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A Study on Densification and CO_2 Gasification of Biocarbon

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Biocarbon is a promising alternative to fossil reductants for reducing greenhouse gas emissions and increasing sustainability of the metallurgical industry. In comparison to conventional reductants (i.e., petroleum coke and coal), biocarbon has low density, poor mechanical strength and high reactivity. Densification is an efficient way to upgrade biocarbon and improve its undesirable properties. In this study, woody biocarbon was compressed into briquettes using two different binders, starch and lignin. The biocarbon densification process, basic fuel properties, mechanical strength and moisture uptake of the biocarbon briquettes were studied. Effects of type and amount of binder on properties of the briquettes were evaluated. The CO_2 gasification behaviours of the biocarbon briquettes were investigated by performing thermogravimetric analyses. The results showed that high mechanical compressing force was required for producing biocarbon briquettes with addition of binder. The biocarbon briquettes produced with addition of starch achieved higher mechanical strength compared to those with addition of lignin. In addition, the mechanical strength of the biocarbon briquettes increased with increasing starch content. For all biocarbon briquettes produced with and without binder addition, there was no moisture uptake after stored for 4 weeks at 35 °C and 98% relative humidity. The saturated moisture content of all briquettes densified with addition of binder were higher than those produced with only biocarbon. Compared to biocarbon powder, conversion of the biocarbon briquettes with and without binder addition took significantly longer time according to thermogravimetric CO_2 gasification tests. The results of the present work indicate that densification of biocarbon is a promising measure to improve biocarbon properties for further handling, logistics and storage and also for final utilization as reductant in metallurgical industries.

1. Introduction

The production of silicon and metals causes intensive greenhouse gas (GHG) emissions due to use of fossilised carbonaceous materials as reductants in their production processes. Reducing GHG emissions is one of the challenges that this industry is facing now and needs to take further actions on. One major opportunity for reducing GHG emissions from metal production is to gradually substitute fossil-fuel based reductants such as coke and coal by renewables based biocarbon (Wang et al., 2016). Biocarbon, as an alternative to fossil coke and coal, can be used as a fuel and reductant in the blast and smelting furnaces together with fluxes to produce hot metal and slag. In addition, biocarbon can also be a promising candidate to replace fossil fuels for energy production. Biocarbon can be produced from a wide range of biomass materials that are available in large amount and at low cost. Recently, more attention has been given to full scale biocarbon production with high solid (fixed) carbon yield and efficient use of by-products such as condensates. In light of this, use of biocarbon in metal production is economically attractive. Additionally, in comparison to fossil reductants, biocarbon has low content of ash and some unwanted inorganic elements (e.g., sulphur and phosphorous), which will help to improve quality of the final products.

Biocarbon is produced by heating biomass material in the absence of oxygen or with lean oxygen to a temperature above 300 °C with a residence time from minutes to days. Biocarbon yield and properties and distribution of by-products depend highly on properties of the raw biomass and production process conditions. During a carbonization process, volatile compounds release from the biomass, leaving behind a lightweight and black biocarbon with 70-90% carbon (Wang et al., 2016). However, compared to coke and coal, the fixed

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carbon content of biocarbon is normally lower. With high porosity and fragile structure, the volumetric energy density and mechanical strength of biocarbon are rather poor (Huo et al., 2013). As a result of this, fines are generated during handling and transportation of biocarbon from production site to end use plant and further storage before final usage. This cause loss of carbon, increase of explosion risk and pollution to the surrounding environment. As the biocarbon is used as reductant in certain metal production processes, the low mechanical strength of biocarbon is also unwanted. For example, during manganese production, the biocarbon fed into the furnace might break into small pieces and fines that are released out together with flue gas without actually involving in the metal production process. Consequently, less biocarbon can reach the slag bed to react with the metal ore and slag, affecting yield and properties of the metal product. It results in loss of both carbon mass and increased energy consumption in the metal production process (Huo et al., 2013). On the other hand, CO_2 gasification reactivity is among the most important properties of carbon materials used as reductant during metal production processes. Less reactive biocarbon is desired for certain metal production processes. However, biocarbon with porous structure and high surface area often has a high reactivity towards CO_2 in a metal production process at high temperature. A considerable fraction of the biocarbon fed into the metal production process might be consumed due to reaction with CO_2, causing loss of carbon mass. Moreover, CO_2 gasification (Boudouard reaction) is an endothermic reaction. Reaction of biocarbon with CO_2 in the smelting furnace will reduce the amount of heat available for the metal production.

