

Impact of Storage Time and Conditions on Properties of Biocarbon

Liang Wang*, Fredrik Buvarp, Øyvind Skreiberg, Roger Khalil

SINTEF Energy Research, Postboks 4761 Torgarden, Trondheim, Norway
liang.wang@sintef.no

Biocarbon is considered as an important alternative to replace fossil carbon as reductant in metallurgical industries. After its production, the properties of the biocarbon might change during long-term transportation and storage under specific conditions. In this work, effects of storage time and conditions on the properties of two kinds of woody biocarbon were investigated. The studied biocarbons were stored under well controlled conditions in a climate cabinet and were sampled along the storage time for moisture uptake measurement and general fuel property characterization. By carrying out the laboratory scale study a more systematic and simultaneous analysis of the impact of relative humidity, storage temperature and time on properties of biocarbon was achieved. Tumbling tests were carried out to investigate the effect of storage time and conditions on the mechanical strength of the biocarbon samples. The results of this work are important for selection of proper biocarbon logistic solutions to secure the desired biocarbon properties for further utilization as reductant in metallurgical industries.

1. Introduction

Intensive greenhouse gas (GHG) emissions are produced from metallurgical industries due to use of fossilised carbonaceous materials as reductants in their production processes. It is important and urgent to reduce GHG emissions and increase sustainability of the metallurgical industry. One solution for this challenge is to replace fossil fuel based reductants such as coal and coke with renewable based carbon (Wang et al. 2016). In addition, biocarbon can also be a promising candidate to replace fossil fuels for producing energy. Biocarbon, often called charcoal, can be produced from various biomass materials that are available in large amount and at low cost. Existing plantations and forest and agricultural residues are all raw materials for biocarbon production. New biomass materials derived from such as short rotation woody biomass and sewage sludge can also be additional sources for biocarbon production. Pilot scale biocarbon production has been carried out for realizing large production capacity, continuous production process and consistent biocarbon properties. Additional attentions are also given to increased fixed carbon yield and efficient use or recycling of by-products such as condensates (Wang et al., 2016). With further gaining of knowledge and development of technology, production and use of biocarbon in metal production processes can become economically attractive and technically feasible. Metal production is an energy intensive process consuming continuously great amounts of biocarbon with certain qualities (Suopajärvi et al., 2013). For this reason, large amounts of biocarbon need to be produced, stored and transported for final utilization. From the production site to use in a plant, transportation and storage of biocarbon might take days, weeks and even months. During transportation and storage, conditions such as temperature and humidity might vary considerably. It in turn affects properties of biocarbon and further utilization of it in a metal production process. Carbonization of biomass is often carried out at a temperature above 300 °C, typically 500 °C, to heat biomass material in the absence of oxygen or with lean oxygen to the desired temperature with a residence time from minutes to days (Wang et al., 2016). Upon carbonization, the volatiles release from the biomass material, with light and brittle biocarbon remaining. Compared to coal and coke, the biocarbon has high porosity and large surface area, which make the properties of the biocarbon more prone to be changed because of changes in ambient conditions. In addition, different than for coal and coke, the biocarbon normally has low mechanical strength and fragile structure (Huo et al., 2013). Therefore, fines are often generated during handling, transportation and storage

of biocarbon before final usage. Generation of fines causes loss of carbon and increased risk of explosion and pollution to surrounding environment. Additionally, as the biocarbon enters the smelting furnace, the biocarbon with low mechanical strength might break into small pieces and fines that reduce the permeability of the smelt or flow together with off- or flue gas out of the furnace (Suopajarvi et al., 2013). This part of the biocarbon cannot reach the zone where the biocarbon react with metal ore or slag. This results in loss of fixed carbon required for the metal production (Huo et al., 2013). However, the property changes of biocarbon associated with its logistic are neither well-known nor properly understood.

