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## **Water vapor adsorption on torrefied corn stover**

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**Abstract.** *The equilibrium moisture content (EMC) of biomass affects transportation, storage, downstream feedstock processing, and the overall economy of biorenewables production. Torrefaction is a thermochemical process conducted in the temperature regime between 200 and 300°C under an inert atmosphere that, among other benefits, aims to reduce the innate hydrophilicity and susceptibility to microbial degradation of biomass. The EMC of raw corn stover, along with corn stover thermally pretreated at three temperatures, was measured using the static gravimetric method at equilibrium relative humidity (ERH) and temperatures ranging from 10 to 98% and from 10 to 40°C, respectively. Microbial degradation of the samples was tested at 97% ERH and 30°C. Fiber analyses were conducted on all samples. In general, torrefied biomass showed an EMC lower than raw biomass, which implied an increase in hydrophobicity. Corn stover torrefied at 250 and 300°C had negligible dry matter mass loss due to microbial degradation. Fiber analysis showed a significant decrease in hemicellulose content with the increase in pretreatment temperature, which might be the reason for the hydrophobic nature of torrefied biomass. The outcomes of this work can be used for torrefaction process optimization, and decision-making regarding raw and torrefied biomass storage and downstream processing.*

**Keywords.** equilibrium moisture content, torrefaction, microbial degradation, corn stover, hydrophobicity.

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## Introduction

Fuels produced from lignocellulosic biomass have recently gained increasing attention due to their positive effects on fossil fuel displacement, greenhouse gas emission reduction, rural development, and national security enhancement. Biomass has characteristics distinct from traditional, fossil energy/carbon sources that make its application more costly and complex than traditional fossil fuels. Moisture increases the cost of transportation, biomass storage, and size reduction which significantly increases overall production cost (Brown, 2003; Jenkins and Sumner, 1986; Shinnars et al., 2007; Bergman et al., 2005; Igathinathane et al., 2009). Gasification of high moisture feedstock produces low quality syngas and deteriorates overall thermal efficiency of the process (Neathery, 2010). Moisture increases char yield and has a mixed effect on bio-oil yield and composition, depending on pyrolysis temperature and mineral matter content of biomass (Gray et al., 1985). The high water content decreases the heating value of biomass, causes ignition issues in combustion systems, demands large process equipment to handle large flue gas volume, and affects the overall combustion quality (Khan et al., 2009).

Equilibrium moisture content (EMC) is established when the moisture content of material in question is in thermodynamic equilibrium with the relative humidity of the surrounding atmosphere at a particular temperature and pressure (Cordeiro et al., 2006). Understanding the relationship between EMC and ERH helps in designing drying, combustion, and thermochemical conversion systems; making decisions regarding storage methods for different biomass types; and improving product quality in general (Singh, 2004).

Torrefaction is a thermochemical process conducted in the temperature range between 200 and 300°C under an inert atmosphere and low heating rate. It is currently being considered as a biomass feedstock pretreatment, particularly for thermal conversion systems. The final solid product, referred to as torrefied biomass, is composed mainly of cellulose and lignin. It is characterized by increased brittleness, hydrophobicity, microbial degradation resistance, and energy density. Thus, torrefaction can play a significant role in decreasing the costs of transportation and storage of biomass in the large quantities needed to sustain biofuels production (Bergman et al., 2005; Yan et al., 2009).

The objective of this work was to assess the hydrophobic nature of thermally treated biomass. Therefore, water adsorption characteristics of raw and torrefied corn stover were determined experimentally at four temperatures and five relative humidity levels. A microbial degradation test was conducted to assess dry matter loss due to microbial growth at high ERH. Furthermore, fiber analysis test was performed to explain the lower water vapor adsorption onto torrefied corn stover.

## Methods

### *Sample preparation*

Corn stover biomass samples harvested in the fall 2010, were obtained from Department of Agricultural and Biosystems Engineering at Iowa State University, Ames, IA. Samples were stored in a cooling chamber at temperature below 5°C to prevent microbial degradation.

Wet material was dried at 60°C for 72h and stored in desiccator until water vapor sorption experiments were conducted. Moisture content of samples before and after experiments was determined according to ASAE standard for forage moisture measurement (ASAE standard,

2003b). All samples were ground and sifted before experiments to obtain physically uniform samples whose particle size was less than 2mm.

Torrefaction of corn stover biomass at 200, 250 and 300°C was conducted according to method developed by Medic et al. (2011). However, all samples were dried before the processing and torrefied for 20 minutes.

