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## Biomass Charcoal Properties Changes during Storage

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### Abstract

In this work, effects of storage time and conditions on the properties of one woody charcoal were studied. Prior to the storage test, the untreated charcoal was characterized by thermogravimetry/mass spectrometry (TG/MS). Weight loss (TG) and evolution profile curves of selected gaseous products were obtained from charcoal pieces that have various appearances, apparent densities and sizes. The result implies that the charcoal pieces have experienced different carbonization conditions. The charcoal samples were collected during the storage test under well controlled conditions and further characterized. It was found that the volatile content of the collected charcoal samples decreases along the storage time. The ash content of sampled charcoal only changed slightly. Accordingly, the fixed carbon content of sampled charcoal decreased about 3% in comparison to the initially loaded untreated charcoal samples. Such decrease of fixed carbon content of charcoal during storage might cause considerable reduction of profitability for an industry that consumes large amounts of charcoal at a relatively high price.

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Keywords: charcoal, storage, thermogravimetry, mass spectrometry, volatile content, fixed carbon

### 1. Introduction

Biomass charcoal is a promising alternative to replace fossil carbon as reductant in metal production [1]. However, carbon reductants with certain quality are required for the various metal production processes. Therefore, large amounts of charcoal need to be produced, stored and transported for final utilization.

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Storage and/or transportation of biomass charcoal might take days, weeks or even months. Consequently, properties of biomass charcoal might change during the long-term storage/transportation process upon variations of storage/transportation conditions like temperature, humidity etc. [2]. In the present work, effects of storage time and conditions on the properties of one woody charcoal were investigated. Thermal conversion behaviors of selected charcoals before storage were also studied by thermogravimetric analysis combined with mass spectrometry (TG/MS).

## 2. Materials and Methods

### 2.1 Samples

Wood charcoal produced in traditional charcoal kilns was studied in the present work and transported to our laboratory in sealed plastic boxes. The charcoal pieces in each box ranged in the size from 1x1 to 10x10 cm. Since properties of charcoal pieces with different sizes might change differently during storage, the charcoal was sorted into small and large pieces before start of the test campaign. The small charcoal pieces in this study are with size in the range of 1x1 to 3x3 cm, whereas the large pieces ranged from 6x6 to 8x8 cm. Sorted charcoal pieces were then separated into two fractions. One fraction was used for the storage test. The second fraction was further sorted according to visual appearances into groups of shiny and dull (charcoal surfaces). Finally, five groups of untreated samples were obtained: shiny&large, shiny&small, dull&large, dull&small, and mix. The mix sample is a representative sample of the whole as loaded sample.

### 2.2 TG/MS analysis of untreated charcoal

The five groups of raw charcoal pieces, sorted according to both size and appearances, were further studied by thermogravimetry/mass spectrometry (TG/MS). Before TG/MS measurements, a few hundred grams of each group of charcoal was ground by a hammer and mortar into powders. Thermogravimetry/mass spectrometry (TG/MS) measurements of untreated charcoal samples were performed by using a modified Perkin-Elmer TGS-2 thermobalance and a HIDEN HAL 2/301 PIC mass spectrometer. Typically, 10 mg sample was heated at a heating rate of 20°C min<sup>-1</sup> up to 900°C in Ar atmosphere. A small proportion of the evolved gas and vapor was introduced into the MS through a glass lined metal capillary transfer line heated to 300°C.

### 2.3 Storage test and analysis of charcoal samples

A climate cabinet (Vötsch VC3 0100) was used in the present work to store charcoal, allowing to control the temperature and relative humidity, between 10°C and 90°C and 10% to 98%, respectively. The charcoal samples were loaded in eight polystyrene containers. The polystyrene containers were selected due to their high heat transfer resistance. Charcoal pieces with sizes in the range of 1x1 to 3x3 cm were loaded in six small containers (#1 to #6). Two large containers (#7 and #8) were filled with big charcoal pieces with size of 6x6 to 8x8 cm. Each container, regardless of piece size, was filled with approximately 3 kg of charcoal. After loading of charcoal samples, each container was covered with a lid, with a certain headspace in each container. In addition, four vents (2x2 cm) were cut near the top and on each side of one container. These vents would allow humid air to enter the container and achieve initial setting conditions in the cabinet.

