



## Full Length Article

# Attempts to produce blast furnace coke from Victorian brown coal. 3. Hydrothermally dewatered and acid washed coal as a blast furnace coke precursor

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## H I G H L I G H T S

- Hydrothermal dewatering reduced reactivity of the products.
- Acid washing reduced reactivity, increased strength and graphitic structure.
- Briquetting at higher temperature reduced reactivity and surface area.
- Air curing reduced reactivity and increased strength.
- Mild conditions gave pore volume similar to that of blast furnace coke.

## A R T I C L E I N F O

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## A B S T R A C T

The products obtained by carbonization of a mixture of hydrothermally dewatered acid washed Victorian brown coal and coking coal tar pitch, which had been briquetted at 150 or 230 °C and air cured were shown to approach blast furnace (BF) coke in many of their properties. The samples had higher strength than BF coke and showed surface areas and reactivities much closer to those of a typical BF coke than products from non-hydrothermally dewatered Victorian brown coal prepared under similar conditions. The reactivity showed a good correlation with the relative amount of graphitic structure determined by Raman spectroscopy.

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## 1. Introduction

Many attempts have been made to convert Victorian brown coal (VBC) into material suitable for use as a blast furnace (BF) coke substitute [1–12]. The products were usually chars rather than cokes and, although some had sufficient strength, their Coke Reactivity Index, CRI [13], values were unacceptably high [10,11]. Recently, the carbonization product of acid washed and briquetted VBC has been tested for reactivity [6], but no comparison was made with a standard BF coke. Thus it remains useful to investigate whether other physico-chemical treatments can give carbonization products of sufficiently low reactivity and high strength. Our earlier studies, in which ground coal and tar as binder were

briquetted at high force at ambient temperature [11] or at 150 °C with optional air curing [14] and then carbonized, gave products of high compressive strength in some cases, but the reactivity was always far higher than that of a BF coke.

Hydrothermal dewatering of low rank coals including VBC involves heating the coal at high temperature (ca 300 °C) and high pressure, so that the water is removed as a liquid rather than as a vapour [15]. (This dewatering process is attractive because the energy consumed in vapourizing the water in more conventional drying processes is saved [15].) It is known that the process of hydrothermal dewatering of VBC gives a product that resembles higher rank coal in some respects, such as lower oxygen content and lower hydrophilicity [16–18]. Since coking coals are of higher rank than VBC, it was hypothesized that the artificial increase in rank produced by hydrothermal dewatering may bring the coal closer in coking properties to a conventional coking coal.

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Experiments in which raw and acid washed Indonesian brown coals of similar rank to VBC have been treated by hydrothermal dewatering and the treated coal hot briquetted and carbonized have recently been reported by Mori et al. [19]. The strength and bulk density of the carbonized products were increased for the products obtained after hydrothermal dewatering at lower temperatures compared to those obtained without hydrothermal dewatering. Commercial application has been seriously considered for the processes of acid washing [20] and hydrothermal dewatering [15,21,22] of low rank coals. These considerations suggest that it might be useful to consider hydrothermal dewatering as a preliminary treatment for the attempted preparation of BF coke from VBC.

Accordingly a typical VBC was subjected to hydrothermal dewatering in both raw and acid washed (to reduce mineral content) form and the hydrothermally dewatered (HTD) products were mixed with binder (coking coal tar pitch) and briquetted, with optional air curing [23–30], and finally carbonized under a range of conditions. Air curing was introduced because previous work showed that under some circumstances air curing increased the strength [23] and reduced the reactivity [14]. Some experiments were carried out at the higher carbonization temperature of 1200 °C, because this was found to reduce the reactivity and surface area [14]. The suitability of the final carbonized products as coke substitutes was tested by measuring strength and reactivity and the products were characterized by a range of techniques to establish the similarities and differences between the structure of these products and that of a BF coke.

## 2. Experimental

### 2.1. Materials

Loy Yang coal (RC) from the Latrobe Valley, Victoria, Australia, was ground to smaller than 3 mm particle size prior to use in this study. Coking coal tar pitch, completely soluble in tetrahydrofuran (THF), with softening point 110 °C and boiling point greater than 300 °C [31], was obtained from Koppers Carbon Materials & Chemicals Pty Ltd, NSW, Australia. Compounds present in the pitch included a large number of polycyclic aromatic hydrocarbons [32]. A conventional BF coke sample was supplied in lump form by Nippon Steel Corporation (NSC), Japan. Further details of material analyses are given in Table 1. Liquid Chromatography grade THF was obtained from Merck Australia and Univar grade sulphuric acid from Ajax FineChem Pty Ltd, Australia.

