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A study of hygroscopic property of biomass pretreated by torrefaction

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Abstract

Torrefaction is a thermochemical conversion process, and it is adopted to improve the drawbacks of raw biomass (such as high hygroscopicity, low calorific values and energy density). During this process, biomass is thermally degraded in an inert or nitrogen environment at temperature range of 200-300 °C for several minutes to several hours. In this study, high homogeneous torrefied wood samples were produced by torrefaction at 200, 210, 220, and 230 °C. The equilibrium moisture content (EMC) of raw and torrefied wood and the contact angle of sample surface are examined to evaluate the hygroscopicity changes of torrefied wood. The results indicate that the EMC of the torrefied wood decreased by 35% or more compared to the EMC of raw material. An increasing of contact angle of torrefied wood surface is observed with increasing torrefaction temperature, and it is in the range of 103-113 ° which is correspond to hydrophobic surface (>90°). Meanwhile, the detailed mechanisms about the changes of biomass hygroscopicity after torrefaction are also illustrated in the present work.

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Keywords: torrefaction, hygroscopicity, equilibrium moisture content (EMC), contact angle

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1. Introduction

Nowadays, energy shortage and environmental issues have been the biggest challenges facing the world. Accordingly, sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of materials, products, and processes [1]. Biomass is regarded as an attractive low-carbon resource, and has the following specific features: (1) it is abundant and easily generated; (2) biomass production is labor intensive and thus conducive to poverty reduction and increase of rural employment; and (3) it is easily converted to thermal energy and electricity [2]. Torrefaction is an eco-friendly process because no chemicals are utilized and added into this process to improve the natural defect of biomass and produce solid fuel. Torrefaction is operated between 200–300 °C under an inert condition. Based on the pretreatment temperature, the conventional biomass torrefaction can be classified into light, mild, and severe torrefaction, where the temperatures are in the ranges of approximately 200–235, 235–275, and 275–300 °C, respectively [3]. Compared to raw biomass, torrefied biomass has a higher calorific values or energy density, lower atomic O/C and H/C ratios and moisture content, lower hygroscopicity, higher grindability, and more uniform properties.

Concerning to the improvement of hygroscopicity, biomass is hygroscopic in nature, because moisture can be absorbed into the cell walls by the hydroxyl groups attract which hold water molecules through hydrogen bonding [4,5]. When biomass undergoes torrefaction, the hydroxyl groups will be partly destroyed through dehydration, and this prevents the formation of hydrogen bonds [4]. Accordingly, hygroscopic biomass tends to be hydrophobic after torrefaction, and the equilibrium moisture content (EMC) in the biomass is reduced significantly [6]. The hygroscopic characteristic of biomass is usually examined by determining the EMC under a humidity range of 50–80%. Some studies pointed out that the hygroscopic property can also be observed via thermogravimetric analysis (TGA), where its weight loss is lower for heating temperatures between room temperature and 105 °C when compared to its parent materials [3].

The aim of this study is to investigate the hygroscopicity of lignocellulosic biomass after light torrefaction, which could produce higher homogeneous torrefied wood compared to mild or severe torrefaction [7]. To achieve this target, the examinations of EMC and contact angle are performed to evaluate the behaviour of water absorption in biomass after torrefaction.

2. Experiment

In this study, a softwood species (fir, *Abies pectinata*) which is abundant in Europe and widely used in the European wood industry have been chosen. The wood sample was dried in an oven at 103 °C until mass stabilization before experiments. The light torrefaction were carried out in a pilot scale system in the temperature range of 200–230 °C with a low heating rate ($0.2^{\circ}\text{C min}^{-1}$) and under low pressure (200 hPa) for 1000 min of experiment to produce a high homogenous torrefied wood. It has been reported that the biochars obtained from low pressure of pyrolysis have more “open” pores and higher reactivity than atmospheric pyrolysis biochars [8], and also could provide torrefied products with greater homogeneity [9]. The proximate analysis was performed according to the ASTM standard procedures (i.e., moisture: E871; volatile matter: E872; fixed carbon: E1534; and ash: D1102) [10]. Before the proximate analysis, the wood samples were crushed with a grinder and sieved to the particle sizes ranging from 0.36 to 1.7 mm (i.e. 12–45 mesh). For the EMC and contact angle determination, the wood samples were cut to the dimensions 20 mm × 20 mm × 20 mm. The sieved and cut wood samples were dried in an oven at 105 °C for 24 h to provide a basis for analysis. Subsequently, the samples were placed in sealed plastic bags and stored in electronic cabinet at room temperature until experiments were performed.

The EMC analysis was carried out in a temperature and humidity chamber at 25 °C with 55 % relative humidity. EMC is defined as the weight ratio of sample with moisture content and the oven dried weight of sample. The measurement of contact angle was performed by using an optical contact angle apparatus, which was consisted of a video measuring system connected and a high-resolution CCD camera. A commercial software (FTA32) was connected with the system to measure and record the results.