### ***Water vapor adsorption experiments***

The equilibrium moisture content of biomass was determined at 10, 20, 30 and 40°C using the static gravimetric method (Spiess and Wolf, 1987). Petri dishes with about 2g (0.0001g resolution) of sample in a thin layer were placed in sealed plastic containers, *i.e.* hygrostats. There were four sample types in duplicates in each container. Five saturated solutions of inorganic salts were used to control equilibrium relative humidity in hygrostats, ranging from about 10% (LiCl) to 98% (K<sub>2</sub>SO<sub>4</sub>) (Greenspan, 1977). All salts were reagent grade (Fischer Scientific, Pittsburgh, PA). Solutions were prepared at 50°C with excess salt to ensure solution saturation condition. Temperature and relative humidity data loggers HOBO U23 Pro v2 (Onset Computer Corporation, Pocasset, MA) were placed in each chamber. Incubator Fischer Scientific Isotemp (Fischer Scientific, Pittsburgh, PA), with refrigeration capability was utilized to control temperature ( $\pm 1^\circ\text{C}$ ) during experiments. Samples were assumed to be in equilibrium with hygrostat atmosphere relative humidity when there was no difference ( $\pm 0.001\text{g}$ ) in three subsequent weight measurements. Moisture content of samples was determined by ASAE standard method (ASAE standard, 2003b) upon completion of each experiment.

### ***Microbial degradation experiment***

The microbial degradation test was conducted using the same equipment and experimental set up that was used for water vapor adsorption tests. The duration of the test was 30 days. During the experiment, temperature was maintained at 30°C with the help of incubator. Relative humidity was maintained at 97% (saturated solution of K<sub>2</sub>SO<sub>4</sub> salt). These parameters were chosen to promote natural microbial growth already present on the biomass. Dry matter content of samples was determined before and after the experiment, according to ASAE standard method D358.2 (ASAE standard, 2003b).

### ***Fiber analysis***

Fiber analysis was done according to the National Renewable Energy Laboratory procedure (Sluiter et al., 2011). In short, carbohydrates present in the biomass were dissolved in two stage sulfuric acid hydrolysis and the resulting monomers were analyzed by means of high performance liquid chromatography with refractive index detector (Varian ProStar 355/356, Varian Inc., Palo Alto, CA) and a column (Bio-Rad Aminex HPX-87P, Hercules, CA). Solid residual was weighed and considered to be acid insoluble lignin, while acid soluble lignin in hydrolysate was determined by visible spectrophotometry.

## **Results and discussion**

### ***Experimental results***

The EMCs of raw and corn stover torrefied at 200 (T200), 250 (T250) and 300°C (T300) are showed in Figure 1. EMC of all four types of biomass decreased with an increase in temperature. This phenomenon is typical for biological products and might be a consequence of the enhanced excitation states of water molecules at higher temperatures, which lowers

cohesive forces between them (Bjork and Rasmunson, 1995). As expected, EMC of biomass increased with an increase in ERH and, with no exception, samples exposed to the lowest and highest ERH also respectively had the lowest and highest EMC, regardless of pretreatment temperature. Dry raw corn stover had the highest EMC values at all temperatures for ERH above 0.4. There was no significant difference between samples below 0.4, according to Tukey-Kramer HSD test (not shown in Figure 1), regardless of environmental temperature. Furthermore, EMC of thermally treated samples decreased with the increase in torrefaction process temperature. This is mainly a consequence of a decrease in the number of water adsorption sites and changes in the material structure due to cleavage of hydroxyl groups from biomass polymers, elimination of hemicellulose and the formation of non-polar unsaturated structures<sup>4</sup>. The difference between hydrophobicity of corn stover torrefied at 250 and 300°C is not statistically significant. Tukey-Kramer HSD test revealed that differences between ERH levels for the same sample and environmental temperature are all significant. This is true regardless of sample type. If the samples of the same kind and ERH, but different environmental temperature, are compared to each other no straightforward conclusion could be established. Moreover, the only exception is the highest ERH value at which all samples were significantly different. Therefore, hydrophobicity of thermally treated material was clearly expressed only at the highest ERH level, regardless of environmental temperature, with raw and samples torrefied at 250°C having highest and lowest EMC, respectively.

