Possible CO$_2$ mitigation via addition of charcoal to coking coal blends

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ARTICLE INFO

ABSTRACT

Processes involving biomass oxidation are considered to be CO$_2$ neutral since the replenishing of the biomass by normal growth will remove CO$_2$ from the atmosphere. Thus the use of charcoal in the production of metallurgical coke, to be used as a reducing agent in the formation of iron, would be a strategy for the reduction of CO$_2$ in the overall ironmaking process. This paper describes experimental attempts to produce industrial grade coke from coking coal blends to which are added amounts of charcoal up to 10%. Coking experiments were carried out partly in a 30 lb coke oven and partly in a sole heated oven. The influence of blend composition, heating rates and charcoal particle size was investigated. Cokes made using fine charcoal addition (–60 mesh) were considerably weaker than cokes made from the base blend. This is interpreted to be the effect of the ash constituents in the charcoal which, among other things, contains much higher calcium than the coals used. However, carefully sized fractions of coarse charcoal (–3/8 +1/4 in) produced much higher quality coke, possibly the result of a different dispersion of the charcoal mineral components.

1. Introduction

Interest in the use of biomass substitutes for traditional fossil fuels has become relatively common these days due to the enhanced interest in global climate change. The underlying rationale is that, since biomass is in principle a renewable resource, the contribution to global CO$_2$ from its combustion, apart from the energy expended in processing and transportation is insignificant. Some countries, such as Canada and Brazil, have extensive quantities of biomass and consequently programs to use this biomass in creative ways such as transformation of biomass cellulose into ethanol [1]. The use of corn to produce ethanol has been important in Brazil for a number of years and is becoming more important in the USA in recent years. Ethanol additions to gasoline may have the potential to reduce the overall generation of CO$_2$ by the transportation sector [2].

The partial substitution of metallurgical coals by charcoal also has the potential to reduce the overall generation of CO$_2$ by the steel industry. The use of carbonized coconut shells in the blast furnace has been proposed [3]. Specialized blast furnaces operating exclusively on charcoal are only found in Brazil [4] where their use has resulted in considerable deforestation. The literature does not contain a wealth of information on the addition of biomaterials to coal. Das et al. [5] have blended biomass with a non-coking coal of high ash content to produce foundry coke. An Australian project, funded by ACARP (Sustainable Technology Australia) [6], investigated the production of charcoal from eucalyptus wood and the costs associated with charcoal production. The project also investigated the production of metallurgical coke from a commercial coal blend with 5% and 10% added charcoal. We will consider these results in more detail below.

In Canada the steel industry uses annually 3.7 Mt of metallurgical coke in the blast furnace, equivalent to 13 Mt CO$_2$, one of the larger generators of this gas in the metals sector [7]. Replacement of 10% metallurgical coke by charcoal

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would result in the reduction of CO_2 emissions by 1.3 Mt annually from this sector, thus providing impetus for work in this area. Our own analysis of the Canadian biomass situation indicates that the requisite amount of charcoal would be available from Canadian sources although this is not the case for many countries in the developed world.

The formation of metallurgical coke from coal is related to the development of thermoplasticity during coking with a variety of factors coming into play [8]. The introduction of anything other than coking coal into a coking coal blend must therefore be given careful consideration. In this paper we investigate the coking of several blends of commercial coking coal with varying amounts of commercial hardwood charcoal. The coking experiments were carried out using both a 30 lb coke oven and a standard sole heated oven. The object of the work was to find those coking conditions which would allow the production of coke of acceptable industrial quality with at least 10% added charcoal.

2. Experimental

The small-scale coking experiments reported were carried out in two different laboratory scale coke ovens. The first was a 30 lb coke oven constructed by the Carbolite Company and designed to bring the coking charge from an initial wall temperature of 860 °C to a final centre temperature of 1100 °C in approximately 2.5 h. This was used for the first two sets of coking experiments. The second was the sole heated oven where the charge (25–30 lb) was heated from the sole, starting at 554 °C and programmed up to 950 °C with continued heating until the top temperature had reached 500 °C, according to ASTM D 2014-97. The charge was water quenched, dried and heated under nitrogen in a retort at 10 °C/min to 1100 °C. The resulting cokes from both coking ovens were characterized by measurement of CSR and CRI according to ASTM D 5341-99, chemical analysis, apparent specific gravity, true specific gravity (helium pycnometer) and optical textures. Ruhr dilatations were carried out according to ASTM D 5515-97 and Gieseler fluidities according to ASTM D 2639-04.

