



Reactivity of bio-coke with CO₂

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ABSTRACT

Incorporation of biomass-derived materials in coal blends for cokemaking is one of the strategies that could reduce the levels of greenhouse gas emissions produced by the steelmaking process. Bio-coke refers to the resultant coke prepared with the addition of charcoal to a coal blend. In this work, characteristics of bio-coke gasification by reacting with CO₂ were examined using Thermal Gravimetric Analysis. Bio-coke samples with different levels of charcoal addition to a coal blend were prepared in the CanmetENERGY pilot-scale coke oven. These samples were heated in CO₂ for identification of the minimum gasification temperature. Sample gasification rates at 1000 °C were also measured. It was observed that mineral content plays an important role in the gasification characteristics of the bio-cokes. Those with low mineral content behave very similarly to the reference coke. Higher mineral content bio-coke reacts with CO₂ at a lower temperature. It was found that the gasification characteristics of the bio-cokes are well described by the alkalinity index.

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1. Introduction

The iron and steel industry is a major greenhouse gas (GHG) emission point source. In 2005, the world wide iron and steel industry released 646 Mt CO₂ to the atmosphere and ranked as the fourth largest CO₂ point source [1]. Global awareness of the adverse effect of increasing atmospheric GHG content on climate change is increasing. As one of the major GHG emitters, the iron and steel industry world-wide is facing increasing pressure to reduce the environmental impact of its production processes.

Numerous technologies have been proposed to reduce the environmental impact and to improve the efficiency of the manufacturing process allowing sustainable development of the iron and steel industry [2]. Among the various proposed strategies, biomass application is potentially capable of significantly lowering the GHG emission of the cokemaking–blast furnace system in the integrated steelmaking process.

By definition, biomass incorporates all plant and animal matter on the earth's surface. It usually refers to material of recent biological origin that can be used as an energy source. Same as fossil fuels, biomass is also a carbon-based fuel. The combustion of a carbon-based fuel releases CO₂, a GHG, to the atmosphere. In terms of GHG emission, the crucial difference between fossil fuel and biomass lies in the time frame over which CO₂ is released. Since the natural process that transforms CO₂ from the atmosphere into fossil fuel takes millions of years, the CO₂

released from combustion of this type of fuel is considered as 'new' GHG. Hence, it contributes to the increase of GHG concentration in the atmosphere. On the other hand, combustion of biomass releases CO₂ that is balanced by the CO₂ captured during its growth. Therefore, the argument is that biomass is considered GHG 'neutral'.

Because of the GHG neutral characteristic of biomass, substitution of fossil fuel consumed in the ironmaking process by biomass is able to maintain both the supply of carbon required by the reduction and energy needed for melting and, at the same time, leading to a reduction in the GHG emission of the process.

In the integrated steelmaking process, the cokemaking–blast furnace system is the major CO₂ emission source and the focus of the present work. Biomass can be applied in two locations in the cokemaking–blast furnace system, Fig. 1. By substituting a portion of the coal blend by biomass, the resultant coke is termed bio-coke to distinguish it from coke produced entirely from coal. As bio-coke is gasified in the blast furnace, a portion of CO₂ released originates from the biomass and thus does not contribute to the increase in atmospheric GHG concentration. Besides cokemaking, biomass can also be used as a substitute for auxiliary fuel directly injected into the furnace. Injection of auxiliary fuel, such as coal, oil and natural gas, in the hearth of the blast furnace via tuyeres is a common practice in industrial operations. Substituting fossil fuel injection by biomass could further reduce the GHG emissions associated with the ironmaking process [3].

Experimental work has recently been performed on preparing bio-coke with various levels of charcoal addition to a coal blend and the properties of the resultant bio-cokes have been assessed [4,5]. It was observed that bio-cokemaking is a challenging task. This is because industrial coke consists of polycrystalline graphitic material produced generally from a carefully selected metallurgical coal blend. The coke