These vents also allows potentially produced gases to slowly escape the container during the test campaign, yet only a small enough amount such that the container's internal conditions would not change drastically. The heat transfer resistance of the containers allows for a potential change of temperature inside them as charcoal degrades, while the limited vent openings allows for a gas atmosphere considerably different from the initial humid air setting of the climate cabinet. The containers with charcoal samples loaded were stored in the climate cabinet for 6 weeks under various conditions. For the first four weeks, the temperature in the cabinet was held constant at 35 °C with 98% relative humidity. Generation of such conditions is to simulate storage and transportation of charcoal in hot and humid weather. In the last two weeks, the temperature in the cabinet was lowered to 10 °C but still with 98% relative humidity. A Testo 350-454 XL gas analyzer was set up to measure concentration of gases in the climate cabinet, including CO, NO, NO<sub>2</sub>, H<sub>2</sub>, and NO<sub>x</sub>. For studying effect of storage time on charcoal properties, the charcoal samples were collected from each container along different storage time. For example for container #1, it was opened almost every week in order to sample charcoal pieces for further analysis. However, container #6 was only opened at week #6 for collecting charcoal samples. In addition, considering possible differences in conditions in the top and bottom of one container, charcoal samples were collected from both the top and bottom of it. Triple proximate analyses were done for both untreated and all charcoal pieces sampled after certain storage test time. The proximate analysis were carried out through following procedures described in ASTM standard D 1762-84, Standard Test Method for Chemical Analysis of Wood Charcoal.

### 3. Results and Discussion

#### 3.1 Characterization of selected untreated samples

The received sample pieces were divided according to the dull or shiny appearance of the charcoal. Three dull and three shiny pieces of charcoal were selected for thermogravimetry-mass spectrometry (TG/MS) measurements. One shiny and one dull piece was cracked into two half pieces. The volatile matter (VM) content and the evolution profiles of the volatiles were determined by TG/MS. As measured by TG, the VM content of the as-received charcoals varied from 5.5 to 11% (see Fig. 1). As the obtained VM values show, the dull charcoals have slightly more VM than the shiny charcoals. The difference between the surface and the middle of the studied charcoal piece is not so significant. The evolution profile of the selected volatiles (Fig. 1) shows moderate differences between the charcoal pieces. The dull samples evolve slightly higher amount of carbon monoxide and hydrogen over 600°C, while the relative amount of carbon dioxide does not differ significantly. Both carbon monoxide and hydrogen start to evolve at about 100°C higher temperature from shiny samples comparing to dull pieces. This observation supports the hypothesis that the shiny pieces may have experienced higher temperatures during carbonization. The five untreated ground samples were characterized by TG/MS measurements. As measured by TG, the VM content of the ground samples varied from 8.4 to 10%. Fig. 2 shows the TG, DTG and evolution profile curves of selected gaseous products of the ground samples. The very similar shape of the DTG curves proved the efficiency of the homogenization. However, the slightly higher VM content of the dull samples comparing to the shiny samples still existed.

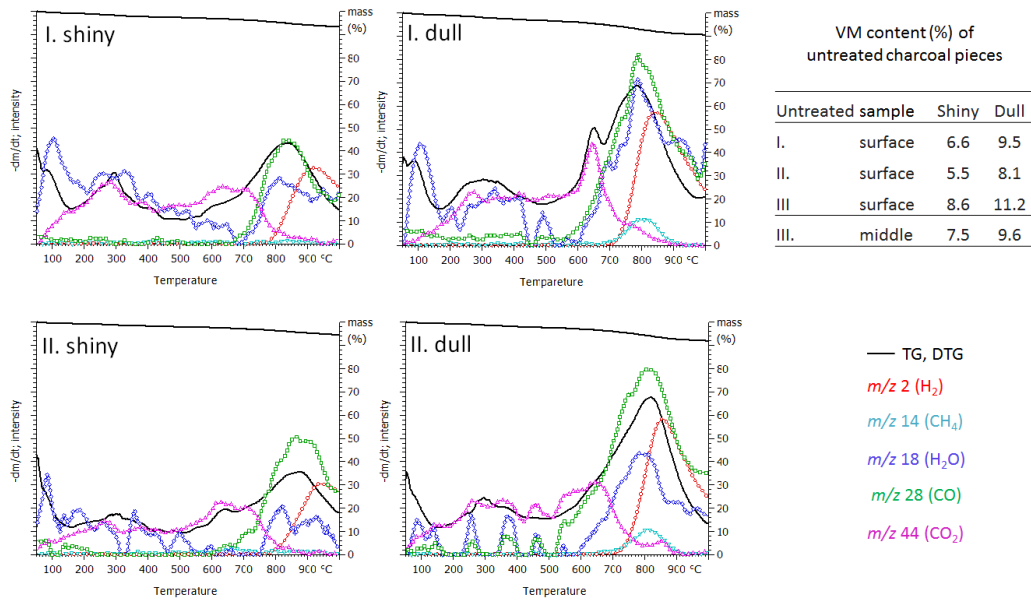


Fig. 1. VM content, TG, DTG and MS ion curves of selected shiny and dull charcoal pieces