Densification can be an efficient measure to upgrade biocarbon, gaining favorable properties. In comparison to raw biocarbon, densified biocarbon, e.g. pellets or briquettes, have superior quality such as enhanced abrasion resistance and increased density, which significantly influence the handling, logistics and storage characteristics of biocarbon (Hu et al., 2015). Furthermore, conversion properties of densified biocarbon towards CO_2 are expected to be considerably different than those of raw biocarbon, due to increased density and lower porosity and surface area (Kawakami et al., 2004). Previous work mainly focused on densification of biomass and torrefied biomass (Kaliyan et al., 2004). Compacting and densification of biocarbon have not been given enough attention, with only limited study results reported. Compared to raw biomass or torrefied biomass, the biocarbon has considerable different physical and chemical properties. Detailed studies are needed to investigate densification behaviors of biocarbon, effects of compacting conditions and the use of binders on bonding mechanisms for different densified biocarbons, as well as their physicochemical properties.

In the present work, the densification process of one industry biocarbon was described and properties of the derived biocarbon briquettes were characterized. The effects of binders on mechanical and moisture uptake properties were studied. The CO_2 gasification reactivity of the produced biocarbon briquettes was also studied.

2. Experimental section

2.1 Materials and binders

In the present work, an industrial charcoal was used for the densification study. The industrial charcoal was produced at atmospheric pressure with slow heating rate and long residence time. The received charcoal was ground by a laboratory mill to particles smaller than 1 mm. Then the ground charcoal particles were further sieved and the fraction with size smaller than 500 μm was used for further densification tests. Alkaline lignin, as a by-product from pulp and paper industry, was used as binder in this work. The alkaline lignin is a dry light brown powder with particle size smaller than 20 μm. Wheat starch was also tested as binder in the current work, which is a white powder, purchased from VWR International, LLC (Norway). Before the compacting test, the charcoal powder was dried at 105 °C for 12 hours first. Then the dried charcoal powder was mixed with water and binder and thoroughly stirred. The amount of water added was 20 % (w/w), and was introduced into the charcoal powder in order to enhance bonding through capillary binding effects. The dosage of binder to the charcoal powder were 5 and 20 % (w/w). The charcoal powder with only addition of water was also tested for comparison purpose. The prepared mixtures of charcoal with water and binders were stored in plastic bags. In total 5 samples were prepared, including biocarbon with 20% water only (w/w), biocarbon with 20% water (w/w) and 5 and 20% (w/w) starch and biocarbon with 20% water (w/w) and 5 and 20% (w/w) alkaline lignin.

2.2 Biocarbon densification

Densification of biocarbon into briquettes was carried out by using a roller press (B050 A, K.R.KOMAREK, INC). Around 500 grams of prepared charcoal powders was fed into a feed hopper and smoothly vertically moved down to the bottom of the hopper with assistance of a vertical agitating screw. As the sample powder arrives at the bottom of the hopper, it falls into a horizontal screw feeder and is pushed into the nip zone and briquetted (compacted) between two rollers. By varying the speed of the vertical agitating screw and horizontal screw, it is possible to control the amount of sample powder for further pressing in the nip zone. The speed of the rollers can also be controlled, and a fully adjustable hydraulic system provides the force holding the rollers together. The gap between the rollers can be changed, which makes it possible to produce briquettes with different thicknesses. In the present work, the roller gap is 0.3 mm for all press tests. The briquettes are collected in a sample bin and stored for further analysis. The feeder screw speed and torque were the same for all compacting tests. Key operational parameters of the roller press were monitored and recorded, including roller torque, speed and force. The morphology and microstructure of ground biocarbon and selected biocarbon briquettes were examined by a scanning electron microscopy (FESEM, Zeiss Ultra).

2.3 Moisture uptake test

The moisture uptake behaviours of the produced briquettes were investigated by storing them in a climate cabinet (Vötsch VC3 0100) under well-controlled conditions. Prior to moisture uptake testing, the briquettes were dried in a drying chamber at 105 °C for 12 hours. Then the dried briquettes were loaded in five glass containers and stored in the cabinet at a temperature of 35 °C and a constant relative humidity of 98%. The mass of the briquettes was measured after storage times of 2, 4, 20, 72 hours, and 4 weeks.

