original

ADDITION OF PITCH BINDERS TO WESTERN
CANADIAN MARGINAL COKING COALS IN
COKEMAKING PART I: EVALUATION OF
PITCHES FROM VARIOUS SOURCES

L.A. CIAVAGLIA, K BELINKO AND B.N. NANDI

SEPTEMBER 1978

ERP/ERL 77-98(R)

INTRODUCTION

Recently at CANMET interest has developed in the addition of bitumen pitches in the upgrading of marginal western Canadian coking coals.(1,2)   This pitch addition would serve a threefold purpose in the upgrading process; first as a source of fluidity, a necessary property of a good coking coal, secondly as a wetting agent for the inert components of the coal during carbonization and thirdly as a source of binder to enhance the bonding action of the reactive vitrinite.

During the carbonization of a blend of coal and bitumen pitch the vitrinite component of the coal and the pitch combine to form one fused mass upon solidification. This reaction occurs provided that the vitrinite has not become badly oxidized and that the melting ranges of the vitrinite and pitch overlap. The greater the extent of this overlapping the more homogeneous is the final structure of the fused mass. The physical properties of the combination of the two components may not be additive, that is, they may differ from either the properties of the pitch and vitrinite.

To further some rheological studies performed on marginal coking coals and various bitumen pitches it was decided to carbonize a series of these blends in a high temperature coke oven using canister coking techniques. (3)

EXPERIMENTAL

Part 1

The coal selected for this study was a western Canadian high inert, partially oxidized coal of low fluidity. The proximate, ultimate and petrographic analyses along with carbonization data from CANMET'S 250 KG movable wall oven are given in Table 1. The pitches used were the vacuum bottoms (+524°C) of Athabasca and Cold Lake bitumen feedstocks, and the thermal hydrocracked residue products of Athabasca and Cold Lake bitumens. The thermally hydrocracked residue from Lloydminster bitumen was also used along with a coal tar pitch obtained from the Aluminum Company of Canada. The analyses of these pitches are given in Table 2.

The coal/pitch blends were used in this study:

Coal + 20% Athabasca Pitch

Coal + 20% Athabasca Residue

Coal + 10% Athabasca Residue

Coal + 20% Cold Lake Pitch

Coal + 20% Cold Lake Residue

Coal + 10% Cold Lake Residue

Coal + 20% Lloydminster Residue

Coal + 10% Lloydminster Residue

Coal + 20% Coal Tar Pitch

Coal + 10% Coal Tar Pitch

Coal (-20 U.S. Sieve) + 10% Athabasca Residue

Coal (-20 U.S. Sieve) + 10% Coal Tar Pitch

With the exception of the particle size study which used -20 U.S. standard sieve coal, all coal was crushed to -6 U.S. standard sieve. The particle size of the pitch was -20 U.S. standard sieve.

The canisters used in the carbonization of the coal blends were constructed of perforated tin plate 0.03 cm thick. The length of each canister was 29.2 cm with a diameter of 7.6 cm. Perforations were 0.1 cm in diameter with 0.17 cm square centres. One end of the canister was capped and spot welded while the other end had a removable cap (Fig. 1). The canisters were lined with wax paper to avoid seepage during packing and handling.

All coal/pitch blends were mixed thoroughly in a mechanical mixer and packed into the canisters to a density of 801 kg/m^3 at a moisture of 4%. After the canisters were filled the open ends were capped and secured with wire. All canisters were labelled with metal tags and arranged in a specially constructed wooden box 91.4 cm by 91.4 cm by 30.0 cm deep, surrounded by a matrix coal. The entire assemble was then charged in the 250 KG movable wall oven using side charging techniques (4) and carbonized for 10.5 hours to a centre temperature of 1010°C. As the coke charge was pushed from the oven the canisters were separated from the matrix coke and quenched with water. After drying overnight the canisters were opened and a visual evaluation was made on the cokes.

In order to test the relative strengths of the canister cokes, a slightly modified version of a small sample tumbler test developed by Bituminous Coal Research (5) was utilized. The apparatus consisted of two stainless steel tubes 30.5 cm in length and 5.1 cm in diameter, each with two removable threaded caps and twelve steel balls 1.3 cm in diameter (Fig. 2). A 30.0 gram coke sample of specified sieve size (-4 + 8 U.S. standard sieve) was placed in each tube along with the twelve steel balls and tumbled at 25 rpm for 800 revolutions. The fragmented coke was sieved and the average coke size reduction (percentage) calculated (5). The stronger the coke, i.e., the greater its resistance to crushing and abrasion by the steel balls and tumbling action the smaller the average size reduction; thus a relative strength index could be calculated for the various cokes. The data for this test is given in Table 3.