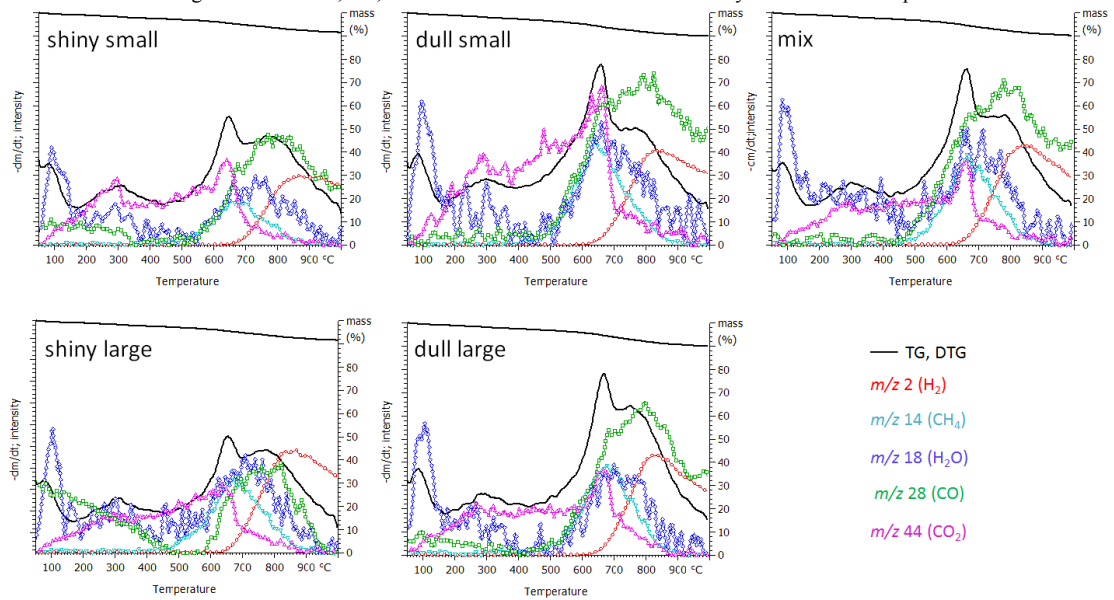


Fig. 2. TG, DTG and MS ion intensity curves of ground untreated samples

### 3.2 Effect of storage time and conditions on charcoal properties

Fig. 3 shows volatile matter content of charcoal samples collected from container #1 and #7 during and after the entire storage test. Fig 3(a) shows that the volatile content of charcoal sampled at week 4 from the top section of container #1 increase significantly, and is 10% higher than that of the initially loaded

charcoal sample. However, the measured volatile content of charcoal samples collected at week 6 decreases, and is only approximately 1% higher than that of initial loaded sample. Fig 3(a) also shows that the deviation of measured volatile content of charcoal samples collected in week 3 and 4 are considerable large. After each sampling, several collected charcoal pieces were ground into powders and 1 gram of powder was used for volatile matter content measurement. As indicated by TG/MS study results, charcoal pieces might be different even they were carefully selected according to appearance and apparent density. Therefore deviation of volatile matter content might be related to heterogeneity of charcoal samples studied in the present work. On the other hand, the volatile content of samples collected from the bottom section in container #1 increases slightly. Fig 3(b) displays that the volatile content of the large charcoal pieces in container #7 varied during the storage test. After 2 and 6 weeks storage time, the volatile content of charcoal samples collected from the bottom section increases from 16% to 32% and 21%, respectively. However, the volatile content of charcoal samples collected from the top section increases to 21% and then decreases to 9%, after 2 and 6 weeks storage time, respectively. Fig. 4(a) shows average values of moisture content, volatile content and ash content measured from the charcoal samples collected from the eight containers during and after the storage test. Generally, the average volatile content of sampled charcoal samples increased about 3% and the ash content of sampled charcoal changed slightly. As a result, the fixed carbon content of charcoal after the storage test decreases about 3% (Fig. 4(b)). Considering that a large amount of charcoal is consumed daily for a metal production industry, such decrease in fixed carbon content of charcoal will cause considerable reduction of useful carbon available in the metal production process and profitability of the industry as well [3].

