Blast Furnace Coke Substitutes from Victorian Brown Coal

By

M. Mamun Mollah

A thesis

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Abstract

Iron is usually produced from its ores using coke in a blast furnace (BF). Coke, a hard and macroporous carbon material, is produced from special coals (coking coals) and acts as fuel, smelting agent, and the permeable support for the charge to the BF. No material can completely replace coke in a BF. Coking coals are becoming harder (and more expensive) to obtain. Victorian brown coal (VBC) is accessible, cheap, with low mineral concentrations, which is favourable for iron production in a BF. However, as-mined, it does not form coke, but a char which is too reactive to be used in a BF. The objective of this project is to produce a substitute for BF coke from VBC by physical and chemical treatments and to investigate the use of cementing agents to reduce the reactivity and strengthen the product finally formed.

VBC from Loy Yang open cut, and its commercial products, briquettes and char, which were obtained from Australian Char Pty Ltd in lump form, were used as starting materials. VBC tar, coking coal tar pitch, and asphaltene (hexane insolubles from VBC tar) were used as binders. Some of the starting material was pre-treated by acid washing (0.5 M H_2SO_4), hydrothermal dewatering (HTD; 320 °C-35 min) or alkali treatment (KOH (aq), 185 °C-10 h). The elemental analysis and NMR of these materials were determined.

Before pelleting, raw VBC, pre-treated VBC, or briquettes were dried at 105 °C under N_2, ground to <0.15 mm, then mixed with the binder in tetrahydrofuran (THF). THF was removed and the mixture was pelleted by a conventional hydraulic press at ambient temperature or using an INSTRON 5569 series Mechanical Tester applying a range of forces, temperatures and times. Some samples were pelleted under N_2 (350 °C-30 min) by “Hot Press Carbonization” (HPC). In some cases, samples were air cured at 200 °C for 2 h. Finally, the samples were carbonised at a range of temperatures and times under N_2 flow, at a low heating rate to minimise cracking of the pellet, then cooled under N_2.

The measurements used to evaluate the suitability of the products as substitutes for BF coke were compressive strength and reactivity. The compressive strengths of pellets were measured by using an INSTRON 5569 series Mechanical Tester. Reactivity was measured using a thermogravimetric balance. The sample was heated to 1000 °C at 20 °C /min under N_2 and held at 1000 °C for 1 h in a flow (70 ml/min) of 1:1 CO_2:N_2. The reactivity, R60CO_2, was calculated from the weight loss. Physical properties of the products were measured in order to understand what factors controlled the compressive strength and reactivity.

Initially, VBC or commercial briquettes were impregnated with tar, pelleted at ambient temperature and carbonized. Products from VBC showed higher compressive strengths (40-60 MPa) and slightly lower reactivity (R60CO_2 87-89 %) and surface areas (790-800 m^2/g) than those from briquettes. The effects of carbonization time, temperature (900 or 950 °C) and tar addition were relatively small. The high reactivity of the samples compared to that of coke (R60CO_2 13 %) is probably related to their higher surface areas and the smaller extent and greater disorder of their graphitic structure as shown by XRD.

The poor results of ambient pelleting and recent literature suggested that hot pelleting of VBC would be advantageous. Therefore, VBC-tar mixture was hot pelleted (150 °C-20 kN for 10 or 30 min), optionally air cured then carbonized (950 °C for 3 h). Products showed higher compressive strength (90-200 MPa) and bulk density (1.17-1.27 g/cm^3) than those obtained following ambient pelleting. A high concentration of tar (10-15 wt%) and air curing increased the compressive strength by a further factor of two. The compressive strength was higher than that of a BF coke (20 MPa), but the surface area remained high and the surface was rough (SEM) and the proportion of graphitic structure was small (Raman spectroscopy). These factors probably contributed to the high reactivity of even the strongest products.

VBC treated by HTD resembles a higher rank coal (e.g. lower O content), suggesting that HTD coal might carbonize to a less reactive product, like a higher rank coal. HTD treatment reduced the reactivity of the carbonization products, without an unacceptable lowering of the compressive strength. More severe briquetting conditions, acid washing before HTD, air curing and severe carbonization conditions (1200 °C-8 h) all together reduced the reactivity to R60CO_2 34 %, still much higher than that of a BF coke. The surface area was reduced, but only to 100 m^2/g, (cf. 18 m^2/g for BF coke) and the proportion of graphitic structure was smaller than in BF coke, so that the higher reactivity may be due to these structural factors.

Alkali treated VBC (ATC) appears to melt and fuse upon carbonization, like a coking coal, suggesting that carbonised product might be similar to a BF coke. The ATC with pitch and air curing had a high compressive strength (up to 230 MPa) after carbonization (1200-1300 °C for 2-8 h). The small surface area (as low as 20 m^2/g) and smooth surface (SEM) of the products under some conditions suggests that fusion occurred during carbonization. However, the proportion of graphitic structure (Raman and TEM) was lower than for a BF coke and the reactivity of the carbonized products did not fall below R60CO_2 30 %. Possibly the alkali treatment changed the chemical structure and inhibited graphitisation. Suitable pore structure is necessary for low reactivity, but the chemical structure is also important.

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Empirical treatments, modifying the structure of brown coal in the direction of higher rank coals, give carbonised products which approach BF coke in reactivity, surface area and the proportion of graphitic structure while maintaining compressive strength.

PART A: General Declaration

Monash University

Declaration for thesis based or partially based on conjointly published or unpublished work

General Declaration

In accordance with Monash University Doctorate Regulation 17.2 Doctor of Philosophy and Research Master's regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original papers published in peer reviewed journals and five unpublished publications. The core theme of the thesis is Blast Furnace Coke Substitutes from Victorian Brown Coal. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the School of Chemistry under the supervision of Prof Alan L Chaffee and Prof W Roy Jackson.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of six my contribution to the work involved the following:

Thesis chapter	Publication title	Publication status*	Nature and extent of candidate's contribution
2	An attempt to produce blast furnace coke from Victorian brown coal	Published in Fuel	● proposed original idea ● prepared and analyzed samples ● identified major issues ● developed interpretations ● fully drafted papers and conclusions
3	The use of a brown coal derived binder and hot briquetting to induce a coke forming ability in Victorian brown coal	To be submitted in Energy&Fuel	
4	Hydrothermally dewatered Victorian brown coal as blast furnace coke precursor	Fully written, to be submitted to Fuel	
5	Alkali treatment to induce the formation of blast furnace coke substitute from Victorian brown coal	Fully written, to be submitted to Fuel	
6		Fully written, to be submitted to Fuel	
7		Fully written, to be submitted to Fuel	

I have / have not (circle that which applies) renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

Signed: ....

Date: 20/5/15

I wish to dedicate this thesis to my brother, Asharaf Faroque Badal and my chemistry teacher, Waliul Hoque; I believe that without the support of both I could not even think of this study.

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List of Publications

Journal publication

Mollah MM, Marshall M, Jackson WR, Chaffee AL. An attempt to produce blast furnace coke from Victorian brown coal. Fuel 2015;148:104-11.

Conference papers

1. Chaffee, AL, Mollah, M, S., RH, Marshall, M, Jackson, WR, *Attempted Production of Blast Furnace Coke from Victorian Brown Coal*, in: 2011 International Conference on Coal Science & Technology, Oviedo, Spain, 2011.
2. Mollah, M, Marshall, M, Jackson, WR, Chaffee, AL, *Attempts to Reduce the Reactivity of Char Obtained from Victorian Brown Coal*, in: 2013 International Conference on Coal Science & Technology, Pennsylvania State University, PA, USA, 2013, pp. 1200-1207.
3. Mollah, M, Jackson, WR, Marshall, M, Chaffee, AL, *Attempt to Induce a Coke Forming Ability in Victorian Brown Coal*, in: 10th Australian Coal Science Conference, Brisbane, QLD, Australia, 2013.
4. Mollah, M, Jackson, WR, Marshall, M, Chaffee, AL, *Hydrothermally Dewatered Coal as a Blast Furnace Coke Precursor* in 2014 Energy Future Conference, Sydney, Australia.

Oral presentations and posters

- Oral Presentation: *Attempts to Reduce the Reactivity of Char of Victorian Brown Coal*
  Event: International Conference on Coal Science & Technology, 2013, PA, USA
- Oral Presentation: *Attempt to Induce a Coke Forming Ability in Victorian Brown Coal*
  Event: 10th Australian Coal Science Conference, 2013, Brisbane, Australia
- Poster: *Coal Derived Liquids to Improve the Coking Ability of Victorian Brown Coal*,
  Event: 2nd International Symposium on the Sustainable Use of Low Rank Coal, 2012, Melbourne, Australia
- Poster: *Hydrothermally Dewatered Coal as a Metallurgical Coke Precursor*,
  Event: 3rd International Symposium on the Sustainable Use of Low Rank Coal, 2014, Melbourne, Australia
- Oral Presentation: *Hydrothermally Dewatered Coal as a Blast Furnace Coke Precursor*
  Event*:* Energy Future Conference, 2014, Sydney, Australia.

Institutions visited as part of PhD studies

- AusChar Pty Ltd, Morwell, Victoria, Australia, Feb 2012
- CSIRO Energy Centre, Newcastle, NSW, Australia, Oct 2012
- Kyoto University, Katsura Campus, Kyoto, Japan, Dec 2012
- Blast furnace operation of Nippon Steel Corporation, Nagoya Works, Japan, Dec 2012
- Pennsylvania State University, Pennsylvania, USA, Sep 2013

List of Symbols and Abbreviations

^{13}C	carbon isotope of atomic weight 13
^{1}H	hydrogen isotope of atomic weight 1
aq.	aqueous
ar	as received
ASTM	American Society for Testing and Materials
ATC	alkali treated coal
AWC	acid washed coal
AWC-HTD	acid washed coal hydrothermally dewatered
BF	blast furnace
C_{al}	fraction of aliphatic carbons
C_{ar}	fraction of aromatic carbons
$C_{c=o}$	fraction of carbonyl carbons
CRI	coke reactivity index
CSR	coke strength after reaction
daf	dry ash free
db	dry basis
DCM	dichloromethane
diff.	difference
Eq.	equation
f_a	Brown-Ladner fraction of aromatic carbons
Fe_2O_3	hematite
Fe_3O_4	magnetite
FeO	wustite
H_{ar}	fraction of aromatic hydrogens
HRTEM	high resolution transmission electron microscopy
HTD	hydrothermal dewatering
H_α	fraction of aliphatic hydrogens adjacent to aromatic ring
H_β	fraction of methylene ($-CH_2-$) hydrogens
H_γ	fraction of methyl ($-CH_3$) hydrogens
ICPAES	inductively coupled plasma atomic emission spectroscopy

LYLA	Loy Yang low ash brown coal
Mt	million ton
NMR	nuclear magnetic resonance
PAH	polycyclic aromatic hydrocarbons
ppm	parts per million
R60CO_2	modified reactivity index determined by heating for 60 min at 1000 °C under CO_2
RC	raw coal
RC-HTD	raw coal hydrothermally dewatered
SAX	X-ray scattering
SEM	scanning electron microscopy
STP	standard temperature and pressure (273.15 K, 101.325 kPa)
t	tonne (1000 kg)
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
tHM	tonne hot metal
VBC	Victorian brown coal
wt	weight
XRD	X-ray diffraction

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Chapter 1

General Introduction

1.1 Background

Iron and its alloy with carbon, steel, play a vital role in civilization, as they are fundamental needs for modern societies and form an almost inexhaustible resource, because iron is one of the most abundant elements in the earth's crust [1, 2]. The use of iron was known to the Egyptians as early as in 4000 BC [1]. It is now one the most important materials in modern society and a range of applications, from food production to healthcare, transport systems, even communication systems, all depend on iron and steel. Urbanization and industrialization are driving the global iron and steel demand to grow every year [3], and the global mining giant BHP Billiton remains confident that growth will continue in the future [4]. The production of crude steel in the world has increased significantly in the past decade; the total production was about 600 Mt in 2000 [1], compared to 1548 Mt in 2012 [5] and 1606 Mt in 2013, when China was the largest producer in the world, with production of about 780 Mt [6].

Most iron is mined in the form of oxides, hematite (Fe_2O_3) and magnetite (Fe_3O_4), which need to be reduced to the metal. This is achieved by a thermochemical process known as reduction at high temperatures in a furnace. The most common reductant used is carbon, which reduces the iron ore in a vessel called a blast furnace (BF). Coke is the form of carbon that remains dominant in the iron and steel industry, but is relatively expensive, so that cheaper substitutes have always been of interest. The reasons that coke won and has retained its place as the principal reductant in blast furnaces will become clear when the history of iron production and the operation of the modern blast furnace are considered, as discussed in the next Sections.

1.2 History of iron production

The smelting of iron from its ore has always been more difficult than the smelting of copper or tin, because the melting point of iron is higher. With the temperatures available in an early BF, the iron would solidify almost as soon as it separated from the ore and form a mixture with the slag of stone-like appearance, not resembling a metal at all. It was necessary to develop the technique of repeated heating and hammering to separate the metal [7]. The fuel and reductant for all early furnaces was carbon in the form of charcoal [7] prepared by heating wood in a restricted supply of air [8].

With the growth of iron production in the 18th century in Britain severe shortages of charcoal appeared, as huge numbers of trees were necessary to smelt a relatively small amount of iron ore. For example, to smelt one tonne of iron ore, required clearing more than three acres (1.2 ha) of forest [9]. Therefore, iron had to be imported from abroad [10]. Attempts to use coal itself as the fuel and reductant were unsuccessful, because of the high sulphur content of the coals available [1, 11]. Abraham Darby in Coalbrookdale heated coal in a restricted supply of air, in the same way as wood was heated to make charcoal, so that the inner section of the coal heap was pyrolysed rather than burnt and this pyrolysed product is referred to as coke [11]. The coke so produced was of lower sulphur content than the original coal and could be substituted for charcoal in a BF for some applications, leading to expansion in iron production. Ultimately coke almost entirely replaced other carbon sources in iron smelting.

It became clear at an early stage that not all coals were equally suitable for making coke. For example, iron smelted with some coke contained too much sulphur to be used for making wrought iron or steel and it was necessary to add large amounts of limestone to combine with the sulphur to give iron of acceptably low sulphur content [12]. Apart from the problem of impurities such as sulphur, it was found that coke which retained its strength in the BF could be most easily prepared from coals which caked or agglomerated on heating [13]. Therefore, attempts were made as early as 1870 to devise laboratory tests which measured agglomeration or melting on a small scale [14], but the correlation between the results of these direct tests of plastic properties and the quality in a practical situation of the coke from a given coal was not generally very good [13]. Instead more indirect tests were used to obtain a specification of coke for particular purposes; the ASTM specification for foundry coke prescribed in 1916 was one of the first standard methods for coal and coke [14]. Older reviews concluded that the important properties for BF coke were structural, in particular the permeability and strength of the coke and its reactivity [15], and that good coking coals were those which gave relatively unreactive coke, which was permeable to the BF gases and of sufficient strength to support the charge without shattering. Coal selection for coke manufacture and measurement of the properties of cokes remain important for efficient and economical BF operation at the present time. These historical considerations provide a background for the description of modern BF practice and coke production and properties which follows.

1.3 The modern blast furnace

Blast furnaces now account for the largest volume of iron production in the world [16, 17]. A modern BF (Figure 1), is a massive refractory structure that can be considered as a vertical shaft reactor superimposed over a crucible-like hearth. For decades this was the symbol of the industrial age. A medium size BF, 28 m high with diameter of 9.1 m at bottom-hearth, 10.2 m at middle-hearth and 7.1 m at the top end, can have a vessel volume of 1500 m^3 with a production capacity of 3000 tonne hot metal (tHM) per day. In contrast, a large BF, with a total vessel volume of 5500 m^3, which can be 34.3 m high and of 16.5 m middle-hearth diameter, can produce 12000 tHM per day [18], or even more. For instance, the Oita BF no.2 of Nippon Steel Corporation (NSC) has a production capacity of 13,500 tHM per day [19]. Generally, a large modern BF producing 1 tHM consumes about 300 kg of coke and 240 m^3 (at standard temperature and pressure of 273.15 K and 101.325 kPa, STP) of blast oxygen [19, 20]. The refractory materials of a BF have to be able to withstand high temperatures (up to 2300 °C in some areas) [18, 19] and a corrosive environment. The outer layer of the BF is a steel shell, then comes a layer of iron castings used as cooling panels and finally the inner wall of refractory firebrick. The hearth of the furnace contains layers of refractory micropore carbon protected by an aluminosilicate layer and also an alumina-carbon layer [21].

A BF can be divided into vertical sections as follows: at the top there is the throat, with provision for loading the charge, then comes the stack, where the charge is heated by the ascending gas and reduction begins, then the belly, where the melting and contraction of the slag and iron begin, the bosh, where the reduction and melting are completed, and finally the hearth, where the slag floating on the molten iron is tapped off and the liquid metal is collected and cast. Above the hearth are inlets to introduce hot oxygen or blast (1200 °C), which are called tuyeres, and inlets for other sources of fuel.

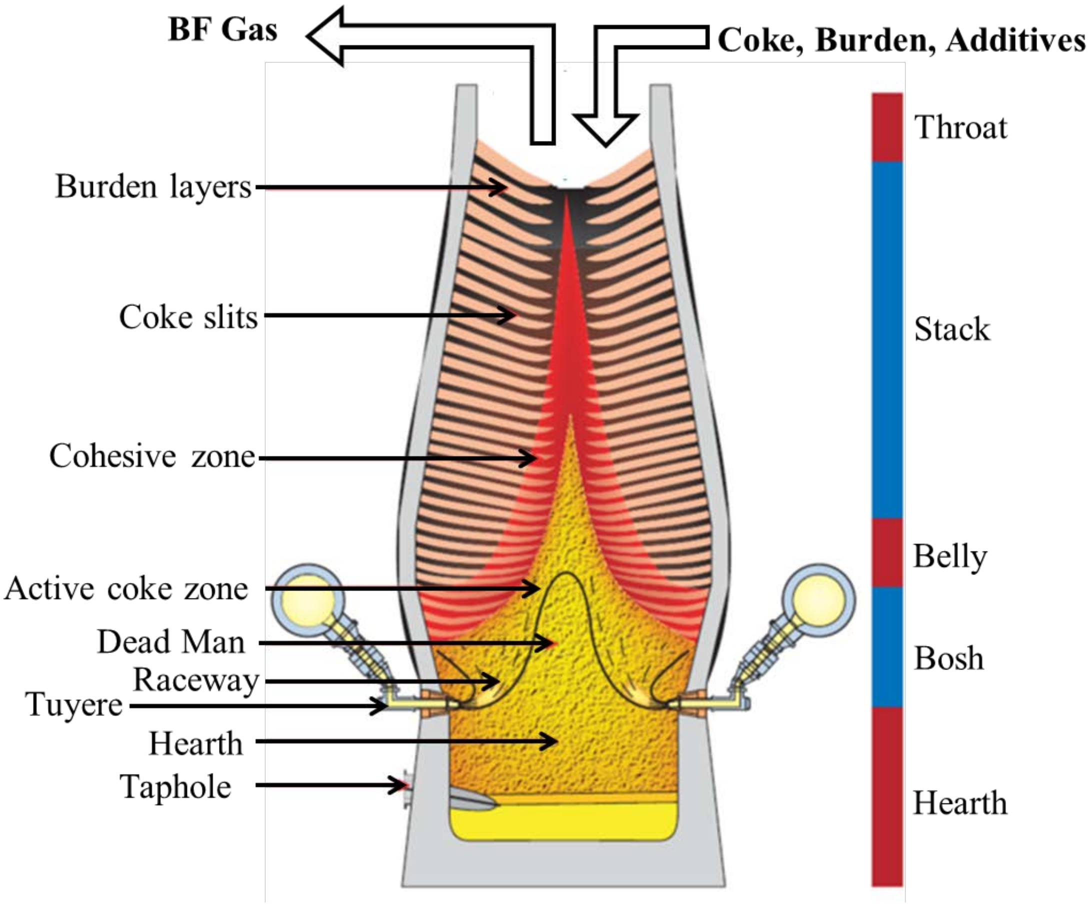


Figure 1: A schematic diagram of a modern BF [19].

1.3.1 Blast furnace reactions

It is to be noted that the reason a BF is effective is that the free energy of reaction favours the reduction of oxides by carbon or, in other words, carbon has greater affinity for oxygen than iron. There are metals such as Al, Ti and Mn for which this is not true and the metal has to be obtained from its ores by other methods.

A BF works on the principle of a counter-current heat and mass exchanger, where the descending ore, coke etc. react continuously under the action of ascending hot gas in a smelting process, which eventually extracts the iron from its ore as molten metal. A simplified picture of the operation of a BF, which concentrates on the reactions involving iron, divides the BF into three thermal zones where different reactions take place [1, 18, 19].

In the upper zone or pre-heating zone, a significant amount of heat is exchanged between the freshly charged materials and the ascending gases (CO, CO_2, H_2, N_2). The temperature of the gases drops from 800-1000 °C to 100-250 °C at the very top, due to heating up of the charge.

The principal reactions occurring in this region are reduction of iron oxides, hematite (Fe_2O_3) and magnetite (Fe_3O_4), by CO, to wustite (FeO).

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \qquad \text{Eq. 1}$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \qquad \text{Eq. 2}$$

The ascending CO is also converted to CO_2 in this zone by the reverse Boudouard reaction (Eq. 3), also known as the solution loss reaction and carbon gasification reaction, because at the relatively low temperatures in this zone the equilibrium favours CO_2 over CO.

$$2CO \rightarrow C + CO_2 \qquad \text{Eq. 3}$$

In the middle zone, at about 1000 °C, most of the wustite is reduced to iron by ascending CO.

$$FeO + CO \rightarrow Fe + CO_2 \qquad \text{Eq. 4}$$

In the lowest zone, where the temperature rises from 1000 °C at the top to 2000 °C at the level of the tuyeres, any remaining iron oxide is reduced directly by the coke (carbon).

$$FeO + C \rightarrow Fe + CO \qquad \text{Eq. 5}$$

The oxygen in the hot blast reacts (burns) with the descending coke to give CO_2 and a large amount of heat which supplies much of the heat required for BF operation, raising the temperature to 1800-2000 °C. In the presence of carbon above 1000 °C the CO_2 in the gas is unstable and is converted to CO by virtue of the Boudouard reaction. This CO then rises up the BF and reduces iron oxides in the upper two zones. It is important that the coke be sufficiently permeable that the gas can rise up the BF without excessive hold up.

$$C + O_2 \rightarrow CO_2 \qquad \text{Eq. 6}$$

$$2C + O_2 \rightarrow 2CO \qquad \text{Eq. 7}$$

The temperature at the hearth is that of the molten metal and slag, about 1500 °C. As the coke burns, void space is created, so that charge and products descend by gravity. This is the driving force which keeps the charge descending at a suitable rate. It is important that the coke be sufficiently strong that it does not break up during its descent into fine particles, which would reduce the permeability to the ascending gases and to the descending molten metal and slag.

Materials charged at the top take 6 to 8 hours to reach the hearth of the BF, where they are in the form of molten slag and iron, which can easily be separated. A BF typically will run for 4-10 years once started, with only occasional halts for maintenance.

1.4 Coke for the modern blast furnace

Coke for the modern BF is as high in carbon content (about 90% carbon [22]) as char, graphite and diamond, but, unlike them, has physical and chemical properties which make it suitable for use in a BF. Its carbon is graphitizable [23] with well ordered, but small graphite-like domains [24, 25], that will form graphite if heated to a high temperature (3000 °C). In contrast, char is non-graphitizable carbon and will not form graphite even at high temperature [24]. Physically, coke is a macroporous (with pores as big as ~200 µm [26]) material containing only a small amount of micropores (~1-25 m^2/g of CO_2 surface area [27]). In contrast, graphite and diamond do not contain such large macropores [26].

Coke is produced as massive, inherently strong lumps that are chemically much less reactive (according to the coke reactivity index, CRI [28]) than conventional coal char. It is manufactured in a conventional coke oven battery, a series of batch reactors, by the carbonization of coking coal (or blends) at a high temperature (e.g. 1000-1200 °C), generally for 18-24 h [11, 29].

In a BF, coke is charged from the top of the furnace along with other charges (iron bearing loads and additives such as limestone). Coke plays important multiple roles in a BF:

i) its carbon (in the form of coke or as CO) chemically reduces the iron containing compounds to molten pig iron [30, 31],

ii) its combustion provides most of the heat required in the furnace [32],

iii) its strength in the BF provides the mechanical support required for the iron bearing charge [32] and this strength is due to its relatively low reactivity towards CO_2,

iv) its large pores provide the permeability to permit the gases to ascend into the stack and for slag and molten metal to pass down to the hearth of the furnace. This permeability property is unique to coke among carbon materials, so that BF operation is not possible without coke [32, 33],

v) the relatively low reactivity of coke with furnace gases such as CO_2 ensures that the coke persists for long enough to reduce the ore and bear the load.

Furthermore, coke is the only material in a BF that descends in solid form to the tuyere level of the BF [18, 34], where carbon (coke) reacts with hot blast and creates a huge amount of heat. Other carbon materials such as charcoal or even coal itself cannot fulfil these requirements, as they soften and become impermeable under the BF conditions. Therefore, coal cannot be used in a BF and has to be converted to coke by carbonization. Only some bituminous coals, so called coking coals, are able to produce coke with the properties required by a modern BF.

1.4.1 Coal for blast furnace coke production

Coking coals, which are generally of bituminous rank, have the peculiar ability to soften when heated [35, 36], which is often described as melting. After softening, coking coals form a plastic phase called mesophase [23, 37-39], and agglomerate, obliterating their original shape, and then resolidify [40] into hard, strong, porous lumps of coke. Generally, conversion of coal to coke occurs in about 75 wt% yield [32]; thus, to produce 1 tonne of coke approximately 1.30 to 1.35 tonnes of coal are needed [41]. Coking coals contain a large number of polycyclic aromatic hydrocarbons (PAH) of the correct size, neither too big as in anthracite nor too small as in low rank coals [23], in their structure and also hydroaromatics. It is these groups that control the formation of mesophase [42]. In contrast, carbonization of low rank coals, that have more aliphatic hydrocarbons in their structure and cross-link easily when heated, forms a non-graphitizable carbon, char [24, 43], which is not suitable as coke because the product of carbonization is too reactive.

Most coals, including many bituminous coals, are not suitable for BF coke production, as will become clear when the coking process is described in Section 1.4.2. The most suitable coals for this purpose, called prime coking coals, are not abundant and the ever increasing demand is seriously depleting the supply of such coals [44]. Therefore, in coking practice, it is common to blend coals to obtain a coke of the required properties [45].

1.4.2 Chemistry of the coking process

In summary, during carbonization, some of the organic compounds in coking coals are converted into small volatile molecules and escape as gas, leaving the non-volatile condensed solid residue, coke (Figure 2), consisting to a large extent of large-molecular-weight polycyclic aromatics [23, 37, 46].

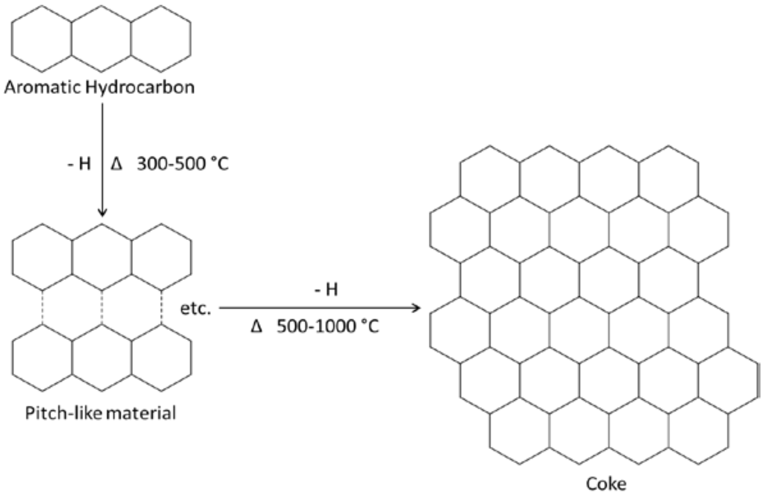


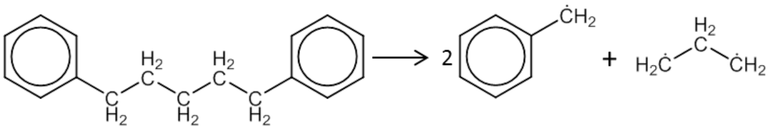
Figure 2: The steps in aromatic polymerization leading to coke formation, taken from [47].

Considering the process in more detail, carbonization of coking coals can be divided into three stages [11, 47, 48]. The first stage at temperatures below 200 °C is common to all coals, whether coking or non-coking, and is where the main volatile products, water, carbon monoxide and dioxide, hydrogen sulphide, etc. are released due to the loss of functional groups. Dehydration of alcohols (Eq.8) or decarboxylation of carboxylic acids (Eq.9) are examples of such reactions, where *R* can be an aliphatic or an aromatic group [11].

$$\text{R-CH}_2\text{-CH}_2\text{-OH} \rightarrow \text{R-CH=CH}_2 + \text{H}_2\text{O} \qquad \text{Eq. 8}$$

$$\text{R-CH}_2\text{-COOH} \rightarrow \text{R-CH}_3 + \text{CO}_2 \qquad \text{Eq. 9}$$

The second stage occurs at 350-550 °C [11]. In this stage, C-C and C-O bonds that bridge aromatic ring systems are cleaved, so that light hydrocarbon gases (e.g. methane, ethylene, etc.) and a mixture of organic compounds that condense on cooling to tar are evolved. Free radicals such as relatively stable benzyl radicals form from the breakage of these bridging bonds in non-coking and coking coals, as for example in the following reaction [11]:



Eq. 10

However, in coking coals the number of such bonds is less than in non-coking coals, so that the free radicals formed can all be stabilized by internal hydrogen atom transfer reactions [11, 49]. The necessary hydrogens are available in coking coals because these coals contain a greater amount of hydroaromatic structures in their molecules than other coals [11, 50]. The stabilized radicals, acting as plasticizers (metaplast) [11, 51], give mobility to the large aromatic structures (PAH), allowing them to move, align and rearrange. Thus when the PAH polymerize to give aromatic sheets of molecular weight about 900 amu [37] (see Figure 2), these sheets can self-organize into liquid crystals, mesophase [23, 24, 37, 39, 46], which are anisotropic. This formation of liquid crystals plays a large role in the ordering of the carbon into graphitic or graphitizable structures [11, 24].

In non-coking coals, these free radicals are formed in the same way, but, their greater number and the smaller concentration of hydroaromatic structures makes it impossible for them to be capped by internal hydrogen transfer. Thus rapid polymerization takes place, rather than the formation of mesophase.

The third stage, beginning above 550 °C, leads to additional polymerization, which inhibits the mobility in the liquid crystals. The liquid crystals increase in size and Van der Waals attractions promote their ordering to give pre-cokes, semi cokes, or green cokes [52]. At the same time more volatile matter, including water, gases and condensable tars etc., are produced due to thermal cracking of the metaplast [11].

$$\text{Metaplast} \rightarrow \text{Semicoke} + \text{Tar Vapors} + \text{Gases} \qquad \text{Eq. 11}$$

As the temperature continues to increase, with the semicokes still maintaining their elastic nature (up to 700 °C), more gases are extruded as a result of pyrolysis of the metaplast. Thus vapour bubbles pass through the plastic mass, creating large macropores, which do not get filled with fluid [11, 51]. With temperature increasing above 700 °C, further polymerization, accompanied by gas production, freezes the structure to give an anisotropic coke [11].

$$\text{Semicoke} \rightarrow \text{Coke} + \text{Gases} \qquad \text{Eq. 12}$$

The formation of liquid crystals and hence of a plastic phase obliterates the original pore structure so that, when solidification occurs, large pores are formed as the structure shrinks, without concomitant formation of micropores. Thus the surface area of the final coke is small and the process gives a permeable, but strong and partially ordered, carbonaceous material of relatively low reactivity in CO_2.

1.4.3 Coke characterization

Coke is the most expensive material [53] among those charged to a BF. In addition, because coke is so critical for iron smelting processes in a BF (see Section 1.3) and its quality is important for efficient and economical BF operation [54], it is important that a coke should be carefully characterized before it is used, so that the BF will operate efficiently. High grade coke is characterized by a limited range of physical and chemical properties. The important properties of a suitable coke are listed below, with the reasons for their importance and techniques of measurement [18].

1.4.3.1 **Physical properties**

Coke Size: Coke size required in a BF varies from plant to plant because the ratio of coke size to ore size should be in the range 3-5:1 to give optimum permeability [18]. Moderately large coke size with a narrow size range gives better permeability and hence better efficiency and productivity [55]. Coke size is mostly controlled by screening, usually in the 40-60 mm range with a 50-55 mm size being ideal [32, 56], but some excellent BF operations prefer a smaller coke size, 40 mm, and even 24 mm (square) coke size has been used in some BFs [19].

Coke Strength: Coke strength is important because coke must descend through the furnace without breaking up into small particles as a result of mechanical, thermal and chemical attack. Coke must remain as almost intact lumps in order to provide the necessary permeability for upward flow of gas and downward flow of molten iron and slag. There are two strength parameters which are important; a) resistance to volume breakage (before and after reaction) and b) resistance to abrasion. The chemical reaction of the coke in the BF is simulated by reaction with CO_2 at 1100 °C for 2 h [28]. The volume breakage before reaction can be determined by the drop shatter test [57] and the abrasion before reaction by a tumbler test [58]. If the coke passes these tests it needs to be evaluated after reaction. Coke strength after reaction can again be measured by a tumbler test to give the coke strength after reaction (CSR) [28]. It would also be possible to carry out a drop shatter test after the reaction under the conditions of [28] to determine the volume breakage after reaction, but this is less frequently used. All of these standard tests require large amounts of material, and alternative measures of coke strength for small samples can be obtained by determining the compressive strength [59, 60] or tensile strength [61, 62] of coke fragments.