3. Results and discussion

Proximate and ultimate analyses for the three coal blends used in this work as well as the two samples of charcoal are shown in Table 1. A word about the three blends is in order. Blend 1 consists of the following composition of commercial coking coals: 25% LV, 30% MV and 45% HV. The LV and HV are Appalachian coals and the MV is from western Canada. Blend 2 has 80% of the same HV and 20% of the same LV; Blend 3 has 70% HV and 30% LV. Blend 1 containing 30% MV coal is different than Blends 2 and 3 which are similar.

Of major importance in cokemaking is the quantity and nature of ash in the coke blend. The ash compositions of the three coal blends and two charcoals used in this work are given in Table 2. The ash compositions of the three coal blends are typical of commercial coking coal blends with silica and alumina dominating, with similar amounts in all three blends. The two hardwood charcoal samples, commercial products from the same producer, show some differences, mainly in the

Table 1 – Proximate and ultimate analysis of coal blends and charcoals						
		Blend 1	Blend 2	Blend 3	Charcoal 1	Charcoal 2
Proximate analysis						
Ash %	%	8.27	6.88	6.60	1.91	4.30
Volatile matter %	%	26.39	30.63	30.00	9.46	13.31
Fixed carbon %	%	65.34	62.49	63.40	88.63	82.39
Ultimate analysis (db)						
Carbon	%	82.24	81.78	81.81	91.65	86.38
Hydrogen	%	4.76	5.02	4.93	2.42	2.30
Nitrogen	%	1.45	1.54	1.56	0.33	0.50
Sulphur	%	0.77	0.93	0.89	<0.05	<0.05
Oxygen by difference	%	2.51	3.85	4.21	3.64	6.47

amount of silica. The important charcoal ash constituent to consider for this work is calcium oxide, which is high for both samples, along with potassium oxide. The calcium content of wood, and consequently charcoal, is something that is inevitably a potential problem with additions of charcoal and other biomass to coke blends.

In assessing the quality of metallurgical coke many parameters are used such as coke size, ASTM stability, CSR, CRI, grindability, hardness and various drum indices. Because the sample size used in this work prevents reliable measurement of a number of these parameters we restrict our analysis of coke quality to measurements of CSR (Coke Strength after Reaction) and CRI (Coke Reactivity Index). We will also discuss coke textural analysis briefly below.

The first set of coking runs involves Blend 1 and Charcoal 1 and was performed in a 30 lb coke oven. Charcoal, ground to pass 60 mesh, was added in amounts of 2, 5 and 10%. The CSR for Blend 1 alone was 56.7 which appears to be low for a coking coal blend. It must be pointed out that the short coking time of our 30 lb oven (~2.5 h) is expected to produce coke of poorer quality than a pilot or industrial scale coke oven where the coking times are of the order of 20 h or so.

Fig. 1 shows the CSRs and CRIs of the cokes produced from Blend 1 as a function of the amount of Charcoal 1 added to the blend. It is evident that there is a sharp, fairly linear, drop in CSR with charcoal addition. For 5% charcoal addition the CSR drops from 56.7 to 35.8, well outside the acceptable range for metallurgical coke. The CSR drop is accompanied, as expected by a concomitant rise in CRI. This behaviour has been observed previously for charcoal addition to a pilot scale charge (Sustainable Technology Australia) [6]. The Australian work involves the addition of −2 mm charcoal (5 and 10%) to a commercial coal blend. They found that the CSR varied from 74.0 to 21.5 to 0.4 with charcoal addition with the CRI varying from 19.0 to 25.3 to 33.0. It is clear that the charcoal addition results in unacceptably low quality coke in this case.