Selected cokes were mounted in epoxy resin and polished for examination under a reflected light microscope in order to study the bonding effect of the pitch additives. The following cokes were related for this examination:

Original Coal

Coal + 10% Athabasca pitch

Coal + 10% Athabasca residue

Part 2

Utilizing the results from part 1, a 250 KG oven charge was carried out using 11% Athabasca residue as an additive for a poor coking coal from western Canada. This pitch was chosen due to its favourable effects in part 1 of this study, and was crushed to -20 U.S. standard sieve while the coal was crushed to -6 U.S. standard sieve. The blend was carbonized in CANMET'S 250 KG movable wall oven. The carbonization data is given in Table 4. An A.S.T.M. stability test, along with a Bituminous Coal Research tumbler test, were performed on both the additive free coke and coke with pitch addition. The data is given in Table 4. Both cokes were also examined under the reflected light microscope to study the effect of the pitch.

RESULTS AND DISCUSSION

Part 1

All of the canister cokes came out reasonably intact with the exception of pitch free coke, which showed virtually no bonding and came out in small individual lumps. Cokes that contained binder pitch appeared to be quite hard while the lumps of the pitch free coke were soft and easily crushed between the fingers. Fig.3 Due to this extreme lack of bonding in the pitch free coke, strength tests were virtually impossible to conduct and obtain any meaningful results.

A blend of the coal and 20% Athabaska pitch yielded a coke with a strength index of 67.5. Upon replacing this pitch with 20% Athabasca residue, the strength index rose to 54.0 and further rose to 42.3 for a concentration of 10% Athabasca residue. However, when 10% Athabasca residue was added to -20 U.S. standard sieve coal, the strength index of the resultant coke dropped slightly to 44.3. The increased surface area of the coal may explain this decrease in coke strength. An increase in the concentration of Athabasca residue may offset the increase in surface area and retain the original strength of the coke. Utilization of a concentration of 20% Cold Lake pitch achieved a strength index of 60.5 and with 20% Cold Lake residue, a strength index of 55.3. As with Athabasca, a concentration of 10% Cold Lake residue, which yielded an index of 47.5, proved to be the most favourable concentration in the upgrading of the coke. Indices of 45.1 and 46.5 were obtained using blends of 10% and 20%, respectively, of Lloydminster residue. No coke was made using Lloydminster pitch due to its soft nature which makes it virtually impossible to crush and blend with the coal.

The blend of the coal with 20% coal tar pitch produced a coke with a strength index of 62.4 which climbed to 41.0 when the coal tar pitch concentration was lowered to 10%. Blending 10% coal tar pitch to -20 U.S. standard sieve coal drastically dropped the strength index to 65.7. Again, the increased surface area of the coal may have been the reason for this decline in coke strength with the binder being spread too thin throughout the blend, although the decrease in coke strength was much more severe than in the case of Athabasca residue binder.

Examination of the cokes under the microscope supported the

strength test results. The lack of bonding between the reacted coke and inert macerals in the pitch free coke is illustrated in Figure 4. This absence of bonding would have given rise to a very low strength of the coke. The addition of Athabasca pitch improved the strength of the coke and this can be supported from the micrograph of the coke structure, Fig.5, which shows the surface bonding effect of the pitch with the inert macerals. The strength of the coke further improved with the addition of Athabasca residue. The micrograph of this coke structure, Fig. 6, shows not only a surface bonding effect but actual penetration into the cavities of the inert macerals which would give additional strength to the structure.

Part 2

The addition of Athabasca residue to the coal improved the strength quality of the coke. The A.S.T.M. stability factor was increased 23% from 36.8 to 45.3 and the A.S.T.M. hardness factor 24% from 55.9 to 69.4. Another factor in the improvement of the quality of the coke was the reduction of the coke breeze which dropped from 7.6% to 3.1% with the addition of the residue. The increase in coke strength was also observed in the small sample tumbler test. The addition of Athabasca residue raised the strength index from 35.1 to 29.2 an increase of 17%.

Although the micrograph of coke showed some bonding between the coke structure and inert macerals, Fig.7, the bonding with binder addition was much superior. The bonding in the latter case not only showed good surface but also penetration into the pores of the inert macerals helping adherement to reinforce the structure. Fig.8

CONCLUSIONS

In the canister study all binders had a beneficial effect on the strength of the coke, with the thermally hydrocracked residues being a much more superior binder than the vacuum bottoms of the feedstocks. Ten percent appears to be the near optimum concentration for Athabasca and Cold Lake residues while the optimum concentration of Lloydminster residue may not have been achieved for this particular coal.