Pore size distribution and surface area: Coking coals soften and resolidify during carbonization, which obliterates the original pore structure so that the final coke has only a small amount of micropores (less than 2 nm), but contains many large macropores (greater than 50 nm) (see Section 1.4 and 1.4.2). Coke porosity and the distribution of pore sizes have an important influence on its strength [63], reactivity [33, 64] and permeability. Therefore, porosity, pore size distribution and surface area are important coke quality parameters.

A number of techniques are available to determine the porosity and surface area of coke. There is a standard method for determining the total porosity of coke using water pycnometry to measure the apparent and true specific gravity and then to calculate the porosity from these quantities [65]. Numerous methods including electron microscopy, mercury intrusion porosimetry and physical adsorption of gases have been developed for analyzing pore structure and surface area in more detail and these can be applied to coke. Mercury porosimetry has also been used to characterize the pore size distribution of coke [33]. CO_2 adsorption at low temperature (273 K) is used to determine the micropore volume and surface area [33]. CO_2 is preferred to N_2 at 77 K for determination of surface area because at 77 K N_2 diffuses very slowly into the pore network, so that equilibrium is attained only after an unacceptably long time [66]. A combination of helium pycnometry to determine the true density and mercury density can be used to determine the total pore volume [33]. Pore structure has also been studied in detail by SEM [67].

Optical texture: The optical texture component in coke, mainly composed of anisotropic carbon as well as some isotropic carbon [9, 11, 23, 37, 39], increases coke strength and decreases coke reactivity to CO_2, but increases the reactivity to alkali metals. Therefore, optical texture in coke is a factor that can affect BF operation. Optical texture can be measured by optical microscopy following an ASTM method [68].

Graphitic structure: Coke contains well-ordered graphite structure [24, 43] and a greater degree of graphitization is found to decrease coke reactivity to CO_2 [69] and to increase coke strength. Therefore, the amount of graphitic structure can influence the efficiency and productivity of a BF. X-ray diffraction (XRD) [70-72], Raman spectroscopy [73, 74] and transmission electron microscopy (TEM) [75, 76] can be used to measure the extent of graphitic structure.

1.4.3.2 **Chemical properties**

The presence of moisture, mineral matter, volatile matter, sulphur, phosphorus and alkali metals such as sodium can degrade coke quality and the quality of the final products, so that their measurement is important [32].

Moisture: Coke for the BF should have minimum and consistent moisture content because drying the moisture will require additional heat, which will have to come from additional fuel. Moisture content can be determined using an ASTM method [77], heating the coke sample at a temperature of 104-110 °C in a drying oven for 1 h, and then calculating moisture content from the mass loss.

Volatile matter: Volatile matter makes it difficult to clean the BF outlet gas [32, 56], so that coke should have less than 1 wt% volatile matter. There is an ASTM method [78], for volatile matter determination in coke. The method involves heating the sample in a closed container at a high temperature. Volatile matter content is calculated from the mass loss, excluding losses due to water.

Carbon: Carbon content in coke is important because the carbon acts as reducing agent and burning of carbon provides most of the process heat. Therefore, carbon content of coke should be as high as possible [55] and most importantly, constant or nearly constant for use in any individual BF in order to minimize variability in the amount of heat produced in the BF [18]. Carbon can be measured by the usual methods of organic elemental analysis [79].

Ash: The mineral matter content of coke should be low because silica, which is usually one of the main components, has to be fluxed with extra limestone. Also, all mineral matter is an inert component which reduces the amount of useful reductant and fuel per unit coke mass [18, 32]. The mineral matter is determined approximately by measuring the ash yield when the coke is heated at high temperature (e.g. 815 °C) in air following a suitable standard method such as ASTM D3174-12 [80].

Sulphur and Phosphorus: The main effects of S and P are on the quality of the product (see Section 1.2 for S) and therefore their minimization is desirable [1, 11]. They can be measured by standard methods such as ASTM D4239-14e2 for sulphur and ASTM D4326-13 for phosphorus in coke ash.

Alkali: Alkali metals and their compounds increase the reactivity and lower the strength of coke [17] and can also attack the refractory walls of the BF [18]. They can be determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) of the solution obtained by borate fusion, followed by acid dissolution of the coke, using a standard such as AS 1038.14.1.

Reactivity: The reactivity of the coke must not be too high or it will be degraded aggressively by the CO_2 produced in the solution loss reaction (Section 1.3.1) in the upper region of the BF [31], and also by reactions with furnace gases before burning at the tuyere level. Such reactions break coke into small particles which will reduce the strength and permeability of the coke [32] and make BF operation uneconomical [23]. The standard test of coke reactivity is ASTM D5341-99R10 [28]. The principle of this method has been described above in discussing coke strength after reaction.

Some of these methods were used in characterizing the products of the current work, modified to take account of the small samples available.

1.5 Victorian brown coals

As noted, coking coals are becoming expensive and scarce (Sections 1.1, 1.4.1) so that it is becoming economically desirable to search for carbonaceous substitutes. Victorian brown coals (VBCs) are abundant and cheap with large deposits of low S, P, N and inorganic matter contents [81, 82], so that it is natural that attention has turned to them as precursors of BF coke substitutes.

In contrast to coking coals, VBCs are brown (low rank) coals, and categorized as non-coking coals, with high moisture content (50-67 wt% [83]). In Victoria, brown coals, covering two-thirds of the State (Figure 3) are found in each of the three major Tertiary basins, the Murray Basin, Otway Basin and Gippsland Basin [81]. According to the Department of Primary

Industry Victoria [25, 84], Victoria has a reserve of 430 billion tons of brown coal. The full potential of VBC can only be realized through a good scientific understanding of the composition and behavior of the brown coal [85]. VBCs are of tertiary age, 15-50 million years old [86]. The coals in the Gippsland Basin vary in age from late Eocene to late Miocene. They are therefore 10-40 million years old [87], much younger than typical Australian coking coals, which are generally of Permian age (180-280 million years old) [88]. VBCs are of much lower rank than coking coals, because they have been subjected to only moderate temperature and pressure for a relatively short time.

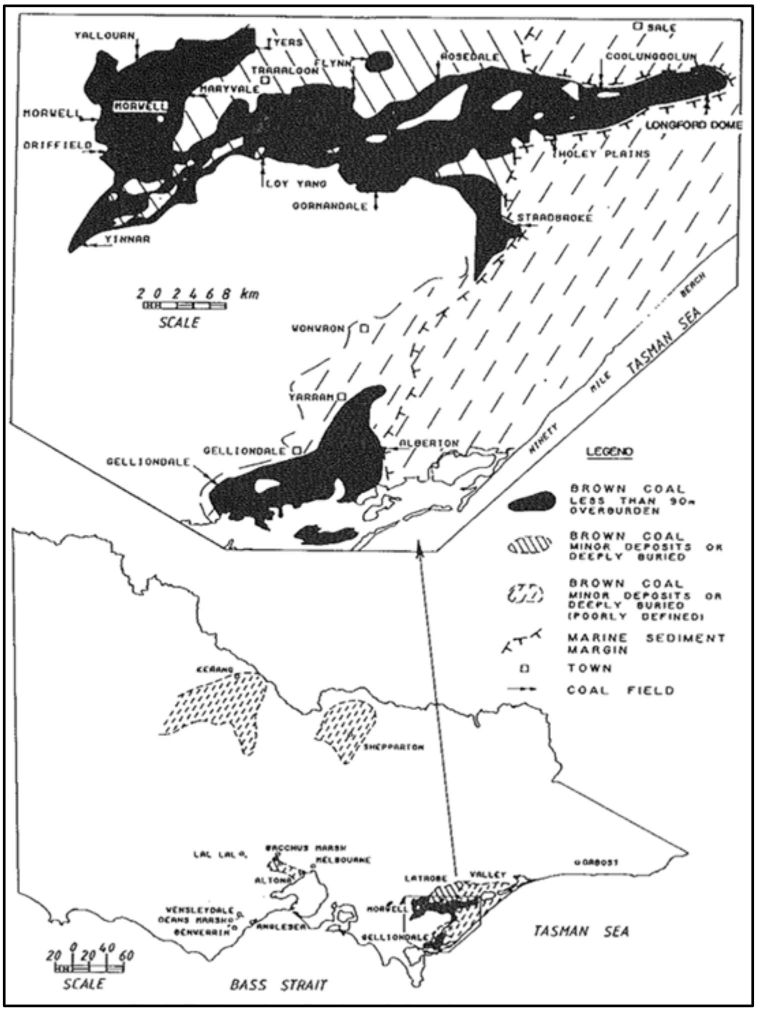


Figure 3: Tertiary coal basins of Victoria (taken from [81]).

The lower rank corresponds to a much higher oxygen content (~25 wt% dry ash free (daf)) than for typical coking coals (~10 wt% [89]). The higher O content leads to a much higher concentration of oxygen functional groups including ether, carbonyl and heterocyclic ring structures as well as acidic functional groups including carboxylic acids and phenols, together with their salts, generally Na, Mg, Ca etc. [90]. The acidic and non-acidic functional groups each account for about half the oxygen content. The acidic functional groups cover a wide range of acidity and are usually grouped as strong and weak acids [91]. The strong acids are predominantly carboxylic, but both carboxyl and phenolic groups can be more strongly acidic, depending on the environment in the coal structure. The presence of the oxygen functional groups, particularly of the acidic functional groups, has important effects on the structure and the properties of VBC. For example, the high polar oxygen functional group content leads to the hydrophilic nature of VBC [92]. The structure of the coal is dependent on the polar interactions between the acid functional groups. Furthermore, the difference between the strongly polar nature of carboxylate and phenolate salts and the much weaker average polarity of the parent carboxylic acid and phenolic groups gives rise to important differences between the properties of raw VBC and VBC subjected to mild acid washing treatment, for example with regard to water adsorption isotherms [91]. Removal of some of the oxygen functional groups, as can be achieved by e.g. hydrothermal dewatering (HTD), will also alter the average polarity of functional groups in the coal and therefore also has an important effect on coal properties [93].

Treatment with alkali has been used to isolate a soluble fraction (humic acid) more amenable to analysis than the solid coal [94] and useful as a soil improver [95]. Treatment with strong alkali at high temperature (185 °C) was found to solubilize coal completely in pyridine and this was felt to be a promising route to more complete organic-group analysis of VBC [96]. Other properties of the coal were also modified by this treatment and, in particular, the alkali treated coal showed evidence of softening on heating.

The relatively low degree of coalification of VBC can also explain its relatively high volatile matter content (45-60 wt% dry basis (db) [97]). Liquefaction and other experiments have shown that the structure of VBC and other low rank coals can be considered as a two-phase system with relatively small long chain aliphatic and terpenoid molecules, “guest”, loosely bound to a rigid lignin derived framework, “host” [98]. These guest molecules can be relatively easily volatilized. As the coal rank increases the bonds, between the guest molecules and the host becomes stronger, and the relative ease with which they can be volatilized decreases [99, 100]. The high volatile matter content of VBC is a disadvantage for producing a coke-like material because the loss of mass during carbonization will be higher and the yield of final product will be lower, and also because the mass loss tends to induce shrinkage of briquette-formed VBC and hence cracking during carbonization, which will affect the integrity of the final carbonized products.

Another important disadvantage of VBC as a coke precursor is that it does not soften on heating [101]. This can be explained by the small size (1-2 rings) of most of the aromatic clusters in brown coals [102], compared to 4-6 in bituminous coals [11], so that when the coal is pyrolysed the aromatic clusters formed are too small to give a plastic mesophase (see Section 1.4). Therefore, on heating under an inert atmosphere, it gives a solid residue which is not fused, thus not massive or inherently strong, and with a relatively small content of graphitic carbon, in contrast to coke (see Section 1.4). The carbonized product is usually referred to as a char, characterized by relatively high reactivity and surface area, and resembles charcoal rather than coke. Thus, carbonization of as mined VBC will not give a BF coke substitute. (It was noted above that treatment with strong alkali gives a product which may melt on heating and could be a BF coke precursor).

However, VBC as a coke precursor has inherent advantages because of its generally low concentration of mineral impurities and cations and consequent low ash yield [82, 103]. Therefore, the contribution of a coke derived from VBC to the slag and minerals in the BF would be small. Furthermore, there are large deposits of VBC which are low in sulphur [104], an important advantage because sulphur has a negative effect on the quality of the iron product (see Section 1.2). There are also economic advantages because the overburden that has to be removed to mine many deposits of VBC is relatively thin (10-20 m) compared to coal thickness of up to and over 100 m [81]. The large deposits, high coal to overburden ratio and easy access of the fields to population centers make VBC very cheap if it is used on the spot. (The high moisture content makes it expensive to transport wet VBC over any distance). These advantages have led researchers to attempt to make a substitute for BF coke with VBC as a starting point. Cheap carbonaceous materials from other countries have also been trialled as BF coke substitutes, and the next Section briefly reviews all these attempts, concentrating most attention on VBC because it is the subject of this study.

1.6 Attempts to produce blast furnace coke from low rank coals

1.6.1 East German attempts

Coke of BF quality was made from brown coal in East Germany by a complicated and expensive process [105, 106] which nonetheless ran commercially for some time.

The steps leading up to the final commercial process have been discussed by Kennedy [107] and what follows is a brief summary of his discussion. The supply of hard coke was a severe problem after World War II, when it was decided to expand the iron and steel industry in East Germany, because no suitable coking coal was available. Therefore, initiatives were taken to use brown coal, based on pre-war research. East Elbe coals were selected because the coals had low ash and sulphur content. The pre-war studies (Lurgi-Krupp process) had shown that carbonising at higher temperature increased the carbon content and strength and reduced the reactivity of the char, which was necessary if the char was to be used as a coke substitute for a BF. The East Germans were able to produce a strong briquette using finely ground coal (0-1 mm particle size) by pressing in an extrusion press. Carbonization was carried out in two stages with a slow rate of temperature rise in the first stage and faster rate in the second stage to a final temperature of 1100 °C held for 20 h. The high final temperature was chosen to reduce the reactivity to an acceptable level. The low reactivity was confirmed by tests in CO_2 at 1300 °C, comparing the coke substitute from brown coal with more conventional cokes [106]. The extreme conditions resulted in a yield of only about half of the final char as briquettes of the required size.

The expense and high wastage of this process, which relied on extreme conditions rather than the use of a binder or other pre-treatment, meant that it was only used until supplies of coking coal from other countries became available [108].

1.6.2 The FMC process

Another process, the FMC process [109-111], was developed in the United States to produce BF coke from different coals including brown coals. The distinctive feature of the FMC procedure was that the coal was pyrolysed and the tar produced was processed to pitch, which was used as a binder.

Ground coal (ideally less than 2.4 mm in particle size) was steam dried to remove moisture, some air being introduced to prevent agglomeration. Then the dried coal was carbonized at 500 °C and the tar and char separated. The char was then calcined at about 800 °C and cooled before mixing with pitch, which was prepared from the tar. The mixture of calcined char and pitch was briquetted at about 100 °C, then the briquettes were air cured to harden them and finally carbonized at 900 °C to obtain the FMC coke. The process ought to have been suitable for brown coal, but unspecified problems were encountered and it was suggested that further work was necessary.

It may be noted that the binder, apart from strengthening the briquettes, may have a composition which would induce formation of mesophase (Section 1.4.2). The tar could be more aromatic and even more hydroaromatic, with fewer crosslinks, than the bulk of the coal, and so would be a potential source of mesophase.

The FMC processes also introduced the idea of air curing the briquettes to increase the strength of the final char. Similar successful use of air curing to increase the strength of final “coke-like” products has been made by later workers [112-118]. The chemistry of the air curing process is discussed in Section 1.7 below.

1.6.3 Indonesian brown coals

Recently, Mori et al. [119] attempted to produce BF coke-like material from Indonesian brown coals of similar rank to VBC. They hydrothermally dewatered raw and acid washed coal separately. Treated or untreated coal was then hot briquetted and carbonized to obtain the final products. They found that the strength and bulk density of the final products were increased for the products obtained after HTD at lower temperatures compared to those obtained without the HTD process. Both HTD and acid washing separately increased the plasticity of the briquettes. These results suggested that HTD treatment should be considered as a preliminary treatment before attempting to prepare a substitute for BF coke from low rank coals. No reactivity measurements were reported.

1.6.4 Attempts using Victorian brown coals

Preparation of BF coke from VBCs has been studied for over 50 years. Extensive investigations were carried out by Higgins, Kennedy and co-workers [107, 120-127] for the Gas and Fuel Corporation of Victoria, Australia in attempts to produce a coke-like material that could be used in metallurgical furnaces including BFs. The initial impulse was the example of hard briquette production from German brown coals by the Lurgi-Krupp process (see Section 1.6.1). Without using any binder, Higgins, Kennedy and co-workers briquetted coals from the Yallourn open cut, of different particle size and moisture content, in a conventional hydraulic press, to form 1 inch diameter cylinder shaped briquettes. These briquettes were pre-dried at different times and temperatures prior to carbonization at 900 °C. They found that coal of smaller particle size (less than 1 mm), a higher briquetting force (three times as high as used in conventional extrusion presses) and a slow heating rate in pre-drying all assisted in increasing the strength of the final products to about 35 MPa compressive strength. Then they made larger briquettes (2 inches in diameter) to match the size of industrial coke, using less than 1 mm particle size VBC, briquetting using the same press but with higher force, followed by slow pre-drying and subsequent carbonization at 900 °C. It was found that the larger briquettes gave cracked final products that had much lower compressive strengths than that of the char obtained from 1 inch briquettes. They also produced some char by the same procedures from ‘Y-type’ commercial briquettes (normal size 2 inches), obtained from the Yallourn briquette factory, that had been briquetted by conventional extrusion presses. Conventional briquetting rather than hydraulic pressing gave a stronger final product. Therefore, the commercial briquettes were used for subsequent investigations. However, the products were still cracked and less strong than those obtained from 1 inch briquettes.

It was discovered that the cracking was due to shrinkage that occurred during the loss of the large amount of volatile matter (about 50 wt%, see Section 1.5). There were differences in shrinkage between the core and the surface of the briquette due to the temperature gradient in the briquette. They found by trial and error that it was desirable to have a low rate of temperature increase up to 600 °C (~1 °C/min), and that above 600 °C a faster rate (~3 °C/min) of temperature increase [127]) could be used without weakening the briquettes. This empirical heating rate procedure gave stronger, less cracked char.

It had been previously suggested by Rummel [128] that ideally the rate of temperature increase should be controlled so that during carbonization the temperature difference between the core and surface of the briquette is constant and small. Experiments in which the heating rate was modified using this criterion were carried out by Megler and Kennedy [129]. However, the modified rate of temperature increase did not closely resemble that which was found to be empirically desirable, and did not give stronger char than that obtained by a constant rate of temperature increase. They then proposed that the rate of temperature increase should be controlled, so that the differential shrinkage between the surface and core of the briquettes should vary as little as possible during the whole period of heating to 900 °C (see Figure 4). This was found to be similar to the empirically suitable rate of temperature increase used previously and the theoretically calculated rate of temperature increase, when applied in practice, gave strong, crack-free char.

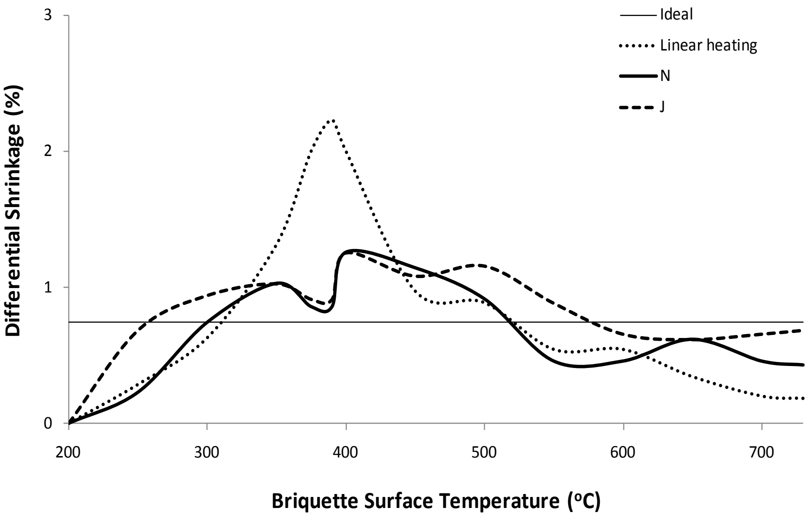


Figure 4: Differential shrinkage for linear heating (100°C/min) compared to differential shrinkage when the theoretical heating cycle was used (experiments J, N) and the ideal theoretical shrinkage. Modified from [130].

Unfortunately, this strong char was found to be too reactive for BF use. They concluded that this was due to the inherent properties of brown coal, so that further work explored only other metallurgical uses, for example in foundries [130].

Recently, Mori et al. [131], attempted to produce a BF coke substitute from VBCs. They briquetted finely ground coal (0.1 mm) without adding any binder at a range of pressures (32-192 MPa) and temperatures (25-230 °C), then carbonized the briquettes at up to 900 °C. By careful choice of briquetting and carbonization conditions, they were able to obtain a coke-like material (char) of high strength and density. They characterized the resulting products by SEM and suggested how the structural changes observed led to high strength. However, they did not comment on the reactivity (CRI) of the product as measured by standard methods [28].

French and Reeves [132] have produced a strong coke-like material of high density from low rank coals, including VBCs. They dried the coal at 5 to 40 °C, then briquetted it, then dried it again at 25-66 °C, prior to carbonization at less than 750 °C for less than 3 h. They stated that the final product was denser than a conventional BF coke and the compressive strength was similar to that of a BF coke. Acid washing was included as an option to remove undesirable components such as sulphur and silica (Section 1.4.3.2). They did not comment on the reactivity with CO_2 at high temperature (CRI).

1.7 Chemistry of air curing

The mechanism by which air curing increases the strength of the final product has been discussed by Metzinger and Huttinger [115] and Unal el al. [118]. During air curing it has been proposed that polar oxygen containing groups (e.g. carboxyl) are formed in the binder, such as pitch or tar [115], and these will interact more strongly with the polar groups in the coal, thus strengthening the structure (reactions 13 and 14, where R and R_1 are aliphatic or aromatic groups).

$$\text{R-OH} + \text{R}_1\text{-COOH} \rightarrow \text{R-COO-R}_1 + \text{H}_2\text{O} \qquad \text{Eq. 13}$$

$$\text{R-COOH} + \text{R}_1\text{-COOH} \rightarrow \text{R-CO-O-OC-R}_1 + \text{H}_2\text{O} \qquad \text{Eq. 14}$$

Furthermore, the new polar groups in the binder (such as pitch or tar) will interact with each other to form cross-links and polymerize the binder, thus strengthening the structure further [114, 117]. During the carbonization process the oxygen containing groups will be replaced by C-C bonds (reaction 15 and 16) [115], so that the enhanced strength will remain.

$$\text{R-COO-R}_1 \rightarrow \text{R-R}_1 + \text{CO}_2 \qquad \text{Eq. 15}$$

$$\text{R-CO-O-OC-R}_1 \rightarrow \text{R-R}_1 + \text{CO} + \text{CO}_2 \qquad \text{Eq. 16}$$

1.8 Aims and approaches

The objective of this project is to induce a coke-forming ability in VBC by a range of physical and chemical treatments including the use of a cementing agent. The treatments used include compression into a briquette of a mixture of VBC or its derivatives and the cementing agent under various conditions, air curing in some cases and carbonization under a range of conditions. As well as VBC itself, derivatives of VBC are investigated, including commercial briquettes, hydrothermally dewatered VBC and VBC treated with strong alkali or mild acid washing.

The quality of the final products is compared with that of a commercial BF coke by measuring the compressive strength and the reactivity. These tests should be considered as screening tests rather than as definitive tests of quality, which would require large amounts of sample and could only be undertaken in a future project, for a VBC product that has at least similar compressive strength and reactivity to conventional BF coke. Other physical and chemical characteristics of the carbonized products are compared with those of a BF coke in an attempt to determine which physico-chemical characteristics are important in determining compressive strength and reactivity and why they are important. The results from the project indicate that it is possible to improve the quality of a coke substitute from VBC by this approach.

1.9 Hypothesis

This research is based on the following hypotheses.

1. A coke-like material can be prepared starting from VBC, by carbonizing a briquetted mixture of suitably treated VBC or its commercial products and tar-like coal derivatives acting as binders.
2. Following on from work of previous researchers, air curing has an effect on the strength, reactivity and general textural and structural properties of the coke-like materials.
3. The reactivity of the final coke-like product can be evaluated on a small scale by a thermogravimetric method.
4. The structural integrity of the coke-like products can be evaluated on a small scale by a series of physical methods e.g. compressive strength of single pellets.
5. Studying the textural and physico-chemical structural characteristics of the coke-like products can cast light on the factors that make for an acceptable BF coke substitute and the mechanisms by which coal, particularly low rank coal, can be converted to a suitable BF coke.

1.10 Methodology

1. VBC or its products, such as commercial briquettes, hydrothermally dewatered coal, acid washed coal or alkali-treated coal, will be used as the primary carbonaceous precursors of the coke-like carbonized product.
2. Binders will be sourced or prepared from higher rank coals and, if possible, from brown

coal, preferably VBC. The binders could be obtained as the liquid products from carbonization of higher rank or brown coals or as fractions therefrom. Alternatively, binder could be prepared as a suitable fraction of liquid product from hydrogenating VBC.

3. Treated or untreated VBC are to be mixed with selected binders. The mixtures will be briquetted under a range of conditions, varying the temperature, time and force. The briquettes will be carbonized under a range of conditions, varying the temperature and time, in all cases under a carefully regulated heating regime, which has been found to be important for obtaining a strong product from VBC (see Section 1.6.4). Some samples will be air cured before carbonization, because this has been found to improve the strength of the carbonized products (see Section 1.6.2).
4. The suitability of the final products as substitutes for BF coke is to be tested by measuring the compressive strength of the carbonized products and the reactivity in a CO_2 atmosphere by small scale tests using a thermogravimetric balance, based on the large scale standard tests used for BF coke.
5. Various physical and chemical characteristics of the original and treated VBC, the binders and the carbonized products will be determined and compared to those of a conventional BF coke, to establish what characteristics are important in giving the best coke-like substitutes and in an attempt to explain why these characteristics are important in giving a good substitute for a BF coke. The characteristics investigated will include bulk density, helium density, CO_2 surface area and the micropore and total pore volume which can be calculated from the densities and the surface area. The proportion of graphitic structure will be determined from Raman spectroscopy, XRD and TEM. The surface morphology of the final products will be observed by SEM to determine the pore structure and to search for evidence of melting or plasticization during carbonization.

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CHAPTER 2

An attempt to produce blast furnace coke from Victorian brown coal

PART B: Suggested Declaration for Thesis Chapter

An attempt to produce blast furnace coke from Victorian brown coal

Monash University

Declaration for Thesis Chapter 2

Declaration by candidate

In the case of Chapter 2, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Proposed original idea; prepared and analyzed samples; identified major issues; developed interpretations; fully drafted papers and conclusions	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Marc Marshall	Aided methods development, input to results analysis, input to manuscript revision	N/A
Alan L Chaffee	Supervision, assisted interpretation in results, editorial assistance	N/A
W Roy Jackson	Supervision, assisted interpretation in results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		**Date** 20/5/15
Main Supervisor's Signature	Alan Chaffee	**Date** 20/5/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

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An attempt to produce blast furnace coke from Victorian brown coal

M. Mamun Mollah, W. Roy Jackson, Marc Marshall, Alan L. Chaffee *

School of Chemistry, Monash University, Clayton 3800, Australia

HIGHLIGHTS

- Products showed satisfactory compressive strength.
- Reactivity and surface area were much higher than those of coke.
- Coal derived products had lower reactivity than briquette derived products.
- Coal derived products had lower surface area than briquette derived products.
- Products had less graphitic structure than coke.

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Reactivity

ABSTRACT

This paper describes attempts to produce blast furnace coke from Victorian brown coals. The attempted method involves combining a coal-derived binder with the original brown coal or its commercial products, briquettes. Briquetting of these mixtures gave composites that were then carbonized to form coke-like materials. Products were characterized by bulk density, helium density, compressive strength, reactivity, surface area, scanning electron microscopy and X-ray diffraction analysis. It was found that the products have sufficient compressive hardness to be used as coke but are still too reactive to be used in a blast furnace.

1. Introduction

Metallurgical coke is a macroporous carbon material of high strength [1], consisting of a partially ordered structure [2]. It is similar in structure and form to many brittle types of foam such as are found in ceramics and glasses [3]. It is produced in large, fused, strong pieces with a much lower reactivity (Coke Reactivity Index, CRI [4] of 18–40% [5,6]) than conventional brown coal chars and is therefore suitable to be used in a blast furnace to produce iron from iron ore. Reactivity and strength are the most important parameters that characterize the quality of the coke [7,8] and its behavior in a blast furnace [1].

Coke is produced by the carbonization of so called coking coals of specific rank or of coal blends at temperatures up to 1200 °C. Coking coals are defined as those coals that possess a plastic stage in carbonization, first soften then swell and resolidify at higher temperature to form coke [5,9–13]. This plastic phase carbonization process produces partially ordered graphite structure which leads to an inherently strong and relatively unreactive coke [5,9–13]. Coking coal is crucial in a modern industrial society, supplies are becoming increasingly scarce and therefore it is becoming progressively more expensive [14,15]. Limited reserves of these coking coals saw the price soar to around US$400/ton in 2011 [16] and, though the price has since fallen to A$120/ton in Sep 2014 [17], uncertainty as to the long term price trend remains. Therefore there is increasing interest in substituting carbon products from cheaper coals for at least part of the coke charged to a blast furnace.

Victorian brown coal (VBC) is accessible and cheap with low concentrations of mineral impurities, which is a favorable requirement for blast furnace coke. Minerals, specially metallic iron and iron sulfides, increase coke reactivity [18] and thus reduce its strength [5] (Coke Strength after Reaction, CSR). Therefore VBC has attracted attention as a coke precursor for over 50 years. However, brown coal does not melt on heating and the solid residue from the carbonization is not massive, fused or inherently strong. It is characterized by relatively high reactivity, resembles charcoal more than coke and is usually referred to as a char [19,20]. Attempts to overcome these problems by Higgins and Kennedy [21–23] involved starting with commercial briquettes, obtained by agglomerating finely ground brown coal under high pressure, and carbonizing them. Preliminary investigations showed that a hard reactive char could be obtained by modulating the heating

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* Corresponding author at: School of Chemistry, PO Box 23, Monash University, Clayton 3800, Australia. Tel.: +61 3 9905 4626; fax: +61 3 9905 4597.

E-mail address: alan.chaffee@monash.edu (A.L. Chaffee).

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rate during carbonization [23], but without any understanding of the processes involved, it was difficult to scale up the experiment or even to allow for variation in the total heating time or the size of the briquettes used. Rummel [24], in earlier work on German brown coals, noted that cracking and weakening of the briquettes occurred because of the differential shrinkage stress caused by the temperature difference between the surface and the core of the briquettes. He suggested that the heating rate should be controlled so that during carbonization the temperature difference between the core and surface of the briquette was constant. Experiments in which the heating rate was modified using this criterion were carried out by Megler and Kennedy [25]. The modified heating rate did not closely resemble that which was found empirically desirable, and did not give a stronger char than that obtained by a constant rate of temperature increase. Finally, Higgins and Kennedy [21–23] showed that careful staged heating in briquette drying and in subsequent carbonization of Yallourn (Victoria) brown coal gave a hard char suitable for a range of applications but still too fragile and too reactive for blast furnace coke.

More recently Mori et al. [26], following earlier work on Turkish lignite by Bayraktar and Lawson [27], briquetted Victorian brown coal at a range of pressures and temperatures and carbonized the resulting briquettes at a relatively moderate temperature of 900 °C. By careful choice of briquetting and carbonization conditions Mori et al. were able to obtain a char of high strength and density. They examined the resulting product by scanning electron microscopy (SEM) and suggested how the structural changes observed led to high strength. They did not comment on the reactivity of the product as measured by standard methods [4] (e.g. coke reactivity index, CRI). French and Reeves [28] were also able to produce a strong, high density product by briquetting and carbonizing low rank coals including Victorian brown coals, but again did not comment on the reactivity of the product.

In further investigation of coke substitutes from VBC, it would therefore be useful to estimate the reactivity of the products. Detailed investigation of the properties of coke substitutes has recently made extensive use of thermogravimetric analysis in a CO_2 atmosphere with a linear rate of temperature rise, to study the reactions occurring as material is lost from reactive products to the gas phase [29,30]. However, for a survey of materials with unknown and possibly high reactivity, it would be sufficient to obtain the reactivity by a simple isothermal test using a thermogravimetric balance, following a procedure based on the standard determination of coke reactivity index (CRI), and this was the approach used in this work.

The research described in this paper took as its starting point the production of char from commercial briquettes pioneered by Higgins and Kennedy [21–23]. In our work an attempt was made to improve the properties of the char by combining a VBC derived binder with commercial briquettes and also with VBC itself. To ensure that valid comparisons could be made between the briquette and coal derived products, the briquettes and VBC were subjected to the same treatments. The composite of binder and coal or briquettes can then be carbonized with the aim of forming a coke-like material of sufficiently low reactivity and high strength to significantly replace coke in a blast furnace. The process could give a substantially cheaper product than the coke currently used in blast furnaces.

2. Experimental

2.1. Materials

Loy Yang coal was obtained from an open cut mine and milled to <3 mm. Briquettes were obtained from Australian Char Pty Ltd and were produced by EnergyBrix Australia. They were made without added binder from a mixture of 80% Loy Yang and 20% Yallourn coal. Tar, a by-product of Victorian brown coal pyrolysis, was obtained from Australian Char Pty Ltd. The tar was completely soluble in Tetrahydrofuran (THF) and dichloromethane. About two thirds of the tar boils between 130 °C and 320 °C [31]. The aromaticity of the tar was calculated to be 0.41 using the Brown Ladner equation [32] from the elemental analysis (Table 1) and the ^{1}H NMR (not shown). A sample of blast furnace coke used for comparisons was obtained from Nippon Steel Corporation, Japan. THF (Liquid Chromatography grade) was obtained from Merck Australia, Kilsyth, Victoria.