Blend 1 consists of three coking coals — low, mid and hi-vol. The influence of blend composition was also of some interest to us so that Blend 2 was formulated without any mid-vol coal to contain 20% LV and 80% HV. The coking results for Blend 2 with added Charcoal 1 are given in Fig. 2. In spite of the differences between the blends the general trend of CSR and
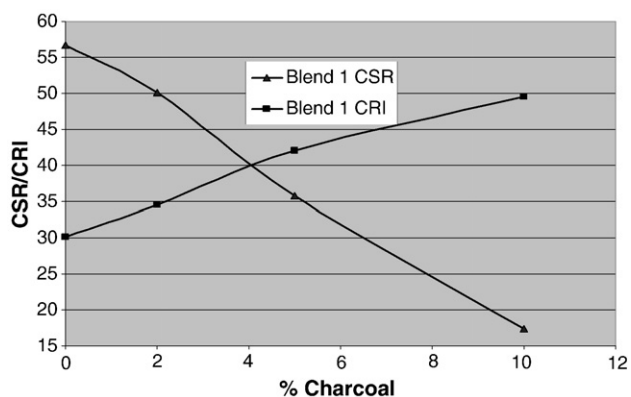
Table 2 – Ash composition of coal blends and charcoals

Ash analysis (db)		Blend 1	Blend 2	Blend 3	Charcoal 1	Charcoal 2
SiO_2	%	54.82	51.51	51.12	3.82	21.47
Al_2O_3	%	31.12	32.83	33.28	1.17	4.82
Fe_2O_3	%	5.84	7.43	7.23	1.14	4.40
TiO_2	%	1.59	1.46	1.49	0.15	0.28
P_2O_5	%	0.71	0.32	0.38	4.04	2.58
CaO	%	1.29	1.33	1.18	53.04	38.45
MgO	%	0.70	0.80	0.86	11.45	4.05
SO_3	%	0.99	1.09	1.11	4.67	2.62
Na_2O	%	0.38	0.65	0.60	0.47	1.62
K_2O	%	1.43	1.54	1.69	4.32	9.28
BaO	%	0.20	0.19	0.16	1.03	0.42
SrO	%	0.12	0.14	0.14	0.28	0.18
NiO	%	0.02	0.02	0.02	0.05	<0.007
V_2O_5	%	0.06	0.06	0.07	0.20	<0.020
LOF	%	0.69	0.59	0.62	5.24	6.36

Fig. 2 – Plots of the CSRs and CRIs for cokes from Blend 2 as function of the amount of charcoal 1 (–60 mesh) added to the blend. Blend 2 consists of 20% LV and 80% HV.
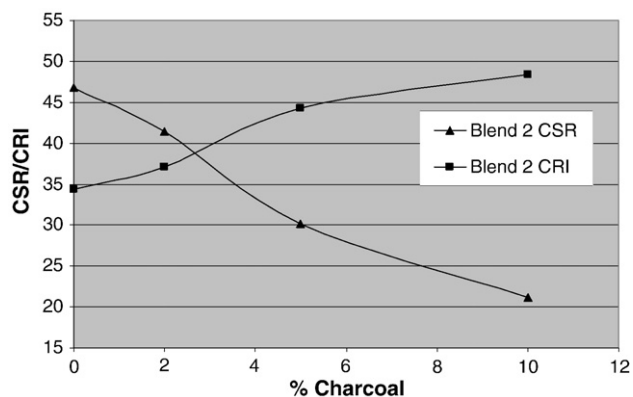
CRI variation are remarkably similar to the results obtained for Blend 1 shown in Fig. 1. It would appear that the change in blend produces no important difference in behaviour when some of the mid-vol coal in the blend is replaced by HV coal.

The third series of coking runs was carried out using the sole heated oven followed by processing the sole heated coke to 1100 °C in a retort under nitrogen. The composition of Blend 3 is slightly different from the composition of Blend 2 with 30% low-vol and 70% high-vol. It is seen from Figs. 2 and 3 that the CSR for Blend 3 (without charcoal) is higher than that for Blend 2 (without charcoal) even though the blends are quite similar. This may be due to the slight differences in the blends but is more probably associated with the manner of preparing the cokes. The 30 lb oven takes only 2.5 h to reach final temperature while the sole heated oven heats the bottom of the charge to 950 °C while the top of the charge attains 500 °C in ~6.5 h. This material is then heat treated to 1100 °C to produce met coke. The more rapid heating in the case of the 30 lb oven probably produces coke with lower CSR than the sole heat process.