An important part of the biocarbon supply chain is transport with further storage. This is challenging when biocarbon is in question, as large quantities are needed for continuous operation of a metal production plant. The aim of the current work was to study the biocarbon suitability and durability against decay with respect to different conditions similar to those experienced during transport and storage. A systematic analysis of the impact of relative humidity, storage temperature and time on biocarbon properties was achieved.

2. Experimental section

2.1 Samples

In the present work, two kinds of biocarbon were used for the storage test. The received biocarbon had a size in the range of 1x1 to 15x15 cm. A previous study showed that properties of different biocarbon sizes change differently during storage at the same conditions. Therefore, the received biocarbon pieces were sorted and samples with size in the range of 3x3 to 5x5 cm were used for storage testing.

2.2 Laboratory storage test

A climate cabinet (Vötsch VC3 0100) was used in the present work to enable the temperature and relative humidity to be set and controlled throughout the storage test period. A matrix of high temperature (55 °C) and low temperature (35 °C) experiments during two storage periods, of 4 weeks and 8 weeks, were investigated. During all storage tests, the relative humidity in the climate cabinet was kept at 98% RH. The climate cabinet enables continuous control of relative humidity to $\pm 3\%$ RH and temperature of ± 1 °C. Approximately 500 grams of received biocarbon was first loaded in an open polystyrene container and conditioned at a desired condition for one week. Afterwards, the conditioned biocarbon was loaded into a plastic container that was put into the climate cabinet with exactly the same condition as the biocarbon was initially conditioned. The container was well-sealed, enabling sampling of possible gases generated during storage of the biocarbon, through a gas outlet on the top of the container that was connected to a gas collection bag. After storage for a desired period, the biocarbon was taken out of the container and subjected directly to further analysis.

2.3 Analysis of charcoal samples

Triple proximate analyses were done for both untreated biocarbon and all biocarbon pieces sampled after a certain storage test time. The proximate analyses were conducted by following procedures described in ASTM standard D1804, Standard Test Method for Chemical Analysis of Wood Charcoal. Mechanical durability tests were carried out on untreated and stored biocarbon samples at the end of the storage period. It was suspected that there already were fines on the outer surface and also inside the as-received biocarbon pieces. Therefore, around 50 grams of biocarbon (10-15 pieces) sample was first cleaned by pressurized air for 1 minute to remove fines that already were present in them. Then the air-blown biocarbon pieces were loaded into a glass jar and rotated in a jar mill. The results were expressed as the percentage of fines fractions (< 500 μm) of the total weight. In such a way, the actual effect of the storage under controlled conditions on changes in mechanical strength of the biocarbon samples could be evaluated. The sampled biocarbon after storage testing was also visually evaluated in terms of change of surface morphology. After 4 and 8 weeks storage at 55 °C and 98% relative humidity (RH), there were white and brown discoloration on the surface of some biocarbon pieces. These pieces were inspected with field emission scanning electron microscopy (FE-SEM) to see whether the fungi had grown on the surface of the pieces.

3. Results and discussion

3.1 Storage test

Table 1 presents proximate analyses results of the untreated biocarbon sample #1 and #2. The properties of the two studied biocarbon samples are rather similar. However, the ash content of biocarbon #1 is three times higher than that of biocarbon #2. As listed in Table 1, concentrations of major ash forming elements in biocarbon #1 are significantly higher than those of biocarbon #2, especially for catalytic elements. Moisture contents of the studied biocarbon samples generally increase along increase of storage temperature and time. Increase of moisture content can be mainly due to adsorption of liquid water by the two studied samples due

to high porosity and large surface area. Upon increase of storage time and temperature, more water can penetrate into small pores and capillaries, into the microstructure of biocarbon pieces, enhancing water adsorption and moisture content consequently.