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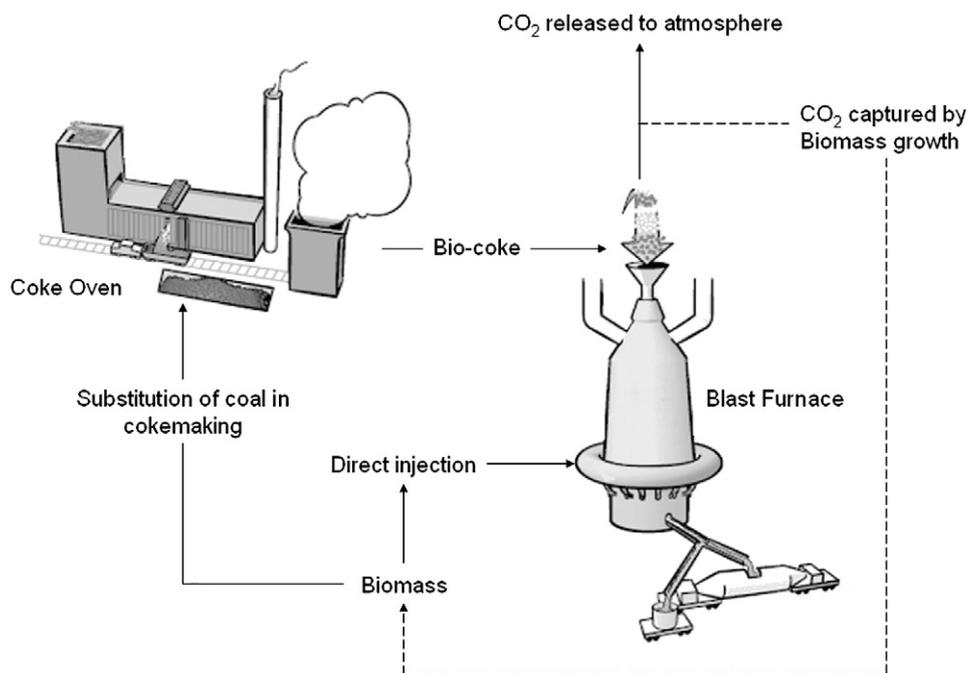


Fig. 1. Biomass application in blast furnace ironmaking.

produced from the selected coal blend must have just the right combination of physical stability and chemical reactivity for it to be compatible with the modern blast furnace processes. Any foreign material introduced into the met coal blend has the potential to interfere with the graphitization process, and hence affect both the physical and chemical properties of the resultant coke. In particular, it was observed that CSR of the resultant bio-coke was decreased as compared to the coke produced from the same coal blend without charcoal addition. Moreover, the CRI was found to be increased [4,5]. Both observations suggested that addition of charcoal to the coal blend enhances the reactivity of the resultant bio-coke.

To further understand the effect of charcoal addition to the coal blend on the properties of the resultant bio-coke, the CO₂ gasification of bio-coke was studied by thermogravimetric analysis (TGA).

2. Experimental

Bio-coke samples studied in this work were prepared using the CanmetENERGY pilot-scale coke oven with different degrees of charcoal addition to the base coal blend as summarized in Table 1. For comparison, the coke sample produced from the base coal blend was also included as the reference. In the TGA tests, gasification of the samples was performed entirely under CO₂ atmosphere. About 1.5 g of sample was heated at 10 °C/min to 1000 °C to obtain the minimum gasification temperatures. Samples were then maintained at 1000 °C for 60 min to determine the isothermal reaction kinetics.

Table 1
Description of bio-coke samples.

Sample	Description	Particle size
Reference	Coke produced from base blend	0.6–1.0 mm
Bio-Coke A	Coke produced from base blend with addition of 2% charcoal	0.6–1.0 mm
Bio-Coke B	Coke produced from base blend with addition of 3% charcoal	0.6–1.0 mm
Bio-Coke C	Coke produced from base blend with addition of 5% charcoal	0.6–1.0 mm

3. Results and discussion

TGA experiments revealed that sample dehydration and devolatilization was completed when the temperature reached about 700 °C and mass was stabilized. Any further change in sample mass was due to the gasification of carbon by reaction with CO₂.

The rate of sample mass change of the cokes during heating from 700 °C to 1000 °C is shown in Fig. 2. Biocokes A and B behaved identically to the reference coke produced from the base coal blend. Biocoke C, however, was the most reactive in CO₂. Its gasification was initiated at a lower temperature and its rate of gasification was also faster as compared to other samples.

The isothermal gasification kinetics of the cokes at 1000 °C was compared, as shown in Fig. 3. In the figure, the sample mass was normalized with respect to the mass reached at 1000 °C for comparison. The gasification kinetics of Biocokes A and B were identical to that of the reference coke. For all samples examined, the mass decreased linearly with time and the slope of the straight line represented the gasification rate constant at 1000 °C. The gasification