Table 1
Analyses of materials.

	Coal	Briquette	Tar	Coke
Proximate analysis				
Moisture (wt%,ar)	60	10	–	3
Ash (wt%db)	3.25	1.35	0.0	11.98
Volatile matter (wt%db)	49.40	49.10	–	–
Fixed carbon (wt%db)	47.35	49.55	–	–
Ultimate analysis (wt%db)				
Carbon	65.70	67.22	74.10	86.2
Hydrogen	4.70	4.76	9.36	0.4
Nitrogen	0.60	0.69	0.62	1.01
Sulfur	0.66	0.30	0.40	0.4
Chlorine	0.11	0.10	–	–
Oxygen (by diff.)	24.80	25.70	15.62	0.3
Physical properties				
Surface area (m^2/g)	237	242		18

Samples of the as received coal, briquettes, tar and coke were dried at 105 °C in a flow of N_2 to determine the moisture content then ashed at 815 °C. The volatile matter content of the as received coal was determined by HRL Technology Pty Ltd, Mulgrave, Victoria. Samples of as received coal were analyzed for C, H, N, S by HRL Technology and of briquettes, tar and coke by the Campbell Microanalytical Laboratory, University of Otago, New Zealand, with O being obtained by difference. The analyses of coal, briquettes, tar and coke are shown in Table 1 and of the coal ash in Table 2.

2.2. Preparation of starting materials

The as received coal and briquettes were treated in the same way to ensure that comparisons between the final products would not be affected by variation in impregnation efficiency or pellet properties. As received coal and briquettes were dried in a flow of N_2 at 105 °C for 24 h, then ground to pass a 0.15 mm sieve then dried again in a flow of N_2 at 105 °C to reduce the moisture content to 1–2 wt% as determined by an OHAUS MB45 halogen moisture analyzer.

2.3. Mixing and pelleting

A solution of Victorian brown coal tar in THF was mixed with ground (Section 2.2) coal or briquettes (0–15 wt%) at room temperature. The coal was impregnated with a THF solution rather than neat tar to ensure optimum dispersion of the tar in the coal. The THF was removed under reduced pressure and the impregnated coal or briquette powder was dried under a flow of N_2 at 105 °C for 24 h. The mixture was ground to <0.15 mm and dried again to 1–2 wt% moisture content under a flow of N_2. This mixture was employed as feedstock. The feedstock was formed into a pellet using a conventional hydraulic pellet press which is usually used for KBr sample preparation for IR analysis. About 1 g of sample was placed into a cylinder shaped die set of 13 mm internal diameter and pressed over 2 min under vacuum until the force reached

Table 2
Ash composition (wt% total ash) of the coal and typical ash composition (wt% total ash) of briquettes. (ND = not determined).

	SiO2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	Na_2O	CaO	SO_3	P_2O_5
Coal	56.5	19.2	2.3	8.0	0.2	2.4	4.1	1.0	5.4	0.2
Briquettes	25	12	15	1	0.8	12.5	10	7.5	16	ND

8 ton and the force held for 10 min. The evacuated die was backfilled with N_2 prior to removing the pellet. The resulting cylinder shaped pellets were about 13 mm in diameter and about 6 mm in height.

2.4. Carbonization

Prepared pellets were weighed in an alumina cup and placed into a muffle furnace and then carbonized in a continuous flow of N_2 (400 L/h). A carefully controlled heating regime was required to prevent cracking of the pellet. This is because of shrinkage of the pellet as a result of volatile matter being given off at temperatures higher than 350 °C [9,20]. Therefore, the carbonization temperature was increased to 500 °C at 2 °C/min then to 900 or 950 °C at 5 °C/min and then held at temperature for 2 or 5 h. The samples were cooled under N_2 overnight and weighed. A relatively low carbonization temperature was used to facilitate comparisons with the earlier work of Higgins and Kennedy [23]. The carbonization yield was determined by the difference in mass between the feedstock that was used to prepare a pellet and the final carbonized product of that pellet, using Eq. (1) [33].

$$\text{Yield} = (B/A) \times 100 \tag{1}$$

where B is the final weight after carbonization and A is the weight of the coal or coal-binder mixture (db) used to prepare a pellet. The estimated uncertainty based on results obtained under similar conditions was ±0.5 wt%.

2.5. Bulk density

Bulk density of carbonized products was calculated from the weight of the pellet and its volume determined from the diameter and height of the cylinder shaped pellet. The uncertainty in bulk density based on duplicate determinations was about ±0.02 g/cm^3.

2.6. Helium density

The helium densities of the samples were determined on dried samples by helium pycnometry [34] using an AccuPyc 1330 model pycnometer (Micromeritics, Norcross, GA, USA). The unit was calibrated on a daily basis and oven-dried sub-samples of between 0.5 and 1 g ($\sim$1 mm particle size) were used for analysis. The sample was purged with helium 99 times to ensure complete removal of air. The helium density was determined from an average of 10 measurements on each individual sample. The uncertainty in helium density based on multiple determinations (standard deviation) was about ±0.04 g/cm^3.

2.7. Compressive strength

The compressive strength of the sample of known height (H) and diameter (D) was measured by using an INSTRON 5569 series Mechanical Tester. The sample was placed on the anvil of the tester and an axial load applied across the plane ends until failure occurred. The displacement and loading were measured during the compression at a displacement rate of 0.05 mm/s. The compressive strength σ_c was calculated using Equation (2), as used by Johns et al. [35]:

$$\sigma_c = (4F/\pi D^2)(\mathrm{H}/D)^{0.5} \tag{2}$$

where force, F is determined from the maximum load the pellets withstood, D is the diameter and H is the height of the pellet. The uncertainty in compressive strength based on duplicate determinations was about ±10–20% of the value.

2.8. Surface area

Surface area was measured by CO_2 adsorption using a Micromeritics TriStar II 3020 analyzer at 0 °C. Experiments were carried out on oven-dried 0.2 g sub-samples, which were further dried under vacuum at 160 °C for at least 8 h to ensure complete removal of adsorbed gases using a Micromeritics VacPrep 061 instrument. CO_2 surface areas and micropore volumes (pores < 2 nm diameter) were calculated using the Dubinin–Radushkevitch equation [36–38]. The reference vapor pressure (p_o) for CO_2 at 0 °C was taken to be p_o = 26141.72 torr. The uncertainty in surface area based on duplicate determinations was about ±2% of the value.

2.9. Reactivity test

Samples were tested for reactivity by a small-scale method based on the standard method ASTM D5341-99R10 [4]. The reactivity test denoted R60CO_2 was carried out in a Setaram TAG 24 symmetrical thermoanalyzer. The gases (nitrogen and carbon dioxide) were dosed into the thermoanalyzer using Bronkhorst programmable mass flow controllers. About 25 mg of sample obtained from the broken pieces of pellets after the compression test (Section 2.7) was weighed into a 70 μL alumina crucible and loaded into the furnace, then purged for 10 min with 35 mL/min N_2 at room temperature. With continuing N_2 flow, the sample was heated to 110 °C at 10 °C/min then held at 110 °C for 30 min to remove moisture. The sample was then heated to 1000 °C at a rate of 20 °C/min in the N_2 flow and held in the N_2 flow at 1000 °C for 10 min. Then the flowing gas composition was changed to 50% CO_2/50% N_2 and the temperature held at 1000 °C for another 60 min. The sample was cooled in a N_2 flow to ambient temperature. After cooling, the crucible was removed and weighed. The coke reactivity index (R60CO_2) was calculated using Eq. (3).

$$\text{R60CO}_2 = [(m_1 - m_2)/m_1] \times 100 \tag{3}$$

where m_1 was the original test sample weight before reaction and m_2 was sample weight after reaction in CO_2. The uncertainty in reactivity based on duplicate determinations was about ±2% in R60CO_2 units.

2.10. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was carried out using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope. This microscope can be operated in two modes; mode 1 with a field free lens and mode 2 with an immersion final lens for high resolution imaging. Prior to loading into the instrument each sample was mounted on conductive carbon tape and coated with platinum (1–2 nm thickness) for 0.5 min using a Cressington Sputter Coater. During the coating process the samples were tilted about 45° and rotated at 50–100 rpm.

2.11. X-ray diffraction (XRD)

Powder X-ray diffraction experiments were performed in reflection mode [39] on a Bruker D8 Focus Powder Diffractometer with Cu K_α radiation (40 kV, 40 mA) as the X-ray source. A divergence slit width of 1.0 mm, scattering slit width of 1.0 mm, detector slit width of 0.2 mm and monochromator slit width of 2.0 mm were used. Samples were pulverized to less than 0.18 mm. Samples were then packed into a silicon holder and scanned over an angular range from 5° to 55° 2θ at a scan speed of 0.6° 2θ per min, using a step size of 0.02° 2θ.

Bragg's Law and the Scherrer Equation were used to calculate the interlayer spacing between aromatic planes of carbon crystallites, d_{002}, and the crystallite size or stacking height, L_c, respectively [40–47].

Diffractogram data was smoothed by MS Excel then OriginPro 8 SR2 software was used for deconvolution according to Li et al. [46] and Sonibare et al. [45] in the 2θ range of 15–35° to resolve 002 and γ bands [48] (Section 3.8).

3. Results and discussion

3.1. Carbonization yield

The yields (Fig. 1) were similar for coal and briquette derived products and almost independent of carbonization time and temperature. The yields decreased linearly with increasing tar content. On the assumption that the tar and coal or briquettes volatilized independently of each other, it was calculated that the yield of tar was 35 ± 3 wt% and did not vary significantly within the range of tar contents used, carbonization conditions or starting material (coal or briquettes). This yield was that expected from the known volatility of the tar (about 66%; see Section 2.1) and supports the assumption of independent volatilization of tar and coal. The yield for 0 wt% tar was similar to that obtained by Mori et al. [26] from Victorian brown coal briquetted at an ambient temperature. This yield was much less than that of coke (75 wt%) [5]) from typical coking coals, which have much lower volatile matter 18–32 wt% [5,6,13,49] than Victorian brown coals (~50 wt%; Table 1).

3.2. Bulk density

The bulk density of the coal derived products tended to be higher than that of the briquette derived products at lower tar content (Fig. 2). It is possible that the process of briquette production, at a temperature of 70–105 °C and a pressure of 120 MPa [50], led to a more rigid structure, which shrank less during carbonization than that of coal and so gave a product of lower bulk density. Rearrangement of coal structure during briquetting at 130–160 °C, which might make the structure more rigid, has been suggested by Mori et al. [26]. Such an increase in rigidity of structure was observed for Victorian brown coals, steam dried at higher temperatures (greater than 180 °C) but much lower pressures (1–2.5 MPa) than those used in briquette production [51]. The bulk density tended to increase with increasing tar content as the tar filled pores in the coal structure so that the difference between coal and briquette derived products disappeared. There was no consistent effect of carbonization conditions on bulk density. As found by Mori et al. [26], the bulk density was always higher than that of BF coke (0.87 g/cm^3 [52]), suggesting that the pore volume of the BF coke was higher than that of the coal and briquette derived products.

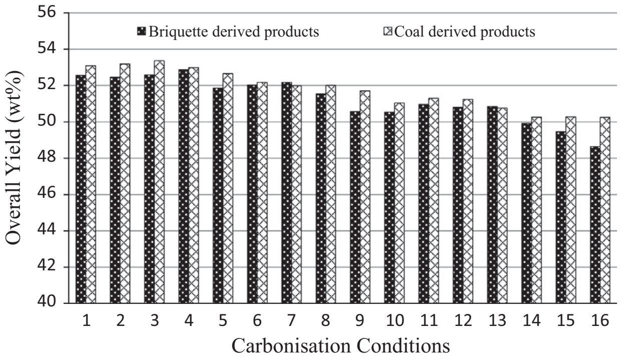

Fig. 1. Overall yield of products - four tar contents were used, samples 1–4, 0 wt%; 5–8, 5 wt%; 9–12, 10 wt%; 13–16, 15 wt%. In each set the first sample (1, 5, 9, 13) was carbonized at 900 °C for 2 h, the second (2, 6, 10, 14) at 950 °C for 2 h, the third (3, 7, 11, 15) at 900 °C for 5 h and the fourth (4, 8, 12, 16) at 950 °C for 5 h.

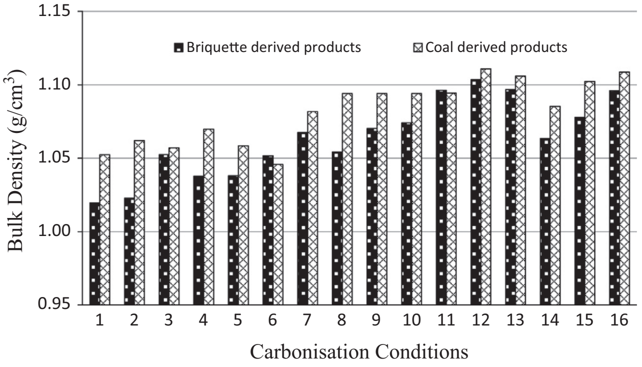

Fig. 2. Bulk density of products – four tar contents were used, samples 1–4, 0 wt%; 5–8, 5 wt%; 9–12, 10 wt%; 13–16, 15 wt%. In each set the first sample (1, 5, 9, 13) was carbonized at 900 °C for 2 h, the second (2, 6, 10, 14) at 950 °C for 2 h, the third (3, 7, 11, 15) at 900 °C for 5 h and the fourth (4, 8, 12, 16) at 950 °C for 5 h.

3.3. Helium density

Comparison of bulk and helium densities (Fig. 3) indicated that briquette derived products had more pore volume per unit mass than the coal derived products and that the pore volume for both coal and briquette derived products tended to decrease as tar was added, probably because the tar penetrated into some of the pores [53]. The helium density of the products was slightly higher than that of a BF coke and, since the bulk density of the products

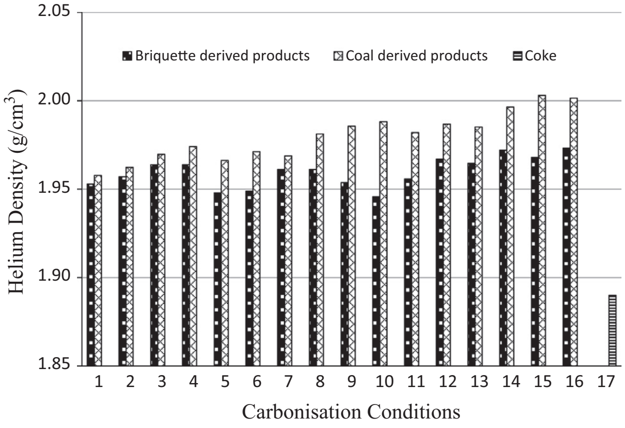

Fig. 3. Helium density - four tar contents were used, samples 1–4, 0 wt%; 5–8, 5 wt%; 9–12, 10 wt%; 13–16, 15 wt%. In each set the first sample (1,5,9,13) was carbonized at 900 °C for 2 h, the second (2, 6, 10, 14) at 950 °C for 2 h, the third (3,7,11,15) at 900 °C for 5 h and the fourth (4, 8, 12, 16) at 950 °C for 5 h.

was considerably higher, the pore volume of a BF coke per unit mass was higher than that of the VBC products. The helium density of products from coal and briquettes was similar when no tar was added, but that of the coal derived products tended to be higher when tar was added. This suggests that there was an interaction between tar and coal during carbonization which tended to increase the density and that such an interaction did not occur, at least not to the same extent, with the briquette derived products. The difference between coal and briquettes in this regard may be due to the higher pore volume of the briquette derived products, increasing the average distance between tar and coal molecules and thus reducing the strength of the interaction between them. Alternatively, it may be due to greater rigidity of the briquette derived product structure.

3.4. Compressive strength

Fig. 4 shows the outstanding difference was between briquettes and coal derived samples, with the latter having much higher compressive strengths, which were all higher than that of the coke sample. In some cases, longer carbonization time, higher carbonization temperature and increased tar content increased the compressive strength but the effects were all relatively small. The greater rigidity of the briquette structure (see above) may have reduced the extent of compression during pressing and weakened the interaction which occurred during carbonization to strengthen the products.

The higher pore volume per unit mass of the briquette derived products (Section 3.3) supports this suggestion. An alternative explanation is suggested by the proposal of Mori et al. [26] that, during pressing of coal, low molecular weight components (the guest [54]) are squeezed out onto the surface of the particles and act as a binder during carbonization to strengthen the product. For the briquettes, these low molecular components would have been squeezed out during the commercial briquetting and subsequent grinding would have dispersed them. When the briquette powder was subsequently pressed again there would be no low molecular weight components to be squeezed out and bind adjacent particles so that the briquette derived product would have been weaker, as observed. Mori et al. [26] measured the strength of their coal derived product by a different method from that used in this paper, so that the numerical values cannot be compared, but they also found that the brown coal derived products were much stronger than a BF coke.

There is literature which suggests that differences in the inorganic analyses of the original coal and briquettes could influence the strength of the final products. Increased Ca would be expected to increase the strength of the products [55], but the higher Ca content of the briquette derived products (see Tables 1 and 2) did not correspond to a higher compressive strength, so that this effect, if it occurred, must have been outweighed by those discussed above. There have been suggestions that changes in silica (quartz) concentrations could affect the strength, but the magnitude and direction of the effect is uncertain. Sukhorukov et al. [56] suggested that quartz would increase the strength of coke and Patrick and Stacey [57] thought that at lower concentration quartz could increase the strength. In contrast, Patrick and Stacey [57] suggested that at higher concentration quartz would decrease the strength and Gornostayev et al. [58] suggested that such a decrease in strength could be due to strain induced by changes in the mineral volume following phase transformations during carbonization. Thus the higher silica content of the coal compared to the briquettes could have been a factor in the higher strength of the coal derived products, but this remains uncertain.

3.5. Surface area

The surface areas (Fig. 5) of the coal derived products fell in the range 790–800 m^2/g and those of the briquette derived products in the range 810–830 m^2/g, all much higher than the surface area measured for coke (18 m^2/g). The low value for the coke may be attributed to the destruction of the original pore structure when the plastic state is formed during carbonization [59]. The high values obtained for the products suggest no melting occurred during their carbonization. There was no significant effect of tar addition or carbonization conditions on the surface area. The coal derived products showed slightly lower surface areas than those derived from briquettes. The higher surface area of the briquette derived products corresponded to their larger pore volume which was possibly related to larger inter molecular distances due to the weaker bonding (Section 3.4) in the briquette derived products. The higher surface area of the briquette derived products was not related to the surface area of the original material because the briquettes and coal had the same surface area within the limits of error (Table 1).

3.6. Reactivity

Fig. 6 shows that the coal derived products were slightly less reactive than the briquette derived products. The carbonization temperature and time and tar content had relatively small effects

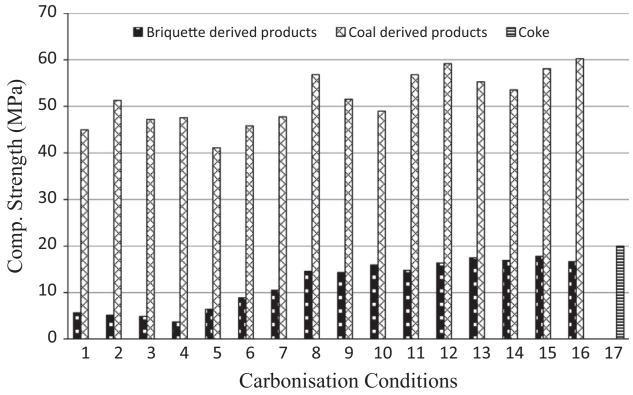

Fig. 4. Compressive strength - four tar contents were used, samples 1–4, 0 wt%; 5–8, 5 wt%; 9–12, 10 wt%; 13–16, 15 wt%. In each set the first sample (1,5,9,13) was carbonized at 900 °C for 2 h, the second (2, 6, 10, 14) at 950 °C for 2 h, the third (3, 7, 11, 15) at 900 °C for 5 h and the fourth (4, 8, 12, 16) at 950 °C for 5 h.

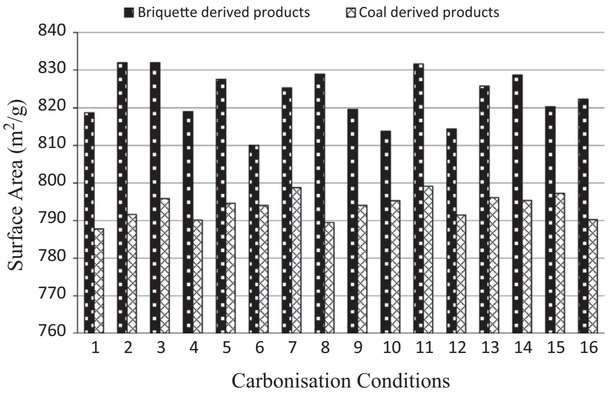

Fig. 5. Surface area of products - four tar contents were used, samples 1–4, 0 wt%; 5–8, 5 wt%; 9–12, 10 wt%; 13–16, 15 wt%. In each set the first sample (1,5,9,13) was carbonized at 900 °C for 2 h, the second (2, 6, 10, 14) at 950 °C for 2 h, the third (3, 7, 11, 15) at 900 °C for 5 h and the fourth (4, 8, 12, 16) at 950 °C for 5 h.

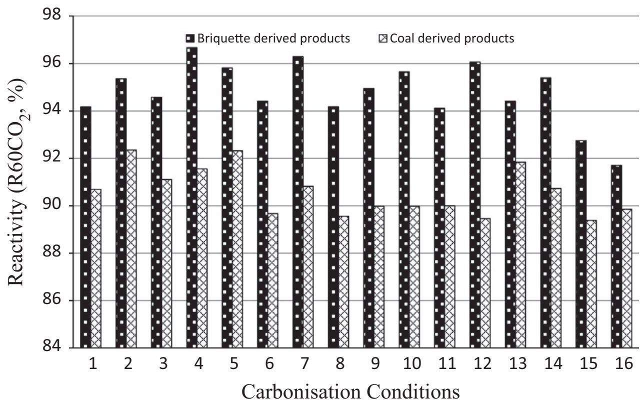

Fig. 6. Reactivity of products - four tar contents were used, samples 1–4, 0 wt%; 5–8, 5 wt%; 9–12, 10 wt%; 13–16, 15 wt%. In each set the first sample (1,5,9,13) was carbonized at 900 °C for 2 h, the second (2, 6, 10, 14) at 950 °C for 2 h, the third (3, 7, 11, 15) at 900 °C for 5 h and the fourth (4, 8, 12, 16) at 950 °C for 5 h.

on reactivity. At low tar content and less severe carbonization conditions the pore volume per unit mass of the briquette derived products was less than that of the coal derived products, but the difference in the $R60CO_2$ for these cases was not greater than for other conditions, so that this factor had little effect on the difference in $R60CO_2$. Possibly the greater rigidity of the briquette structure and the absence of the bonding effect of low molecular weight components (Section 3.4) led to greater intermolecular distances and weaker bonding of the structure of the briquette derived products and so increased their reactivity. All the products were much more reactive than the BF coke ($R60CO_2$ 13%). Thus even addition of a binder did not alter the conclusion of Higgins and Kennedy [21–23] that brown coal char was much more reactive than coke. The mineral content of the products is not likely to have increased their reactivity because the concentrations of precursors of possible catalysts, iron and calcium [18], in the original coal and briquettes were relatively small and no crystalline iron or calcium minerals, which are believed to be the only catalytically active species [18] were observed by XRD (Section 3.8) in the products from either coal or briquettes. The difference in reactivity between brown coal derived products and coke could be at least partly due to the large difference in surface area [60] (Section 3.5). The larger pore volume of the BF coke (Section 3.2) compared to that of the brown coal derived products did not lead to a higher $R60CO_2$ than that of these products, implying that surface area rather than pore volume controls the $R60CO_2$.

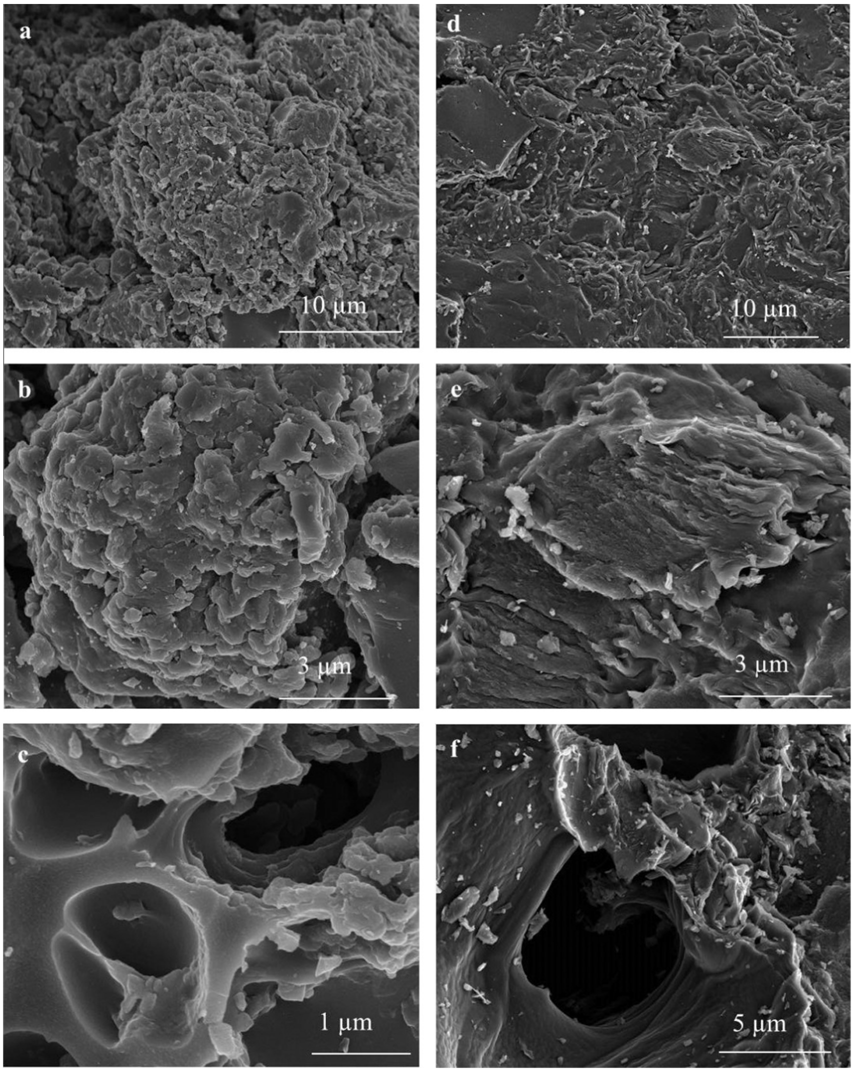

Fig. 7. SEM images of products (a, b) and coke (d, e) at the same magnification to show differences in surface morphology, and images of pores in products (c) and coke (f) to show differences in pore structure.

3.7. Scanning Electron Microscopy (SEM)

Fig. 7(a) and (d) show low magnification images of a typical final product and coke respectively and Fig. 7(b) and (e) show medium magnification images of the same final product and coke respectively. There were no clear effects of tar addition, carbonization conditions or starting material (coal, briquettes). For all the final products a grainy irregular surface was observed with cracks and fissures. The morphology of the products was similar to that observed for carbonized brown coal briquettes by Mori et al. [26]. If images at the same magnification are compared, the coke surface (Fig. 7(d) and (e)) was much smoother than the surface of the products (Fig. 7(a) and (b)). The coke surface showed evidence of melting and subsequent resolidification, with no cracks (Fig. 7(e)). The pores in the coke surface were well-defined, deep and large (see Fig. 7(f)), whereas the pores on the product surface were shallow and tended to be smaller (see Fig. 7(c)). This difference in surface morphology may also help to explain the difference in reactivity between coke and coal/briquette derived products.

3.8. X-ray diffraction

In XRD experiments, for all samples a sharp peak (not shown in the figure, removed for deconvolution purposes) for quartz was observed at around 26° 2θ, but no significant peaks for iron, calcium or magnesium crystals were observed. A broad peak was found in the 2θ range of 15–35° (Fig. 8) and another peak in the 2θ range of 40–50° (not shown). Li et al. [46,48], Sonibare et al. [45] and Siddiqui et al. [61] also observed a similar peak structure in carbonized coal, sub-bituminous/bituminous coals and asphaltenes respectively. The shape of the 15–35° 2θ peak in the products indicated that two symmetrical components were required to deconvolute it, as for BF coke.

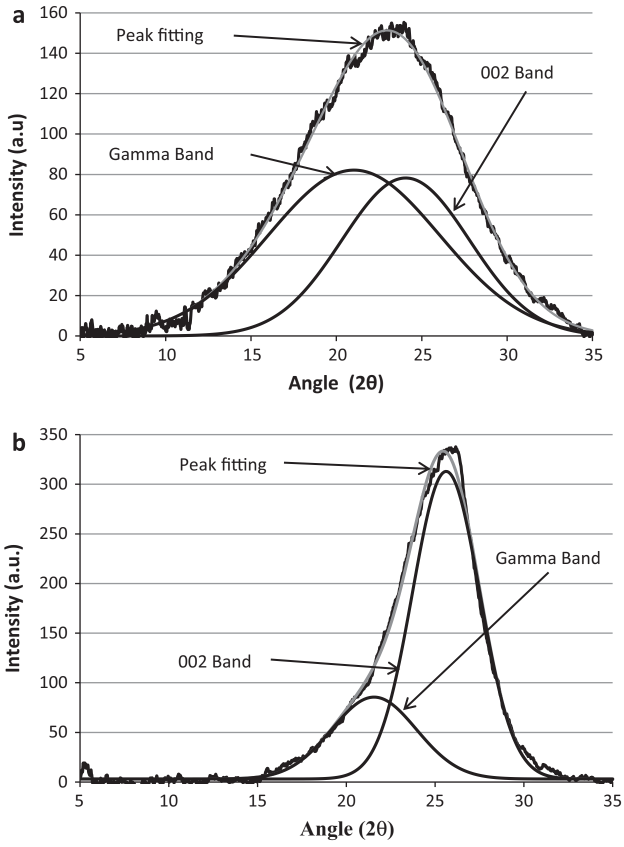

Fig. 8. An example of curve-fitting Gaussian peaks to the XRD pattern of (a) product (b) BF coke.

The 002 and 100 bands, at about 25° and 45° 2θ respectively are related to stacking in aromatic layers and the distance between points in an aromatic layer respectively [40–47]. For crystalline graphite the band at 25° 2θ is symmetrical and narrow [44,62], so that broadening and apparent asymmetry of this peak in BF coke and the products imply the existence of bands on the low 2θ side other than the 002 band. One of these extra bands, the γ band, is associated with the packing distance of saturated structures grafted on the edges of coal crystallites, such as aliphatic side chains, or with the irregular packing of buckled aromatic layers [42,45,46,61].

The ratio of the areas of the 002 band and γ band is taken to be a measure of the ratio of ordered graphitic carbon to amorphous carbon [63]. For the products obtained in this work, this ratio was about 0.8 for coal derived and 0.7 for briquette derived products, whereas for BF coke it was about 3.0, indicating that the proportion of carbon in well-ordered graphitic structures in the products was much less than in the BF coke. The spacing, d_{002} between the planes in the graphitic structure in the products, 3.7 Å, was greater than that in the BF coke, 3.48 Å or in graphite (3.35 Å), indicating poorer crystallinity or a lower degree of graphitization [64] and the presence of some aliphatic carbon in the products. Furthermore, the 002 band for the products was broader than the corresponding band in the BF coke, again indicating a lower degree of crystalline order [47] than in the BF coke. The stacking height, L_c in the products was only about 9.05 Å compared to about 18.07 Å for the BF coke; smaller crystallite size in the products indicating a poorer degree of graphitization than in BF coke.

Along with other properties, the smaller proportion of well-ordered graphitic structure, the poorer crystallinity of the graphitic structure and the smaller size of the crystallites in the products, would all help to explain their higher reactivity compared to that of a BF coke, as discussed by earlier workers [7,62].

4. Conclusion

Cokes prepared from ground brown coal showed higher compressive strengths and slightly lower reactivity and surface areas than those prepared from ground brown coal briquettes. The effects of carbonization conditions (time, temperature and tar addition), at least over the range of conditions examined, were relatively small. The high reactivity of the samples compared to that of coke is probably related to their higher surface areas, together with the smaller extent and greater disorder of their graphitic structure. It is in these directions that improvements will have to be sought.

Acknowledgements

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CHAPTER 3

The use of a brown coal derived binder and hot briquetting to induce a coke forming ability in Victorian brown coal

PART B: Suggested Declaration for Thesis Chapter

The Use of a Brown Coal Derived Binder and Hot Briquetting to Induce a Coke Forming Ability in Victorian Brown Coal

Monash University

Declaration for Thesis Chapter 3

Declaration by candidate

In the case of Chapter 3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analyzed samples; identified major issues; developed interpretations; fully drafted papers and conclusions	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Marc Marshall	Aided methods development, input to results analysis, input to manuscript revision	N/A
Alan L Chaffee	Supervision, assisted interpretation in results, editorial assistance	N/A
W Roy Jackson	Supervision, assisted interpretation in results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		**Date** 20/5/15
Main Supervisor's Signature	Alan Chaffee	**Date** 20/5/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

The use of a brown coal derived binder and hot briquetting to induce a coke forming ability in Victorian brown coal

M. Mamun Mollah, Marc Marshall, W. Roy Jackson and Alan L. Chaffee

School of Chemistry, Monash University, Clayton 3800, Australia

Corresponding Author: Alan L. Chaffee

School of Chemistry, PO Box 23, Monash University, Australia

Email: alan.chaffee@monash.edu, Tel: +61-3-9905-4626, Fax: +61-3-9905-4597

Abstract

Victorian brown coal with its tar, which is a by-product of commercial char production, was investigated to produce a blast furnace coke substitute. Coal-tar mixture was briquetted applying 20 kN force at 150 °C for 10 or 30 min. Briquettes of about 13 mm diameter and 8 mm height were optionally air cured at 200 °C for 2 h and carbonized at 950 °C for 3 h in a muffle furnace to obtain the final coke-like products. Products were characterised by overall yield, bulk density, helium density, compressive strength, CO_2 surface area, reactivity to CO_2 at 1000 °C, scanning electron microscopy (SEM) and Raman spectroscopy and also compared with a conventional blast furnace coke. Products showed significantly improved strength, far higher than a typical BF coke, but the reactivity and surface area remained too high.