Table 2 and Table 3 show general properties of biocarbon samples collected after storage tests. The volatile content of biocarbon after storage testing increases evidently, with slight decrease of the ash content as well. As a result, the fixed carbon content of the analysed biocarbon samples decrease. These findings agree with those observed in our previous study (Wang et al., 2016). The main composition of volatile matter in biomass and biocarbon mainly includes short- and long-chain hydrocarbons/aromatic hydrocarbons. Increase of volatile matter content indicates degradation of biocarbon into gases and vapor, which partially explains the decrease of fixed carbon content in the stored samples (Wang et al., 2016). Considering that a large amount of biocarbon is consumed daily in a metal production plant, useful carbon available for the metal production will be considerably reduced due to decrease of the fixed carbon content. It gives significant impact on profitability of the industry and economic consequences in the biocarbon value chain.

Table 1: Proximate and ultimate analysis of the untreated biocarbon

	Biocarbon #1	Biocarbon #2
Moisture content (as received, wt %)	10.28	8.74
Volatile matter (wt %, d.b.)	13.93	12.51
Ash (wt %, d.b.)	6.64	2.09
Fixed carbon *(wt %, d.b.)	79.43	85.40
C (wt %, daf)	85.69	84.50
H (wt %, daf)	1.96	2.02
N (wt %, daf)	0.54	0.48
S (wt %, daf)	<0.02	<0.03
O* (wt %, daf)	11.79	12.97
Si (mg/kg, d.b.)	11734	4128
Al (mg/kg, d.b.)	2988	24
Ca (mg/kg, d.b.)	23834	3865
K (mg/kg, d.b.)	8044	3638
Na (mg/kg, d.b.)	239	61
Fe (mg/kg, d.b.)	8253	312
Mg (mg/kg, d.b.)	1682	1186

d.b.: dry basis; daf: dry ash free; *: by difference to 100%.

Table 2: Properties of biocarbon #1 after storage test

	35°C, 98% RH		55°C, 98% RH	
	4 weeks	8 weeks	4 weeks	8 weeks
Moisture content (as sampled, wt %)	11.0	13.9	14.0	16.3
Volatile matter (wt %, d.b.)	16.8	18.9	20.4	23.1
Ash (wt %, d.b.)	5.4	5.0	4.3	3.9
Fixed carbon *(wt %, d.b.)	77.8	76.1	75.4	73.0

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

Table 3: Properties of biocarbon #2 after storage test

	35°C, 98% RH		55°C, 98% RH	
	4 weeks	8 weeks	4 weeks	8 weeks
Moisture content (as sampled, wt %)	10.7	11.2	12.5	14.2
Volatile matter (wt %, d.b.)	14.9	15.5	16.2	20.1
Ash (wt %, d.b.)	3.2	3.0	2.9	2.2
Fixed carbon *(wt %, d.b.)	81.9	81.5	80.9	77.7

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

3.2 Generation of fines

Table 4 shows that the percentage of fines were highest in the raw biocarbon samples. After storage tests, less fines were generated from both raw biocarbon samples. However, the percentage of fines generated from biocarbon #1 is consistently higher than that of biocarbon #2, regardless storage conditions. Figure 1 shows

finer generated after the tumbling test for raw biocarbon #1 and after 8 weeks storage. Figure 1-a shows the dispersed fines without evident agglomeration. However, Figure 1-b shows that many small fines particles stick on the surface of a large grain. In addition, there are many particles with different sizes aggregated together. During storage, the biocarbon samples have capacity to adsorb water, which is observed as an increase of moisture content. Because of this, the fines generated from stored biocarbon samples might be moister and stickier, compared to those from untreated biocarbon samples. Therefore, fines generated from the stored biocarbon samples have higher tendency to aggregate together. In addition, the fines particles are more hygroscopic and have a larger relative surface area, which permits more microbial activity and fungi growth compared to the bulk of biocarbon (Kymäläinen et al., 2014).