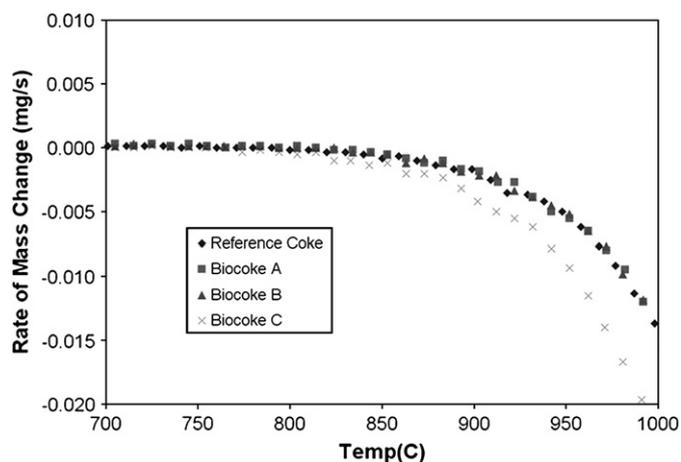


Fig. 2. Rate of mass change of coke samples with temperature.

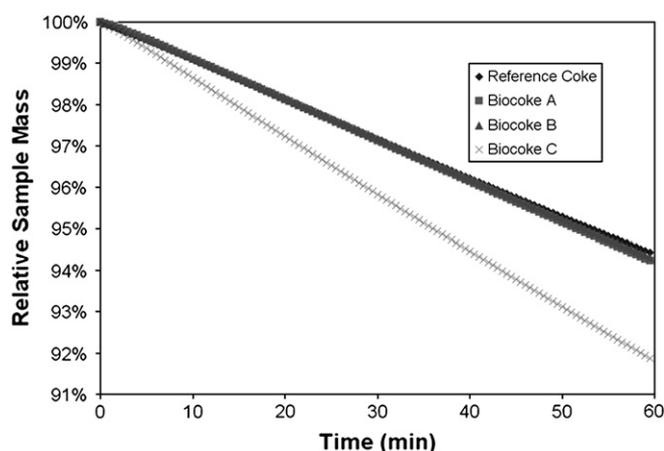


Fig. 3. Gasification kinetics of cokes at 1000 °C.

rate of Biocoke C was 0.14%/min whereas the gasification rates of the reference coke and Biocokes A and B were only 0.10%/min.

The minimum gasification temperatures and reaction rates at 1000 °C are summarized in Table 2.

TGA results revealed that addition of 2% and 3% charcoal to the coal blend did not change the CO₂ gasification behaviour of the resultant biocoke as compared to the reference coke. However, when charcoal addition was increased to 5%, the resultant biocoke had a lower initial gasification temperature and a higher reaction kinetics at 1000 °C.

Nomura et al of Nippon Steel Corp. [6] have proposed the use of reactive coke to improve the reaction efficiency of the blast furnace. The use of reactive coke signifies that its gasification by CO₂ can proceed at a relatively lower temperature and thus result in a reduction in the thermal reserve zone temperature (TRZT) of the blast furnace. A lowering in the TRZT shifts the equilibrium of reaction (1) to the right. Consequently, the CO₂ proportion in the furnace top gas is increased, which leads to a better utilization of the input carbon for reduction of the iron ore and to a lower coke rate.



As found in the TGA experiments, addition of charcoal to the coal blend may increase the reactivity of the resultant biocoke. Besides substituting fossil fuel by renewable fuel, addition of charcoal to the coal blend in bio-cokemaking could further reduce the total fuel consumption, hence reducing the GHG emission of the blast furnace ironmaking process.

The reduction in GHG emission upon using Biocoke C in the blast furnace process was calculated using a blast furnace heat and mass balance model developed at CanmetENERGY [3]. For modeling purposes,

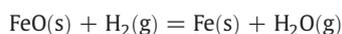
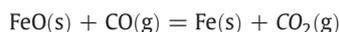
Table 2
Summary of TGA results.

Sample	Description	Alkalinity index	Min gasification temp	Rate of mass loss at 1000 °C
Reference	Coke produced from base blend	1.69%	810–830 °C	0.10%/min
Bio-Coke A	Coke produced from base blend with addition of 2% charcoal	1.73%	810–830 °C	0.10%/min
Bio-Coke B	Coke produced from base blend with addition of 3% charcoal	1.70%	810–830 °C	0.10%/min
Bio-Coke C	Coke produced from base blend with addition of 5% charcoal	1.83%	760–780 °C	0.14%/min

the blast furnace was divided into three zones. The two boundaries that define these three zones are:

1. the 1000 °C isotherm, and
2. the bosh region where CO is the only carbon containing gas.

The 1000 °C isotherm represents the thermal reserve zone temperature (TRZT) of the furnace. Above the thermal reserve zone, the temperature is too low to allow gasification of coke by CO₂ to proceed. Moreover, the gas composition at the 1000 °C isotherm is assumed governed by the equilibrium of the following reactions:



In the bosh region of the blast furnace, the gases produced in the hearth ascend through a bed of hot coke and all of the CO₂ and moisture are reduced into CO and H₂, respectively. These two boundaries provide information on the composition of the gas phase, which allows stage by stage mass balance calculation.

