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The effect of feedstock origin and temperature on the structure and reactivity of char from pyrolysis at 1300–2800 °C

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ABSTRACT

This study reports the effect of feedstock origin, residence time, and heat treatment temperature on CO_2 and O_2 reactivities, nanostructure and carbon chemistry of chars prepared at 1300, 1600, 2400, and 2800 °C in a slow pyrolysis reactor. The structure of char was characterized by transmission electron microscopy and Raman spectroscopy. The CO_2 and O_2 reactivity of char was investigated by thermogravimetric analysis. Results showed that the ash composition and residence time influence the char reactivity less than the heat treatment temperature. The heat treatment temperature and co-pyrolysis of pinewood char with biooil decreased the CO_2 reactivity, approaching that of metallurgical coke. Importantly from a technological standpoint, the reactivities of char from high temperature pyrolysis (2400–2800 °C) were similar to those of metallurgical coke, emphasizing the importance of graphitizing temperatures on the char behavior. Moreover, graphitization of chars from wood and herbaceous biomass increased with the increasing heat treatment temperature, leading to formation of graphitizing carbon.

1. Introduction

Ferroalloy production is energy-intensive, consuming large amounts of both electricity and coke. Coke is used in this process to reduce metal oxides naturally present in ores to produce the base metal. Development of cost-effective, renewable reductants is environmentally desirable because global ferroalloy production releases about 55 Mt of CO_2 emissions annually [1]. Using carbon sources from renewable, plant-based feeds has potential to replace fossil-based reducing agents and effectively reduce CO_2 emissions. In recent years, much progress has been made on conversion of plant-based materials to carbonaceous char materials; some of these materials may have potential as reductants. However, metallurgical production continues to rely on fossil-based reductants due to limited knowledge of char properties, knowledge gaps in the conditions required to produce chars with acceptable reactivity, and high costs.

Ferroalloys are defined as iron-rich alloys which contain high proportions of Si, Mn, C, Cr, etc. which improve tensile strength, wear, corrosion resistance, and toughness [1]. Ferroalloys are produced in submerged-arc furnaces at temperatures > 1500 °C. Within the furnace, a three-phase electrode is inserted into a mixture consisting of metal oxide and carbonaceous reductants, typically metallurgical coke and coal [2]. The carbonaceous materials serve many roles, with the primary function being to reduce the metal oxide to form the base metal [3]. Additionally, the carbonaceous materials improve gas distribution during the reduction process, trap SiO gas, and enhance electrical resistance of the reaction mixture [4,5]. The most important properties of the carbonaceous reductant are high reactivity, high conversion, and low levels of impurities (such as sulphur and phosphorus) [6]. Low ash content is important, as each additional percent of ash in carbonaceous reductant increases slag volume by about 10–15 kg t^{-1} of ferroalloy, thereby increasing the electric power required for smelting [5].

In recent years, many studies investigated production and/or co-production of carbonaceous solids by pyrolysis treatment of wide variety of renewable feedstocks [3,5,7–11]. In comparison with the metallurgical coke traditionally used in ferroalloy production, carbon produced from renewable feedstocks contains less fixed carbon and a greater percentage of volatile components and may need to be

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graphitized prior to use as a reductant [11]. Although different types of biomass can be converted into biochar, herbaceous biomass species are especially promising candidates for the use as carbonaceous reductants in ferroalloy industries because of their high growth rate and relative ease of harvest [7]. Despite these arguments in favor of herbaceous biochars, the majority of previous investigations have studied charcoals produced at temperatures $< 1000\,^{\circ}C$ [12–18]. Thus, the effects of feedstock composition, treatment at temperatures greater than $> 1250\,^{\circ}C$, and residence time on the char reactivity and structure have not been studied in depth. In particular, herbaceous feedstocks contain high amounts of alkali metals which promote faster devolatilization rates and suppress tar formation, leading to higher char yields and higher CO_2/O_2 reactivity than charcoals produced from wood [19]. The high reactivity of biochar reductant may be advantageous in some cases within the ferroalloy industries. However, the use of a reductant more reactive than metallurgical coke may increase maintenance costs due to the decreased electrical conductivity [20,21]. Therefore, reductant reactivity becomes a key variable that must be understood in potential replacements for metallurgical coke. Likewise, the effect of residual alkali metal content in biochar produced from pyrolysis of herbaceous biomass must be considered. Previous studies report that nearly 50% of the potassium in the herbaceous biomass is released in the temperature range from 900–1250 °C, with residual potassium likely being present as counter ions in phenolate groups [22,23]. In addition, alkali metal ions (K^+ and Ca^{2+}) promote catalytic conversion of tars to small molecule products in a temperature range from 700 to 900 °C [24]. However, treatment at temperatures greater than 1250 °C will be required to produce graphitic or turbostratic carbons suitable as metallurgical coke, and the fate of potassium at these temperatures is not clear. In addition to knowledge gaps in reactivity and composition, the cost of biochar reductants is not competitive with metallurgical coke, in part due to low biochar yields. Previous studies have examined deposition of biooil and tar recycling to increase char yields and to decrease char reactivity [11,25]. For example, impregnating biooil within an existing char increased the total char yield with minimal effect on char microporosity and adsorption properties [26]. Similarly, deposition of biooil on biochar prior to pyrolysis promoted formation of oxygen-containing functional groups and transformation of small aromatic rings to larger aromatic rings [27]. However, literature data are scarce that describe the effect of biooil deposition on resulting char properties that impact metallurgical applications, adding uncertainty to the use of biooil impregnation as an approach to increase char yields and decrease char reactivity.