Keywords: Victorian brown coal, Blast furnace coke, Strength, Reactivity, Surface area

1. INTRODUCTION

Iron and steel have played a vital role in civilization. Most iron is mined as oxides, which have to be reduced to the metal. The most popular method of doing this is to react the ore with carbon in a blast furnace (BF). The source of the carbon is usually coke, because it is sufficient to use a relatively low proportion of coke relative to the amount of iron ore [1]. Coke, a hard and macroporous carbon material, is produced from coking coals in a coke oven. Coking coals are bituminous coals which, when heated, soften, become plastic and coalesce into a coherent mass that swells and resolidifies to form a solid porous residue (coke) [2]. The coke acts as fuel source and the smelting agent in a blast furnace and also provides the permeable support and mechanical support for the burden of iron ore being charged from the top of the furnace. High mechanical strength is preferred for an efficient BF operation [3]. To date, there is no other material that can completely replace coke in a blast furnace.

Coking coals are becoming increasingly harder (and more expensive) to obtain as global steel demand grows [4] and the more easily mined coking coal becomes depleted [5]. Victorian brown coal (VBC) is very accessible, very cheap, and has very low concentrations of mineral impurities, which are favourable factors for iron production in a blast furnace [6-8]. However, unfortunately, in its as-mined condition it does not form coke in a coke oven, only producing a char which is too reactive to BF gas, to be used in a blast furnace. Low reactivity is an important requirement for a BF coke [9] or its substitute, because low reactivity ensures that the coke retains its strength in the BF, so that it can support the charge.

In earlier work it was shown that products obtained from VBC by ambient temperature briquetting of a mixture of VBC and tar obtained from VBC and subsequent carbonization had a high compressive strength, but too high a reactivity in CO_2 to be used as BF coke [10, 11]. Recently, French and Reeves [12] patented a process in which low rank coals were briquetted at low temperature (<66 °C) and subsequently carbonized without added binder to give a product of comparable compressive strength and bulk density to BF coke. However, no information was given on reactivity in CO_2 or strength of the product after exposure to CO_2 at high temperature (1100 °C). Mori et al. [13] briquetted VBC at a high force and high temperature, up to 230 °C, without binder, and again obtained a product after carbonization of high compressive strength. They examined the effect of changes in the briquetting conditions and carbonization temperature on the strength, bulk density and microscopic structure of the products and related their results to earlier work on the properties of low rank coals. They did not examine the reactivity in CO_2 at high temperature of their products.

These prior studies suggested to us that it might be useful to attempt to produce a BF coke from VBC by hot briquetting, rather than ambient temperature briquetting following carbonization. Since air curing has often been found to be beneficial in improving the strength of carbonized materials [14-16], its effects on the properties of hot briquetted samples have also been examined in the present study. The crucially important reactivity, as well as the compressive strength, of the products are determined and these properties are then related to other characteristic of the final carbonized products, such as bulk density [17], surface area [18] and microscopic structure [13, 19]. In addition, the extent of graphitisation [20, 21] was estimated by Raman spectroscopy.

It can be noted that some investigations of the reactivity of coke substitutes in recent years have used dynamic TGA [22] to make detailed comparisons of reactivity, but, since it was expected that some of the products prepared in this study might be too reactive, as found in previous work [10, 23, 24], it was decided to use a simple reactivity test based on the ASTM standard [25] to determine the relative reactivity of different products.

2. MATERIALS AND METHODS

2.1 Materials

Raw coal (RC) was obtained from an open cut mine located in Loy Yang, Victoria, Australia and milled to <3 mm. Victorian brown coal tar, which was a by-product of coal pyrolysis to produce char, was sourced from Australian Char Pty Ltd, Morwell, Victoria. The tar was completely soluble in tetrahydrofuran (THF) and dichloromethane [10]. About two thirds of the tar boils between 130 °C and 320 °C [26]. A BF coke sample was obtained from Nippon Steel Corporation, Japan to compare with the final products. THF of Liquid Chromatography grade was obtained from Merck Australia, Kilsyth, Victoria.

2.2 Preparation and analyses of materials

The moisture content of RC and BF coke were determined as the loss in weight when a sample was heated in flow of N_2 at 105 °C for 4 h. For ashing, samples of RC, tar and coke were dried at 105 °C in a flow of N_2 for 4 h to determine the moisture content, and then heated in air at 815 °C for 2 h. The volatile matter content of the RC was determined by HRL Technology Pty Ltd, Mulgrave, Victoria. Analyses for C, H, N and S were carried out by HRL Technology (RC) and by Campbell Microanalytical Laboratory, University of Otago, New Zealand (tar, coke). O was obtained by difference. The oxygen content of RC was obtained using the minerals plus inorganics content (2.25 wt%db), calculated from the ash yield of acid washed coal and the Mg+Na+Ca+Fe content of RC rather than the ash yield of RC [27, 28]. The analyses of RC, tar and coke are shown in Table 1. The standard deviations of the ash yields, based on duplicate determinations, were ± 0.02 wt%db (RC) and 0.7 wt%db (coke). The uncertainties in the RC analyses were ± 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 and those for coke and tar analyses. The composition of the ash of RC is given in Table 2.

Table 1: Proximate and ultimate analyses of materials.

Analysis[a]	**RC**	**Tar**	**Coke**
Proximate			
Moisture (wt%ar)	60.0	-	3.0
Ash (wt%db)	3.25	0.0	12.0
Volatile Matter (wt%db)	49.4	-	-
Fixed Carbon (wt%db)	47.4	-	-
Ultimate (wt%db)			
Carbon	65.7	74.0	86.2
Hydrogen	4.70	9.36	0.4
Nitrogen	0.60	0.62	1.01
Sulphur	0.66	0.40	0.4
Oxygen (by diff.)	26.1	15.6	0.03
Atomic H/C ratio	0.85	1.51	0.06

[a] The uncertainty in the ash yield given as standard deviations based on duplicate analyses was less than 0.1 wt%db. The uncertainty in volatile matter and fixed carbon given by HRL Technology was given as ± 0.4 wt%db. The uncertainty in RC ultimate analysis given by HRL Technology 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. For coke and tar analyses, standard deviations based on duplicate results were ± 0.15 wt%db for C, ± 0.06 wt%db for H, ± 0.04 wt%db for N, negligible for S and ± 0.9 wt%db for O content obtained by difference in all cases.

Table 2: Ash composition of RC (wt% of the total ash).

SiO_2	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**K_2O**	**MgO**	**Na_2O**	**CaO**	**SO_3**	**P_2O_5**
56.5	19.2	2.3	8.0	0.2	2.4	4.1	1.0	5.4	0.2

2.3 Mixing and briquetting

Victorian brown coal tar was dissolved in THF then mixed with ground coal (Section 2.2) at room temperature so as to incorporate 0 to 15 wt%db tar. The coal was mixed with a THF-tar solution rather than neat tar to promote optimum dispersion of the tar in the coal. The THF was removed under reduced pressure and the mixture was dried under a flow of N_2 at 105 °C for 24 h then ground to <0.15 mm and dried again under a flow of N_2 to 1-2 wt%db moisture content, as determined by an OHAUS MB45 halogen moisture analyser. This mixture was employed as the starting point for further treatment.

About 1.2 g of coal-tar mixture was placed into a 13 mm diameter die set. Then the die was heated to 150 °C by a heating element attached to it at a rate of 10 °C/min. After confirmation that the contents had reached the required temperature, force was applied using an INSTRON 5569 series Mechanical Tester at a rate of 10 kN/min until the force reached 20 kN and the force held for 10 or 30 min. The force was then released and the die was cooled to ambient temperature to recover the briquette, which was weighed. The typical diameter and thickness of the briquettes were about 13.0 and 8.0 mm respectively.

2.4 Air curing

The briquettes were heated in a flow of air (300 mL/min) at 200 °C for 2 h [14, 15, 29] and then cooled to ambient temperature with the air flow continuing. During air curing the briquettes lost 1-2 wt%, indicating that some oxidation took place, but there was no cracking or white ash spots, so that combustion did not occur.

2.5 Carbonization

For carbonization, a relatively low carbonization temperature was used to permit comparison with the earlier work of Mollah et al. [10, 11] and with the earlier work of Higgins and Kennedy [30-35]. Prepared briquettes were weighed in a ceramic cup placed into a muffle furnace in a flow of N_2 (400 L/h). A controlled heating regime was required to prevent cracking of the briquettes because of shrinkage [34, 36], resulting from volatile matter being given off at temperatures higher than 350 °C [37]. Therefore, the carbonization temperature was increased to 500 °C at only 2 °C / min, then to 950 °C at 4 °C / min. The samples were held at 950 °C for 3 h, cooled under N_2 overnight and weighed.

2.6 Analyses of the products

Some of the procedures were identical to those of Mollah et al. [10] and therefore are only given in the supplementary material. The yield for each of the three stages of the process, briquetting, air curing and carbonization, was calculated from the change in mass during the process divided by the mass before the process. The overall yields were determined from the three separate yields. The estimated uncertainty of the overall yields based on the variation in results from duplicate experiments was ± 0.5 wt%.

Bulk density of carbonized products was calculated from the weight of the pellet and its volume determined from the diameter and height of the cylinder shaped pellet. Helium densities of carbonized products [38] were determined as described in the supplementary material. The uncertainty in bulk density based on duplicate determinations was about ± 0.02 g/cm^3 and in helium density based on multiple determinations (standard deviation) was always less than ± 0.03 g/cm^3.

The compressive strengths of carbonized products and a BF coke sample were measured using an INSTRON 5569 series Mechanical Tester by the method of Johns et al. [39] as detailed in the supplementary material. The uncertainty in compressive strength based on multiple determinations was always less than ± 11% of the average value.

Surface area was measured by CO_2 adsorption using a Micromeritics TriStar II 3020 analyser at 0 °C using the Dubinin–Radushkevitch equation [40-42] as described in the supplementary material. The uncertainty in surface area based on duplicate determinations was about ± 2% of the average value. Scanning Electron Microscopy (SEM) of the products was carried out using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope as described in the supplementary material.

The reactivity test denoted R60CO_2 was carried out in a Setaram TAG 24 symmetrical thermoanalyzer as described by Mollah et al. [10]. The flow rates of N_2 and CO_2 were controlled by a Bronkhorst programmable mass flow controllers. About 25 mg of sample obtained from broken briquettes after the compressive strength test (Section 2.6) was weighed into a 70 µL alumina crucible and loaded into the furnace. After 10 min with 35 mL/min N_2 flow at room temperature, the sample was heated to 110 °C at 10 °C/min then held at 110 °C for 30 min to remove moisture under continuing N_2 flow. The sample was then heated to 1000 °C at a rate of 20 °C/min in the N_2 flow and held in the N_2 flow at 1000 °C for 10 min. Then the flowing gas composition was changed to 35 mL/min CO_2/35 mL/min N_2 and the temperature held at 1000 °C for another 120 min. The sample was cooled in a N_2 flow to ambient temperature. After cooling, the crucible was removed and weighed. The coke reactivity index (R60CO_2) was calculated using the following equation:

$$R60CO_2 = [(m_1 - m_2) / m_1] \times 100$$

where m_1 was the original test sample weight before reaction and m_2 was sample weight after reaction in CO_2 for 60 min. The uncertainty in reactivity based on duplicate determinations was about ± 2% in R60CO_2units. A similar calculation can be made to obtain R120CO_2 from the sample weight after reaction in CO_2 for 120 min, but it was found that R120CO_2 did not discriminate between the relativities of different products as clearly as R60CO_2.

A Renishaw inVia Raman Microscope, using a 632.8 nm HeNe laser light as the incident beam, was used to record the Raman spectra in air at room temperature. A power of 1.1 mW and spot size of 0.7 µm were used and the laser exposure time for each scan was 30 s. Multiple areas were scanned and spectra were recorded between 1900 and 900 cm^{-1}.

Earlier workers [43-45] identified two broad peaks at about 1600 cm^{-1} and 1340 cm^{-1}, referred to as G and D bands respectively, in samples of similar carbonized products. In this work, the peak positions were in slightly different positions, which can, according to Li et al. [43, 46], be explained by differences in the excitation wavelength. As the spectra could not be adequately interpreted based solely on these two broad bands, the spectra were deconvoluted and fitted to four bands, as by earlier workers [47-50]. The fits were made using OriginPro 8 SR2 software. The lowest frequency band, the S band, at ~1160 cm^{-1}, has been assigned to alkyl-aromatic bonds; the next band, the D' band, at ~1330 cm^{-1}, to ordered but not graphitic aromatic carbon; the G_R band at ~1530 cm^{-1} to amorphous carbon; and the highest frequency band, the G' band at ~1600 cm^{-1}, to ordered graphitic structures [21, 43].

3. RESULTS AND DISCUSSION

3.1 Overall yield

Figure 1 illustrates the overall yields of the products. The yield of the final products, which varied from about 50 to 53 wt%, was lower than that from conventional coking coals (75 wt%, [51]), because coking coals have lower volatile matter content (18-38 wt%, [51-53]) than VBC (49.4 wt% db, Table 1). The yield was similar to that of the products obtained from same coal by ambient briquetting following carbonization [10]. The yield from tar in the final products was calculated (uncertainty ± 3% of the value) based on the assumption that the yield from coal was the same regardless of the proportion of tar. For this purpose the yield from tar is given by the following equation:

Yield from tar = (Overall yield – Proportion of coal X Yield from coal)/Proportion of tar

where the yield from coal was calculated from the yield of products when no binder was added (samples 1 and 2 in Figure 1)

It was found that in the carbonized products, the yield from tar decreased with increasing tar content. For non-air cured samples the yield from tar decreased from 48 wt% for 5 wt% tar content to 35 wt% for 10 and 15 wt% tar content. For air cured samples the yield from tar decreased from 70 wt% for 5 wt% tar content to 55 wt% for both 10 and 15 wt% tar content. This suggests that at lower tar concentration the coal-tar interaction was higher. This is probably because the tar molecules penetrated the coal pores at low concentration and, as the pores were filled, the coal could not accommodate more tar. Hence the excess tar could not interact so strongly with coal particles, resulting in an increase in volatilisation during carbonization. In the case of air curing, polymerisation [14] due to cross-linking reactions between oxygen containing functional groups [16, 54, 55] in coal and tar during air curing reduced the volatility of the tar resulting in an increase in yield from tar.

The overall yield tended to decrease as the proportion of tar increased. This is probably because of the greater volatility (about 66 wt%, [10]) of the tar at higher tar concentration compared to coal. The yield at low tar content was reduced by air curing, as a result of oxidation of the coal (as noted above, the polymerisation of the tar led to lower volatilisation of tar than coal), but as the tar content increased the effect of air curing on the yield changed. At higher tar content the interaction of the air cured tar and coal particles was less, because the coal pores could not accommodate the extra tar, leading to a reduction in the yield of tar (see above) and a smaller effect of air curing. Briquetting time had negligible effect on the yield.

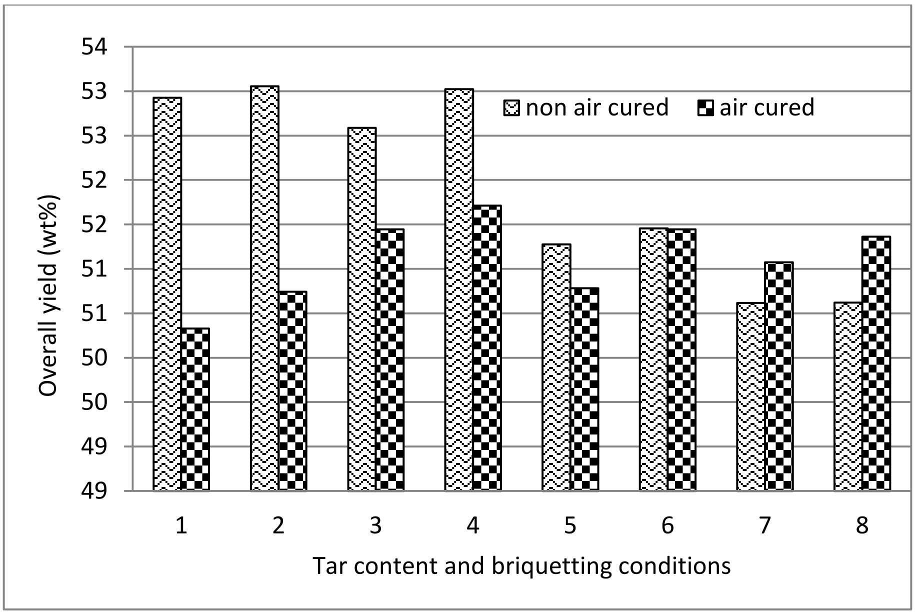

Figure 1: Overall yield of the products. Four tar contents, 0, 5, 10, and 15 wt% were used for samples 1 & 2, 3 & 4, 5 & 6, and 7 & 8 respectively. All samples, were briquetted at 150 °C with 20 kN, 10 min for odd samples, 30 min for even samples, carbonized at 950 °C for 3 h.

3.2 Bulk density

The bulk density (Figure 2) was notably higher than that of a typical BF coke (0.87g/cm^3, [18, 56]) and slightly higher than that of a product obtained following ambient briquetting of the same coal (1.05-1.10 g/cm^3) [10]. The higher briquetting temperature may have promoted flow of the coal mass and therefore increased the effect of the compressive force. The bulk density was increased by longer briquetting time, probably because force applied for a longer time had a greater compressive effect and this carried through the carbonization process. Air curing also tended to increase the bulk density when tar was present, probably because the polymerisation of the tar induced by air curing [16, 36, 57] densified the tar components and thus increased the bulk density. Addition of tar did not have any consistent effect on bulk density.

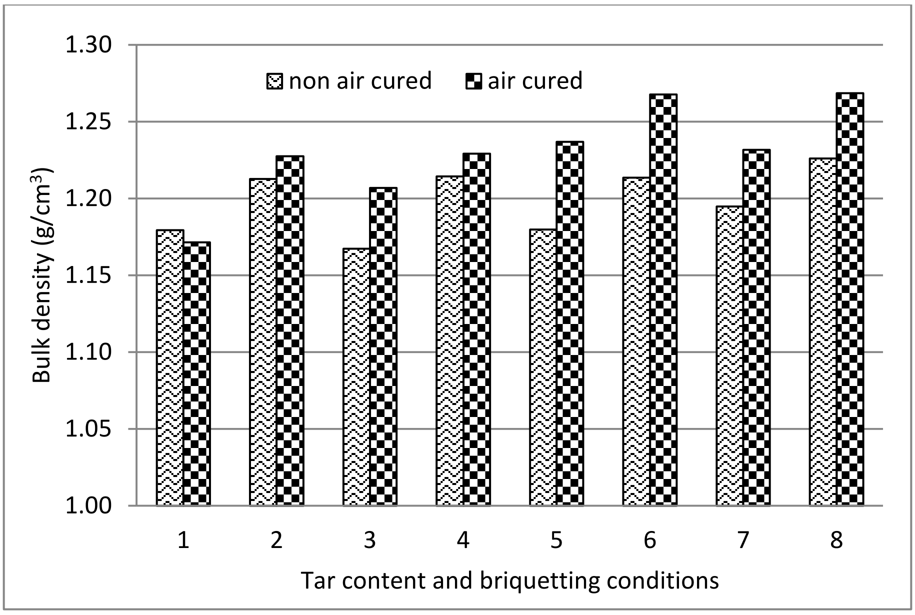

Figure 2: Bulk density of the products. Four tar contents, 0, 5, 10, and 15 wt% were used for samples 1 & 2, 3 & 4, 5 & 6, and 7 & 8 respectively. All samples, were briquetted at 150 °C with 20 kN, 10 min for odd samples, 30 min for even samples, carbonized at 950 °C for 3 h.

3.3 Helium density

The products had slightly higher helium density (Figure 3a) than a typical BF coke (1.89 g/cm^3, measured with the same apparatus) and similar helium density to products obtained by ambient briquetting from the same coal. Since the bulk density of the products was much higher than that of a typical BF coke, the pore volume per unit mass of the BF coke must also have been higher than that of the products. Similarly the pore volume of the products obtained by ambient briquetting must have been slightly higher than that of the products obtained in this work. The helium density increased when the tar content was 10 or 15 wt% and also with longer briquetting time with these two tar contents. It appeared that the carbonized tar was denser than the carbonized coal. Air curing magnified the effect of incorporating tar and thus increasing the helium density of the products, probably because of the polymerisation [16, 36, 58] of the tar components occurring during air curing.

Comparison of the helium and bulk densities indicates that adding small amounts of tar did not change the pore volume (Figure 3b) significantly. However, air curing often reduced the pore volume by up to 10%. The oxidation of the coal and the tar during air curing led to greater mobility of the molecules at higher temperature, so that the larger pores tended to shrink (as noted in Section 3.5 none of the treatments reduced the micropore volume and surface area appreciably). Longer briquetting time also reduced the pore volume by up to 10% by promoting movement of coal and tar molecules into the larger pores.

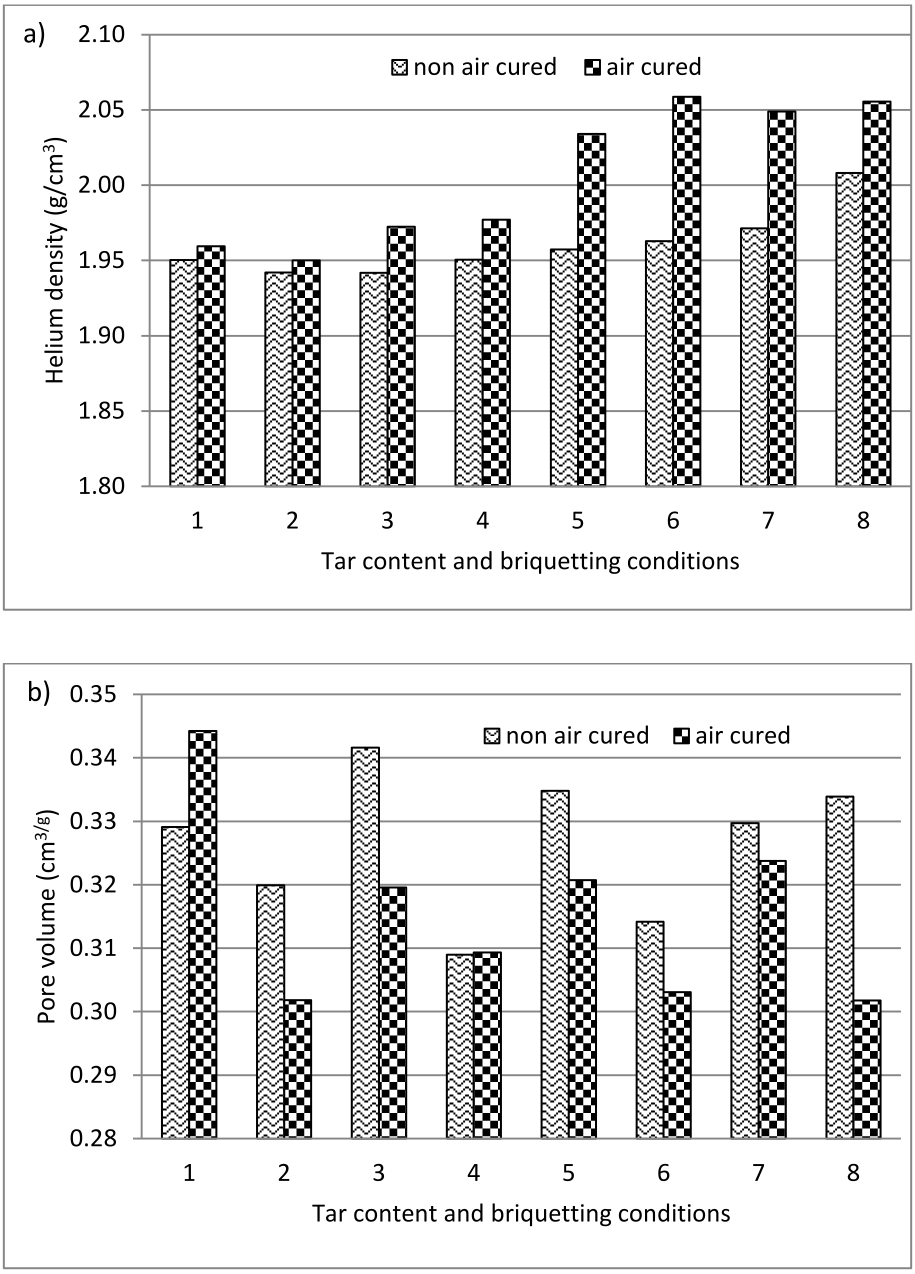

Figure 3: a) Helium density and b) pore volume of the products. Four tar contents, 0, 5, 10, and 15 wt% were used for samples 1 & 2, 3 & 4, 5 & 6, and 7 & 8 respectively. All samples, were briquetted at 150 °C with 20 kN, 10 min for odd samples, 30 min for even samples, carbonized at 950 °C for 3 h.

3.4 Compressive strength

Figure 4 shows the compressive strength of the final products. All the products had much higher compressive strength than the BF coke sample (20 MPa, measured with the same apparatus under the same conditions) and the products obtained by ambient briquetting of the same coal (40-60 MPa) [10]. Smaller pore volume of the products of this work may explain why the compressive strength was higher (Section 3.3) than that of the products obtained by ambient briquetting of the same coal. As for the helium density, only the combination of high tar content and air curing significantly increased the compressive strength of the products above the general level. This can be explained by noting that chemical changes in binders such as tar during air curing increase the capability of the tar to bind the coal particles together [59]. Small tar additions were insufficient to obtain a significant binding effect, but 10 or 15 wt% tar was sufficient to increase the binding significantly when the tar was cured. The decrease in pore volume following air curing (Section 3.3) would probably also help to increase the compressive strength.

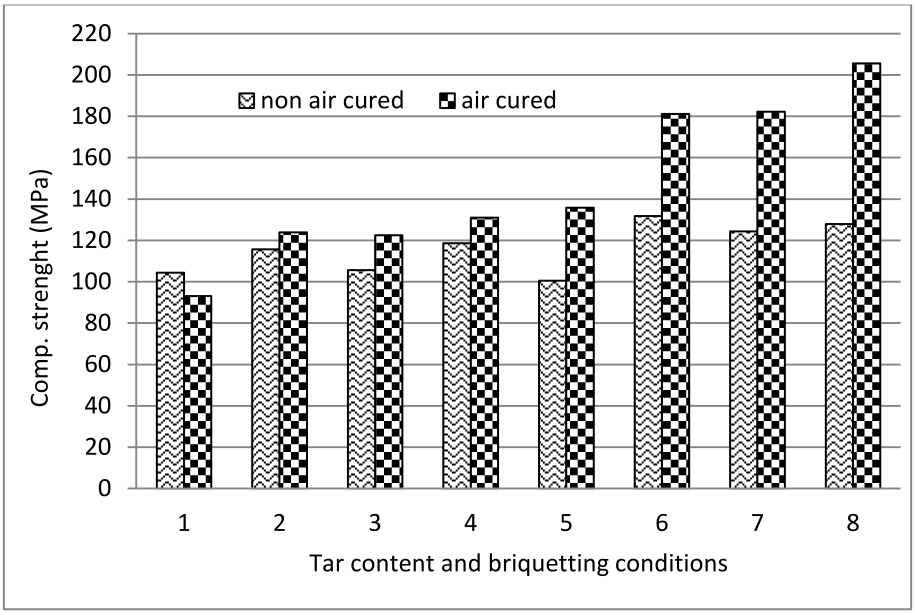

Figure 4: Compressive strength of the products. Four tar contents, 0, 5, 10, and 15 wt% were used for samples 1 & 2, 3 & 4, 5 & 6, and 7 & 8 respectively. All samples, were briquetted at 150 °C with 20 kN, holding time for odd and even samples were 10 or 30 min respectively, then carbonized at 950 °C for 3 h.

3.5 Surface area

The surface area of the products (Figure 5) was much higher than that of a BF coke (18 m^2/g, measured with same apparatus, similar to that found by Eatough et al. [60]) and only a little lower than that of products of ambient briquetting (790-800 m^2/g, [10]. The low surface area of BF coke is due to melting of the parent coals as melting destroys the original pore structure and only large pores are formed as resolidification occurs during carbonization [61-63]. The high surface area of the products, obtained in this work, suggests no melting or plasticization occurred. Adding a significant amount (10-15 wt%) of tar combined with long briquetting time did decrease the surface area, indicating that tar was forced into the pores and helped to close some of them. Air curing also decreased the surface area at short briquetting time, perhaps because chemical changes in the tar reduced its volatility, so that the tar continued to block pores during the carbonization process. However, the surface area of the final products was much greater than that of the original VBC (230 m^2/g), so that the favourable effects of tar and air curing were apparently insufficient to counter the opening of micropores due to loss of volatile matter during carbonization.

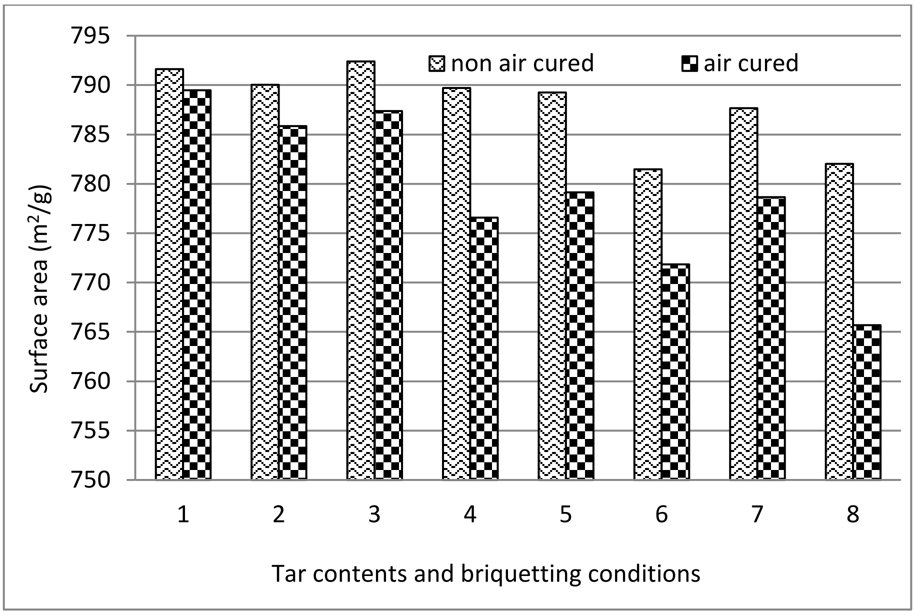

Figure 5: Surface area of the final of the products. Four tar contents, 0, 5, 10, and 15 wt% were used for samples 1 & 2, 3 & 4, 5 & 6, and 7 & 8 respectively. All samples, were briquetted at 150 °C with 20 kN, holding time for odd and even samples were 10 or 30 min respectively, then carbonized at 950 °C for 3 h.

3.6 Reactivity

Figure 6 shows the reactivity ($R60CO_2$) of the final products. The reactivity of the products was again much higher than that of a BF coke (13%, measured with same apparatus) and similar to that of ambient briquetting products (89-92%, [10]). Earlier work [6, 64] suggested that iron and calcium minerals affect coke reactivity, but the very low concentrations of such minerals in the original coal (Table 2) imply that the high reactivity was probably not due to the minerals present. Air curing had little effect in general. Adding tar and increasing the briquetting time did decrease the reactivity slightly, probably because the reduction in surface area [65] caused by filling of micropores and the effect of time on bonding between the tar components and coal particles and migration of tar into the micropores had some influence. However, these effects on surface area and reactivity were small.

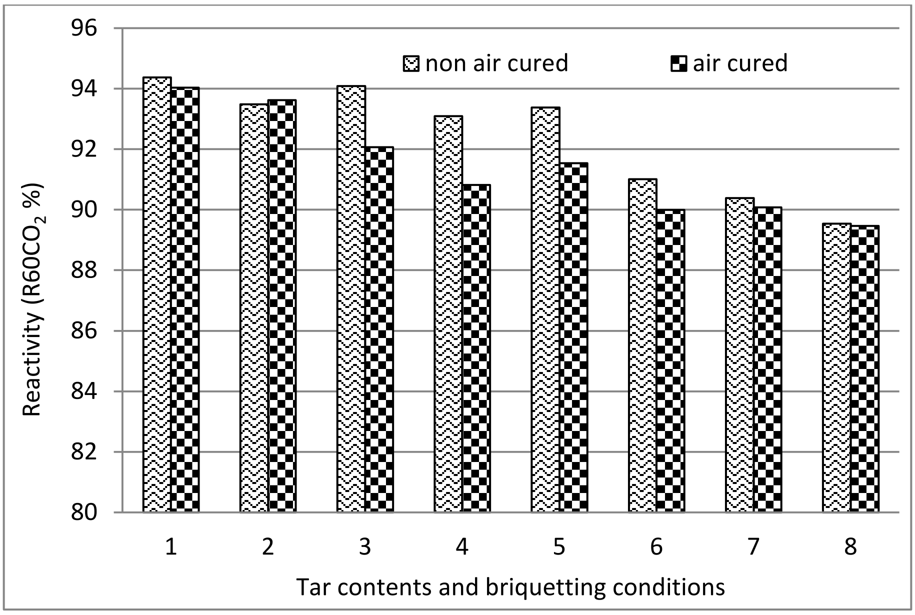

Figure 6: Reactivity of the products. Four tar contents, 0, 5, 10, and 15 wt% were used for samples 1 & 2, 3 & 4, 5 & 6, and 7 & 8 respectively. All samples, were briquetted at 150 °C with 20 kN, 10 min for odd samples, 30 min for even samples, carbonized at 950 °C for 3 h.