2.4 CO_2 gasification reactivity test

The reactivity of densified biocarbon towards CO_2 was studied by using a thermogravimetric analyser (Mettler Toledo TGA 851^e). Before one experiment, one small piece (around 10 mg) was cut from a densified biocarbon briquette. The small sample piece was loaded in an alumina crucible that was heated up in the TGA for the gasification test. After loading the sample, the TGA was first purged by N_2 gas flowing upwards, for 30 minutes at room temperature. Then the temperature was increased from room temperature to 850 °C with a heating rate of 13 °C/min in the presence of N_2. When the temperature reached 850 °C, the N_2 flow was shifted to CO_2 and the sample was exposed at 850 °C for 120 minutes. The sample weight loss was continuously recorded as one experiment started at room temperature. However, only the weight loss measured in the isothermal stage was used for further treatment and comparison. After the isothermal stage, the gas flow was shifted back to N_2 and the TGA furnace cooled down to room temperature. For each sample, at least three sample pieces were cut from different briquettes and then gasified with exactly the same experimental procedures and at the same conditions. There was no significant difference in the weight loss behaviours of the tested sample pieces from one kind of sample.

3. Results and discussion

3.1 Densification of biocarbon

Table 1 presents proximate analyses results of the studied biocarbon and the two binders, alkaline lignin and wheat starch. It is interesting to see that the alkaline lignin has rather high ash content. The alkaline lignin is a by-product from pulp and paper production plants. Calcium bisulfite is used for pulping and making of paper, which results in abundance of calcium and sulphur in the alkaline lignin and its ash as well. According to an ash analysis, a significant amount of calcium is retained as oxide in the ash residues, partially explaining the high ash content of the alkaline lignin.

Table 1: Proximate analysis of the biocarbon, alkaline lignin and wheat starch

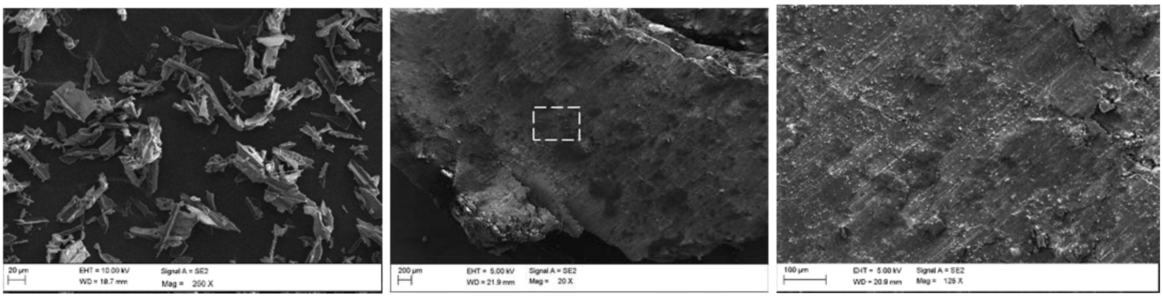
	Biocarbon	Alkaline lignin	Wheat starch
Volatile matter (wt %, d.b.)	10.1	61.4	96.5
Ash (wt %, d.b.)	3.3	18.4	0.6
Fixed carbon *(wt %, d.b.)	86.6	20.2	2.9

d.b.: dry basis; *: by difference.

Figure 1 shows photos of (a) biocarbon powder, and briquettes made from (b) biocarbon, (c) biocarbon + 20% alkali lignin and (d) biocarbon + 20% starch, after drying at 105 °C for 12 hours. It can be seen that biocarbon briquettes produced without binder addition cracked into pieces, and can easily be crushed by fingers. It indicates that, for the biocarbon briquettes with only water addition, the bonds between adjacent particles are rather weak. Therefore, these briquettes have low mechanical strength and will lose mass due to breakage during handling, logistics and storage. On the other hand, the biocarbon briquettes with binder addition showed compact structure and smooth surface and no clear cracks could be observed even after drying at 105 °C for 12 hours. All the briquettes produced with addition of binders could not be broken by fingers before or after drying. Upon densification, particles are compacted and bonded together via different binding forces.

