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Research article

Characterization and behavior of water in lignocellulosic and microalgal biomass for thermochemical conversion

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ABSTRACT

Behavior and nature of water in biomass significantly influence the thermochemical conversion processes. This study investigates the characteristics and behavior of water in lignocellulosic and microalgal biomass using differential scanning calorimetry (DSC) and low-temperature X-ray diffraction (XRD) methods. Pine sawdust (PS), peanut shell (PT), and microalgae (MA) samples with different water contents were used and analyzed systematically. Freezable free water was detected in all biomass samples through DSC analysis. Different from PS and PT, a shift in the position of freezable free water peaks was observed during freezing process of MA on DSC, which was attributed to the strong hydrophilicity of this biomass. No freezable bound water was observed in the biomass samples. However, significant amount of non-freezable bound water was detected in all biomass samples. The freezing enthalpies of freezable free water in PS, PT, and MA ranged between 319.04 and 297.7 kJ/kg which were in good agreement with that of bulk water. The boundary between freezable and non-freezable water in the biomass samples was clearly defined combining DSC and XRD analyses. The amount of non-freezable bound water in biomass samples directly correlated with the relative concentration of oxygen functional groups in biomass samples.

1. Introduction

Extensive use of fossil fuel resources has led to their depletion [1,2], global warming and environmental pollution [3–6]. Therefore, researchers have focused on using alternative and sustainable energy sources such as biomass to ensure the energy security and curb greenhouse gas emissions. The two main routes to convert biomass into thermal energy and biofuels are thermochemical [7–9] and biochemical [9,10] processes. Direct biomass combustion and co-combustion with coal account for >90% of the global biomass utilization [9]. Biomass utilization for power generation faces some challenges such as high moisture content which significantly complicates its applications [9]. Biomass commonly contains water in the range of 50 to over 150% (dry basis) [3]. High water content in biomass decreases the heating value of the fuel, reduces the conversion efficiency, and increases the transportation costs [9]. Furthermore, corrosion of downstream equipment may occur as a result of water vapor condensation in flue gas. Thermochemical conversion processes have been considered as the most promising biomass conversion technologies [3]. Pre-drying of biomass is critical for increasing the conversion efficiency and decreasing the emissions during biomass thermochemical conversion.

Drying behavior of lignocellulosic and algal biomass has been reported in the literature [3,11–14]. Boriouchkine et al. [15] studied the influence of moisture in wood chips on boiler operation. They reported that low water content in biomass can result in higher particle temperatures during combustion, while higher water content decreases the overall conversion efficiency of fuel as some heat is consumed for water evaporation. Boiler efficiency can be increased by drying biomass prior to combustion. Pre-drying could decrease air emissions and improve boiler operation [1]. The boiler efficiency can be increased by 5–15% by using pre-dried instead of wet biomass [11]. The optimum water content of biomass for thermochemical conversion technologies is normally in the range of 15–25% [3]. Bennamoun and co-workers [13] investigated the changes in algae structure during drying process. They observed that drying of algae at temperatures higher than 60 °C can result in destruction of majority of proteins, lipids and the vitamins in algae. They suggested an optimum drying temperature of 55–60 °C.

A detailed understanding of water-biomass interaction is critical for designing efficient drying systems. The characteristics of water in other energy resources such as low-rank coals have been studied in detail [16–26]. However, there have been limited studies on type and properties of water in biomass feedstock. Generally, water in brown coal has been classified as two major forms of freezable and non-freezable

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water [27]. More detailed classification of water in low-rank coals involves three forms of "Freezable free water", "Freezable-bound water", and "Non-freezable bound water" [16,18]. Freezable free water refers to the water condensed on particle surface or in macropores [20]. Bound water refers to the type of water present in micropores (D < 10 nm) [28]. The latter type usually shows lower freezing heat compared with bulk water [21]. The shift of DSC freezing peak to lower temperatures happens when water clusters in micropores are very small (<10 molecules) [20,29]. In such confined environment, water forms hydrogen bond with active sites.

Previous studies have been reported on the effects of water content on biomass conversion as well as biomass drying processes [1–3,9,11,15]. However, there is a significant knowledge gap in types of water and their characteristics and behavior in biomass. The changes in types of water at different biomass moisture contents and the critical moisture contents at which each type of water is removed is not fully understood. The main objective of this study is to expound the nature of water in biomass, its behavior and characteristics using a number of analytical techniques to understand the interaction of water with lignocellulosic and microalgal biomass.

2. Materials and methods

2.1. Sample preparation

Two lignocellulosic biomass samples, pine sawdust (PS) and peanut shell (PT) (both from North China), and one microalgae samples, *Chlorella vulgaris* (MA) (supplied by Spirulina Bio-Engineering Co. Ltd., China) were used in this study. The proximate and ultimate analyses of the samples are given in Table 1. The PS and PT samples were grinded and sieved to a particle size range of 125–300 μm. MA sample was supplied in powder form. In order to obtain samples with highest possible water content, about 15 g of each biomass samples was stirred in deionized water for 16 h at room temperature and then filtered. In order to obtain biomass samples with lower water contents, wet biomass samples were dried in a vacuum drying oven at 35 °C and 0.1 MPa. Biomass samples with lower water contents were obtained by controlling the residence time in the vacuum oven. Biomass samples were prepared immediately before DSC and low-temperature XRD analysis to avoid changes in water content. The moisture contents in PS, PT, and MA samples for DSC analysis were in the range of 38.3–60.64%, 29.61–59.81%, and 33.51–72.8% on wet basis, respectively.