Growth of fungi colonies was observed at the highest ERH values on raw samples at 20°C and 30°C, and on T200 and T250 samples only at 30°C. This might affect EMC of the samples. However, samples with mold contamination did not show any abnormally high EMC values caused by dry matter loss due to microbial degradation. Hence, the aforementioned samples were also included in the statistical analysis and fitting of water adsorption isotherms.

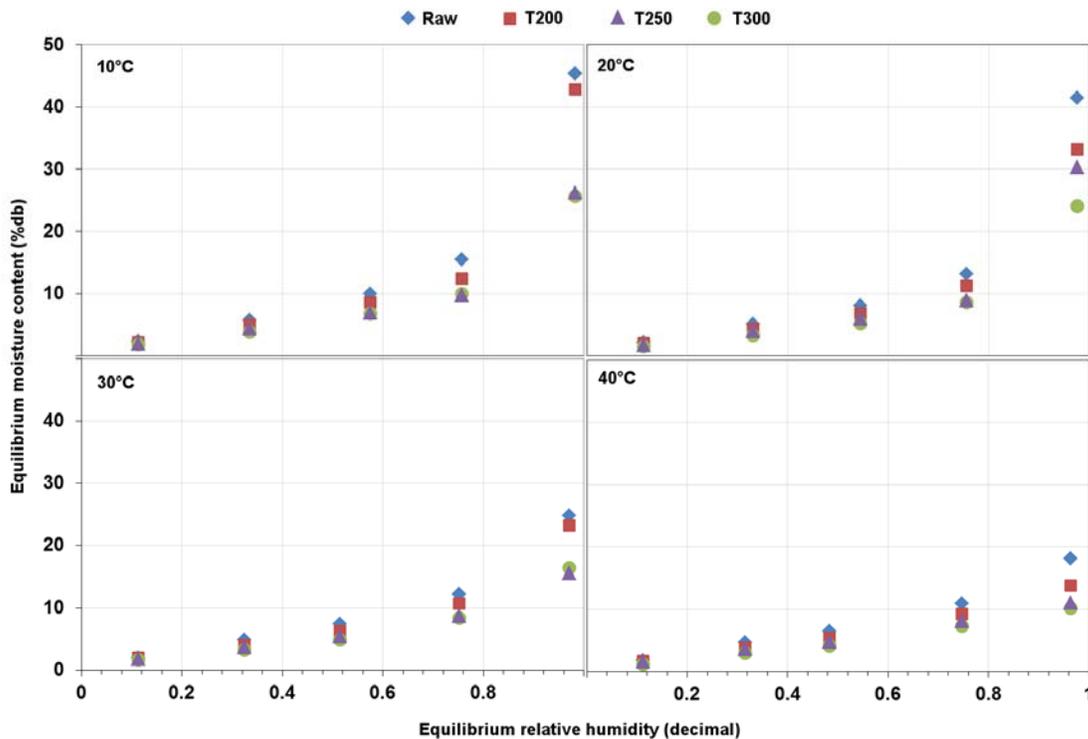


Figure 1. Moisture content of raw and thermally treated biomass

### **Microbial degradation results**

Microbial degradation tests were conducted at 30°C and ERH of 0.97 as there was not any mold growth at other conditions. The results are presented in Figure 2. Dry matter loss (DML) of the raw corn stover sample was about 17% after 30 days, and was the highest among all samples (Figure 2).

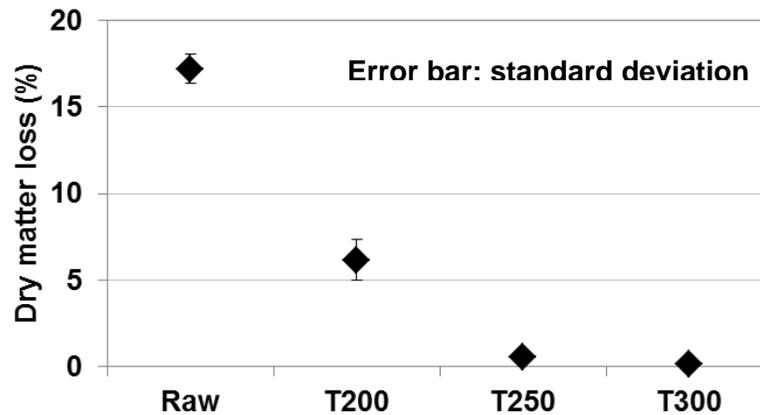


Figure 2. Dry matter loss due to microbial degradation at 0.97 ERH and 30°C

This value was about 3 times higher than the dry matter mass loss of T200 sample. DML for corn stover torrefied at 250 and 300°C were less than 1%.