Table 4: Fines in biocarbon #1 and #2 after storage test

	Initial	35°C, 98% RH		55°C, 98% RH	
		4 weeks	8 weeks	4 weeks	8 weeks
Biocarbon #1 (wt %)	1.9	1.7	1.6	1.4	1.3
Biocarbon #2 (wt %)	1.5	1.4	1.2	1.1	1.0

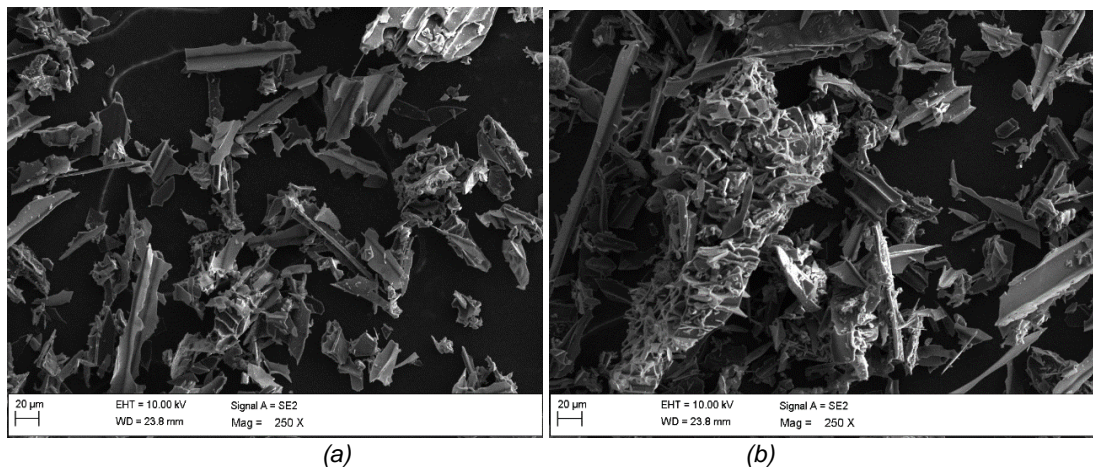


Figure 1: SEM image of fines from (a) untreated biocarbon #1, and (b) biocarbon #1 after storage at 55°C and 98% RH for 8 weeks

3.3 Fungal growth

Visible changes over time to the samples proved most significant and noticeable for biocarbon #1 after storage tests. Figure 2 shows clear white and brown discoloration on the surface of biocarbon #1 after storage for 4 weeks at 55°C and 98% RH. After 8 weeks storage, significant amount of white mildew-like materials can be seen. Figure 3 shows SEM images of biocarbon #1 after 4 weeks storage at 55°C and 98% RH.

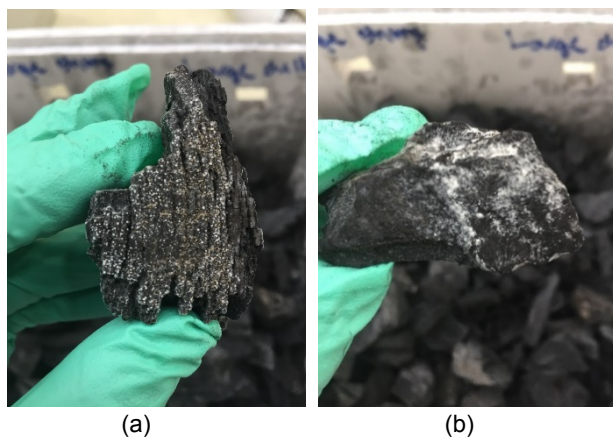


Figure 2: Growth of fungi on biocarbon #1 after (a) 4 weeks and 8 weeks storage at 55 °C and 98% RH in the climate cabinet

