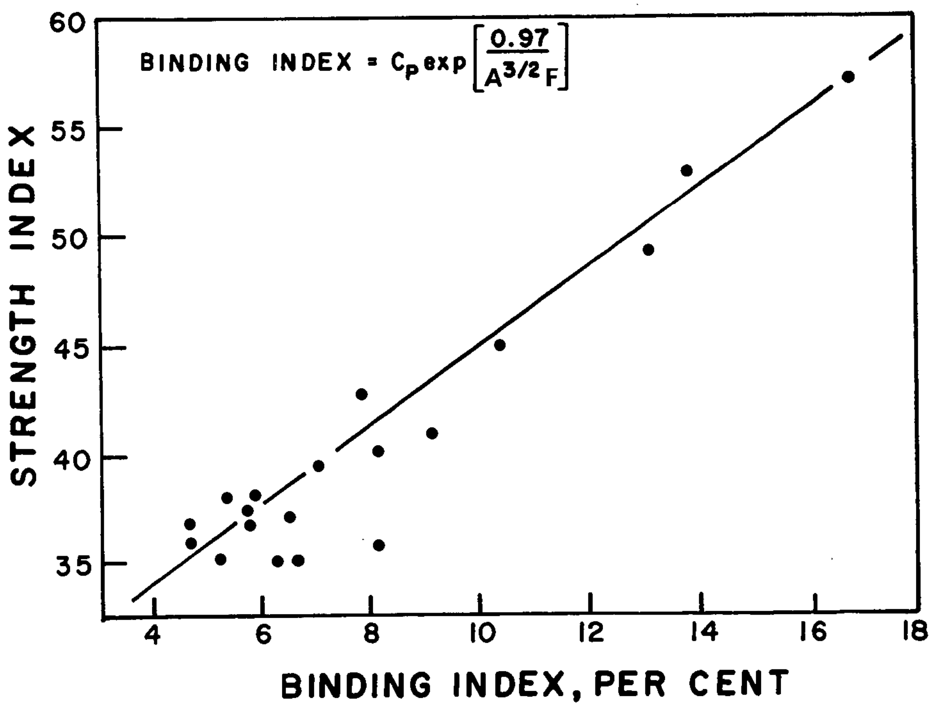

FIGURE 2: Relative Strength Indices for Various Coal/Pitch Blends

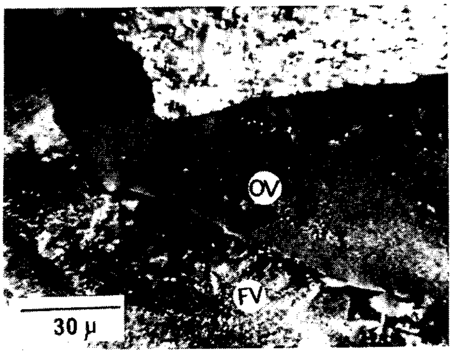

FIGURE 3: Optical Micrograph of Coke Produced from Coal With No Additive Showing Poor Bonding Between Fused Vitrinite (FV) and Oxidized Vitrinite (OV)

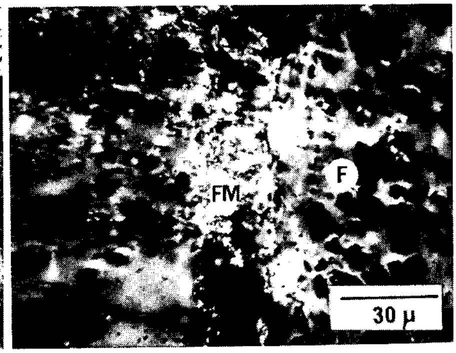

FIGURE 4: Optical Micrograph of Coke Produced from Coal + 5% Pitch D Showing Discontinuous Bonding of Fused Mass (FM) With Fusinitic Structure (F)

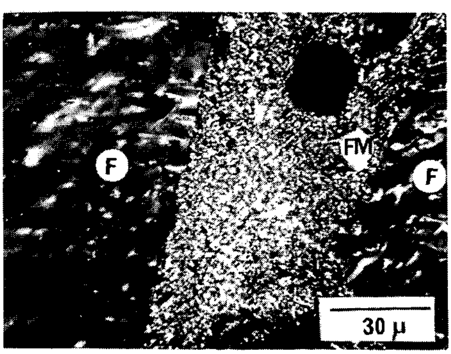

FIGURE 5: Optical Micrograph of Coke Produced from Coal + 10% Pitch D Showing Excellent Bonding of Fusinitic Structure (F) by Fused Mass (FM)

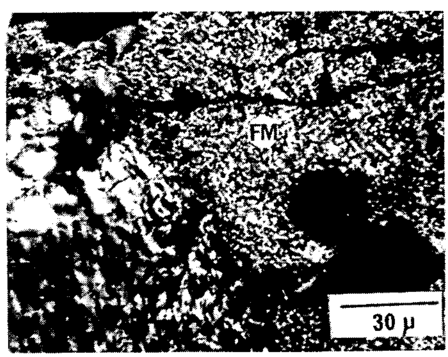

FIGURE 6: Optical Micrograph of Coke Produced From Coal + 16% Pitch D Showing Development of Micro-cracks Within Fused Mass (FM)