As discussed in the section 3.1, even though torrefied biomass is comparatively more hydrophobic in nature than raw biomass, it still adsorbs a relatively significant amount of water vapor. At the temperature and ERH used in the microbial degradation experiment, raw and T200, and T250 and T300 samples had EMC values of about 25 and 15%<sub>db</sub>, respectively. However, DML was significantly lower in the case of corn stover torrefied at 250°C and 300°C than in the case of raw biomass. This might be not only due to the elimination of hemicelluloses and an increase in hydrophobicity, but also the formation of sugar and lignin degradation products toxic to microorganisms, such as furan and phenol derivatives that are trapped in the pores of torrefied material.

### **Fiber analysis results**

The results of the fiber analysis are shown in Figure 3. There was an overall trend of decrease in both xylan and arabinan quantity with increase in torrefaction temperature. These two compounds represent the hemicelluloses fraction of corn stover. As expected, raw and biomass pretreated at 300°C had respectively the highest (28%) and the lowest (4%) amount of hemicelluloses. Similar trend was also observed by several other researchers (Bergman et al., 2005; Yan et al., 2009). Increase in the torrefaction temperature from 250 to 300°C caused cellulose degradation and decrease in its contents from about 45 to 20%, respectively. Nevertheless, there was no significant difference between raw, T200, and T250 in regards to cellulose content, which was expressed as a glucan percentage. Relative total lignin content increased from 20 to 75% with the temperature increase, probably due to carbohydrate elimination and conversion to acid insoluble products during the thermal pretreatment.

■ Acid soluble lignin ■ Acid insoluble lignin ▨ Glucan ▩ Xylan □ Arabinan

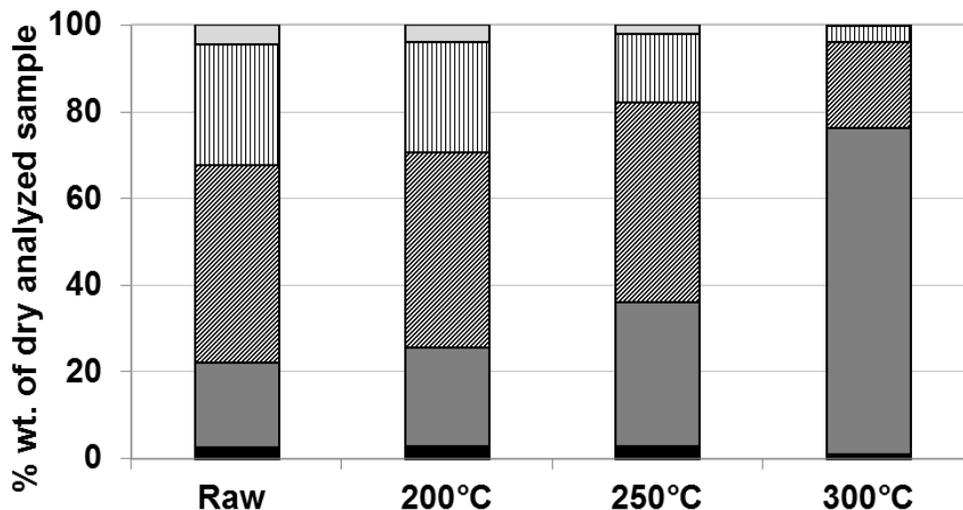


Figure 3 Fiber analysis of raw and torrefied corn stover

## Conclusion

Corn stover undergoes chemical and physical changes during torrefaction that increases its hydrophobicity. Thermal treatment at 200 °C, since very mild did not induced enough changes in biomass properties to make its water adsorption properties different from raw biomass, except at highest ERH value. However, corn stover torrefied at 250 and 300 °C had adsorption properties significantly different from raw biomass. When compared among themselves, torrefied samples differed only at two highest ERH values. Raw biomass had about 17% dry matter mass loss due to microbial degradation. It was followed by corn stover torrefied at 200 °C. Nevertheless, samples torrefied at 250 and 300 °C had negligible mass loss when compared to raw and T200. This is consequence of higher hydrophobicity and probably formation of degradation products toxic to fungi.

Fiber analysis showed drastic decrease in hemicelluloses content and relative increase in lignin content of torrefied corn stover. Torrefaction may have increased hydrophobicity of biomass through elimination of hydrophilic carbohydrate fraction and its partial conversion into non-polar, hydrophobic degradation products.

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