3.7 Scanning electron microscopy (SEM) studies

The SEM photographs (Figure 7 a) may be compared with those of products prepared by hot briquetting without added binder from a Loy Yang coal, as in this work, but of much lower ash yield 0.8wt%db) by Mori et al. [13]. The products showed a rougher surface than those of Mori et al., with many small protuberances and grains. The higher silica and clay contents (Table 2) of the Loy Yang coal used in this work may have contributed to the greater surface roughness, because of cracking and distortion following phase changes in these minerals [66]. Like the products of Mori et al., the products showed no evidence of macropores. The surfaces of the products were similar to those of the carbonized products obtained by ambient briquetting [10]. The surface of the product with binder obtained following air curing (Figure 7 b) appeared to be smoother under lower magnification than the surface of the product prepared without tar or air curing. This smoothness could be due to tar derived polymer spreading over the surface and coating and binding the coal particles. This could help to explain the increase in compressive strength following tar addition and air curing as suggested in Section 3.4. However, under high magnification (Figure 7 c, d) the surface appeared rough with many indentations in the sample, consistent with the high surface area observed (Section 3.5) and the high reactivity (Section 3.6).

The surface of these products contrasted with that observed for a BF coke [10] which is much smoother and exhibits large macropores, helping to explain why BF coke is less reactive than these products.

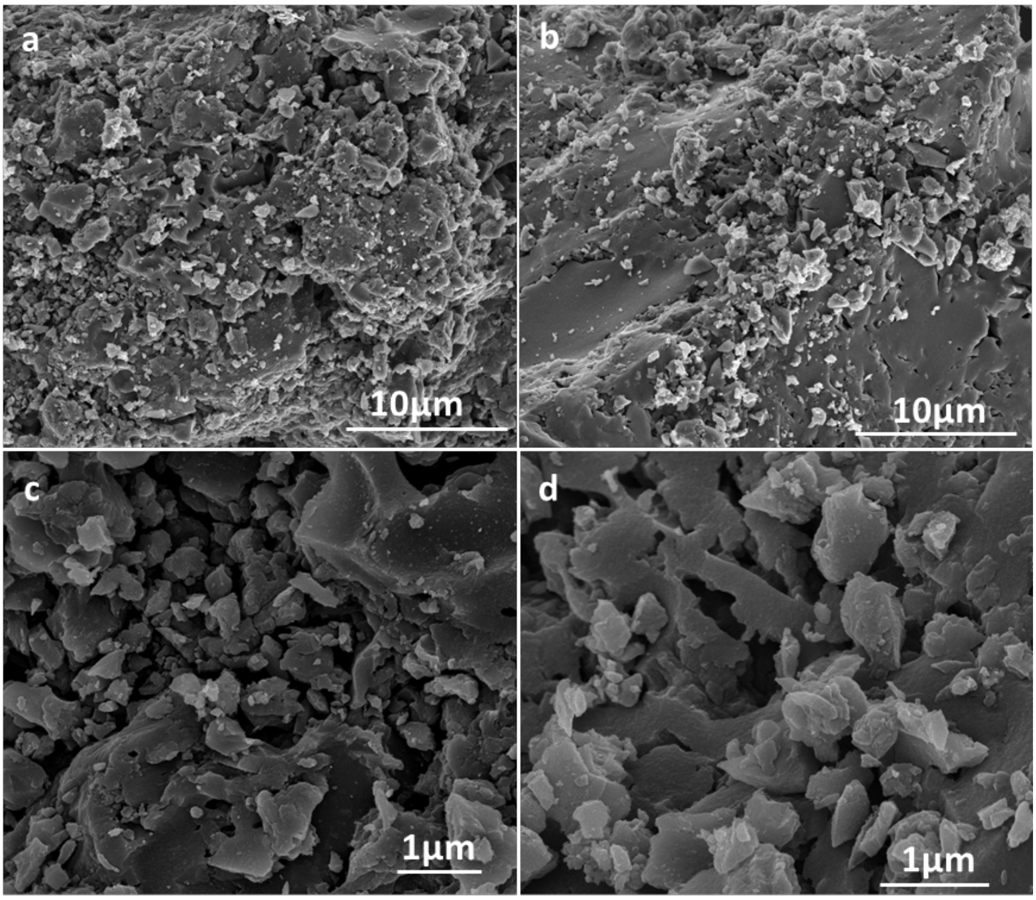

Figure 7: SEM micrographs of products prepared without tar or air curing with 10 min briquetting time (a, c) and with 15 wt% tar, air cured, with 30 min briquetting time (b, d).

3.8 Raman spectroscopy

All the products gave a similar Raman spectrum (Figure 8) for a typical example). The ratio of D and G band intensities (areas) has been found to be inversely correlated with the amount of graphitic structure [49]. For all the products produced in this work the ratio (D'/G' in this work, Figure 8) was about 5, compared to 1.2 for a typical BF coke (measured under the same conditions) and similar values for BF coke reported by other workers [20, 21], implying that the amount of graphitic structure was similar in all the products and much less than that in BF coke. This is another factor that may explain the high reactivity of the products as suggested by earlier workers [67].

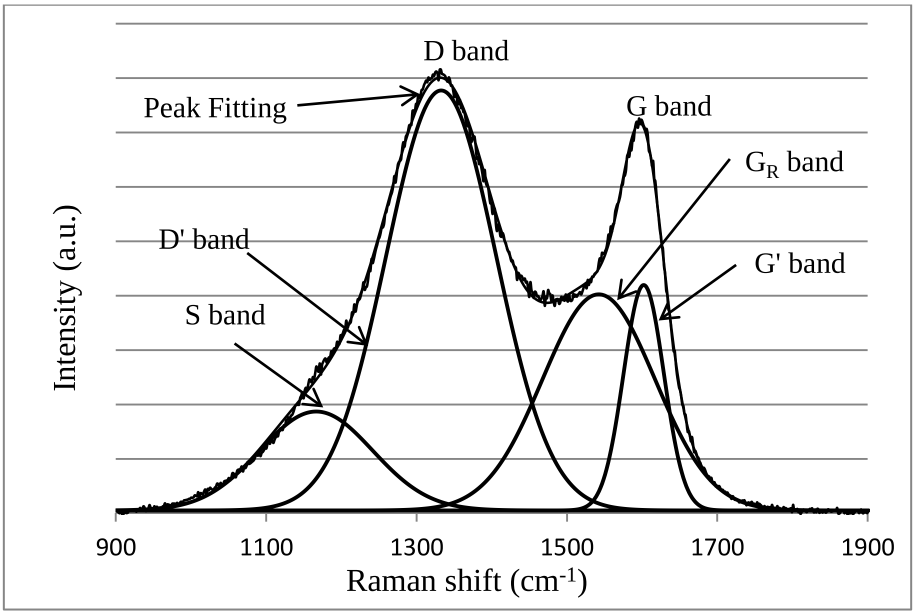

Figure 8: An example of deconvolution of the Raman spectrum of a product.

4. CONCLUSION

Products obtained by hot briquetting and subsequent carbonization showed higher compressive strength and bulk density than those obtained following ambient briquetting and carbonization of the same coal and binder. Addition of binder combined with air curing increased the compressive strength by up to a factor of four. Electron micrographs showed that these strong products had a smoother surface than the products obtained without air curing, possibly because the tar polymerized and flowed onto the surface, binding the coal particles together more strongly and thereby giving a less compressible product. The compressive strength was much higher than that of a BF coke.

However, the surface area of the products remained high, similar to that of a conventional brown coal char, and the surface was highly irregular on a µm scale. Furthermore, the proportion of graphitic structure was small. These factors probably contributed to the high reactivity of even the strongest products, similar to that the reactivity of products obtained from the same coal following ambient briquetting and much higher than the reactivity of a typical BF coke. Procedures will have to be devised to obtain a product of lower surface area and higher proportion of graphitic structure to achieve the aim of reducing the reactivity and obtaining a substitute for BF coke from VBC.

5. ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

(Chapter 3)

Analytical techniques

Helium density

The helium densities of the samples were determined on dried samples by helium pycnometry using an AccuPyc 1330 model pycnometer (Micromeritics, Norcross, GA, USA). The unit was calibrated on a daily basis. Oven-dried sub-samples of between 0.3 and 0.7 g were used. The sample was purged with helium 99 times to ensure complete removal of air. The helium density was determined from an average of 10 measurements on each individual sample. The uncertainty in helium density based on multiple determinations (standard deviation) was about ± 0.03 g/cm^3.

Compressive strength

The compressive strengths of the sample of known height (H) and diameter (D) were measured by using an INSTRON 5569 series Mechanical Tester. The sample was placed on the anvil of the tester and an axial load applied across the plane ends until failure occurred. The displacement and loading were measured during the compression at a displacement rate of 0.05 mm/sec. The compressive strength σ_c was calculated using the following equation:

$$\sigma_c = (4F / \pi D^2)\ (H / D)^{0.5}$$

where force F is determined from the maximum load the pellets withstood, D is the diameter and H is the height of the pellet. The uncertainty in compressive strength based on multiple determinations was always less than ± 11% of the average value.

Surface area

Surface area was measured by CO_2 adsorption using a Micromeritics TriStar II 3020 analyzer at 0 °C. Experiments were carried out on oven-dried 0.2 g sub-samples, which were further dried under vacuum at 160 °C for at least 8 h to ensure complete removal of adsorbed gases using a Micromeritics VacPrep 061 instrument. CO_2 surface areas and micropore volumes (pores <2 nm diameter) were calculated using the Dubinin–Radushkevitch equation. The saturation vapour pressure (p_o) for CO_2 at 0 °C was taken to be $p_o = 26141.72$ torr. The uncertainty in surface area based on duplicate determinations was about ± 2% of the average value.

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was carried out using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope. This microscope can be operated in two modes; mode 1 with a field free lens and mode 2 with an immersion final lens for high resolution imaging. Prior to loading into the instrument each sample was mounted on conductive carbon tape and coated with platinum (1-2 nm thickness) for 0.5 min using a Cressington Sputter Coater. During the coating process the samples were tilted about 45 ° and rotated at 50-100 rpm.

CHAPTER 4

Hydrothermally dewatered Victorian brown coal as blast furnace coke precursor

PART B: Suggested Declaration for Thesis Chapter

Hydrothermally dewatered Victorian brown coal as blast furnace coke precursor

Monash University

Declaration for Thesis Chapter 4

Declaration by candidate

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major issues; developed interpretations; fully drafted papers and conclusions	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Marc Marshall	Aided methods development, input to results analysis, input to manuscript revision	N/A
Alan L Chaffee	Supervision, assisted interpretation in results, editorial assistance	N/A
W Roy Jackson	Supervision, assisted interpretation in results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		**Date** 20/5/15
Main Supervisor's Signature	Alan Chaffee	**Date** 20/5/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Hydrothermally dewatered Victorian brown coal as blast furnace coke precursor

M. Mamun Mollah, Marc Marshall, W. Roy Jackson and Alan L. Chaffee

School of Chemistry, Monash University, Clayton 3800, Australia

Corresponding Author: Alan L. Chaffee

School of Chemistry, PO Box 23, Monash University, Australia

Email: alan.chaffee@monash.edu, Tel: +61-3-9905-4626, Fax: +61-3-9905-4597

Abstract

Victorian brown coal does not soften or melt on heating, leading to the formation of coal chars rather than a coke suitable for use in a blast furnace. The chars have very high reactivity (coke reactivity index, CRI) and low strength (coke strength after reaction, CRS). In this study, hydrothermal dewatering treatment of the coal in conjunction with acid washing of the coal, addition of coal tar pitch, hot briquetting and air curing have been evaluated in attempts to reduce the reactivity and strengthen the products finally formed. Products were characterized by bulk density, helium density, compressive strength, reactivity to CO_2, surface area (CO_2 adsorption), scanning electron microscopy, Raman spectroscopy and X-ray diffraction analysis and were compared with a conventional blast furnace coke. Products of sufficient compressive strength could be obtained, but the reactivity was still too high for them to be used as a blast furnace coke replacement.

Keywords: Blast furnace coke, Victorian brown coal, Coke strength and reactivity

1. INTRODUCTION

Carbon is the reducing agent in a blast furnace (BF) to produce iron from its ore. The form of carbon used, produced from coking coals in lump form, is called metallurgical coke. Metallurgical coke is inherently strong and macro-porous (which permits it to act as permeable support) and has much lower reactivity than conventional brown coal char. Coking coals, generally of bituminous rank, are blended [1-3] to make BF coke of high strength and acceptable reactivity [1]. They contain 18-38 wt%db volatile matter [2, 4, 5], melt when heated, and then agglomerate, thus obliterating their original shape, to form metallurgical coke. It is well known that the properties of coke are determined by the parent coals [6]. Therefore, coal quality is very important for BF coke production. However, limited reserves, transport costs and high demand are making these coals a more and more expensive commodity, with the price rising to about $400/t in 2011 [7], but long term cost uncertainty remains even though the price has dropped sharply in 2014.

Brown coals are abundant and cheap in Australia especially in Victoria. Victorian brown coal (VBC) often has low concentrations of mineral impurities and sulfur which is a favorable requirement for BF coke. Therefore VBC is an attractive feedstock for the iron and steel industry. However, like other low rank coals, VBC does not form a liquid phase during carbonization, and thus it does not produce BF coke. Chars obtained on carbonization are so far unable to replace the coke in a BF either because of their very low strength or their very high reactivity [2] (Coke Reactivity Index, CRI [8]). Attempts to improve these properties have been made for more than fifty years [9-13]. Char of high strength has been obtained from VBC [9, 12-16], but the reactivity of these high strength products was too high [12, 14, 15] or not reported [9, 13, 16].

In an earlier study [17] ground coal and binder were pelleted at high force (8 ton) at ambient temperature, then carbonized to make a coke-like material. However, these products had too high reactivity for a BF coke. Another attempt [18] was made to induce a coking ability in VBC, in which coal-binder mixture was pelleted with heating, optionally air cured then carbonized. Again, the products showed too high reactivity to be used in a BF.

Hydrothermal dewatering (HTD) 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 vapor [19]. (This dewatering process is attractive because the energy consumed in vaporizing the water in more conventional drying processes is saved [19].) It is known that the process of HTD of VBC gives a product that resembles higher rank coal in some respects, such as lower oxygen content and lower hydrophilicity [20-22]. Since coking coals are of higher rank than VBC it was hypothesized that the artificial increase in rank produced by HTD may bring the coal closer in coking properties to a conventional coking coal. Experiments in which raw and acid washed Indonesian brown coals of similar rank to VBC have been treated by HTD and the treated coal hot briquetted and carbonized have recently been reported by Mori et al. [16]. The strength and bulk density of the carbonized products were increased for the products obtained after HTD at lower temperatures compared to those obtained without HTD. These considerations suggest that it might be useful to consider HTD as a preliminary treatment before attempting to prepare a substitute for BF coke from VBC.

Accordingly a typical VBC was subjected to HTD in both raw and acid washed (to reduce mineral content) form and the HTD products were mixed with binder and briquetted, then with optional air curing [23-30] 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 [18]. In this study the carbonization temperature was increased to 1200 °C, higher than those used earlier [17, 18] to approximate the carbonization temperature used in preparing conventional BF coke. 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 a BF coke.

2. EXPERIMENTAL SECTION

2.1 Materials used

Loy Yang brown coal from the Latrobe Valley, Victoria, Australia, has been used in this study. Coal was obtained from the open cut mine containing about 60 wt% moisture, then milled to <3 mm particle size and defined as raw coal (RC) in this paper. Coking coal tar pitch, softening point 110 °C, completely soluble in tetrahydrofuran (THF), was obtained from Koppers Carbon Materials & Chemicals Pty Ltd, NSW, Australia. Compounds present included a large number of polycyclic aromatic hydrocarbons and the boiling point was greater than 300 °C [31]. A sample of BF coke used for comparisons was obtained in lump formed from Nippon Steel Corporation (NSC), Japan. Further details of the analyses of these materials are given in Table 1. THF (Liquid Chromatography grade) was obtained from Merck Australia, Kilsyth, Victoria and sulphuric acid (Univar grade) from Ajax FineChem Pty Ltd, Taren Point, NSW, Australia.

2.2 Acid washing the coal

A sample of RC was acid washed as described by Redlich et al. [32] with 0.1 M sulphuric acid. The acid solution was added to the coal at a solution to coal (db) ratio of 20:1 by weight, 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 de-ionised water then stirred for 24 h and filtered. Mixing with de-ionised water, stirring and filtering were repeated until the pH value of the filtrates was constant (pH 4.5 – 5.5).

2.3 Hydrothermal dewatering (HTD)

1 kg of RC or wet acid washed coal (AWC) was charged into a 4 L autoclave with sufficient de-ionised water to give a 3:1 water:dry coal [20, 22, 33, 34] weight ratio. The autoclave was evacuated and filled with 3 MPa (cold) of N_2. 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. Both the hydrothermally dewatered coals were dried in a flow of N_2 at 105 °C for 24 h, then ground in a ball mill to pass a 0.15 mm sieve, and then dried again in a flow of N_2 at 105 °C for another 4 h to reduce the moisture content to 1-2 wt%db as determined by an OHAUS MB45 halogen moisture analyser. The yield was about 85 wt%db for RC and 83 wt%db for AWC.

2.4 Analyses of materials

The moisture content of the coals and the BF coke were measured by the mass loss when a sample was heated in flow of N_2 at 105 °C for 4 h. Samples of the RC, AWC, RC hydrothermally dewatered (RC-HTD), AWC hydrothermally dewatered (AWC-HTD), pitch and BF coke were dried at 105 °C in a flow of N_2 then ashed at 815 °C for 2 h [35, 36]. The volatile matter content of the RC was determined by HRL Technology Pty Ltd, Mulgrave, Victoria. Samples of RC were analysed for C, H, N, S by HRL and samples of AWC, HTD coals, pitch and BF coke were analysed for C, H, N, S by the Campbell Microanalytical

Laboratory, University of Otago, New Zealand. O was obtained by difference.

For ^{1}H NMR, a sample of pitch was dissolved in $CDCl_3$ and a spectrum was obtained using a Bruker Ultrashield 400 MHz instrument with a 90 ° pulse flip angle (9.5 μs). Solid state ^{13}C NMR spectra of the coals were recorded at room temperature using a Bruker Avance 400 spectrometer. Samples were packed into zirconia rotors with a Kel-F cap. Spectra were recorded using cross-polarization magic angle spinning (CP-MAS) techniques at 10 kHz spin rate with 25 ms acquisition time. Spectra were referenced to a glycine external reference.

To aid interpretation, ^{1}H NMR spectra were divided into four regions [37, 38]: protons attached to aromatic rings (H_{ar}, 6−9 ppm); protons attached to aliphatic carbon adjacent to aromatic rings (H_{α}, 4.5−1.96 ppm); protons attached to carbons further away from aromatic rings (methylene protons) and protons of paraffin groups (H_{β}, 1.95−1 ppm); and protons in -CH_3 (H_{γ}, 1−0.5 ppm). In an analogous manner, the ^{13}C NMR spectra were divided into three regions, as suggested by Kelemen et al [39]: carbonyl carbon ($C_{c=o}$), 165−240 ppm; aromatic carbon (C_{ar}), 90−165 ppm; and aliphatic carbon (C_{al}), 0−90 ppm. The proportions of the four hydrogen types and the three carbon types were determined using Bruker's Topspin 3.1 software. The fraction of aromatic carbon in the pitch was calculated using the Brown-Ladner equation [40, 41] from the elemental analysis (Table 1) and the ^{1}H NMR Figure 1. The fraction of aromatic carbon in the RC, calculated from the solid state ^{13}C NMR [41] spectrum Figure 2.

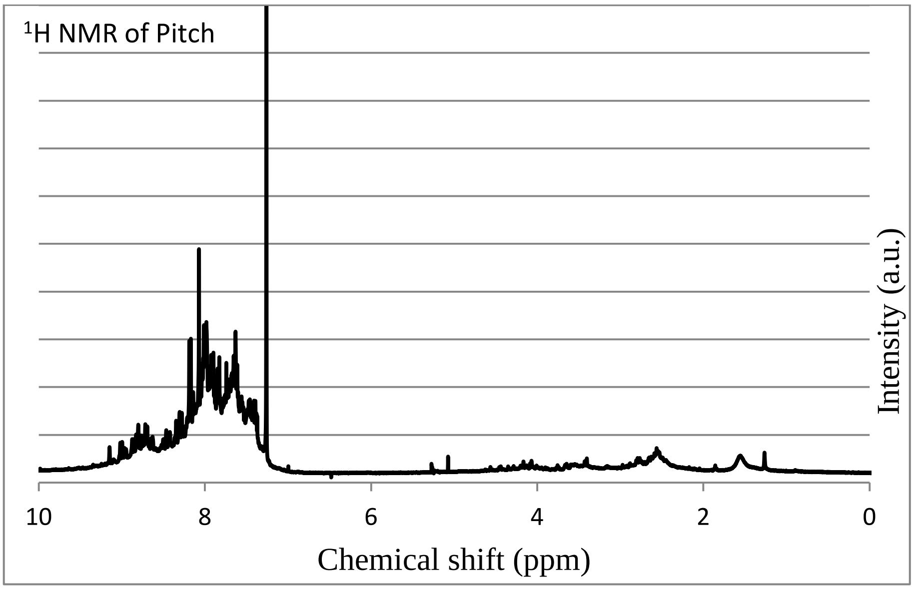


Figure 1: ^{1}H NMR analysis of pitch.

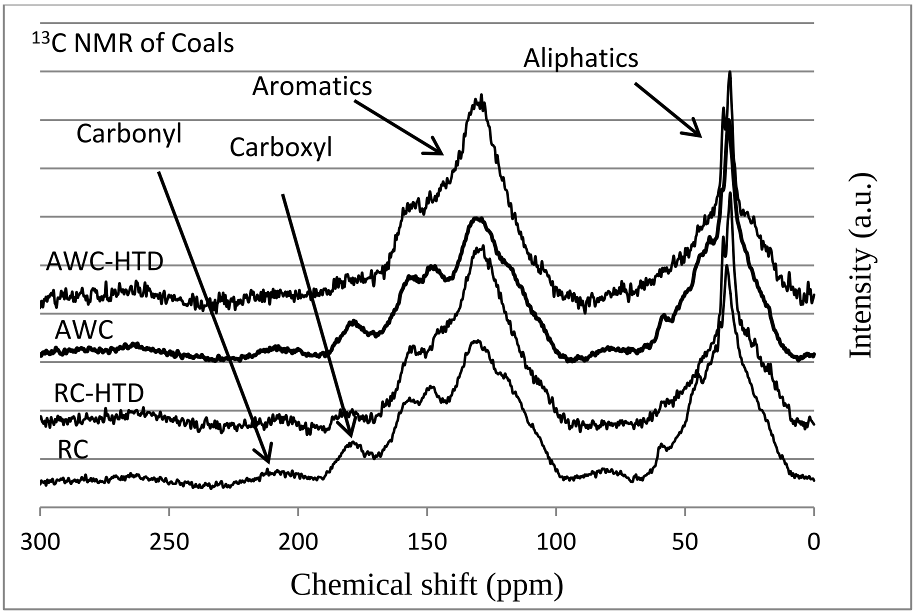


Figure 2:^{13}C NMR of RC, RC-HTD, AWC and AWC-HTD.

2.5 Mixing and briquetting

Coal tar pitch in THF solution, 15 wt% of the dried RC-HTD or AWC-HTD coal weight, was mixed with the ground and dried HTD coals by continual stirring at 80 °C for 1 h. The THF was removed under reduced pressure and the impregnated coal was dried in a flow of N_2 at 105 °C for 24 h. The coal was impregnated with pitch from solution in order to obtain a uniform distribution of pitch in the coal. The mixtures were ground to <0.15 mm and dried in a flow of N_2 to 1-2 wt%db moisture content as measured by a OHAUS MB45 halogen moisture analyser . These mixtures were employed as feedstocks.

About 1.3 g of feedstock was placed into a 13 mm diameter die set. Then the die was heated to 150 °C or 230 °C by a heating element attached to it at a rate of 10 °C/min. After confirmation that the contents had reached the required temperature, force was applied using an INSTRON 5569 series Mechanical Tester at a rate of 10 kN/min until the force reached 7 or 20 kN and the force held for 30 min. The force was then released and the die was cooled to ambient temperature to recover the briquette, which was weighed. The typical diameter and thickness of the briquettes were about 13.0 and 8.0 mm respectively.

2.6 Air curing and carbonization

Half of the samples were air cured. The briquettes were heated in a flow of air (300 mL/min) at 200 °C for 2 h [42]. Then the briquettes were cooled to ambient temperature in a continuous air flow. During air curing the briquettes decreased in weight by 1-2 wt%, but as the pellet did not crack or exhibit white ash spots, no combustion took place. For carbonization, prepared briquettes were weighed into a ceramic cup which was placed into a tube furnace. A slow heating rate (e.g. 2 °C/min) was required, particularly in lower temperature (ambient-500 °C), to prevent cracking of the briquette because of shrinkage [23, 43] as a result of volatile matter being given off at a temperatures higher than 350 °C [24]. Therefore, the carbonization temperature was increased from ambient to 500 °C at 2 °C/min, then to 950 or 1200 °C at 4 °C/min, then held at the final temperature for 2 or 8 h. The samples were cooled under N_2 overnight and weighed.

2.7 Product characterization

Some of the analysis methods have been previously described [17, 18]. Brief details are given in the supplementary material. The yields of the HTD process were not taken into account in determining the overall yields, the basis of which was the HTD coal. The overall yields were calculated from the separate yields for the three stages of briquetting, air curing and carbonization. The yields for each stage were obtained by dividing the change in mass for the stage by the mass before the stage. The uncertainty of the overall yields based on the variation in results from duplicate experiments was ± 0.5 wt%.

Bulk and helium densities of carbonized products and BF coke were determined as described in supplementary material. The uncertainty in bulk density based on duplicate determinations was ± 0.02 g/cm^3 and in helium density based on multiple determinations (standard deviation) was always less than ± 0.03 g/cm^3. The compressive strengths of briquettes and BF coke were measured by using an INSTRON 5569 series Mechanical Tester (see supplementary material). The uncertainty in compressive strength based on duplicate determinations was always less than ± 13% of the average value.

Surface area and micropore volume were calculated from the CO_2 adsorption isotherm determined using a Micromeritics TriStar II 3020 analyser at 0 °C (see supplementary material). The uncertainty in surface area and micropore volume based on duplicate determinations was about ± 2% of the value. Scanning electron microscopy (SEM) of the products was carried using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope (see supplementary material).

The reactivity test denoted R60CO_2 was carried out in a Setaram TAG 24 symmetrical thermoanalyzer with Bronkhorst programmable mass flow controllers for the N_2 and CO_2 flow rates. About 25 mg fragmented briquette or BF coke pieces (less than 1.4 mm particle size) from the compressive strength tests (Section 2.7) was weighed into a 70 µL alumina crucible and loaded into the furnace. Moisture was removed by starting with 10 min under 35 mL/min N_2 flow at room temperature, then heating the sample to 110 °C at 10 °C/min and holding at 110 °C for 30 min. The sample was then heated to 1000 °C at a rate of 20 °C/min and held at 1000 °C for 10 min in the same N_2 flow. Then the flowing gas composition was switched to 35 mL/min CO_2/35 mL/min N_2 and the temperature held at 1000 °C for another 60 min. Then the sample was held for 10 min at 1000 °C in 35 mL/min N_2 flow, cooled to ambient temperature in the same N_2 flow and weighed. The R60CO_2 was calculated using the following equation:

$$R60CO_2 = [(m_1 - m_2) / m_1] \times 100$$

where, m_1 was the original test sample weight before reaction and m_2 was sample weight after reaction in CO_2 for 60 min. The uncertainty in reactivity based on duplicate determinations was about ± 2% in R60CO_2units.

Raman spectra were measured and the spectra deconvoluted as described in the supplementary material. Multiple areas were scanned and spectra were recorded between 1900 and 900 cm^{-1}. The four peaks obtained by the deconvolution were assigned as follows. The lowest frequency band, the S band, at ~1160 cm^{-1} was assigned to alkyl-aromatic bonds, the next band, the D’ band, at 1330 cm^{-1} to ordered but not graphitic aromatic carbon, the G_R band at 1530 cm^{-1} to amorphous carbon and the highest frequency band, the G’ band at 1600 cm^{-1} to ordered graphitic structure [44, 45].

3. RESULTS AND DISCUSSION SECTION

3.1 Analyses of materials

Table 1 gives the ultimate and proximate analyses and NMR data for the materials used and the analysis for the comparison BF coke. The ash yield of the AWC and AWC-HTD were lower than that of RC and RC-HTD respectively because the cations attached to carboxylate anions and acid soluble minerals were washed out with the acid. The acid washing had no significant effect on the elemental analysis or the proportion of carbonyl carbon. The oxygen content of RC was obtained by difference using the minerals plus inorganics content (2.25 wt%), calculated from the ash yield of AWC and the Mg+Na+Ca+Fe content of RC [46, 47]. For AWC the inorganics have been removed and the ash yield can be used to obtain O by difference. The values of O for RC and AWC were the same within the limits of error. The effect of HTD was to remove carboxylate groups, which reduced the proportions of carbonyl carbon in the ^{13}C NMR spectrum (Figure 2 and Table 1) and the oxygen content and was partially responsible for the increase in the carbon aromaticity (Table 1). The carbon aromaticity was increased further by the loss of water soluble organic acids and short chain

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

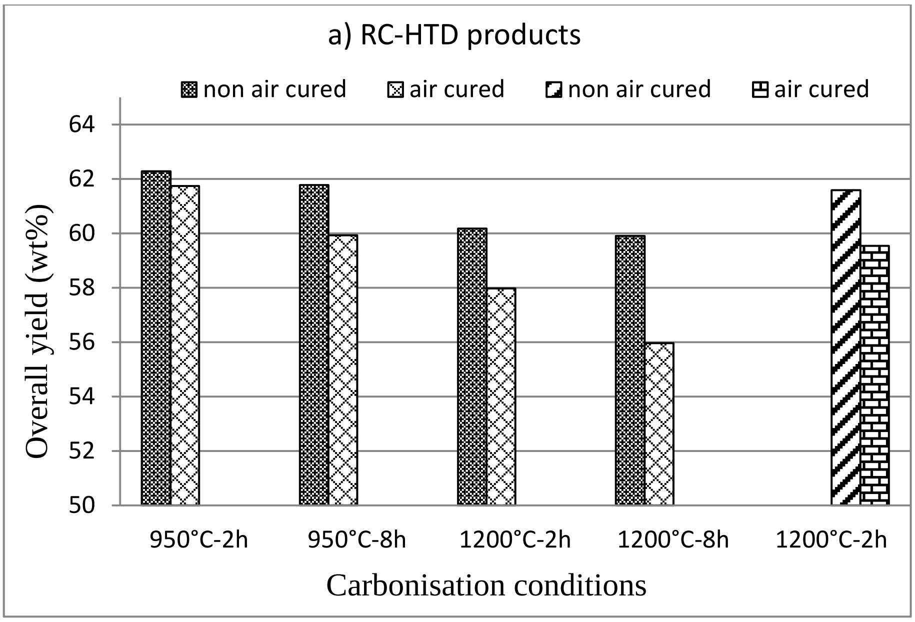
Analysis [a]	**RC**	**AWC**	**RC-HTD**	**AWC-HTD**	**Pitch**	**Coke**
Proximate						
Moisture (wt%ar)	60.0	-	-	-	-	3.00
Ash (wt%db)	3.25	2.03	3.70	2.93	0.0	11.98
Volatile Matter	49.4	-	-	-	-	-
Fixed Carbon	47.4	-	-	-	-	-
Ultimate (wt%db)						
Carbon	65.7	64.0	69.9	70.7	93.0	86.2
Hydrogen	4.70	4.86	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
^{13}C NMR: $C_{C=O}$ (Fraction)	0.09	0.09	0.04	0.05		
^{13}C NMR: C_{ar} (Fraction)	0.49	0.49	0.58	0.60		
Brown-Ladner: C_{ar} (Fraction)					0.95	
Atomic H/C ratio	0.85	0.90	0.79	0.77	0.56	0.06

[a] The standard error of ash yields based on multiple analyses was 0.2 wt%db. The uncertainty (HRL Technology) in volatile matter and fixed carbon was ± 0.4 wt%db and in ultimate analysis of RC 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, ± 0.03 wt%db for N and 0.06 wt%db for S, and therefore for O which was obtained by difference 0.9 wt%db.

alcohols, ketones and aldehydes etc. into the aqueous phase [48]. Apart from the ash yields the analyses of RC-HTD and AWC-HTD were similar. The ^{1}H NMR spectra showed that the pitch was highly aromatic (Figure 1 and Table 1); its carbon aromaticity calculated by the Brown Ladner method [40] was 0.95.