The charcoal used in the third series of coking (Blend 3 with Charcoal 2) consisted of a carefully sized coarse fraction of –3/

8 +1/4 in. which was combined with Blend 3 at 5 and 10% concentration. The CSRs and CRIs of the cokes prepared from Blend 3 are shown in Fig. 3. It is clear that the increased particle size has a dramatic effect on the quality of the coke produced from the addition of 5 and 10% charcoal. The CSR and CRI lines do not cross each other as is observed in Figs. 1 and 2. This difference is shown more clearly in Fig. 4 where the CSR/CRI results for all three sets of experiments are plotted.

The explanation of why there is such a difference in coke quality between Blends 1 and 2, on the one hand, and Blend 3, on the other, is probably related both to the mineral matter content of the charcoal, particle size and the way the CSR/CRI tests are carried out. The cokes are heated to 1100 °C and maintained at that temperature for 2 h in an atmosphere of CO_2. CRI corresponds to the % weight loss during this process and CSR to the tumble strength of the resulting coke. Finely dispersed calcium (as in the case of Blends 1 and 2) would have a greater effect on weight loss than the same quantity of calcium dispersed in discrete pockets in the coke (as for Blend 3) which could result in less reactive, stronger coke.

These results obtained for small-scale coke ovens (30 lb and sole heated oven) demonstrate that it is possible to incorporate charcoal into industrial coking blends. Pilot scale tests are now required as this work moves forward. A recent paper by

Fig. 1 – Plots of the CSRs and CRIs for cokes from Blend 1 as a function of the amount of charcoal 1 (–60 mesh) added to the blend. Blend 1 consists of 25% LV, 30% MV and 45% HV.
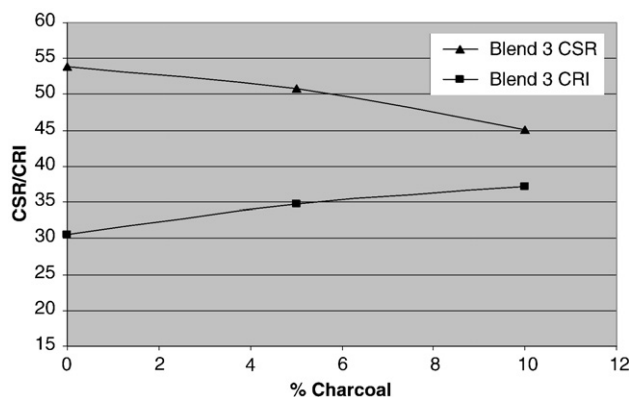

Fig. 3 – Plots of the CSRs and CRIs for cokes from Blend 3 as function of the amount of charcoal 2 (coarse –3/8 in. +1/4 in.) added to the blend. Blend 3 consists of 30% LV and 70% HV.
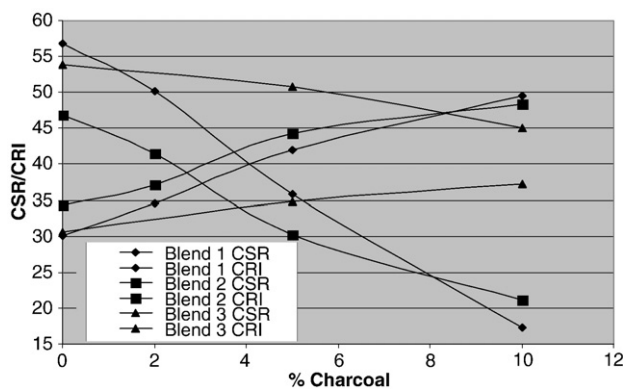
Fig. 4 – Combined plots of the CSRs and CRIs for cokes from all three blends as function of the amount of charcoal added to the blend.
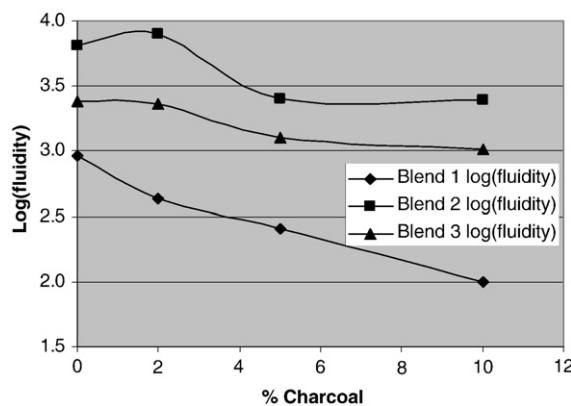

Fig. 5 – Variation of log(fluidity) of the blends with charcoal addition.