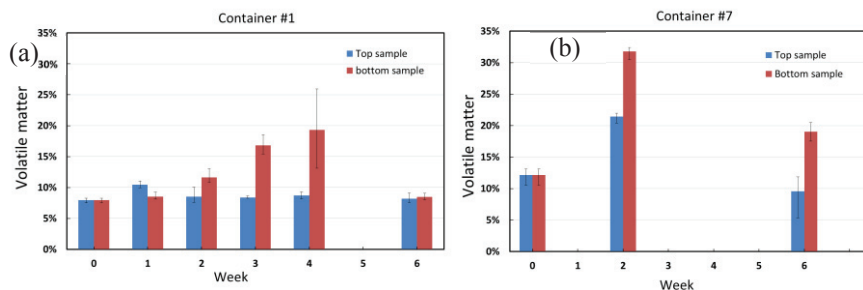


Fig. 3. (a) Volatile content of charcoal sampled each week from container # 1. (b) Volatile content of charcoal sampled at week 2 and 6 from container #7

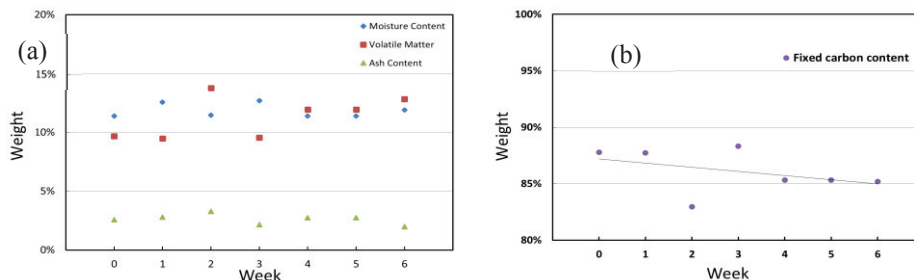


Fig. 4. Overall changes of properties of charcoal sampled from eight containers at different weeks (a) moisture, volatile matter and ash content, (b) fixed carbon content

Volatile matter in the biomass and charcoal is mainly a mixture of short- and long-chain hydrocarbons/aromatic hydrocarbons. Increase of volatile matter content might be attributed to

degradation of charcoal during the storage in the container, which are plausibly converted to gases and vapors [2]. Biomass and charcoal might decompose due to biological and chemical reactions under controlled conditions in the container. Under certain conditions, some bacteria, fungi and microorganisms can modify and decompose dry and charred wood and even lignite, resulting in formation of low molecular carbohydrates on charcoal surfaces [4]. In addition, with presence of oxygen, heat induced degradation might also take place due to oxidization or caramelization of organic constituents in the wooden materials [5]. This process is also accompanied by formation of one-carbon gases such as CO, CH<sub>4</sub> and CO<sub>2</sub>. In this work, slight increase of CO concentration in the cabinet from 0 to 4 ppm was monitored during the test, indicting possible heat induced decomposition of the studied charcoal.

#### 4. Conclusion

In this work, thermal decomposition behaviors of one type of wood charcoal was studied by thermogravimetric analysis combined with mass spectrometry. TG, DTG and evolution profile curves of selected gaseous products imply that untreated charcoal samples have different properties and might experience different carbonization conditions. Effects of storage time and conditions on the properties of the woody charcoal were also studied. It was observed that volatile content of the collected charcoal samples generally increased along the storage time, whereas the fixed carbon content of the samples decreased on average by about 3%. Findings of the present work indicate that properties of charcoal might change considerably after certain storage and transportation time. Such changes are related to storage conditions, and charcoal properties and size. Further work is needed to establish the mechanisms behind the changing charcoal properties.

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#### Biography

Liang Wang is a research scientist at SINTEF Energy Research in Trondheim Norway. His research focus on characterization of biomass and wastes using combined analytical instruments and techniques, advanced biomass carbonization technology, experimental and kinetic study of torrefaction, pyrolysis, gasification and combustion, of biomass and charcoal, ash chemistry during biomass and waste thermal conversion.