3.2 Overall yield

The yields for a range of conditions are shown in Figure 3. The yields for both RC-HTD and AWC-HTD were much less than that of coke from typical coking coals (75 wt%) [2]). The yields as a proportion of the starting coal were in the range 47-51 wt%, similar to those when RC was used as the starting material (50-53 wt%; see Section 3.1 of Chapter 3). There was a small decrease in yield with increasing carbonization temperature. In the absence of air curing, the yield was consistently slightly higher when metallic cations were present than when the cations had been removed by acid washing. This can be explained by the reduction in volatilization of low rank coal when cations are present [49-52]. Mori et al. [16] also noted that volatilization and tar formation would be enhanced by acid washing. There was a small but variable loss in weight during air curing. In addition, air curing led to an increase in weight loss during carbonization, with the effect of air curing for AWC-HTD being greater at lower carbonization temperature. Apart from any weight loss during air curing itself, the oxidation during air curing must have increased slightly the volatility of certain components of the HTD coal and/or the binder. At higher temperature these components would volatilise anyway and air curing would not make a difference. In contrast, for RC-HTD coal, the effect of air curing was greater at higher carbonization temperature. The minerals and inorganics may have had a catalytic effect on volatilisation [49-52] and this could alter the temperature dependence of the effect of air curing. The yields for a given carbonization temperature increased with the severity of the briquetting conditions, probably because the pore volume was reduced and the pore structure became less open (see Section 3.6) which would inhibit volatiles escaping from the sample. In addition, the effect of air curing was small or negligible for the more severe briquetting conditions; possibly the increased severity pushed the binder more deeply into the pore structure and hindered volatilization to some extent. Overall all these effects were small such that, if air curing, change in carbonization conditions and acid washing were beneficial in other respects, the small decreases in yield would probably be acceptable.



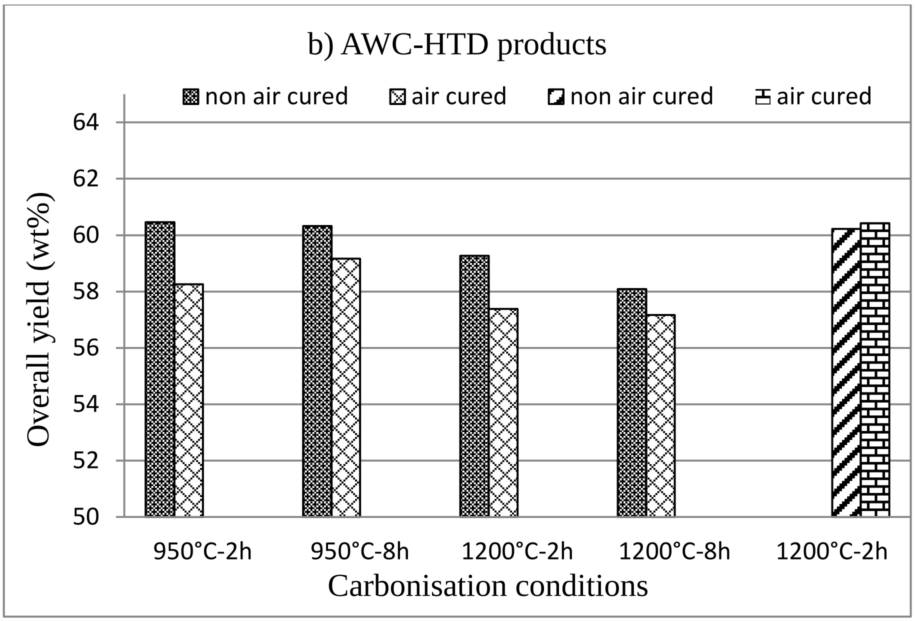


Figure 3: Overall yields of the products as a function of carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150 °C-7 kN-30 min.

3.3 Bulk density

The bulk density of the products from RC-HTD and AWC-HTD is shown in Figure 4. More severe briquetting conditions led to a substantial increase in bulk density to a value much higher than that of BF coke (0.87 g/cm^3 [53]). This was probably due to the collapse of the pores under the more severe conditions. Under these severe conditions acid washing gave a slightly higher bulk density, and air curing, whether for RC-HTD or AWC-HTD, increased the bulk density to a small extent. Mori et al. [16] also found that the bulk density of carbonized products of acid washed hydrothermally dewatered coals was always higher than that of raw hydrothermally dewatered coals. The greater bulk density of the AWC-HTD products can be explained in terms of the changes in pore volume in AWC-HTD and RC-HTD during carbonization (see Section 3.6). Under the less severe briquetting conditions,

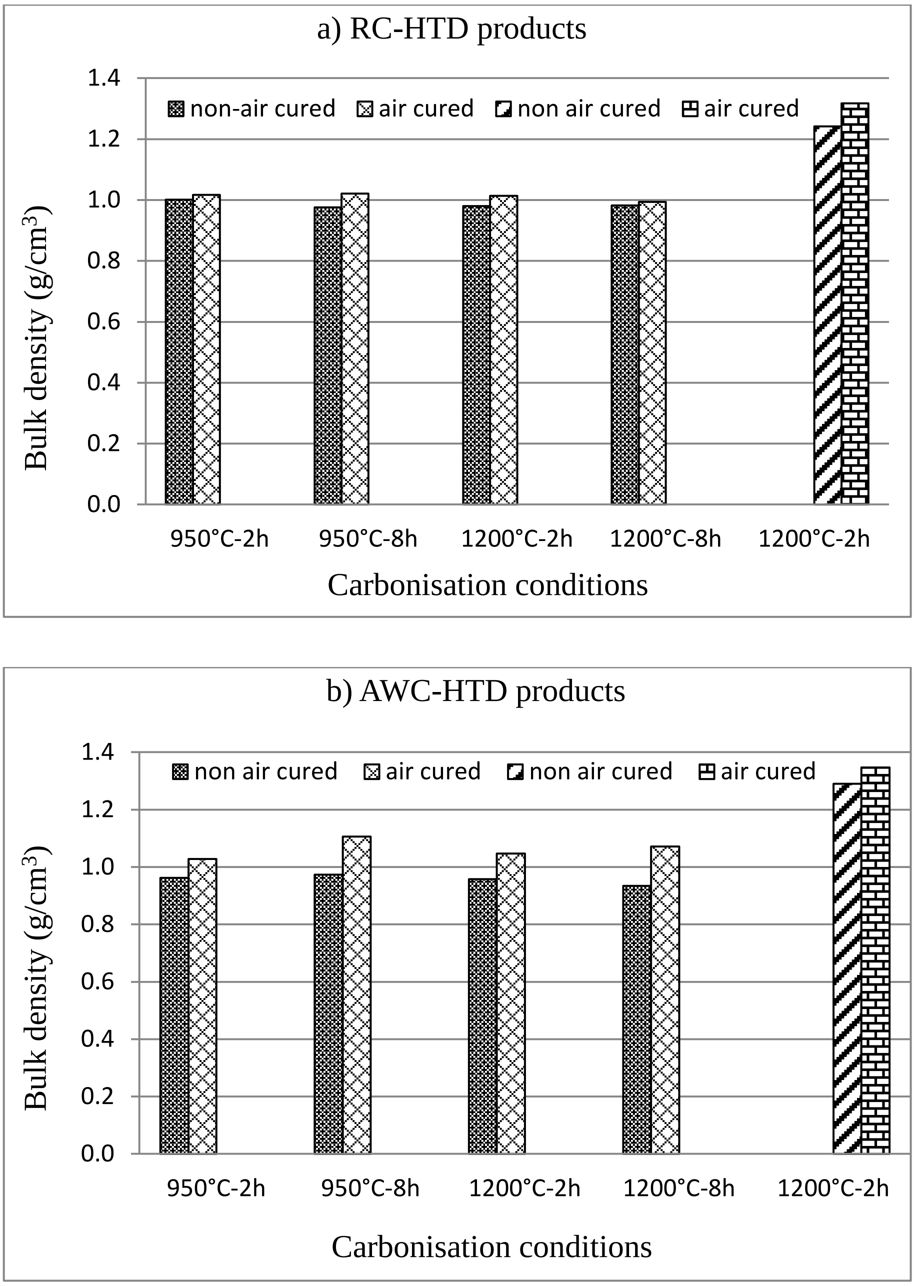


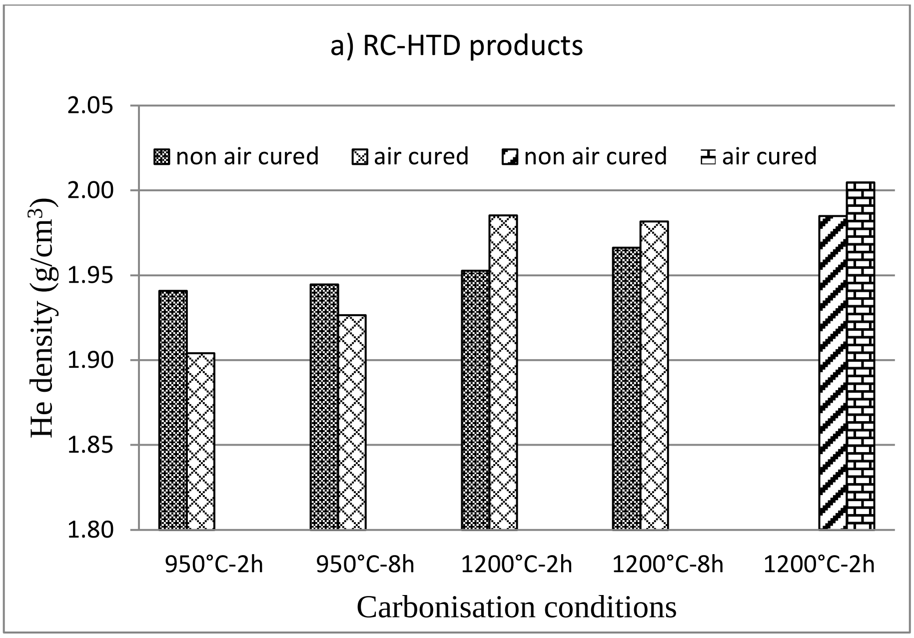
Figure 4: Bulk density of the products as a function of carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150 °C-7 kN-30 min.

there was no consistent effect of carbonization conditions. However, there were two differences in the effects of air curing and acid washing to those which were observed for more severe briquetting conditions. The RC-HTD had a higher bulk density than AWC-HTD in the absence of air curing, but the effect of air curing was greater for AWC-HTD than for RC-HTD, so that the bulk density of air cured AWC-HTD was greater than that for RC-HTD (compare Figure 4a with Figure 4b).

3.4 Helium density and pore volume

Figure 5 (a, b) shows the helium density as a function of acid washing, briquetting conditions, air curing and carbonization severity. Acid washing tended to increase the helium density of the products. As noted above the presence of cations inhibits the loss of volatiles which would be expected to have a lower helium density than non-volatile components [49-52] of the products and so would tend to lower helium density. More severe briquetting conditions, other factors being kept constant, tended to increase the helium density. Possibly enhanced mobility of molecular structures at more severe briquetting conditions (higher temperature, greater force) caused a rearrangement into a more compact structure, which, perhaps because of stronger bonding, remained more compact during carbonization, leading to a higher helium density of the final products. Air curing decreased the helium density at lower carbonization severity but increased it at higher carbonization severity. A possible explanation of the effect at low carbonization severity is that the polymerisation of the binder promoted by air curing fixed the size and shape of the coal derived molecules, thus “freezing” the bond structure so that its rearrangement to higher helium density form was inhibited. At greater carbonization severity this effect disappeared and the increase in helium density resulting from polymerisation of the binder caused by air curing was the main factor governing change in helium density of the products following air curing. Increased carbonization severity promoted loss of side chains and volatiles in general; the side chains and other volatiles would tend to have lower helium density than the r other components and so their loss would increase helium density [54].

The pore volume calculated from the bulk and helium densities Figure 6 (c, d) was generally reduced by air curing, probably because, the polymerization [55, 56] in the curing stage enhanced the interaction between coal and pitch, which inhibited volatilisation during carbonization so that the pores remained blocked. There was a much bigger decrease in pore volume when the briquetting conditions were more severe, because the higher force and temperature promoted molecular flow and tended to close the pores, which remained small during carbonization. Acid washing the coal had relatively little effect on the final pore volume.



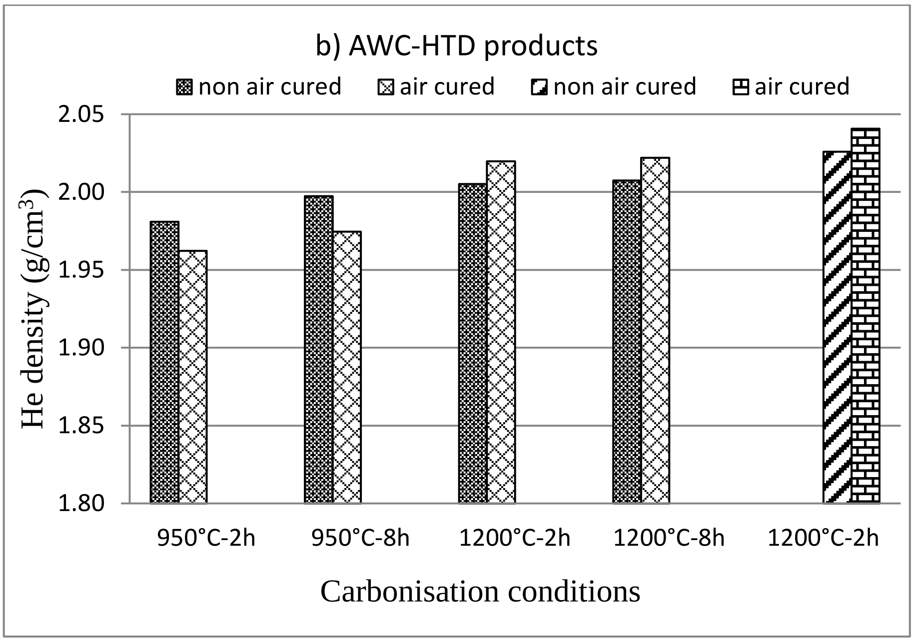


Figure 5: Helium density of the final products as a function of briquetting & carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150 °C-7 kN-30 min.

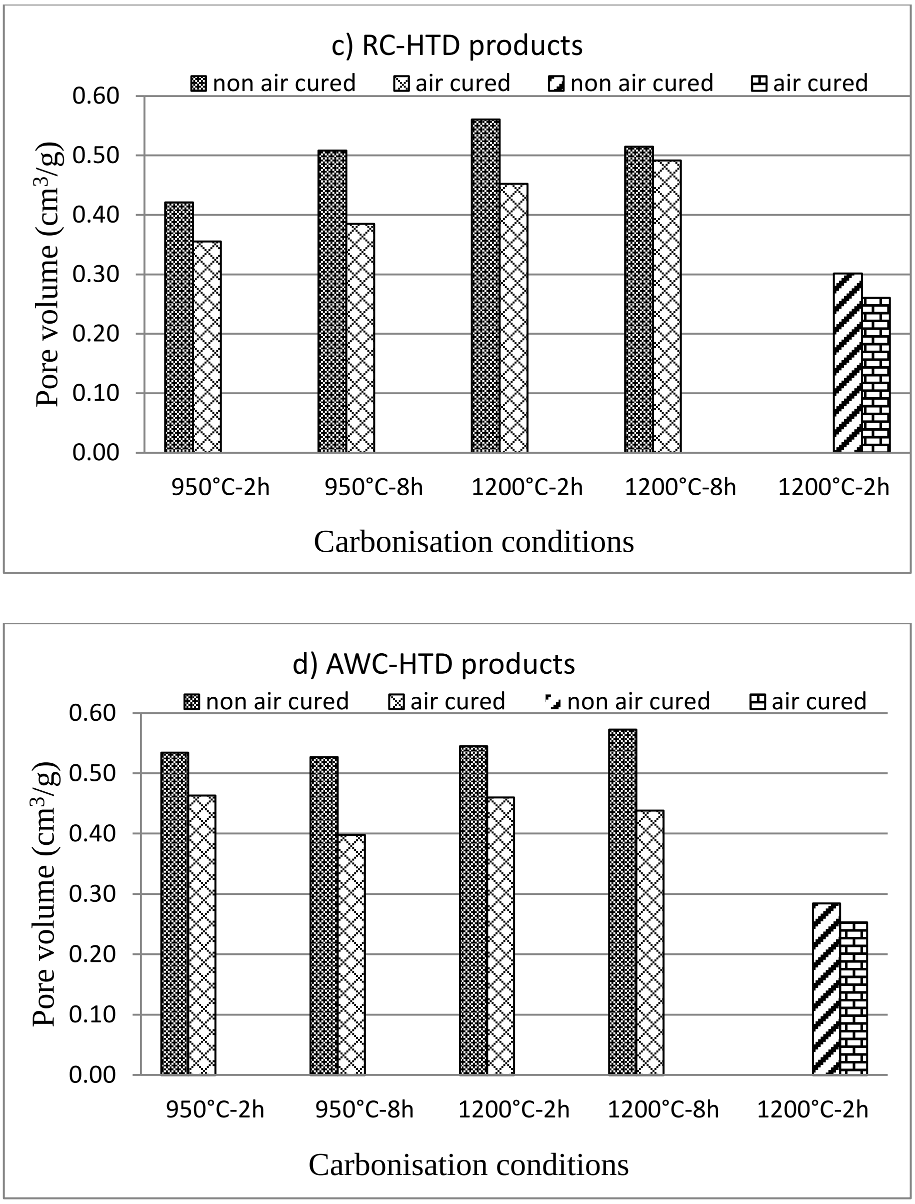
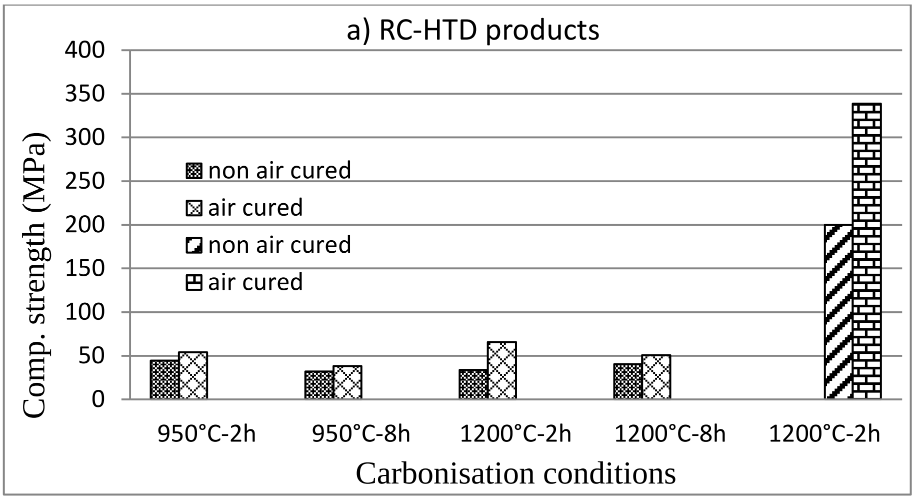


Figure 6: Pore volume of the final carbonised products as a function of briquetting & carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150 °C-7 kN-30 min.

3.5 Compressive strength

Figure 7 gives the compressive strength of the final carbonized products. There was little effect of carbonization time and temperature on compressive strength, but air curing always had a positive effect. Probably the polymerization of the binder induced by air curing (Section 3.4) strengthened its binding effect and thus increased the compressive strength [23, 55-57]. However a much larger effect on compressive strength was found when the briquetting force and temperature were increased. Thus it appears that the more severe briquetting conditions eliminated small pores which weaken the structure, consistent with the increase in bulk density (Section 3.3) and reduced pore volume. The severe briquetting conditions (higher temperature and greater force) reduced interatomic distances and also possibly promoted chemical reactions, both of which factors could have strengthened the product material. These effects may have been the factors increasing the compressive strength. It should be noted that even the weakest samples had a compressive strength comparable to that of a BF coke (20 MPa).



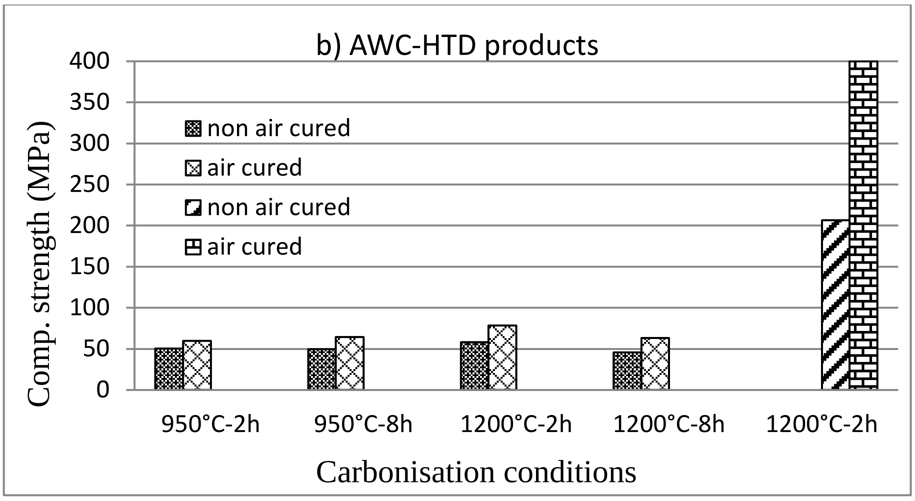


Figure 7: Compressive strength of the products as a function of carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150 °C-7 kN-30 min.

For the less severe briquetting conditions the compressive strength of the AWC-HTD products tended to be slightly higher than that of the RC-HTD products. A similar effect for tensile strength was noted by Mori et al. [16]. They suggested that the removal of the cations made the structure of the coal or the hydrothermally dewatered coal less rigid and more plastic, and this, together with changes in the pore structure (see Section 3.6) increased the tensile strength of the final products.

3.6 Surface area

Figure 8 shows CO_2 surface area of the final carbonized products. The most significant factor influencing the surface area was the carbonization severity (time, temperature). More severe carbonization conditions reduced the surface area, probably because they mobilised the molecules to block micropores and give a more ordered structure. The effect of air curing depended on the briquetting conditions, in that for lower briquetting force and temperature, air curing led to an increase in the surface area of the final products, whereas for higher briquetting force and temperature, air curing led to a decrease in the surface area of the final products. Under the less severe briquetting conditions air curing could increase the proportion of volatile components, whose loss would lead to an increase in porosity (Section 3.2). Under the more severe briquetting conditions the increased force and temperature pushed the binder deeper into the pores of the coal, inhibiting volatilisation and therefore ensuring no increase in porosity from this cause. Possibly more severe briquetting condition modified the state of the binder so that after air curing this led to a more ordered, less porous structure at the higher carbonization temperature.

Comparison of the changes in micropore volume and total pore volume with the severity of briquetting conditions showed that for AWC-HTD the decrease in total pore volume was similar to the decrease in micropore volume, so that the pores which tended to close at higher briquetting force and temperature, were the micropores; larger pores were not affected. For RC-HTD the decrease in micropore volume was greater than the decrease in total pore volume, implying that the volume of larger pores increased under more severe briquetting conditions. This may have been due to formation of microcracks. The more polar bonding in the RC-HTD due to the presence of the cations may have made the physical structure more rigid and therefore more liable to crack. This increase in macropore volume during carbonization for RC-HTD, but not for AWC-HTD, explains why the bulk density of AWC-HTD carbonized products was higher than that of RC-HTD carbonized products (Section 3.3).

The increase in volatilisation when AWC-HTD briquettes were carbonized (Section 3.2) was not reflected in an increase in surface area, which tended to be lower for products from AWC-HTD than for products from RC-HTD. The less rigid structure of the AWC-HTD coal may have led to molecular rearrangements which closed pores, more than making up for the increase in pore volume following volatilization.

Even the sample of lowest surface area, AWC-HTD briquetted under more severe conditions and air cured, had a surface area (79 m^2/g) considerably higher than that of a BF coke (18 m^2/g [28, 58]), but much lower than a conventional brown coal char (about 800 m^2/g [17]).

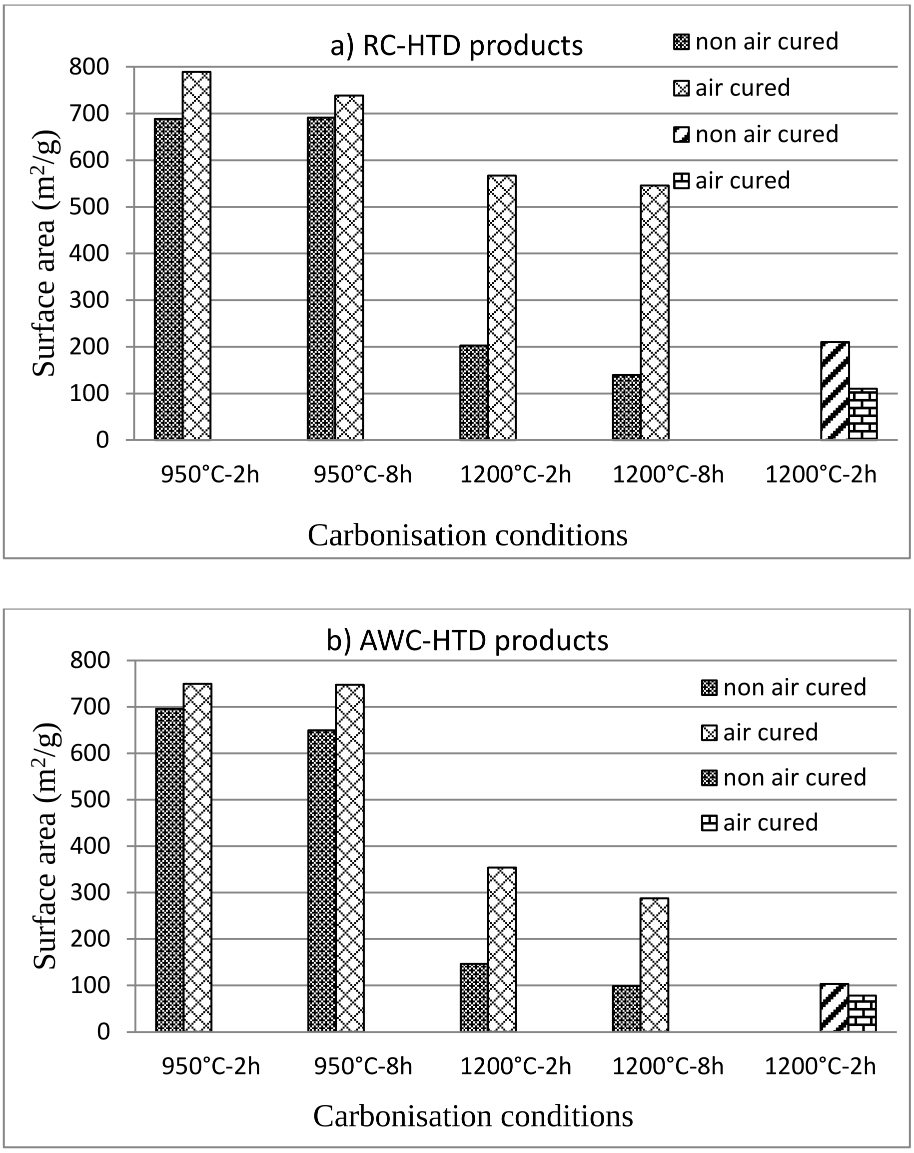


Figure 8: Surface area of the products as a function of carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150°C-7 kN-30 min.

3.7 Reactivity

Figure 9 shows the R60CO$_2$ for the products. For the non-air cured samples there was a correlation between lower surface area and lower R60CO$_2$, but other factors also clearly had a strong influence on R60CO$_2$. For example, air curing often increased surface area but always reduced R60CO$_2$. The reduction in reactivity following acid washing of the original coal can be explained by the lower surface areas of the carbonized products found following acid washing (Section 3.6). A reduction in catalytic species (Ca, Fe, etc.) following acid washing could also conceivably contribute to reduction in reactivity. However, it is believed

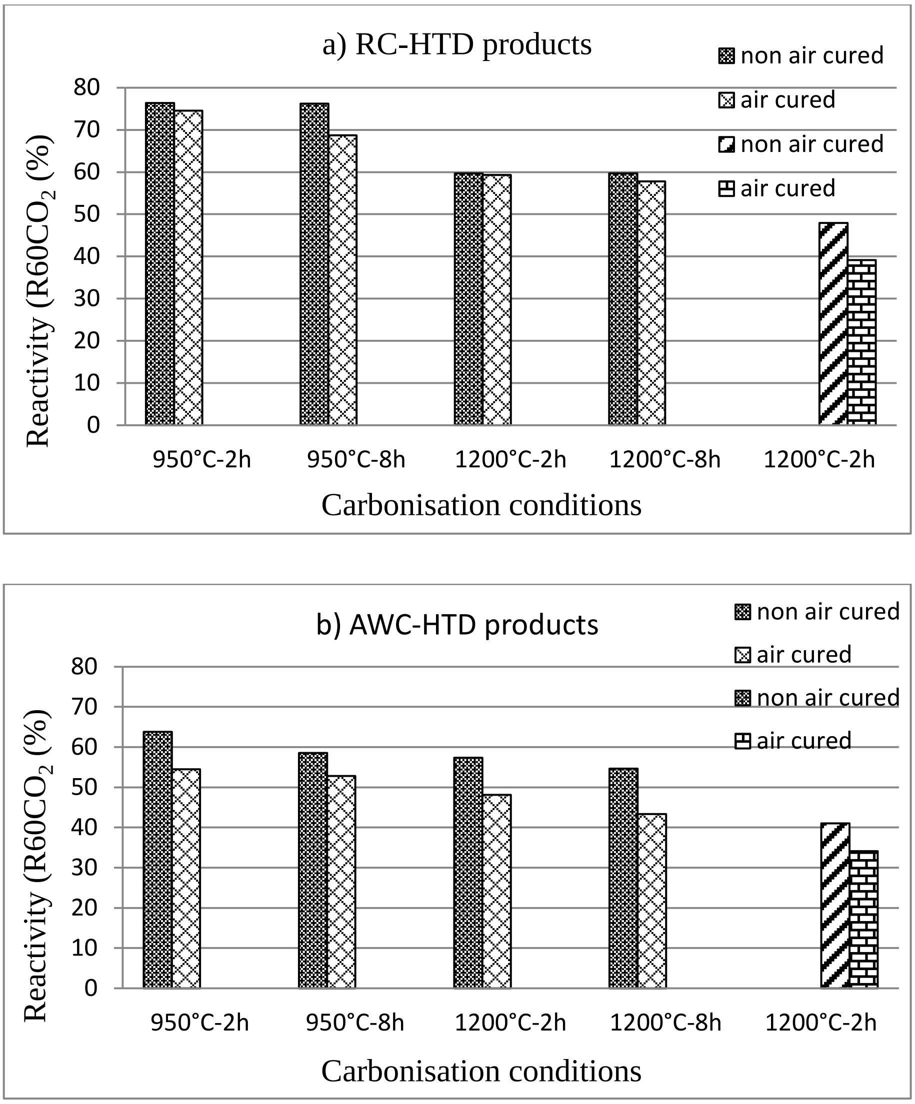


Figure 9: Reactivity of the final products as a function of carbonization conditions and air curing. 15 wt% pitch was used as binder. Briquetting conditions for the pair of samples on the right (1200°C-2h) 230 °C-20 kN-30 min and for the other samples 150 °C-7 kN-30 min.

that only crystalline compounds of these species are catalytically active [59] and no crystalline phases of these species were observed in the XRD of the carbonized products from RC-HTD, so that it is unlikely that removal of the cations would reduce any catalytic effect on reactivity.

The samples of highest compressive strength, obtained using severe briquetting conditions, had a lower $R60CO_2$ than the others, but as for surface area there was no consistent relation between $R60CO_2$ and compressive strength. This suggests that once the surface area is reduced sufficiently and the compressive strength increased beyond a certain level other factors become important in controlling the $R60CO_2$ and this is discussed below.

All the products were much more reactive than a BF coke ($R60CO_2$ 13%). Even the three treatments, acid washing, HTD treatment and addition of a pitch binder, did not alter the conclusion of Kennedy and Higgins [15, 60, 61] that brown coal char was much more reactive than coke. The products were too reactive to permit measurement of strength after reaction with CO_2 implying that Coke Strength after Reaction (CSR) [8], which has been proposed as the most important usage parameter [2], would be too low as CRI and CSR are inversely proportional [62, 63]. However, these three treatments did reduce the $R60CO_2$ below the level for products obtained by simpler procedures in our earlier study [17, 18].

3.8 Scanning electron microscopy (SEM) studies

Figure 10 shows SEM micrographs of the products obtained under the most severe briquetting conditions. The surface for both products was cracked and grainy, much rougher than the surface of a typical BF coke [17]. The products from RC-HTD and AWC-HTD were similar in appearance at both the 10 µm and 1 µm scales (compare Figure 10 (a,b) with Figure 10 (d,e)). Thus the improvement in $R60CO_2$ for the AWC-HTD products was not related to the surface structure on the scale.

Air curing gave a smoother surface for both RC-HTD and AWC-HTD products (compare Figure 10 (a) with (c)) and (b) with (f), which may help to explain why the reactivity was lower for the air cured samples. The smoother surface of air cured products was not necessarily related to a lower surface area because surface area is mainly controlled by much smaller scale (less than 10nm) features than those contributing to the appearance of the micrographs. Thus reactivity depends on µm size features as much as on smaller scale structures. The smoother surfaces for air cured products may be due to the improved binding and mechanical strength (Section 3.5) which tend to inhibit cracking and fragmentation which would occur during the shrinkage which accompanies carbonization.