As shown in Fig. 2, the initial gasification temperature of Biocoke C is lower than that of the reference coke. Typically, the TRZT of an industrial blast furnace is about 1000 °C. Below this threshold temperature, the gasification reaction is virtually halted. Assuming the reference coke behaves similarly to a typical industrial coke, the rate of mass loss of the reference coke at 1000 °C is 0.014 mg/s. Biocoke C reaches the same rate of mass loss with a temperature as low as 970 °C.

Using the blast furnace heat and mass balance model developed at CanmetENERGY, blast furnace coke rates operating with TRZT at 1000 °C and 970 °C were calculated. In the calculation, it was assumed that the PCI rate for both TRZT was maintained at 140 kg/tHM. Moreover, the CO₂ emission by the process was calculated.

The calculations found that the amount of CO₂ emitted using the reference coke was 1.20 t CO₂/tHM. When Biocoke C was used, the emission level was lowered to 1.14 t CO₂/tHM. The CO₂ reduction was contributed by both a decrease in coke rate due to the lowering of TRZT and substitution of fossil carbon by bio-carbon. The annual blast furnace iron production in Canada is about 8.7 Mt/yr [7]. Assuming that the entire Canadian hot metal production capacity utilizes bio-coke produced by addition of 5% charcoal to the coal blend, the annual CO₂ emission associated with the blast furnace operation in Canada can be reduced from 10.4 Mt CO₂/yr to 9.9 Mt CO₂/yr, approximately 5%.

It should be apparent from the results presented and ensuing discussion that increasing the charcoal loading in the coal blend could further reduce the CO₂ emission of the blast furnace ironmaking process. However, as shown by the TGA data, an increase in charcoal loading could significantly increase the reactivity of the resultant biocoke. In order to maintain the hot strength coke properties required for efficient blast furnace application, the amount of charcoal that can be added to a coal blend is limited.

Reactivity with CO₂ is one of the most important characteristics that influences the hot strength of a coke. One of the factors influencing the coke reactivity is its mineral matter content. It is well known that alkaline metals catalyze the gasification reaction of coke. As suggested by Kaczorowski et al. [8], the reactivity of coke is closely related to the alkalinity index, defined as follows:

$$\text{Alkalinity Index} = \frac{[\text{Fe}_2\text{O}_3] + [\text{CaO}] + [\text{MgO}] + [\text{K}_2\text{O}] + [\text{Na}_2\text{O}]}{[\text{SiO}_2] + [\text{Al}_2\text{O}_3]} \% \text{Ash}$$

Alkalinity indices of the biocokes were calculated from the ash content and composition analyses and are listed in Table 2. Alkalinity indices of the reference coke, Biocokes A and B are very similar but that of Biocoke C is significantly increased. This observation supports the TGA results obtained. For the bio-cokes studied in this work, the

alkalinity index is found to be a useful indicator that can be used for estimating the maximum amount of charcoal that can be added to a coal blend without sacrificing the hot strength property of the resultant biocoke.

4. Conclusions

Bio-coke samples were prepared in CanmetENERGY's pilot-scale coke oven by carbonization of a coal blend with varying charcoal addition levels. The CO₂ reactivity of the biocokes was measured via TGA. The bio-cokes produced from 2% and 3% charcoal addition to the coal blend behave similarly to the reference coke in terms of their reactivity in CO₂. As the charcoal addition to the coal blend increased to 5%, the resultant biocoke had a lower initial gasification temperature and a higher reaction kinetics at 1000 °C.

Heat and mass balance calculations revealed that utilization of bio-coke with 5% charcoal addition to the coal blend in blast furnace ironmaking process could reduce the CO₂ emission from 1.20 t CO₂/tHM to 1.14 t CO₂/tHM. Projecting this result to the entire Canadian blast furnace annual iron production capacity, the CO₂ emission associated with the process can be reduced from 10.4 MtCO₂/yr to 9.9 MtCO₂/yr, approximately 5%. The reduction in CO₂ achievable is contributed by both a decrease in thermal reserve zone temperature of the blast furnace due to the increased coke reactivity and from the substitution of fossil fuel by carbon neutral bio-fuel.

Reactivity of the bio-cokes was found to be well correlated to the alkalinity index. This indicator can be used for estimating the maximum amount of charcoal that can be added to a coal blend without sacrificing the hot strength property of the resultant biocoke.

Acknowledgements

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