### 2.2. Acid washing the coal

A sample of RC was acid washed as described by Redlich et al. [33] with 0.1 M sulphuric acid to give acid washed coal (AWC). The acid solution was added to the coal at a solution to coal (db) ratio of 20:1 by weight and the slurry was stirred for 1 h under vacuum to ensure wetting of the coal, followed by 24 h stirring at atmospheric pressure. The slurry was then filtered. The filter cake was mixed with deionised water then stirred for 24 h and filtered. Mixing with deionised water, stirring and filtering were repeated until the pH value of the filtrates was constant (pH 4.5–5.5) to ensure complete removal of sulphate.

### 2.3. Hydrothermal dewatering

1 kg of RC or wet AWC was charged into a 4 L autoclave with sufficient deionised water to give a 3:1 water:dry coal [16,18,34,35] weight ratio. The autoclave was evacuated and charged with 3 MPa (cold) of N<sub>2</sub>. With continual stirring, the slurry was heated to 320 °C in 2 h and held at 320 °C for 35 min. After reaction, the autoclave was cooled overnight, and then the solid product was filtered and washed with deionised water. The yield of HTD product was about 85 wt%db for RC (RC-HTD) and 83 wt%db for AWC (AWC-HTD). Both the HTD coals were dried in a flow of N<sub>2</sub> at 105 °C, then ground to <0.15 mm, and then dried again to reduce the moisture content to 1–2 wt%db, as determined by an OHAUS MB45 moisture analyser with a halogen heating element.

### 2.4. Analyses of materials

The coal and BF coke water contents were measured by the mass loss when a sample (5–10 g) was heated in flowing N<sub>2</sub> at 105 °C for 4 h. Samples of the RC, AWC, RC-HTD, AWC-HTD, pitch and BF coke were dried at 105 °C in flowing N<sub>2</sub>, weighed, then the ash yield was measured by heating at 815 °C for 2 h [36,37]. HRL Technology Pty Ltd, Victoria, measured the volatile matter content and the CHNS contents of the RC. Campbell Microanalytical Laboratory, University of Otago, New Zealand measured the CHNS contents of AWC, RC-HTD, AWC-HTD, pitch and BF coke. O content was then calculated by difference. For O content calculation of RC and RC-HTD, mineral and inorganic contents of the coal were used rather than the ash yield.

For <sup>1</sup>H NMR, a sample of pitch was dissolved in CDCl<sub>3</sub> and a spectrum was obtained at room temperature using a Bruker

**Table 1**  
Proximate and ultimate analyses and NMR data of materials.

Analysis <sup>a</sup>	RC	AWC	RC-HTD	AWC-HTD	Pitch	Coke
Proximate						
Moisture (wt%ar)	60.0	–	–	–	–	3.00
Ash (wt%db)	3.25	2.03	3.70	2.93	0.0	11.98
Volatile Matter (wt%db)	49.4	–	–	–	–	–
Fixed Carbon (wt%db)	47.4	–	–	–	–	–
Ultimate (wt%db)						
Carbon	65.7	64.0	69.9	70.7	93.0	86.2
Hydrogen	4.70	4.86	4.64	4.54	4.36	0.4
Nitrogen	0.60	0.66	0.78	0.79	1.36	1.01
Sulphur	0.66	0.57	0.55	0.54	0.40	0.4
Oxygen (by diff.)	26.1	27.9	20.4	20.5	0.9	0.03
<sup>13</sup> C NMR: C <sub>C=O</sub> (fraction)	0.09	0.09	0.04	0.05		
<sup>13</sup> C NMR: C <sub>ar</sub> (fraction)	0.49	0.49	0.58	0.60		
Brown–Ladner: C <sub>ar</sub> (fraction)					0.95	
Atomic H/C ratio	0.85	0.90	0.79	0.77	0.56	0.06

<sup>a</sup> The standard error of ash yields based on multiple analyses was 0.12 wt%db for RC, RC-HTD, AWC and AWC-HTD and 0.7 wt%db for coke. For RC, the uncertainty (given by HRL Technology) in volatile matter and fixed carbon was ±0.4 wt%db and in ultimate analysis was ±0.3 wt%db for C, ±0.1 wt%db for H, ±0.05 wt%db for N and ±0.03 wt%db for S. The maximum standard deviations based on multiple analyses for the other ultimate analyses were ±0.4 wt%db for C, ±0.16 wt%db for H, ±0.05 wt%db for N and 0.1 wt%db for S, and therefore for O which was obtained by difference 0.9 wt%db.

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