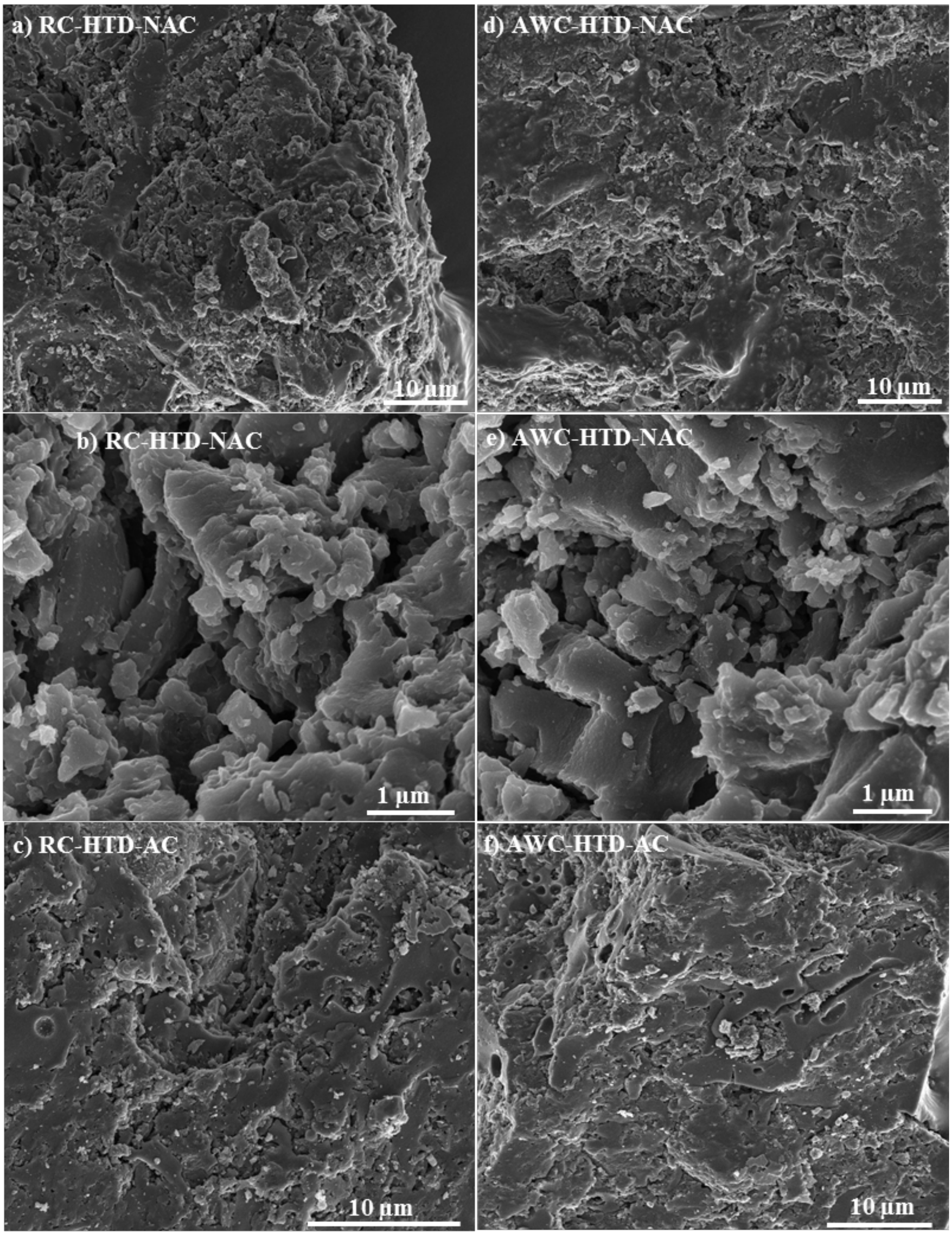


Figure 10: SEM images of products. a) RC-HTD-NAC lower magnification, b) (Note- NAC stands for non air cured and AC stands for air cured samples).

3.9 Raman spectroscopy

A typical Raman spectrum is shown in Figure 11. Earlier workers [45, 64, 65] have suggested that the ratio between areas of D and G bands can be used as a measure of the proportion of graphitic structure in the products as the ratio being inversely correlated with the proportion of graphitic structure. For the products of this study the ratio varied from 4.58 for the product of highest reactivity ($R60CO_2$ 76%) to 3.15 for the product of lowest reactivity ($R60CO_2$ 34%). The increase in the proportion of graphitic structure following acid washing can be explained by the more flexible structure of the less polar acid washed coal which can therefore rearrange more easily to a more stable graphitic structure. Air curing will enhance the interaction between coal particle and pitch so that the polycyclic pitch can promote graphitization in the composite. These results can be compared with 1.2 for the BF coke, which is similar to the ratio found by Kawakami et al. [66] for a BF coke also obtained from NSC. Thus all the products contained a relatively small proportion of graphitic material but the proportion did increase as the reactivity decreased (Figure 12).

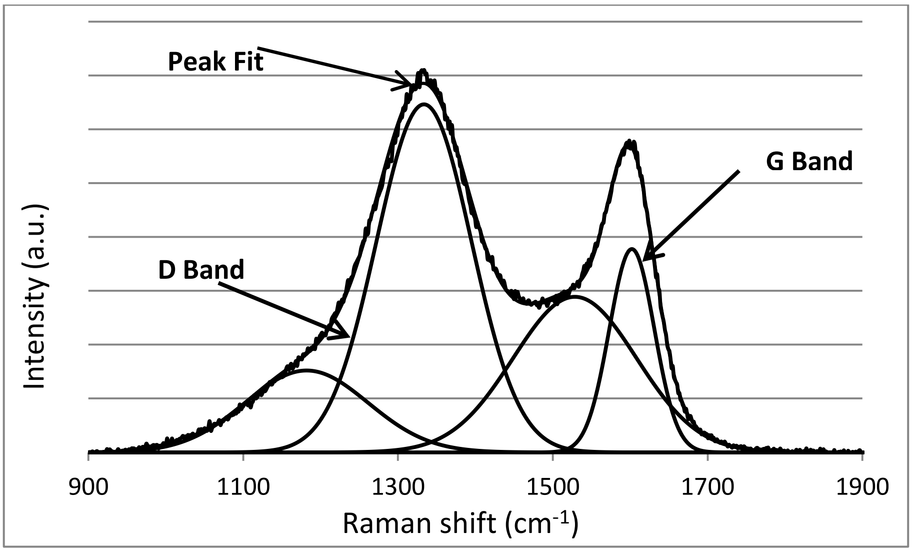


Figure 11: An example of deconvolution (peak fitting) of a Raman spectrum.

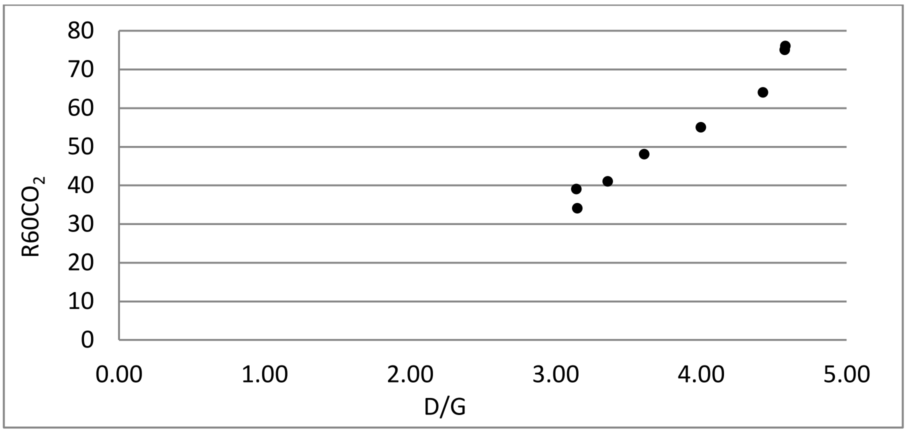


Figure 12: Relation between the proportion of graphitic structure and coke reactivity.

4. CONCLUSION

Comparison with our earlier work [17, 18] on RC indicated that preliminary HTD treatment reduced the reactivity of the carbonization products. More severe briquetting conditions, acid washing of the coal before HTD, air curing and severe carbonization conditions all reduced the reactivity further. However, while the compressive strength of the products was adequate, the reactivity even under the most favorable conditions remained much higher than that of a BF coke. It was possible to reduce surface area significantly, but not to the level of a conventional BF coke. Also, the proportion of graphitic structure and the average pore size remained much smaller than in BF coke. Hence the higher reactivity may be attributed to the low values of these structural factors. Further improvements will be necessary to obtain a substitute for conventional BF coke from VBC.

5. ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

(Chapter 4)

Analytical Techniques

Bulk and helium density

Bulk density of carbonized products was calculated from the weight of the pellet and its volume determined from the diameter and height of the cylinder-shaped pellet. The helium densities of the samples were determined on dried samples by helium pycnometry using an AccuPyc 1330 model pycnometer (Micromeritics, Norcross, GA, USA). The unit was calibrated on a daily basis. Oven-dried sub-samples of between 0.3 and 0.7 g were used. The sample was purged with helium 99 times to ensure complete removal of air. The helium density was determined from an average of 10 measurements on each individual sample. The uncertainty in bulk density based on duplicate determinations was ± 0.02 g/cm^3 and in helium density based on multiple determinations was always less than ± 0.03 g/cm^3.

Compressive strength

The compressive strengths of the sample of known height (*H*) and diameter (*D*) were measured by using an INSTRON 5569 series Mechanical Tester. The sample was placed on the anvil of the tester and an axial load applied across the plane ends until failure occurred. The displacement and loading were measured during the compression at a displacement rate of 0.05 mm/sec. The compressive strength σ_c was calculated using the following equation:

$$\sigma_c = (4F / \pi D^2)\ (H / D)^{0.5}$$

where force *F* is determined from the maximum load the pellets withstood, *D* is the diameter and *H* is the height of the pellet. The uncertainty in compressive strength based on multiple determinations was always less than ± 13% of the average value.

Surface area

Surface area was measured by CO_2 adsorption using a Micromeritics TriStar II 3020 analyzer at 0 °C. Experiments were carried out on oven-dried 0.2 g sub-samples, which were further dried under vacuum at 160 °C for at least 8 h to ensure complete removal of adsorbed gases using a Micromeritics VacPrep 061 instrument. CO_2 surface areas and micropore volumes (pores <2 nm diameter) were calculated using the Dubinin–Radushkevitch equation. The reference vapour pressure (p_o) for CO_2 at 0 °C was taken to be 26141.72 torr. The uncertainty in surface area based on duplicate determinations was about ± 2% of the average value.

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was carried out using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope. This microscope can be operated in two modes; mode 1 with a field free lens and mode 2 with an immersion final lens for high resolution imaging. Prior to loading into the instrument each sample was mounted on conductive carbon tape and coated with platinum (1-2 nm thickness) for 0.5 min using a Cressington Sputter Coater. During the coating process the samples were tilted about 45 ° and rotated at 50-100 rpm.

Raman spectroscopy

A Renishaw inVia Raman Microscope, using 632.8 nm HeNe laser light as the incident beam, was used to record the Raman spectra in air at room temperature. A power of 1.1 mW and spot size of 0.7 µm were used and the laser exposure time for each scan was 30 s. Multiple areas were scanned and spectra were recorded between 1900 and 900 cm^{-1}.

Earlier workers identified two broad peaks at about 1600 cm^{-1} and 1340 cm^{-1}, referred to as G and D bands respectively, in samples of similar carbonized products. In this work, the peak positions were in slightly different positions, which can be explained by differences in the excitation wavelength. As the spectra could not be adequately interpreted based solely on these two broad peaks, the spectra were deconvoluted and fitted to four peaks, as by earlier workers. The fits were made using OriginPro 8 SR2 software.

CHAPTER 5

Alkali treatment to induce the formation of blast furnace coke substitute from Victorian brown coal

PART B: Suggested Declaration for Thesis Chapter

Alkali treatment to induce the formation of blast furnace coke substitute from Victorian brown coal

Monash University

Declaration for Thesis Chapter 5

Declaration by candidate

In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Proposed original idea; prepared and analysed samples; identified major issues; developed interpretations; fully drafted papers and conclusions	75

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Marc Marshall	Aided methods development, input to results analysis, input to manuscript revision	N/A
Ying Qi	Aided methods development, input to manuscript revision	N/A
Gregory Knowles	Assisted in surface area and thermogravimetric analysis, input to manuscript revision	N/A
Jamileh Taghavi Moghaddam	Assisted in scanning and transmission electron microscopy, input to manuscript revision	N/A
Alan L Chaffee	Supervision, assisted interpretation in results, editorial assistance	N/A
W Roy Jackson	Supervision, assisted interpretation in results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		**Date** 20/5/15
Main Supervisor's Signature	Alan Chaffee	**Date** 20/5/15

Alkali treatment to induce the formation of blast furnace coke substitute from Victorian brown coal

M. Mamun Mollah, Marc Marshall, Ying Qi, Gregory Knowles, Jamileh Taghavi Moghaddam, W. Roy Jackson and Alan L. Chaffee

School of Chemistry, Monash University, Clayton 3800, Australia

Corresponding Author: Alan L. Chaffee

School of Chemistry, PO Box 23, Monash University, Australia

Email: alan.chaffee@monash.edu, Tel: +61-3-9905-4626, Fax: +61-3-9905-4597

Abstract

Alkali treated Victorian brown coal was evaluated as a starting material for the production of a substitute for blast furnace (BF) coke. Coal was treated with KOH in a 4 L autoclave at 185 °C for 10 h. Treated coal was optionally mixed with coal tar pitch as binder, then hot briquetted at 200 °C for 30 min. The briquettes were optionally air cured then carbonized at a range of temperatures and times. The carbonized products were tested and compared with a conventional BF coke with respect to properties such as densities, strength, reactivity to CO_2, surface area and pore volume, surface morphology by scanning electron microscopy (SEM) and graphitic structure by Raman spectroscopy and transmission electron microscopy. Some of the products were found to have much higher compressive strength and similar surface areas to BF coke. Their reactivity to CO_2 was much less than that of a carbonized brown coal product, but higher than that of a BF coke, even though the surface appeared very smooth under SEM. The proportion of graphitic structure was also found to be much lower than that of BF coke.

Keywords: Victorian brown coal, Alkali treatment, Blast furnace coke, CO_2 reactivity

1. INTRODUCTION

Urbanization and industrialization are driving the global iron and steel demand to grow every year [1]. Iron is extracted from its ore in a blast furnace (BF) by reduction with coke (carbon) and carbon monoxide, the latter being produced by reaction of the coke with oxygen.

Coke is the most expensive material [2] of those charged to a BF and there is no other material that can replace coke completely in a BF [3]. This is not only for its reducing ability but also for its other properties such as strength, which is required to hold the heavy iron bearing load, relatively low reactivity (coke reactivity index, CRI [4, 5]) with the gas in the BF and permeability to the gas and molten products under BF conditions. Only some bituminous coals are able to produce BF coke. They soften when carbonized under an inert atmosphere [6, 7], and then without any external force resolidify at higher temperatures, to form an inherently low reactivity, macroporous, strong lumpy material [8]. However, the global reserves of these coking coals are limited [9], and because of the shipping cost, these coals are becoming more expensive over a medium time scale.

In contrast, brown coals are abundant in Victoria, with estimated reserves of about 430 billion tonne [10, 11]. Victorian brown coals (VBCs) are very cheap with a low concentration of mineral impurities, which is an advantage for BF coke, as some minerals influence coke reactivity [12-14] and strength [15]. However, its usefulness as a starting material for BF coke has so far been limited by the powdery nature of the carbonized products, which will not form lumps unless pressed; also, the resulting material has high surface area and reactivity. These problems are believed to arise because the brown coal does not melt or plasticize when heated. Nonetheless, substitutes for BF coke from brown coal have been studied for many years. Earlier workers [16-22] suggested that a hard char can be obtained by carbonizing VBC commercial briquettes with a slow heating rate, but the resulting char cannot replace the coke in a BF because of its high reactivity.

In an attempt to improve the properties of the carbonized product, VBC was mixed with a binder and compressed into briquettes before carbonization to obtain a dense lumpy material which resembled coke in appearance. However, the products so formed continued to have a high reactivity to CO_2, high surface area and a low proportion of graphitic structure, even though they were much stronger than BF coke [23, 24]. These lumpy materials did not melt or plasticize during carbonization and it was felt that improvements might be possible if a material could be produced from VBC that would melt during carbonization, like coking coals. Brooks and Sternhell [25, 26] found that the product of alkali treatment of brown coals melted and swelled like coking coal when carbonized. However, they did not carry out any reactivity test for the product. Therefore, in our work Loy Yang raw coal was treated following the procedure of Brooks and Sternhell to see if the final carbonized product had low reactivity. The alkali treated coal was processed in the same way as raw coal in earlier work [23, 24], then carbonized and the properties of the carbonized materials were compared with those of the products obtained earlier and with those of BF coke.

2. EXPERIMENTAL

2.1 Materials

VBC, a soft low rank coal, was used in this study. Raw coal (RC), which had about 60 wt% moisture, was obtained from an open cut mine, located in Loy Yang, Victoria, Australia. Coal was milled to less than 3 mm in particle size and was kept in an airtight polybag. The binder used was coal tar pitch, softening point 110 °C [27], derived from coking coals, and obtained from Koppers Carbon Materials & Chemicals Pty Ltd, Newcastle, NSW, Australia. Lumps of a BF coke were sourced from Nippon Steel Corporation, Japan, to compare with the products. Tetrahydrofuran (THF) (Liquid Chromatography grade) and potassium hydroxide (KOH, pellet form, analytical grade) was obtained from Merck Australia, Kilsyth, Victoria. Sulphuric acid of Univar grade was obtained from Ajax FineChem Pty Ltd, Taren Point, NSW, Australia. More details of the analyses of the coals, pitch and BF coke are given in Table 1 and Table 2.

2.2 Alkali treatment of the coal

VBC was treated with aqueous alkali solution by the method of earlier workers [25, 28]. 320 g KOH was dissolved in 800 g deionized water in a beaker kept in cold water in a tote box to prevent overheating. 320 g RC as received (~60 wt% moisture) was charged into a 4 L autoclave (Figure 1). The KOH (aq.) solution was added to the autoclave. 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 N_2 (cold). The mixture was stirred at a speed of 115-125 rpm using the built-in stirrer. It was heated to 185 °C ± 5 °C and held at temperature for 10 h, then cooled overnight.

The product was recovered and the autoclave was washed out with deionized water. 280 g H_2SO_4 (98%) was dissolved in 2 L deionized water, and then slowly added in a glass container to the product which was stirred slowly in a fume hood. The glass container was kept in a tote box full of cold water to prevent overheating. Water from the product was removed by heating (hot plate) at about 80 °C under N_2 flow in a fume hood for 24 hours. The product was dried at 105 °C under flowing N_2 and then the dried product was washed with deionized water and filtered to remove K_2SO_4. Washing with deionized water and filtering were repeated another nine times. The pH after this was 6.2 and $BaCl_2$ was used to check if SO_4^{2-} was present. There was no precipitate. The product was dried under N_2 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).

2.3 Analyses of materials

The moisture contents of RC, ATC and BF coke were determined as the loss in weight when a sample was heated in flow of N_2 at 105 °C for 4 h. Representative samples of RC, ATC and BF coke to be ashed were first dried at 105 °C in a flow of N_2 for 4 h, then heated in air at 815 °C for 2 h [29, 30]. The RC volatile matter was determined by HRL Technology Pty Ltd, Mulgrave, Victoria, using Australian standard method AS 2434.2. C, H, N and S contents of RC were measured by HRL (RC) using a Leco CHN analyzer for C, H, N and Australian standard method AS 1038.6.3.3 for S. The C, H, N and S contents of BF coke, pitch and ATC were determined by microanalysis methods by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. O content in all cases was obtained by difference. The composition of RC ash was determined by HRL. The details of ^1H NMR and ^{13}C solid state NMR procedures were described in Mollah et al. [31] and are given in the supplementary material. The aromaticity of the pitch was determined from the elemental analysis and the ^1H NMR by the Brown Ladner equation [32]. 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 the ATC was, what would be expected from the ash yield of the RC if the loss of cations [31] 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, calculated from the solid state ^{13}C NMR [33] spectrum (Figure 1), was found to be 0.49, similar to literature values for a Loy Yang coal [34, 35]. The fraction of carbonyl (C=O) carbon was 0.09. The fractions of aromatic carbon in ATC (0.52) was slightly higher than in RC (0.49), as expected, because the fulvic acid (acid/alkali soluble material) removed during the alkali and acid treatment tends to have a lower carbon aromaticity than the whole coal [36]. However, the relative amounts of different aliphatic and aromatic groups within each of these domains were different from those in RC (Figure 1). The carbonyl (C=O) carbon (0.09) in ATC was similar as found by earlier workers [37]. The fraction of aromatic carbon in the pitch was found to be 0.95 using the Brown-Ladner equation [32, 33] from the elemental analysis (Table 1) and the ^{1}H NMR (not shown), indicating the high aromaticity of the pitch.

Table 1: Analyses of coals, pitch and coke.

Analysis [a]	**RC**	**ATC**	**Pitch**	**BF Coke**
Proximate				
Moisture (wt%ar)	60.0	-	-	3.00
Ash (wt%db)	3.25	3.67	0.0	11.98
Volatile Matter	49.4	-	-	-
Fixed Carbon	47.4	-	-	-
Ultimate (wt%db)				
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: Car (Fraction)			0.95	
Atomic H/C ratio	0.85	0.87	0.56	0.06

[a] The uncertainty (standard deviations) 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 given as ± 0.4 wt%db. The uncertainty in RC ultimate analysis given by HRL was given as ± 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, ± 0.03 wt%db for N, 0.06 wt%db for S and 0.9 wt%db for O (by diff).

Table 2: Analysis of ash of raw coal (wt% of the total ash).

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	Na_2O	CaO	SO_3	P_2O_5
56.5	19.2	2.3	8.0	0.2	2.4	4.1	1.0	5.4	0.2

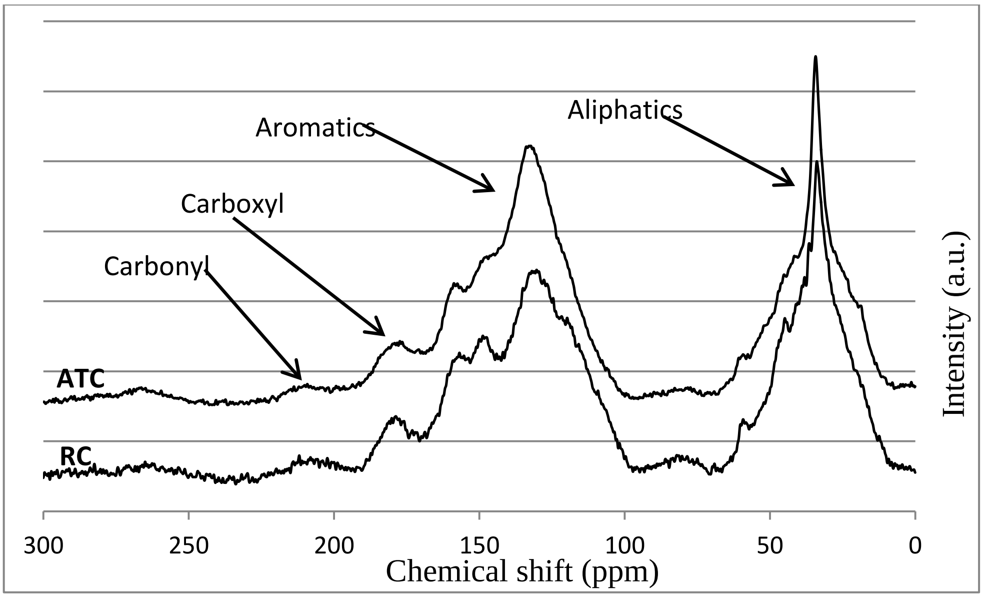

Figure 1 ^{13}C solid state NMR analysis of RC and ATC.

2.4 Mixing the coal with binder

Two samples of ATC (Section 2.2) were set aside for further treatment. One sample was mixed with coal tar pitch at a concentration of 15 wt% as described by Mollah et al. [31] and the other was not impregnated with binder, but was subjected the same procedure. The materials were dried and re-ground to less than 0.15 mm particle size. These materials constituted the feedstocks for further treatment.

2.5 Briquetting

To briquette samples of ATC, about 1.3 g of feedstock was placed into a 13 mm diameter die capable of being heated. Then the die was heated to 200 °C by a heating element attached to it at a rate of 10 °C/min. After confirmation that the temperature of the contents had reached 200 °C, force was applied using an INSTRON 5569 series Mechanical Tester at a rate of 10 kN/min until the force reached 20 kN and the force held for 30 min. The force was then released and the die was cooled to ambient temperature to recover the briquette which was weighed. The typical diameter and thickness of the briquette were 13.0 and 8.0 mm respectively. Two feedstocks were used: alkali treated coal and alkali treated coal-binder mixture. The procedure was similar to that used by Mollah et al [31], except that the briquetting temperature was 200 °C and a high briquetting force (20 kN) was used. This was because lower briquetting temperature (150 °C) and lower briquetting force (7 kN) were found to give poorer results for the hydrothermally dewatered coal than the more severe conditions [31]. It was also found that a higher briquetting temperature (230 °C) led in some cases to overheating and burning, so that a compromise briquetting temperature of 200 °C was used in order to give reliably good results without burning.

2.6 Air curing and carbonization

Samples were air cured at 200 °C for 2 h [38-41] in a flow of air using procedures described in our earlier work [23, 31] (also in supplementary material). For carbonization, prepared briquettes were weighed into a flat-bed alumina dish, which was placed into a tube furnace and then carbonized according to [20, 40, 42] at up to 1200 °C or 1300 °C under a carefully controlled heating regime (see below) and held at temperature for 2 h or 8 h under a flow of N_2 (8 L/min). A carefully controlled heating regime was required, to prevent cracking of the briquette because of shrinkage as a result of volatile matter being given off at higher temperature (around 400 °C) [42, 43]. Therefore, the carbonization temperature was increased at a rate of 2 °C/min. The briquettes were cooled to ambient temperature in a continuing flow of N_2 and weighed. Despite this care, the briquettes sometimes cracked during carbonization.

2.7 Product characterization techniques

Some of the characterization techniques used in this study were similar to those of Mollah et al. [23, 24]. Therefore, these common techniques are described briefly and are detailed in the supplementary material. The overall yields of the products were measured taking account of mass loss in the three stages of the process, briquetting, air curing and carbonization, and were calculated from the change in mass during the process divided by the mass before the process. The estimated uncertainty of the overall yields based on the variation in results from duplicate experiments was ± 0.3 wt%.

The bulk density of carbonized products was calculated by dividing the mass of the cylinder shaped briquette by its volume calculated from the radius and height. The helium density of carbonized products was measured by helium pycnometry [44]. The standard deviation in the bulk density based on duplicate determinations was about ± 0.03 g/cm^3 and in helium density based on multiple determinations was always less than ± 0.04 g/cm^3.

A Mechanical Tester, INSTRON 5569 series, was used to determine the compressive strengths of the final carbonized products and a sample of BF coke. The compressive strengths were measured by using the method of Johns et al. [45]. The uncertainty (standard deviation) in compressive strength based on multiple determinations was usually less than ± 20% of the average value.

CO_2 surface area was measured by adsorption of CO_2 at 0 °C using a Micromeritics TriStar II 3020 analyzer and then calculating the micropore volume and surface area from the Dubinin–Radushkevitch equation [46-48]. The standard deviation in surface area based on multiple analyses was about ± 5-10% of the average value. Scanning electron microscopy (SEM) images of the carbonized products were obtained using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope.

The reactivity test denoted $R60CO_2$ utilized a Setaram TAG 24 symmetrical thermoanalyzer as described by Mollah et al. [24]. N_2 and CO_2 flow rates were fixed by Bronkhorst programmable mass flow controllers. About 25 mg of broken briquettes left after the compressive strength test (Section 2.7) were weighed into a 70 µL alumina crucible and hung in the furnace. The sample was held at room temperature for 10 min with 35 mL/min N_2 flow, then heated to 110 °C at 10 °C/min and held at 110 °C for 30 min under continuing N_2 flow to dry the sample. The sample temperature was then raised to 1000 °C at a constant rate of 20 °C/min in the N_2 flow and held at 1000 °C in the same N_2 flow for 10 min. Then the gas flow was altered to 35 mL/min CO_2/35 mL/min N_2 and the temperature held at 1000 °C for 120 min. The temperature was held at 1000 °C for a further 10 min, but in 35 mL/min N_2 flow. The sample was cooled in the same N_2 flow to room temperature. After cooling, the sample was weighed. The reactivity index ($R60CO_2$) was calculated by the equation:

$$R60CO_2 = [(m_1 - m_2) / m_1] \times 100$$

where m_1 was the original test sample weight before reaction and m_2 was the sample weight after reaction in CO_2 for 60 min. The uncertainty in reactivity based on duplicate determinations was about ± 2% in $R60CO_2$ units.

Raman spectra were recorded in air at room temperature using 632.8 nm HeNe laser light as the incident beam, with a Renishaw inVia Raman spectrometer. The spectra were deconvoluted by OriginPro 8 SR2 software and adequately fitted to four peaks, which had also been found to give a reasonable fit previously [49-52]. The S band, at ~1160 cm^{-1}, has been assigned by earlier workers [53, 54] to alkyl-aromatic bonds; the next band, the D' band, at ~1330 cm^{-1}, to ordered but not graphitic aromatic carbon; the G_R band at ~1530 cm^{-1} to amorphous carbon; and the highest frequency band, the G' band at ~1600 cm^{-1}, to ordered graphitic structures.

Carbon structure in the carbonized products was observed by high resolution transmission electron microscopy (HRTEM) using a Field Emission Electron Microscope (JEOL 2100F). The electron microscope was operated at an accelerating voltage of 200 kV. Each sample was ground in a marble mortar to an ultra-fine powder. A carbon coated copper grid (0.053 mm) was then manipulated to scoop up some of the powder. Excess powder on the grid was then blown off with N_2.

3. RESULTS AND DISCUSSION

3.1 Overall yields

Figure 2 shows the overall yields of the final carbonized products. In all cases, the yields were much less than from a coking coal (75 wt% [3]). Without the binder there was little effect of carbonization conditions or air curing. This was in contrast to what was observed for products from untreated or hydrothermally treated coal, for which the yield dropped significantly after air curing [23, 31]. Thus the alkaline treatment made the coal more resistant to oxidation than untreated coal, in that the weight loss during air curing was less (3 wt% rather than 5-6 wt%). This could be because the more easily oxidized components were lost during the alkaline treatment, which is known to have a marked effect on the coal structure [28]. However, air curing consistently increased the overall yield for samples to which binder was added. This could be because, during the air curing, new bonds are established between the binder and the coal molecules, which inhibit volatilization during carbonization. In the absence of air curing, the volatile components of pitch will be lost during carbonization, reducing the overall yields. It was indeed found that pitch carbonized alone lost about 60 wt% on carbonization under these conditions.

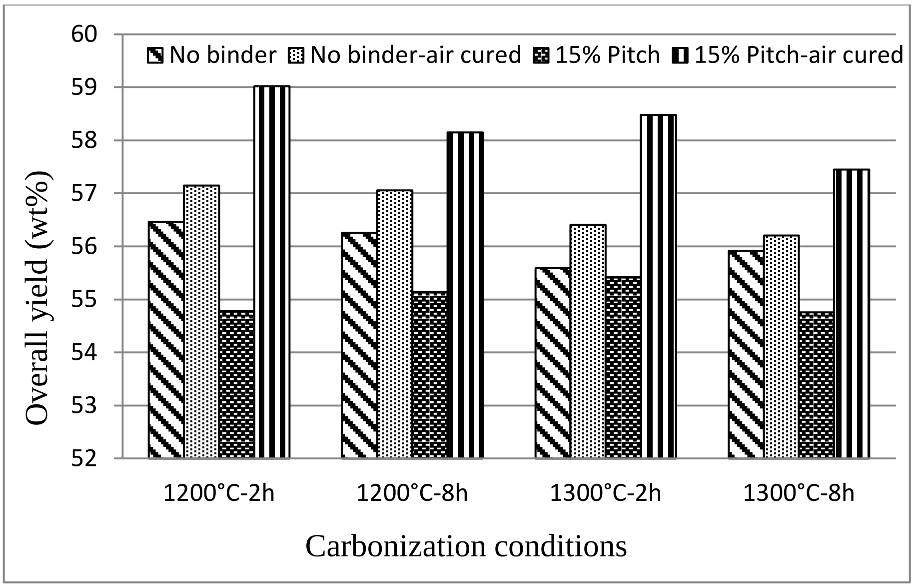

Figure 2: Overall yield of the final carbonized products as a function of carbonization condition and air curing.

3.2 Bulk density

Figure 3 gives the bulk density of the final carbonized products, which was always much higher than that of a conventional coke (0.87 g/cm^3) [55]. Carbonization conditions had little effect on the bulk density. However, adding binder led to a significant increase in bulk density, perhaps because the binder filled pores in the original coal or those formed during

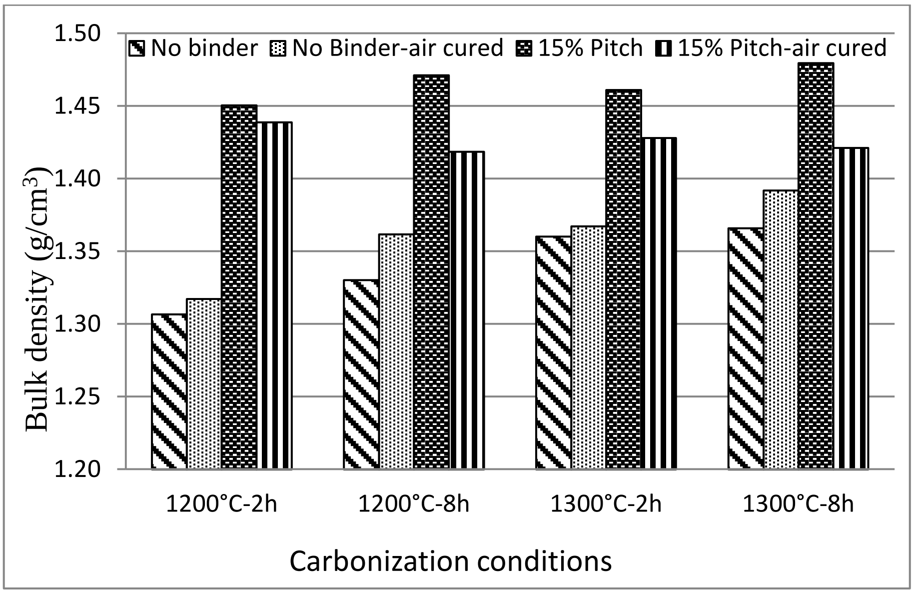

Figure 3: Bulk density of the final carbonized products as a function of carbonization condition and air curing.

carbonization. In contrast, air curing of the products with added binder decreased the bulk density significantly, as also evidenced by swelling of the briquettes observed after air curing. Possibly the volatile species released from the binder during the air curing process [56] could not diffuse out of the briquettes and thereby caused them to swell. At the same time the improved binding of the coal particles to each other consequent on polymerization of the binder [40] tended to freeze the structure, so that at least some of the additional pore volume was retained after carbonization.