Macroscopically, the particles can be together with and without a solid bridge between the particles. Without presence of a solid bridge, the particles can interlock and fold with each other resulting in interlocking bonds, which are short range binding forces and weak as well (Kaliyan et al., 2004). On the other hand, the solid bridge binding of particles is mainly related to crystallization of some ingredients, plasticization, melting and further hardening of certain materials, and chemical reactions etc. (Kaliyan et al. 2004). During densification of biomass, the main biological components lignin and hemicellulose will undergo plastic deformation and act as viscous nature binders to glue particles together. After cooling, the solid bridge formed due to presence of these natural binders becomes even stronger. Water is also one of the most important useful agents in the biomass material, which acts as a binder and lubricant (Hu et al., 2015). However, as a result of carbonization, the amounts of natural binders and water in the biocarbon are significantly decreased or even eliminated. Therefore, the biocarbon particles are difficult to bind together and densify as well. This partially explain cracking of biocarbon briquettes with only water added. Alkaline lignin contains a certain amount of water soluble polymers and the wheat starch is an ordered semi-crystalline polymer in the form of fine granules. With presence of water, softening, glass transition and gelatinization of these polymers take place, which become viscous and adhesive. Consequently, the particles are bond together due to adhesive force at the interface of solid particles and the adhesive binder, and cohesion force within the viscous binder. Figure 2 shows SEM images of the biocarbon particles and the surface of a biocarbon briquette produced with addition of 20% water and 20% starch. As shown in Figure 2 (b) and (c), the briquette surface is intact and dense, without observation of isolated biocarbon particles. This is probably due to softening and melting of starch that binds the biocarbon particles together closely. After briquetting, subsequent hardening of the starch might cause formation of a rigid and smooth layer on the briquette surface.

Figure 1: Photo of (a) biocarbon powder, and briquettes made from (b) biocarbon + water 20%, (c) biocarbon + +20% water + 20% alkali lignin and (d) biocarbon + 20% water + 20% starch, after drying at 105 °C for 12 hours



(a) *(b)* *(c)*

Figure 2: SEM image of (a) biocarbon particles, (b) surface of a biocarbon briquette with addition of 20% water and 20% starch, and (c) zoomed view of the area selected in (b)

3.2 Moisture uptake test

Figure 3 shows the moisture uptake rate of biocarbon briquettes produced with two kinds of binders in various quantities as they were stored in the climate cabinet at 35 °C and 98% relative humidity over four weeks. For comparison purpose, the moisture uptake capacity of no-binder briquettes and biocarbon powders used for briquette production were also tested. It clearly shows that the biocarbon powder, no-binder briquettes and briquettes produced with addition of 5% (w/w) binder reached moisture saturation in 20 h. It is interesting to see that there is no evident difference in moisture uptake capacity for the no-binder biocarbon briquette and the one with addition of 5% (w/w) starch. This indicates that addition of 5% (w/w) starch did not affect the hygroscopicity of the biocarbon briquettes. Hu et al. reported increase of moisture content of biochar pellets with addition of starch as binder, which is related to presence of oxygen-containing functional groups in the starch (Hu et al., 2015). The saturated moisture content of the biocarbon briquettes increased with increasing binder addition amount. The biocarbon briquettes with addition of 20% alkaline lignin (w/w) had the highest moisture uptake capacity, about 26% (w/w). Additionally, it was found that briquettes with lignin added have high saturated moisture content compared to those of briquettes with starch added. The high hygroscopicity of the alkaline lignin is mainly due to its high content of inorganic elements, which have high water adsorption capacity. The alkaline lignin contains calcium bisulphite that will adsorb water during the hydration process.

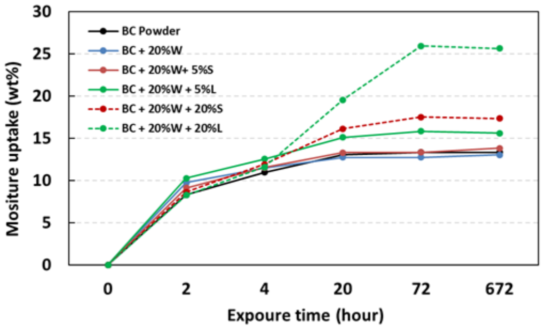


Figure 3: Moisture uptake rate of the biocarbon powder, no-binder briquettes and briquettes made with addition of different binders

