



Full Length Article

Attempts to produce blast furnace coke from Victorian brown coal. 4. Low surface area char from alkali treated brown coal



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HIGHLIGHTS

- Alkali treated coal became plastic during carbonization.
- The treatment could give a low surface area product.
- Product reactivity was relatively low, but higher than for a blast furnace coke.
- Product reactivity decreased with increase in the amount of graphitic structure.
- The product had a small macropore volume and a smooth surface.

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ABSTRACT

A Victorian brown coal (VBC) has been heated with strong aqueous KOH under severe conditions, neutralized with dilute H_2SO_4 and then hot-briquetted with or without coking coal tar pitch as a binder, optionally air cured and finally carbonized. The final products were evaluated as a blast furnace (BF) coke substitute. The least reactive final product had a much lower reactivity than the product obtained by carbonizing a hot-briquetted VBC-VBC tar mixture. Furthermore, the final product obtained from alkali treated coal had a surface area as low as that of a BF coke. However, the reactivity remained higher and the amount of graphitic structure lower than those of a BF coke. In addition, although the coal/coal-binder mixture, like coking coal, appeared to have fused during carbonization, the final products had virtually no meso + macropore volume, in contrast to a typical BF coke.

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1. Introduction

At present the production of blast furnace (BF) coke requires coals, called coking coals, which have the property on carbonization of giving a strong, porous, relatively unreactive [1] and low-surface-area carbon [2]. There has been recent interest in trying to obtain a suitable substitute for BF coke from cheaper and more readily available coals than the currently used coking coals in order to reduce the cost of iron smelting. These have included attempts to convert low rank Indonesian coals into coking coal substitutes by hydrothermal dewatering (HTD) or by acid washing followed by HTD [3]. These treatments gave materials of high strength but unknown reactivity. A subsequent paper [4] by the same group involved acid washing a Victorian brown coal (VBC) which, after

hot briquetting and carbonization, gave strong material with low reactivity. However, the CO_2 surface area of these products was high ($740\text{ m}^2/\text{g}$) and no comparisons were made with the reactivity of coke prepared under standard coking conditions from a conventional coking coal. The products from acid washed coal showed evidence of plasticity, but not of melting and fusion during carbonization.

Another approach has involved addition of binder to VBC prior to briquetting at either ambient temperature [5] or at $150\text{ }^\circ\text{C}$ [6] and carbonization. Both treatments led to materials of high strength, but high reactivity and surface area, making them unacceptable as a BF coke substitute. More recent work has involved preliminary treatment of the same VBC by HTD, or acid washing followed by HTD, prior to addition of a binder, hot briquetting, optional air curing and carbonization [7]. The strength of the product and the volume of the larger pores remained high and reactivity and surface area were much lower than for the products

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prepared from untreated VBC [5,6]. Raman spectroscopy showed a good negative correlation between the amount of graphitic structure in the materials and their reactivity. However, the reactivity remained higher than that of a BF coke and there was again no evidence of melting and fusion during carbonization.

Experiments carried out in the 1950s showed that heating VBC with strong alkali followed by neutralization gave a material which melted and fused during carbonization. No other structural properties were reported [8,9]. Similarly, Khemani and Sarkar [10] found that non-caking bituminous coals became fluid during carbonization after preliminary heating at 250–300 °C in alcoholic alkali and attributed this change to partial decomposition of the polymeric structure into smaller molecules during the alkali treatment. Since coking coals melt and fuse during carbonization [11,12], it was thought that carbonization of the alkali treated VBC may lead to products of low reactivity, high strength and high meso + macroporosity that resemble BF coke more closely than materials previously tested. The properties relevant to the use of these materials, both with and without added binder, as BF coke substitutes are reported in this paper. In addition, the fulvic acids, the fraction of the coal soluble in alkali and acid, which are a by-product of the alkali-neutralization treatment, have commercial value as fertilizers for a range of cultivated plants and have been investigated for this purpose in Victoria [13,14].