3.3 Helium density

In contrast to the bulk density, the helium density of a conventional coke (1.89 g/cm^3, measured in the same way [24]) was higher than that of the products (Figure 4). Thus the difference between bulk density and helium density was much higher for conventional coke than for the products, so that the pore volume of the conventional coke was much greater. The difference between the bulk density and helium density for the products without binder was greater than for products with binder, implying a greater pore volume for the products without binder (Figure 4). This was probably due to the binder filling pores in the mixture of coal and binder. Air curing increased the helium density except at the most severe carbonization conditions, perhaps because under the milder conditions some of the oxygen introduced during air curing remained after carbonization, and since oxygen has a higher atomic weight than carbon or hydrogen the oxygen would tend to increase the helium density. The increased bonding (as mentioned in Section 3.1) resulting from the introduction of oxygen would also tend to increase the helium density. Under the most severe carbonization conditions all the extra oxygen might have been eliminated so that the air curing had no effect on helium density. Air curing increased the difference between helium and bulk density in the presence of binder and so increased the pore volume, as noted in Section 3.2.

As well as filling the pores, the binder under some carbonization conditions may interact chemically with the coal, making the structure more compact, thus increasing the helium density. This was not the case under the mildest and most severe carbonization conditions, for which the helium density of the products with and without binder was similar.

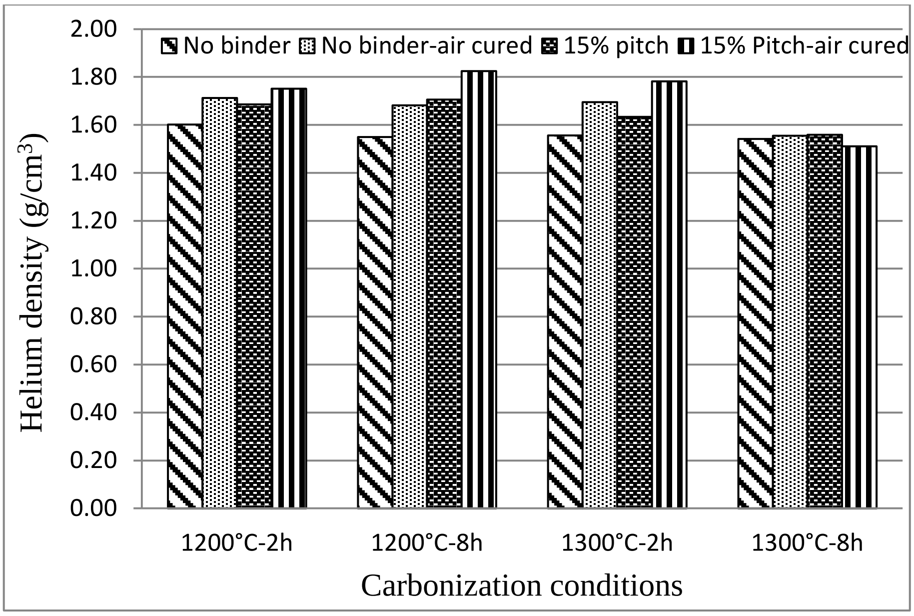

Figure 4: Helium density of the final carbonized products as a function of carbonization condition and air curing.

3.4 Compressive strength

Figure 5 shows the compressive strength of the carbonized products. Even when binder was not added, the compressive strength of the products was higher than that of a conventional coke (20 MPa, tested with the same instrument and conditions). Addition of binder greatly increased the compressive strength. Air curing had little effect when binder was not added, but reduced the compressive strength when binder was added. Nonetheless, the compressive strength remained much higher than in the absence of binder and higher than for a conventional coke. Our previous work [23, 31] on mixtures of binder and raw or hydrothermally dewatered coal found that air curing increased the compressive strength, suggesting that the decrease observed in this work was due to the effect of air curing on the alkali treated coal rather than on the binder. The chemical structure of ATC has been found to be substantially altered by air oxidation [57] and it is possible that this change weakened the physical structure of the coal and reduced the interaction of the coal particles with the binder, thus decreasing the compressive strength [41, 58, 59].

In the absence of binder the highest compressive strength was obtained for the higher carbonization temperature (1300 °C) and at the lower carbonization time (2 h). The lower compressive strength after long carbonization time (8 h) for binderless products suggests that reactions weakening the product structure continued for a long time at carbonization temperature. In contrast, when binder was added, longer reaction time was modestly beneficial. It is well known that pitch heated at these temperatures changes in structure [60] and the change in pitch structure may at longer times increase the interaction with the coal particles and the compressive strength of the carbonized products. This effect more than compensated for the reduction in strength due to reactions of the ATC during carbonization at longer times.

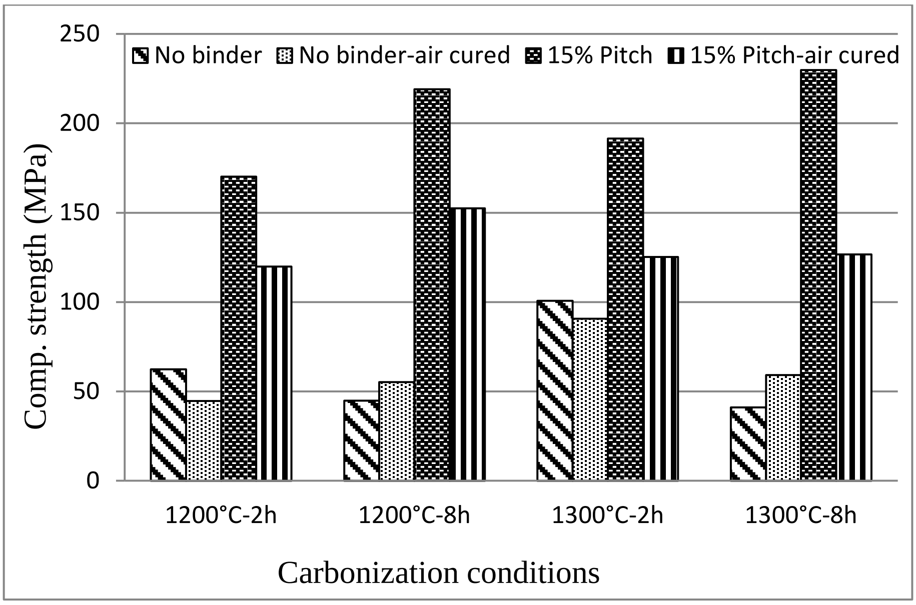

Figure 5: Compressive strength of the final carbonized products as a function of carbonization condition and air curing.

3.5 Surface area

Figure 6 shows the surface areas of the carbonized products obtained from ATC. The products always had significantly lower surface area than conventional brown coal char (800 m^2/g) produced at 900 °C [61] and much lower than that of the products obtained from the same coal reported in our earlier work [23, 24, 31]. This significant reduction in the surface area was probably due to collapse of the pore structure during alkali treatment, which has been observed in an earlier study [62]. Possible melting of part of the structure [25, 26] during carbonization may also have contributed to the collapse of pore structure. Surface area decreased with increasing carbonization severity. Perhaps greater flexibility of the structure at higher temperatures closed more pores.

Air curing in the absence of binder tended to increase surface area at lower carbonization temperatures. This increase may have been due to the opening of the new pores consequent on the oxidation and mass loss (3 wt%) occurring during air curing. Binder helped to reduce the surface areas, probably because binder filled some of the pores. In contrast to what was observed in the absence of binder, air curing further reduced the surface area. The new pores presumably created during air curing were probably filled by binder flowing into them at 200 °C as found by Sakurovs et al. [63], so that the surface area was reduced in the final products.

Thus combination of binder addition, air curing and carbonizing under severe conditions brought the surface area of the products down to the coke level. Some of the products showed surface areas as low as that of BF coke (18 m^2/g, measured with the same instrument under the same conditions).

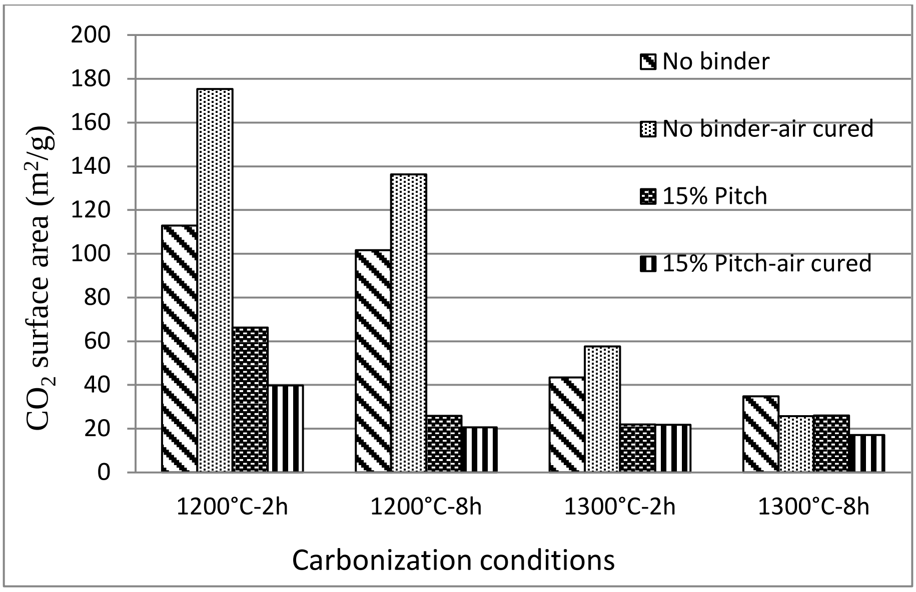

Figure 6: CO_2 surface area of the final carbonized products as a function of carbonization condition and air curing.

3.6 Reactivity

The reactivity of all the products (Figure 7) tested was unacceptably high when compared with that of BF coke (R60CO_2 13%, measured by the same method under the same conditions).

Increased carbonization severity and addition of binder reduced the reactivity modestly, and the reactivity level was much lower than that of brown coal char or products obtained from untreated VBC [23, 24]. However, even the least reactive products were not significantly better than the least reactive products obtained from hydrothermally dewatered coal reported in our earlier paper [31] despite their lower surface area. It would be expected that higher aromaticity would lead to lower reactivity for the final products and thus the lower aromaticity of the ATC relative to the hydrothermally dewatered coal (0.52 and 0.60 respectively) may have nullified the favorable effect of the lower surface area. Raman spectroscopy and TEM will permit testing of this suggestion. Air curing increased the reactivity, possibly because of the weakening of the chemical structure discussed above (Section 3.4) and the increase in surface area (Section 3.5).

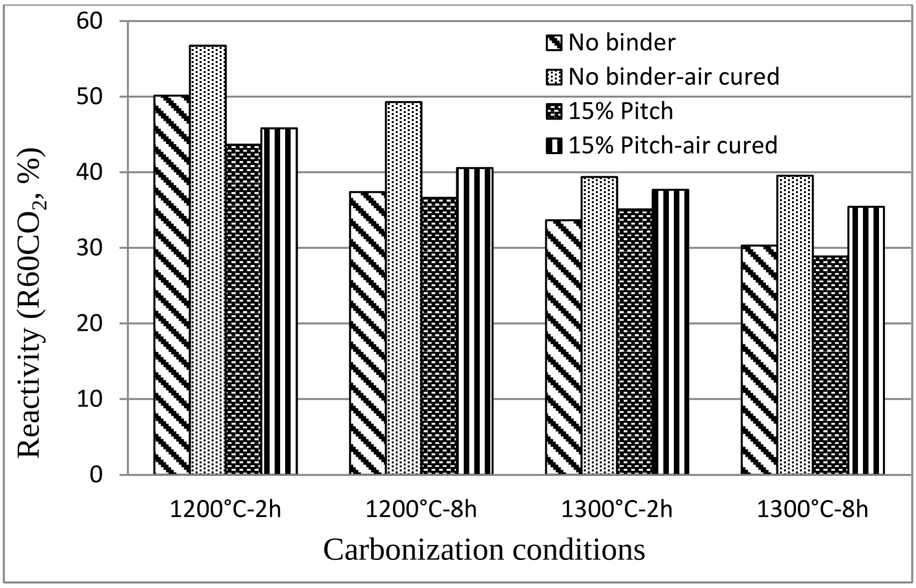

Figure 7: CO_2 reactivity of the final carbonized products as a function of carbonization condition and air curing.

3.7 Raman spectroscopy

The ratio of intensity (areas) of D and G bands is believed to be inversely correlated with the proportion of graphitic structure [51, 54, 64, 65]. It was found that the products of lowest reactivity ($R60CO_2$ 29%) had a lower intensity ratio (2.6) than products of higher reactivity e.g. a product of $R60CO_2$ 57% gave a ratio of 3.6. However, both of these ratios were much higher than the 1.2 observed for a BF coke of $R60CO_2$ 13%. This suggests that the less reactive products had more graphitic structure than the more reactive (Figure 8), but a much smaller proportion than a BF coke. For the less reactive products, the $R60CO_2$ was lower and the proportion of graphitic structure higher than for the products obtained from untreated VBC [23] or hydrothermally dewatered VBC [31].

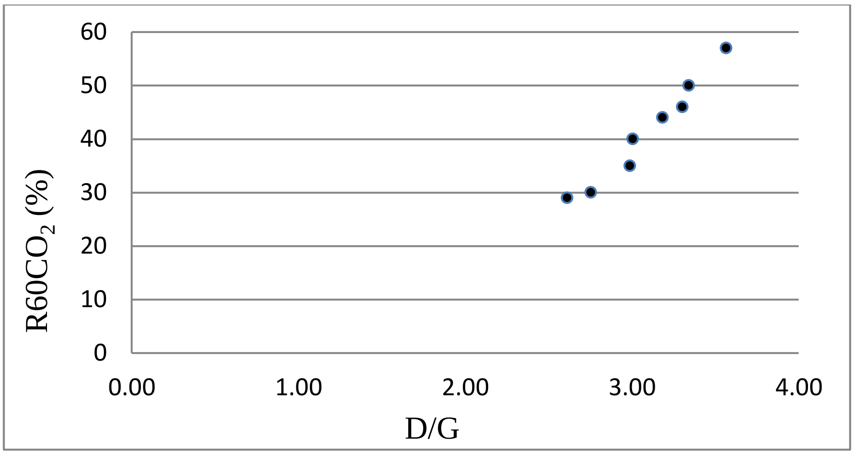

Figure 8: The relation between the proportion of graphitic structure and coke reactivity.

3.8 Scanning electron microscopy (SEM)

Figure 9 shows the SEM images obtained for the least reactive product. Comparison with the images of carbonized products from ambient or hot briquetted VBC or hydrothermally dewatered coal shows that the products from ATC had a much smoother surface with no

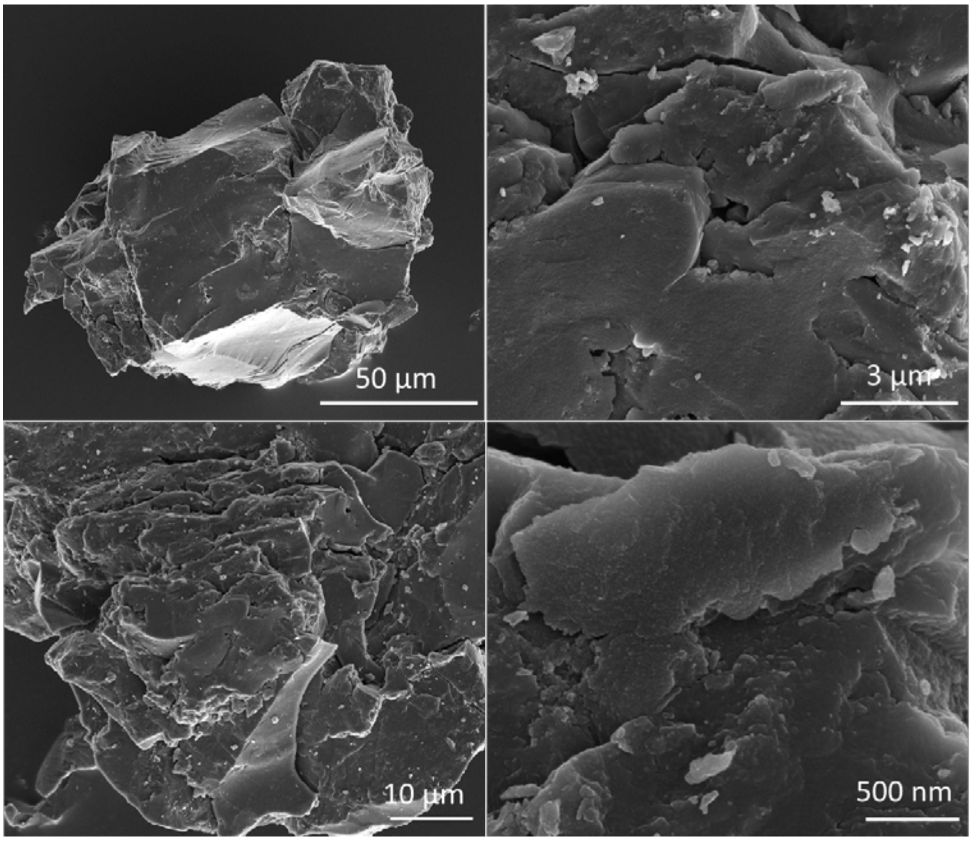

Figure 9: SEM images of a final carbonized product; ATC with 15 wt% pitch briquetted at 200 °C for 30 min and carbonized at 1300 °C for 8 h.

grains or rough jagged edges. There were also fewer cracks and pores. These observations are consistent with melting and subsequent pore filling or fusing (i.e. melting or softening and subsequent resolidification) of pores during alkali treatment. Unlike BF coke there were no obvious macropores.

3.9 Transmission electron microscopy (TEM)

Figure 10 shows a HRTEM micrograph of the least reactive product, with a micrograph of a carbon-rich region of a typical BF coke for comparison. Most of the surface of the carbonized

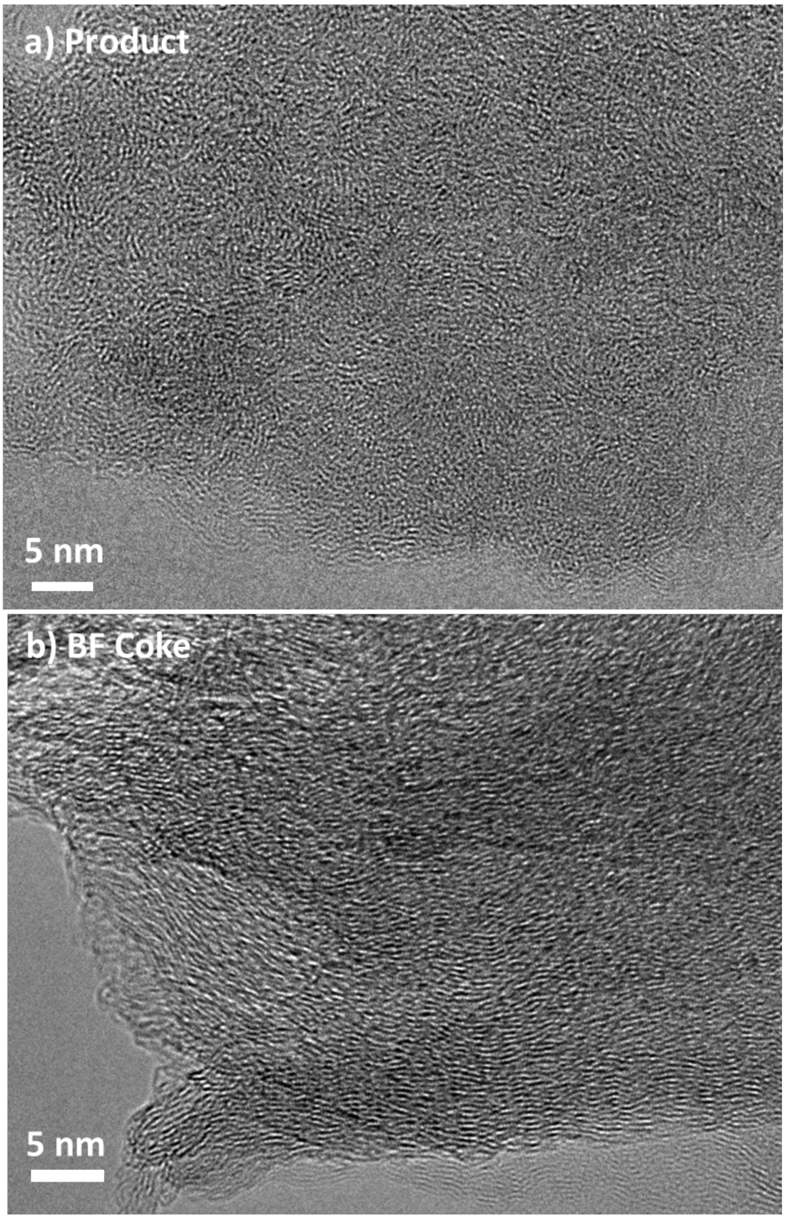

Figure 10: HRTEM images of a) a final carbonized product (ATC-15 wt% pitch briquetted at 200 °C for 30 min and carbonized at 1300 °C for 8 h) and b) BF coke.

product showed only small isolated islands of ordered graphitic structure, whereas the BF coke showed larger regions of such structure much closer to each other. These results are in agreement with the results of Raman spectroscopy. However, in the vicinity of an iron oxide crystal the carbonized product showed extensive regular regions of graphitic structure (not shown), with parallel layers extending over considerable distances. This induction of graphitic structure by iron oxide has been observed previously [66-69]. Unfortunately these regions were only a small part of the total surface. If there were some way of generating large amounts of graphitic structure by suitable deliberate addition of suitable materials, this might be a useful method of reducing the reactivity of the carbonized material.

4. CONCLUSION

The alkali treated coal with a suitable binder showed a high compressive strength after carbonization and the small surface area obtained for the carbonized products under some conditions suggests that melting or plasticization did occur during carbonization. However, the reactivity of the carbonized products was unacceptably high. Possibly the alkali treatment changed the chemical structure of the products in such a way as to increase the reactivity. Clearly suitable values for the physical factors (e.g. surface area) are necessary to obtain a product of low reactivity, but are not sufficient; the chemical structure, for example, the proportion and perfection of graphitic structure in the material, is also important.

5. ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

(Chapter 5)

NMR techniques

For ^{1}H NMR, a sample of tar was dissolved in $CDCl_3$ and spectra was obtained using a Bruker Ultrashield 400 MHz instrument with a 90 ° pulse flip angle (9.5 μs). Solid state ^{13}C NMR of RC was recorded at room temperature using a Bruker Avance 400 spectrometer. Samples were packed into zirconia rotors with a Kel-F cap. Spectra were recorded using cross-polarization magic angle spinning (CP-MAS) techniques at 10 kHz spin rate with 25 ms acquisition time. Spectra were referenced to a glycine external reference.

To aid interpretation ^{1}H NMR spectra were divided into four regions: protons attached to aromatic rings (H_{ar}, 6−9 ppm); protons attached to aliphatic carbon adjacent to aromatic rings (H_α, 4.5−1.96 ppm); protons attached to carbons further away from aromatic rings (methylene protons); and protons of paraffin groups (H_β, 1.95−1 ppm); and protons in $-CH_3$ (H_γ, 1−0.5 ppm). In an analogous manner, the ^{13}C NMR spectra were divided into three regions: carbonyl carbon ($C_{c=o}$), 165−240 ppm; aromatic carbon (C_{ar}), 90−165 ppm; and aliphatic carbon (C_{al}), 0−90 ppm. The proportions of the carbon types were determined using Bruker's Topspin 3.1 software.

Air curing procedure

The prepared briquettes were heated in a flow of air (300 mL/min) at 200 °C for 2 h and then cooled to ambient temperature with the air flow continuing. During air curing the briquettes lost 1-2 wt%, indicating that some oxidation took place, but there was no cracking or white ash spots, so that combustion did not occur.

Helium density measurement

The helium densities of the samples were determined on dried samples by helium pycnometry using an AccuPyc 1330 model pycnometer (Micromeritics, Norcross, GA, USA). The unit was calibrated on a daily basis. Oven-dried sub-samples of between 0.3 and 0.7 g were used. The sample was purged with helium 99 times to ensure complete removal of air.

The helium density was determined from an average of 10 measurements on each individual sample. The uncertainty in helium density based on multiple determinations (standard deviation) was always less than ± 0.04 g/cm^3.

Compressive strength measurement

The compressive strengths of the sample of known height (*H*) and diameter (*D*) were measured by using an INSTRON 5569 series Mechanical Tester. The sample was placed on the anvil of the tester and an axial load applied across the plane ends until failure occurred. The displacement and loading were measured during the compression at a displacement rate of 0.05 mm/sec. The compressive strength σc was calculated using the following equation:

$$\sigma c = (4F / \pi D^2)\ (H / D)0.5$$

where force *F* is determined from the maximum load the briquettes withstood, *D* is the diameter and H is the height of the briquette. The uncertainty in compressive strength based on multiple determinations was always less than ± 20% of the average value.

Surface area analysis

Surface area was measured by CO_2 adsorption using a Micromeritics TriStar II 3020 analyzer at 0 °C. Experiments were carried out on oven-dried 0.2 g sub-samples, which were further dried under vacuum at 160 °C for at least 8 h to ensure complete removal of adsorbed gases using a Micromeritics VacPrep 061 instrument. CO_2 surface areas and micropore volumes (pores <2 nm diameter) were calculated using the Dubinin–Radushkevitch equation. The saturation vapour pressure (p_o) for CO_2 at 0 °C was taken to be p_o = 26141.72 torr. The uncertainty in surface area based on duplicate determinations was about ± 5-10% of the average value.

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was carried out using a FEI Nova NanoSEM 450 field emission gun scanning electron microscope. This microscope can be operated in two modes; mode 1 with a field free lens and mode 2 with an immersion final lens for high resolution imaging. Prior to loading into the instrument each sample was mounted on conductive carbon tape and coated with platinum (1-2 nm thickness) for 0.5 min using a Cressington Sputter

Coater. During the coating process the samples were tilted about 45 ° and rotated at 50-100 rpm.

Raman spectroscopy

A Renishaw inVia Raman Microscope, using 632.8 nm HeNe laser light as the incident beam, was used to record the Raman spectra in air at room temperature. A power of 1.1 mW and spot size of 0.7 µm were used and the laser exposure time for each scan was 30 s. Multiple areas were scanned and spectra were recorded between 1900 and 900 cm^{-1}.

Earlier workers identified two broad peaks at about 1600 cm^{-1} and 1340 cm^{-1}, referred to as G and D bands respectively, in samples of similar carbonized products. In this work, the peak positions were in slightly different positions, which can be explained by differences in the excitation wavelength. As the spectra could not be adequately interpreted based solely on these two broad peaks, the spectra were deconvoluted and fitted to four bands, as by earlier workers. The fits were made using OriginPro 8 SR2 software.

CHAPTER 6

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CHAPTER 7

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Chapter 8

General Conclusion and Future Work

8.1 Conclusion

This work examined the properties of carbonized products prepared from Victorian brown coal (VBC) or suitable derivatives of VBC and binders (VBC derived tar denoted “tar”, the asphaltene fraction of tar, denoted “tar asphaltene” and coking coal tar pitch denoted “pitch”). The properties studied were those particularly relevant to the use of carbonized products as substitutes for blast furnace (BF) coke, including CO_2 reactivity, compressive strength and surface area (micropore volume).

Previous work by the Gas and Fuel Corporation of Victoria in 1950-1964 investigated commercial VBC briquettes as a substitute for BF coke with regard to strength and reactivity and was taken as the starting point. The current work began by pelleting (briquetting) a mixture of ground commercial briquettes of VBC and, optionally, tar at ambient temperature and carbonizing the pellets. The carbonized pellets were compared with those obtained by carbonizing a mixture of ground VBC and, optionally, tar pelleted (briquetted) at ambient temperature. Products prepared from ground VBC, with optional tar addition, showed higher compressive strengths and slightly lower reactivity and surface areas than those prepared from ground commercial VBC briquettes. The effects of carbonization conditions (time, temperature and tar addition), at least over the range of conditions examined, were relatively small. However, all the carbonized products, though of acceptable compressive strength, were much more reactive than BF coke probably of their much higher surface areas. There was also much less, and more disordered, graphitic structure than in BF coke.

Hot rather than ambient temperature briquetting and air curing before carbonization of VBC-tar composites increased the compressive strength and bulk density by up to a factor of four. Scanning electron microscopy (SEM) showed that the strong products had a much smoother surface, which could be explained by polymerization of the tar following air curing and flow of tar onto the surface, thus binding the coal particles together more strongly. However, the surface remained grainy and rough (SEM) and the surface area and reactivity were not much lower than those obtained following ambient briquetting and the amount of graphitic structure remained small. It is suggested that low surface area and a reasonable amount of graphitic structure are necessary for low reactivity.

These experiments suggested that it would be necessary to modify VBC structure to be closer to that of a higher rank coal, at least in some particulars, to obtain a carbonized product closer in its properties to BF coke. The binder ideally should contain the polycyclic aromatic hydrocarbon (PAH) and hydroaromatic structures found in coking coals, in order to promote the creation of graphitic structure, so that pitch was substituted for tar. The first VBC product trialled was hydrothermally dewatered (HTD) VBC, which had a lower carboxylate content and was less hydrophilic than VBC, making it closer to a higher rank coal in some respects. The reactivity of the carbonized HTD product (RC-HTD), was less than that from untreated VBC and more severe briquetting conditions. Using acid washed coal (AWC) as a precursor for HTD (AWC-HTD), air curing and higher carbonization temperature all reduced the reactivity further. HTD in itself will reduce the polarity of the initial coal structure and acid washing will enhance the reduction of polarity so that the coal structure may become more flexible and rearrange more easily into a form with adequate compressive strength, lower pore volume and lower surface area and with a greater proportion of graphitic structure, tending to reduction in reactivity. Severe briquetting conditions could drive the binder deeper into the pores, reducing pore volume and surface area and severe carbonization conditions could increase the mobility of the coal structure, facilitating molecular rearrangement to a more stable and less porous form of low reactivity. Air curing could enhance the interaction between coal and binder and subsequently promote graphitization during carbonization which will give a more stable, less reactive structure. These suggestions can explain why acid washing, HTD and air curing gave a less reactive product. However, the reactivity of even the lowest reactivity products derived from HTD coals remained much higher than that of BF coke and there was less graphitic structure. Since the surface area of the less reactive products was similar to that of the BF coke, this implies that reduction in surface area will only reduce reactivity to a certain limiting value and that further decrease in reactivity requires a more stable structure, with greater extent of graphitization needing to be developed during carbonization.

All the products described above were much stronger than a BF coke and the surface area was significantly low in some cases, but all had a high relatively high reactivity to CO_2 and a low proportion of graphitic structure. It was thought that the low proportion of graphitic structure might be connected to the fact that, unlike coking coals, the materials in the briquettes did not melt during carbonization. Thus improvements in the properties of the final products might be possible if a starting material could be produced from VBC that would induce melting of the briquette material during carbonization. It is known that VBC treated with strong alkali will melt and then resolidify to some extent during carbonization. Therefore, Loy Yang raw coal was treated with alkali, which would remove the fulvic materials and the remaining humic acid and humin briquetted and carbonized. The carbonized products showed a smooth surface under SEM and a low surface area, suggesting that melting and subsequent resolidification did take place. However, the reactivity was only slightly lower than that of products from AWC-HTD and the amount of graphitic structure was only slightly higher. The values were a long way from those for BF coke. Clearly melting or plasticization alone is not a sufficient condition for low reactivity and a large amount of graphitic structure.

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In summary, a carbonized product of much greater compressive strength and with reactivity approaching that of a BF coke can be produced entirely from derivatives of VBC. Low surface area and melting or plasticization were found to be necessary but not sufficient conditions for a product of low reactivity; a reasonable proportion of graphitic structure was also required.

8.2 Future work

The next stage in studying the process of preparing coke-like material from VBC would have two aspects. The first would involve improving the process and testing the products under more realistic conditions, the second would involve more fundamental study to determine what factors control the desirable properties of the products.

8.3 Improvements in production and testing

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4. CRI tests should be conducted on whole briquettes in a furnace rather than on fragments by TGA. The remaining product after such a CRI test could then be subjected to a CSR test, which is of greater interest than a compressive strength test before reaction under CO_2.

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8.4 Fundamental studies of mechanism of graphitization and reduction in reactivity

1. It would be useful to study the evolution of the important characteristics of the products during briquetting and carbonisation. This could be attempted by stopping the briquetting and carbonisation processes before completion of briquetting and after different temperatures and times during carbonisation and then investigating the properties of products by the methods used in the thesis.
2. The properties of the products after reactivity testing should also be investigated. For this purpose it would be desirable to carry out reactivity testing on whole briquettes (see above). This may indicate how the properties of the products change during reaction with CO_2 and therefore how the reactivity could be reduced.
3. Other techniques for determining in more detail the porosity characteristics, which have an important effect on reactivity, strength and permeability, could be applied such as mercury porosimetry and small angle X-ray scattering (SAX).
4. XRD as used in the thesis could not distinguish different degrees of graphitization in the products. More sophisticated treatment of the data and possibly in situ XRD could make useful contribution here.
5. The TGA tests used were isothermal. It has been found that important mechanistic information can be obtained by carrying out TGA under dynamic conditions i.e. rising

the temperature at constant rate (see section 1 of chapter 2) and it would therefore be useful to apply such TGA techniques.