3.3 CO_2 gasification reactivity test

Figure 4 shows fractional weight loss as function of time for CO_2 gasification of the studied biocarbon powder and a briquette piece at a temperature of 850 °C. As can be seen, the CO_2 gasification conversion of densified biocarbon is evidently slower than for the biocarbon powder. The gasification reactivity tests in the present work were performed in the TGA under well controlled conditions and at the same conditions for all tested biocarbon powder and briquette samples. Therefore, the different gasification reactivities shown in Figure 4 can be directly linked to effects of densification on the properties of the studied biocarbon samples. The time used for complete gasification conversion of a 10 mg biocarbon powder sample took around 90 minutes, while it was about 120 minutes the briquette, with the same mass. During a densification process, the biocarbon powder will lose porous structure and surface area due to the mechanical compressing and interlocking of particles with the surrounding ones. As a result of this, a briquette has much higher density compared to biocarbon powder with the same mass, and hence low gas voidage. As the gasification conversion progresses, resistance to mass transfer can be very high, limiting transportation and diffusion of reactive CO_2 into the biocarbon briquette and products of gasification reactions out of the biocarbon briquette (Hu et al., 2016). It consequently slows down mass loss and extends conversion time for gasification of the biocarbon briquette. On the other hand, while the conductivity of the biocarbon briquette is expected to be higher than for biocarbon powder, which alone would increase the rate of temperature increase in the biocarbon briquette and gasification reaction conversion consequently, the effective conductivity should at some temperature decrease due to the less effective radiative heat transfer in the biocarbon briquette. However, the combined effect is a reactivity reducing one. In brief, densification can be an effective way to alter properties and reduce reactivity of biocarbon.

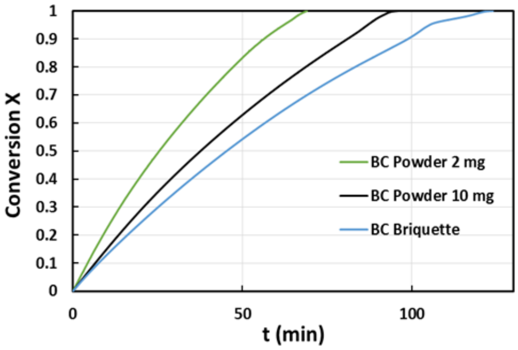


Figure 4: Weight loss as function of time for CO_2 gasification of biocarbon powder and biocarbon briquette at a temperature of 850 °C

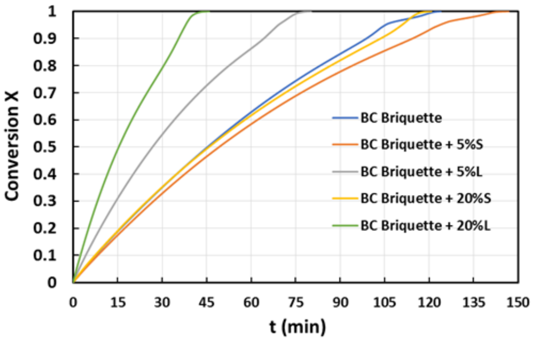


Figure 5: Weight loss as function of time for CO_2 gasification of biocarbon briquette with and without binder addition at a temperature of 850 °C

Figure 5 shows fractional weight loss as function of time for CO_2 gasification of the studied biocarbon briquette produced with and without binder addition. It can be seen that addition of binder gives significant effects on the gasification reactivity of the biocarbon briquette. With addition of wheat starch as binder, the weight loss rate of the biocarbon briquette is slightly lower. In contrast, the CO_2 gasification conversion of biocarbon briquettes with alkaline lignin added is evidently faster than that of the no-binder briquette. The alkaline lignin contains considerable amount of calcium and trace amount of sodium. These elements will give a catalytic effect and promote the CO_2 gasification reaction of biocarbon.

4. Conclusions

In this work, an industry biocarbon was compressed into briquettes with two kinds of binder, namely alkaline lignin and wheat starch. The briquettes densified with binders have higher mechanical strength than that of no-binder briquettes. No-binder briquettes and briquettes produced with addition of 5% (w/w) binder reached moisture saturation in 20 h. Compared to no-binder briquettes, the briquettes produced with binder addition have higher moisture uptake capacity. The biocarbon briquettes with addition of 20% alkaline lignin (w/w) had the highest moisture uptake capacity. Biocarbon briquettes produced with binder addition have evidently different CO_2 gasification reactivity. Use of alkaline lignin as a binder significantly promoted weight loss and increased the gasification reactivity of the biocarbon briquettes. This is most probably related to presence of inorganic elements in the alkaline lignin, which act as catalysts to boost the CO_2 gasification of biocarbon. The results of the present work show that it is feasible to densify biocarbon and achieve better mechanical properties through using different binders. However, biocarbon briquettes produced with addition of different binders have different properties and reactivities, which affect handling, logistics and storage and as well final applications of these briquettes.

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