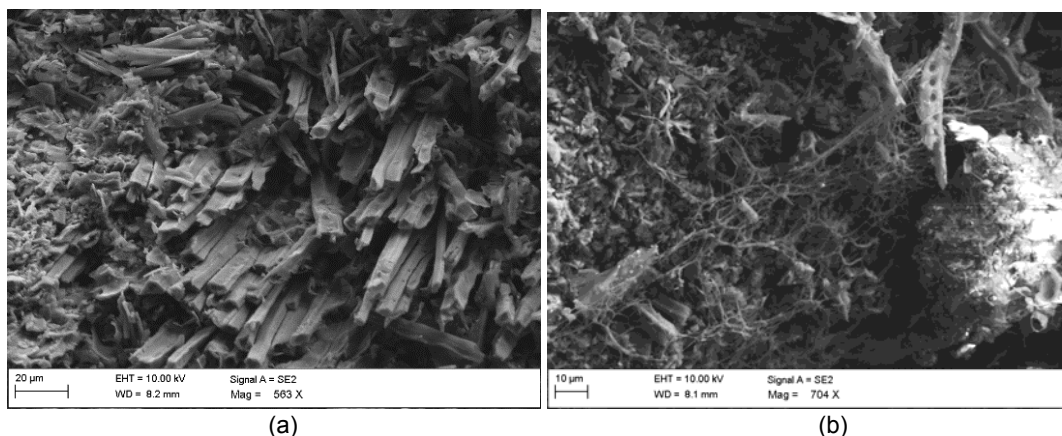


Figure 3: SEM image of biocarbon #1 after 4 weeks storage at 55 °C and 98% RH in the climate cabinet

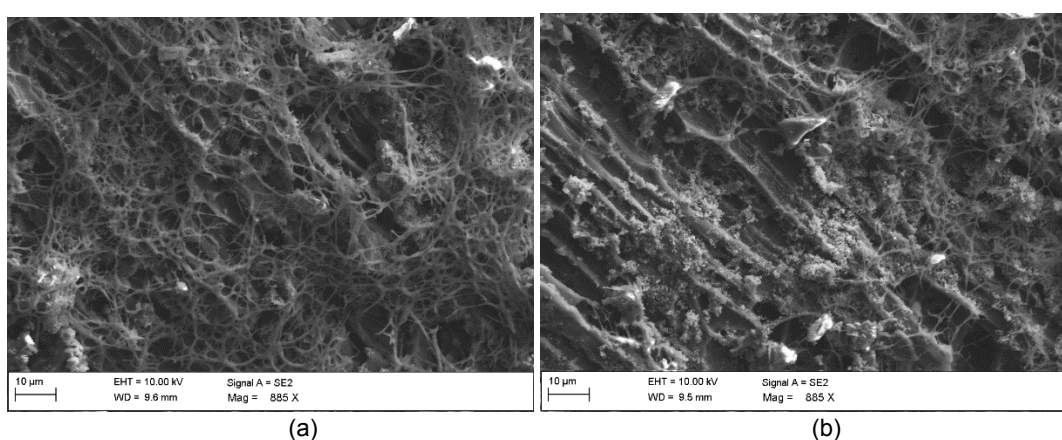


Figure 4: SEM image of biocarbon #1 after 8 weeks storage at 55 °C and 98% RH in the climate cabinet

Figure 3-a displays a scanned area from a biocarbon piece with clean surface and open structure. From the sample, materials with a web-like structure can be clearly seen, covering the surface of the scanned sample. Figure 4 shows that, in addition to the web-like structure material, there is also aggregation of large amounts of fine grains. Similar web-like structure materials have been observed from the surface of raw biomass, torrefied wood and charcoal during artificial storage of them in different laboratory environments (Kymäläinen et al., 2014; Graham et al., 2012). These web-like materials are considered as microbial matter or fungi growing on the surface of the raw wood and heat-treated wood. Normally, the heat-treated wood should be less suitable for fungi growth. The amount of substances such as simple sugars, starch, fats, and proteins are normally quite small in heat-treated wood, while they are critical as nutrients for fungi growth (Svedberg et al., 2008). Moreover, the water content, which is the other important factor for fungi growth, of heat-treated wood is rather low. However, there are still several types of fungi that can cause decomposition and degradation of dry and seemingly unfavourable materials such as heat-treated wood, charcoal, lignite, and even hard coal. It was reported that several micro-organisms (bacteria and fungi) have the ability to live even on charred wood from forest fires, and they are potential utilizers of heat-treated wood in a storage, causing biodegradation (Kymäläinen et al., 2014; Graham et al., 2012; Graham et al., 2016). Although fungi usually do not significantly affect the properties of heat-treated wood, they still can cause mass loss and health problems for workers and pose a threat for working safety. Therefore, storage of biocarbon in a confined space with abundant humidity will lead to increase of moisture content and growth of various fungi. It in turn moistens the biocarbon and initiate biodegradation and possible dry matter loss of biocarbon.