2. Experimental

2.1. Materials

Raw coal (RC), which had about 60 wt% moisture, was obtained from Loy Yang, Victoria. Coal was crushed to less than 3 mm in particle size and was kept in an airtight polybag until use. The binder used was coal tar pitch (referred to below as pitch), softening point 110 °C [15], derived from coking coals, and obtained from Koppers Carbon Materials & Chemicals Pty Ltd, Newcastle, NSW, Australia. The pitch was entirely soluble in tetrahydrofuran (THF). Lumps of a BF coke were sourced from Nippon Steel Corporation, Japan, to compare with the products. THF (Liquid Chromatography grade) and potassium hydroxide (KOH, pellet form, analytical grade) were obtained from Merck Australia, Kilsyth, Victoria. Sulphuric acid of Univar grade was obtained from Ajax FineChem Pty Ltd, NSW, Australia. More details of the analyses of the coals, pitch and BF coke are given in Tables 1 and 2.

2.2. Alkali treatment of the coal

VBC was treated with aqueous alkali solution by the method of earlier workers [9,16]. 320 g KOH was dissolved in 800 g deionized water (7 M) in a beaker kept in cold water in a tote box to prevent overheating and then added to a 4 L autoclave containing 320 g RC as received (~60 wt% moisture). The mixture was stirred with a glass rod until it was converted to slurry. The autoclave was evacuated, then pressurized with 0.2–0.3 MPa N₂ (cold). The mixture was stirred at a speed of 115–125 rpm using the built-in stirrer. It was heated to 185 ± 5 °C and held at temperature for 10 h, then cooled.

The product was recovered and the autoclave was washed out with deionized water. 280 g H₂SO₄ (98%) was diluted in 2 L deionized water to 1.4 M, and then slowly added to the product in a glass container kept under a fume hood. The mixture was stirred slowly during the addition. The product container was kept in a tote box full of cold water to prevent overheating. Water from the product was removed by heating (on a hot plate) at about 80 °C under N₂ flow in a fume hood. The product was dried at 105 °C under flowing N₂ and then the dried product was washed with deionized water and filtered to remove K₂SO₄. Washing with deionized water and filtering were repeated another nine times, until the pH was 6.2 and no SO₄²⁻ was detected by addition of BaCl₂. The product was dried under N₂ at 105 °C in an oven, and then ground to less than 0.15 mm. The final yield of alkali treated coal (ATC) was 103 ± 3 g (80 ± 3 wt% db). The K content of the ATC as measured by the Campbell Microanalytical Laboratory, University of Otago, New Zealand was 0.19 wt% db.

2.3. Material analysis procedures

The determination of water contents, ash yields, volatile matter contents and CHNS elemental analysis, measurement of ¹H NMR and solid state ¹³C NMR spectra and calculation of the Brown-Ladner parameters [17] have been described in a previous paper [7] and are included in the supplementary material. The results of the analyses of RC, ATC, pitch and BF coke are given in Table 1 and the ash composition of the RC is given in Table 2.

The ash yield of ATC was what would be expected from the ash yield of RC if the loss of cations [7] and organic matter during the alkali treatment is taken into account. The ultimate analyses of RC and ATC were similar, despite the loss of organic material during the alkali treatment. The fraction of aromatic carbon in the RC,

Table 1
Analyses of coals, pitch and coke.

Analysis ^a	RC	ATC	Pitch	BF coke
<i>Proximate</i>				
Moisture (wt% ar)	60.0	–	–	3.00
Ash (wt% db)	3.25	3.67	0.0	11.98
Volatile matter (wt% db)	49.4	–	–	–
Fixed carbon (wt% db)	47.4	–	–	–
<i>Ultimate (wt% db)</i>				
Carbon	65.70	66.58	93.0	86.2
Hydrogen	4.70	4.70	4.36	0.4
Nitrogen	0.60	0.67	1.36	1.01
Sulphur	0.66	0.67	0.40	0.4
Oxygen (by diff.)	26.1	23.6	0.9	0.03
¹³ C NMR: C _{C=O} (fraction)	0.09	0.09		
¹³ C NMR: C _{ar} (fraction)	0.49	0.52		
Brown-Ladner: C _{ar} (fraction)			0.95	
Atomic H/C ratio	0.85	0.87	0.56	0.06

^a The uncertainty (standard deviation) in the ash yields based on duplicate analyses was 0.1 wt% db. The uncertainty in volatile matter and fixed carbon given by HRL Technology Pty Ltd, Mulgrave, Victoria, Australia, was ±0.4 wt% db. The uncertainty in RC ultimate analysis given by HRL 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 by the Campbell Microanalytical Laboratory, University of Otago, New Zealand were ±0.4 wt% db for C, ±0.16 wt% db for H, ±0.03 wt% db for N, 0.06 wt% db for S and 0.9 wt% db for O (by diff).

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