A concentration of 10% coal tar pitch along with 10% concentration of Athabasca residue yielded the cokes with the highest strength respectively. However Athabasca residue does not appear to be as sensitive to changes

in coal particle size as does the coal tar pitch during carbonization. The coal tar pitch could not seem to cope with the increase in surface area of the coal resulting in a weak coke structure while Athabasca residue appeared to compensate in some form with the surface area increase and the resultant coke retained almost all of its original strength.

The addition of the Athabasca residue improved the quality of the coke in the full scale 250 KG oven test by increasing the A.S.T.M. stability and hardness factor while decreasing the percentage of coke breeze.

Athabasca residue appears to be an excellent binder for poor coking coals due to its bonding and penetration effects along with its insensitivity to changes in the particle size of the coal with which it is to be blended.

A further study to look at the various parameter of thermally hydrocracked bitumen and their most useful concentration as a binder is presently being undertaken.

TABLE   I

Properties of Coal

Proximate Analysis

Ash	9.8 %
Volatile matter	21.2 %
Fixed carbon	69.0 %

Ultimate Analysis

Carbon	78.2 %
Hydrogen	4.3 %
Sulphur	0.82%

Petrographic Analysis

Vitrinite	51.8 %
Semi-fusinite	34.2 %
Fusinite	11.2 %
Micrinite	2.6 %
Exinite	0.2 %
Mean Reflectance in Oil (Ro)	1.17%

Coke Evaluation

Breeze	26.2 %
ASTM Stability	34.8 %
ASTM Hardness	48.9 %

TABLE 2

Physical and Chemical Properties
of the Binders Used in these Studies

		Athabasca Bitumen Residue	Athabasca Bitumen Pitch	Cold Lake Bitumen Residue	Cold Lake Bitumen Pitch	Lloydminster Residue	Coal Tar Pitch (Alcan)
Volatile Matter	%	54.5	76.9	68.2	81.8	61.6	55.5
Ash	%	6.6	1.45	0.21	0.15	0.16	0.22
Sulphur	%	4.05	5.78	5.06	5.87	5.64	0.56
Nitrogen	%	1.25	0.62	0.80	0.66	0.73	0.94
Oxygen (by difference)	%	7.79	2.76	2.65	0.10	0.94	0.46
Softening point (Ball and Ring)	°C	143	94	112	79	95	100**
CCR***	%	70.6	23.7	48.1	26.8	44.6	58.7
Specific Gravity		1.25	1.08	1.22	1.08	1.16	1.30
Benzene Insolubles	†	16.8	Nil	14.7	Nil	8.0	32.9
Quinoline Insolubles	†	4.1	Nil	Nil	Nil	–	15.8
Asphaltenes		50.3	30.2	44.6	35.3	41.1	51.5
H/C		0.90	1.27	1.14	1.40	1.14	0.53

** Cube in air (Alcan Method)
***Conradson Carbon Residue
† Ash-free basis

TABLE 3

Coke	BCR Strength Index
Pitch Free	NA
+ 20% Athabasca Pitch	67.5
+ 20% Athabasca Residue	54.0
+ 10% Athabasca Residue	42.3
+ 20% Cold Lake Pitch	60.5
+ 20% Cold Lake Residue	55.3
+ 10% Cold Lake Residue	47.5
+ 20% Lloydminster Residue	46.5
+ 10% Lloydminster Residue	45.1
+ 20% Coal Tar Pitch	62.4
+ 10% Coal Tar Pitch	41.0
(-20 U.S. Sieve) + 10% Athabasca Residue	44.3
(-20 U.S. Sieve) + 10% coal tar pitch	65.7

TABLE 4

CHARGE DATA	COAL	COAL + 11% ATHABASCA RESIDUE
Moisture (%)	3.0	2.6
Oven b d (Kg/M^3)	817	818
Coke Yield (d) (%)	74.8	74.1
Pressure (KP)	1.59	2.96
Coking Time (Hr-Min)	9-45	10-40
Centre Temperature (^{o}C)	1015	1010

EVALUATION		
Breeze (%-1.27 cm)	7.6	3.1
Mean Coke Size (cm)	5.23	5.03
Stability Factor	36.8	45.3
Hardness Factor	55.9	69.4
B.C.R. Strength Indes	35.1	29.2