Nomura et al. [9] argues convincingly for increased efficiency in the blast furnace when the metallurgical coke used has larger than usual calcium content. Nomura indicates that increased reactivity of coke shifts the thermal reserve zone in the blast furnace to lower temperatures which has the result of increasing the blast furnace efficiency. This has been demonstrated by full scale testing at two Japanese steel plants. This would also suggest that the incorporation of charcoal into metallurgical coke would have a similar effect.

Although outside the scope of the present study, the economics of charcoal production and byproduct streams is important. Some recent papers discuss these topics in some detail [10,11]. The paper by Mohan et al. [10] reviews exhaustively the pyrolysis of wood/biomass to produce bio-oil and solid residue and proposes improved methodologies for improved yields of bio-oil. Syred et al. [11] propose a new process for the simultaneous production of charcoal, heat and power with low emissions and virtual carbon neutrality.

3.1. Other parameters of relevance

3.1.1. Expansion/contraction (E/C) properties
The sole heated oven permits the measurement of the expansion/contraction characteristics of blends and is of use industrially to predict high oven pressures and sticking coke charges. The E/C values for the blends used in this work as a function of added charcoal are given in Table 3.

For Blends 1 and 2 the E/C is independent of charcoal content. It must be emphasized that the charcoal added to these blends is finely divided, passing a 60 mesh screen. For Blend 3 it is evident that 5 and 10% of coarse charcoal additive

causes a definite decrease in blend contraction. This is a point of some interest since an industrial blend with an E/C of −10% would be considered a safe blend to charge to a battery and an E/C of −3% would be cause for concern. Further work is needed to see if this behaviour is a general occurring phenomenon.

3.1.2. Coke textures
Optical coke textures for all the cokes produced in this work have been measured. In all cases it was seen that, even up to 10% charcoal addition, there were no notable change in optical textures. What this means is that there is no significant incompatibility between the graphitizing coking coals and the added charcoal that would contribute to poor coke quality and is an encouraging result for this work.

3.1.3. Rheological properties of coal blends
Fluidity and dilatation tests were performed for all blends with the corresponding charcoal used in the coking runs. The fluidity results are given in Fig. 5 where we see a gentle decrease in log(fluidity) in all cases. This effect is smaller for Blends 2 and 3 compared with Blend 1 presumably the result of blend composition. Fig. 6 shows the dilatation results for the three blends. In all cases there is a reduction in % dilatation

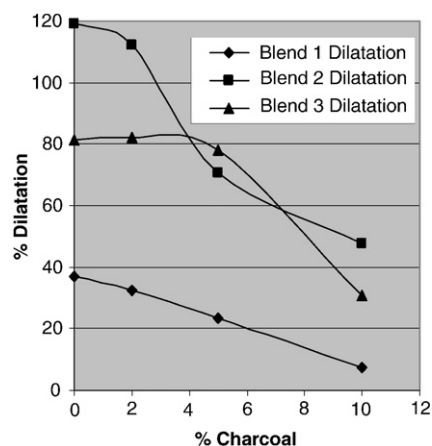| Table 3 – Expansion/contraction of blends with added charcoal				
% Charcoal	0	2	5	10
Blend 1	−14.6	−14.5	−14.5	
Blend 2	−18.2	−19.4	−18.1	−19.1
Blend 3	−10.4	−10.6	−9.0	−2.8
Blends 1 and 2 with fine (−60 mesh) charcoal Blend 3 with coarse (−3/8 +1/4) charcoal.				

Fig. 6 – Variation of dilatation of the blends with charcoal addition.

with charcoal addition but even at 10% added charcoal the dilatation remains at a workable level for a coking coal blend. This positive result is of importance for this work.

4.   Observations and conclusions

- Introduction of finely divided charcoal into a coking coal blend produces low quality coke.
- This may be the result of the high calcium concentration as well as other ash constituents in the charcoal which produces a coke that is more reactive to CO_2.
- Within a narrow range, variation blend composition does not affect coke quality.
- Larger particle size charcoal (−3/8 +1/4 in.) produces significantly better coke pointing the way to further work in this area.

Acknowledgements

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