2.2. Sample characterization

The chemical structure of the PS, PT, and MA biomass samples with different water content were investigated by using a Thermo Fisher Nicolet IS5 mid-FTIR spectrometer. Sample pellets were prepared by mixing 1 mg of sample with 100 mg of KBr. IR spectra of biomass samples were recorded in the wavenumber range of 4000–400 cm^{-1}. Curve-fitting analysis using Gaussian function was carried out to calculate peak areas of different functional groups in biomass samples. The IR bands were assigned based on literatures data [30,31]. The surface morphology of biomass samples was analyzed by a ZEISS Sigma HD scanning electron microscopy.

The wetting properties of biomass samples were measured by analyzing the contact angle formed in water-biomass interface using a POWEREACH static sessile drop analyzer (Shanghai Zhongchen Digital Technology Apparatus Co. Ltd.) equipped with a high resolution camera to record the moment when pure water came into contact with biomass pellets. The angle formed at the water-biomass interface was measured with an accuracy of approximately ±2°. Smaller contact angles indicated higher hydrophilicity and wettability of biomass samples. The contact angle results reported here are the average of three measurements.

Table 1
Proximate and ultimate analyses of biomass samples.

Sample	PS	PT	MA
Moisture (wt%, ar)	9.47	8.03	6.26
Volatiles matter (wt%, db)	72.51	58.39	81.21
Ash (wt%, db)	1.69	11.3	6.52
Fixed carbon (wt%, db)	25.8	30.31	12.27
C (wt%, daf)	46.49	37.87	47.32
H (wt%, daf)	6.22	5.18	6.89
N (wt%, daf)	0.13	1.57	8.48
S (wt%, daf)	<0.01	0.14	0.85
O[a] (wt%, daf)	47.15	55.24	36.46

ar = as received; db = dry basis; daf = dry ash free.
[a] Calculated by difference.

2.3. Low-temperature DSC analysis

The behavior of water in biomass samples were investigated by low-temperature differential scanning calorimetry (DSC). DSC analysis was carried out by using NETZSCH DSC 200-F3 with internal cooling system. DSC was equipped with an external liquid nitrogen cooling accessory which allowed DSC analysis at low temperatures. About 5 mg of biomass sample was used in DSC experiments. During cooling process, the samples were cooled down from 20 °C to −60 °C, followed by heating up to 110 °C at 3 °C/min. The sample chamber was purged with 80 ml/min of nitrogen throughout the experimental run. All experiments were repeated at least twice and the experimental errors were calculated.

2.4. Low-temperature XRD analysis

The changes in crystalline nature of ice in biomass samples with different water content were studied by low-temperature XRD analysis at −60 °C [19]. Low-temperature XRD experiments were carried out using Rigaku Ultima IV X-ray diffractometer with a cooling accessory. The X-ray patterns were recorded in the range of 2θ = 10–90°.

3. Results and discussion

3.1. DSC analysis of biomass samples with different water contents

The DSC thermograms of biomass samples during cooling and heating processes showed three peaks, including one exothermic and two endothermic peaks. Fig. 1a, b, and c show the DSC thermograms of PS, PT, and MA with different water contents under cooling process. The exothermic peaks shown in Fig. 1 were attributed to the phase transition of the water into ice. Similar results have been reported in the literature for low-rank coals [16,18].

The DSC thermograms of PS samples with different water contents under cooling processes are shown in Fig. 1a. Water contents of PS samples were in the range of 38.3–60.64% on wet basis. As can be seen, with temperature decreasing, one exothermic peak appeared at around −8.6 °C. The appearance of one type of water during the cooling process revealed the presence of freezable water, i.e. "freezable free water". The freezable free water refers to water condensed in the large capillaries on biomass surface and intraparticle water. It can be seen that when the moisture content of PS decreased from 60.64% to 39.05%, the intensity of the peak at around −8.6 °C (freezable free water) decreased monotonically and disappeared when the water content reached 38.3%. No exothermic peaks were observed during the cooling process in case of samples with moisture contents below 39.05%. Fig. 1d, e, and f show the DSC thermograms of PS, PT, and MA as a function of water content during heating process. Two endothermic peaks appeared in the temperature range of 0–100 °C. The smaller endothermic peak at around 0 °C corresponded to the melting of ice. The larger endothermic peak in the temperature range of 0–100 °C was attributed to the evaporation of water. The comparison of Fig. 1a and Fig. 1d revealed that although no freezing peak was detected for PS samples with water contents of <