In summary, renewable feeds have potential as environmentally benign replacements to fossil-based reductants used in ferroalloys production, but knowledge of relationships between feedstock, operating conditions, and biochar properties is limited. In this study, the impacts of feedstock, heat treatment temperature (from 1600 to 2800 °C), residence time, and nanostructure on the CO_2/O_2 reactivity of woody and herbaceous biomass were investigated. The specific objectives of this study were to: (1) develop structure–property relationships governing the CO_2 and O_2 reactivity of biochar at high-temperatures, and (2) determine the treatment conditions and feedstock composition which decrease char reactivity to levels that are suitable for application in ferroalloy industries.

2. Materials and methods

Pinewood, beechwood, wheat straw, leached wheat straw and alfalfa straw were chosen for the fast pyrolysis study in a drop tube furnace (DTF). The low-ash containing wood (pinewood, beechwood) of syringyl (S) or guaiacyl-syringyl (GS) lignin types and herbaceous biomass (wheat straw, alfalfa straw) of hydroxy phenol-guaiacyl-syringyl (HGS) lignin type, which are rich in K, Ca and Si elements, were selected to investigate the effect of differences in ash composition and organic matter (cellulose, hemicellulose, lignin, extractives) on the char structure and reactivity. The wheat straw was leached in deionized water (room temperature) by continuous stirring for 12 h, followed by drying at 30 °C in an oven desiccator without any ventilation. Due to leaching of wheat straw, the metal content was reduced to ≈60% of the original value and the Cl, S, K, Na and P contents were strongly reduced. Char samples were generated in the drop tube reactor at 1250 °C, as described in detail by Trubetskaya et al. [28]. The temperature of 1250 °C that is the wall temperature of the DTF was selected to ensure the complete pyrolysis. The reactor consists of an alumina tube (internal diameter: 54 mm, heated length: 1.06 m) heated by four heating elements with independent temperature control. The experiments were conducted by feeding ≈5 g of biomass at a rate of 0.2 g min^{-1}. Both primary (0.18 l min^{-1} measured at 20 °C and 101.3 kPa) and secondary (4.8 l min^{-1} measured at 20 °C and 101.3 kPa) feed gases were N_2. The residence time of fuel particles was estimated to be about 1 s, taking into account density changes during pyrolysis. The char samples generated at 1250 °C were further heated up to 1300, 1600, 2400, and 2800 °C in high-temperature furnaces. The effect of residence time on the char properties was studied by keeping samples at 1300 or 1600 °C for 2 or 12 h.

Pinewood biooil was supplied by BTG BioLiquids. When used, 10 g of pinewood char mixed with 20 mL of biooil were stirred at 40 °C for 5 days and further reacted at 1600 °C in a high-temperature furnace. The CO_2 and O_2 reactivity of all char samples was investigated in a thermogravimetric analyzer. Reactivities of biomass chars and metallurgical coke were compared using reaction rates calculated from the derived kinetic parameters. TEM analysis and Raman spectroscopy were performed to characterize the effect of temperature, residence time, and feedstock on the char carbon chemistry and nanostructure.

2.1. Raw biomass characterization

The ultimate and proximate analysis of pinewood, beechwood, wheat straw, leached wheat straw, alfalfa straw, metallurgical coke and pinewood biooil is shown in Table 1.

The fuels were milled on a Retsch rotor mill RZ200 and sieved to a particle size fraction of 0.2–0.425 mm. The analysis of biomass constituents (cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, and extractives) was conducted according to NREL technical reports [29–31] and Thammasouk et al. [32], and shown in Table 2.

2.2. High-temperature furnace (1300–2400 °C)

The char samples were further treated in the high-temperature furnace LHTG 200–300/20-1G (Carbolite Gero, Germany), as shown in Fig. 1. The furnace can be operated at temperatures up to 1800 °C and at heating rates up to 20 °C min^{-1}. Prior to each experiment, 5 g of the char sample was loaded into the A_2O_3 crucible (Almath Crucibles Ltd, UK) placed in the graphite retort middle. Prior to pyrolysis, the furnace was repeatedly evacuated and purged by argon. The char sample was heated at 10 °C min^{-1} up to 1300 and 1600 °C and kept at that temperature for 2 h. The sample was cooled to room temperature at a rate of 20 °C min^{-1}. Another high-temperature furnace 200–300/30-1G (Carbolite Gero, Germany) was used to heat the char sample to 2400 °C. Samples were stored in sealed plastic containers.

2.3. High-temperature furnace (2800 °C)

The biochar was treated in a vacuum induction furnace (max. 60 kW, max. 10 kHz) with a chamber volume of 0.5 m^3, as shown in Fig. 2. The heating vessel consists of a three-part crucible with an outer alumina crucible (outer diameter: 130 mm, inner diameter: 110 mm, height: 300 mm), a middle carbon crucible (outer diameter: 90 mm, inner diameter: 50 mm, height: 145 mm) and an inner glass carbon crucible (outer diameter: 50 mm, inner diameter: 38 mm, height: 125 mm). The three-part crucible was positioned in an induction coil.