4. Conclusions

In this work, effects of storage time and conditions on the properties of woody biocarbons were studied. It was observed that the volatile content of collected biocarbon samples generally increased along the storage time and temperature, whereas the fixed carbon content of the samples decreased. The biocarbon seems to not have full resistance towards fungi establishment and growth. Findings of the present work indicate that, after certain storage and transportation time, properties of biocarbon might change considerably. Such changes are

related to several factors, including storage conditions, initial charcoal properties etc. This creates additional problems that have to be taken into account when planning the logistic of biocarbon, considering long transportation and storage time in confined spaces.

Acknowledgement

The authors acknowledge the financial support by the Research Council of Norway and a number of industrial partners through the project BioCarb+ ("Enabling the biocarbon value chain for energy").

References

- Graham S., Eastwick C., Snape C., Quick W., Degradation of Biomass Fuels during Artificial Storage in a Laboratory Environment, *International Journal of Low-Carbon Technologies*, 2012,7(2),113-119.
- Graham S., Ogunfayo I., Hall MR., Snape C., Quick W., Weatherstone S., Eastwick C., Changes in Mechanical Properties of Wood Pellets during Artificial Degradation in a Laboratory Environment, *Fuel Processing Technology*, 2016,148,395-402.
- Hu Q., Shao J., Yang H., Yao D., Wang X., Chen H., Effects of Binders on the Properties of Bio-char Pellets, *Applied Energy*, 2015, 57, 508-516.
- Kymäläinen M., Havimo M., Keriö S., Kemell M., Solio J., Biological Degradation of Torrefied Wood and Charcoal, *Biomass and Bioenergy*, 2014, 71,170-177.
- Suopajärvi H., Pongrácz E., Fabritius T., The potential of Using Biomass-based Reducing Agents in the Blast Furnace: A Review of Thermochemical Conversion Technologies and Assessments Related to Sustainability, *Renewable and Sustainable Energy Reviews*, 2013, 25, 511-528.
- Svedberg U., Samuelsson J., Melin S., Hazardous Off-Gassing of Carbon Monoxide and Oxygen Depletion during Ocean Transportation of Wood Pellets, *Annals of Occupational Hygiene*, 2008, 52, 259-266.
- Wang L., Hovd B., Bui H.H., Valderhaug A., Buø T.V., Birkeland R.G., Skreiberg Ø., Tran K.Q., 2016. CO₂ Reactivity Assessment of Woody Biomass Biocarbons for Metallurgical Purposes, *Chemical Engineering Transactions*, 50, 55-60.
- Wang L., Skreiberg Ø., Van Wesenbeeck S., Grønli M., Antal Jr. M.J., 2016, Experimental Study on Charcoal Production from Woody Biomass, *Energy & Fuels*, 30(10), 7994-8008.
- Wang L., Barta-Rajnai E., Hu K., Higashi C., Skreiberg Ø., Grønli M., Czégény Z., Jakab E., Myrvågnes V., Várhegyi G., Antal Jr. M.J., Biomass Charcoal Properties Changes During Storage, *Energy Procedia*, 2017,105, 830-835.