3. Results and discussion

The values of solid yield, which is the weight ratio of torrefied wood and raw, under various torrefaction temperatures are given in **Table 1**. The solid yield is in the range of 87-97 wt%. When the biomass is torrefied at 200 °C, the solid yield is 96.18%, which means a very light thermal decomposition occurs. While the torrefaction temperature is at 230 °C, the solid yield is decreased to 87.71%. Overall, the decreasing of solid yield is mainly due to the thermal decomposition of hemicelluloses in this temperature range [11]. The HHVs of the samples are between 16.55 MJ kg⁻¹ (raw) and 18.26 MJ kg⁻¹ (230 °C of torrefaction), also shown in **Table 1**. The enhancement factor of HHV, which is the HHV ratio of torrefied biomass and raw biomass can be regarded as energy density, it has been widely used to examine the performance of torrefaction [12]. The enhancement factor of treated wood at the end of treatment is in the range of 1.02-1.10. This result is with a good agreement to the light torrefied wood [13]. The results of proximate analysis indicate that the volatile matter (VM) in the samples decreases after torrefaction, whereas the fixed carbon (FC) increases, resulting from the devolatilization reaction during treatment [4,14]. The increasing of FC could also be owing to the carbonaceous materials are formed during treatment due to thermal reticulation reactions [11].

Table 1. Solid yield, HHV, and proximate analysis of raw and torrefied wood.

Material	Solid yield (wt%)	HHV (MJ kg ⁻¹)	Enhancement factor	Volatile matter (wt%)	Fixed carbon (wt%)
Raw	100.00	16.55	1.000	85.53	14.28
200 °C	96.18	16.90	1.021	83.31	16.49
210 °C	93.92	17.08	1.032	82.59	17.18
220 °C	90.36	17.61	1.064	80.88	18.87
230 °C	87.71	18.26	1.103	79.72	20.03

The EMC is used in relation to a hygroscopic material, like biomass, and the lower EMC values examined means the lower behavior of water absorption [6]. The EMC of the torrefied wood is decreased while increasing torrefaction temperature, and it is in the range of 2.34-3.60 %. Moreover, the EMC decreased by 34-58 % of reduction compared to EMC of the raw material (**Fig. 1**).

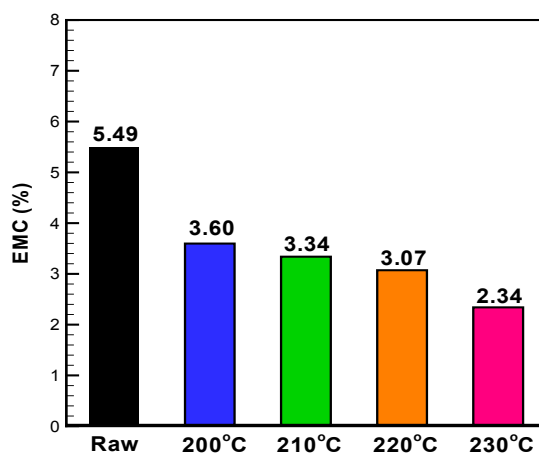


Fig. 1. EMC distribution of raw and torrefied biomass

The reduction of EMC is reflected to the improvement of biomass hygroscopicity. The hygroscopic property of biomass is contributed to the hydroxyl groups in biomass attract and hold water molecules through hydrogen bonding. The hemicelluloses and the amorphous reign of the cellulose chains are more prone to attract water due to

the availability of hydroxyl groups. While biomass after torrefaction, the hemicelluloses and the amorphous reign of cellulose are thermally decomposed. These results prevent the formation of hydrogen bonding to catch water molecules, so that the torrefied biomass tends to be hydrophobic. It is worthy to note that the solid yield of 200 °C torrefied wood is 96.18%, and it is implied a very light degradation of biomass. However, the reduction of EMC is as high as 34.9%, and it could be attributed the released of extractives which are mainly consisted of organic volatile products condensed inside the wood pores. The related study has reported that the lower saturated moisture content in torrefied biomass could also result from tar condensation inside the pores of torrefied biomass, obstructing the passage of moist air through the solid, and then avoiding the condensation of water vapor. In addition, the apolar character of condensed tar on the solid also prevents the condensation of water vapor inside the pores [4].

The measurement of contact angle is conducted by the sessile drop technique. This method is based on the observation of the profile of a drop deposited on a solid surface [15]. After the measurement, the small contact angles ($<90^\circ$) correspond to hydrophilic surface (with hygroscopic property), while large contact angles ($>90^\circ$) correspond to hydrophobic surface (with low wettability) [16,17]. **Fig. 2** and **Fig. 3** display the results of contact angle on the surface of raw and torrefied wood. **In Fig. 2**, The water absorption behavior with time can be observed. The contact angle of raw biomass surface is around 86° in the beginning, and after 20 s, the contact angle of the surface tends to 0° . In contrast, the contact angles of torrefied biomass are always maintained at a certain value and higher than 90° , the range is from 103 to 113° . Overall, the contact angels of all the torrefied samples in the present study are higher than 90° , indicating the reduction of wettability (or increase of hydrophobicity). In the related study, Li et al. [18] performed the contact angle determination of biomass (corn cob) surfaces after torrefaction under N_2 and CO_2 . They revealed that the contact angel increased as the torrefaction temperature elevated, and the high hydrophobicity of corncobs could be obtained while torrefaction occurred at a high temperature.

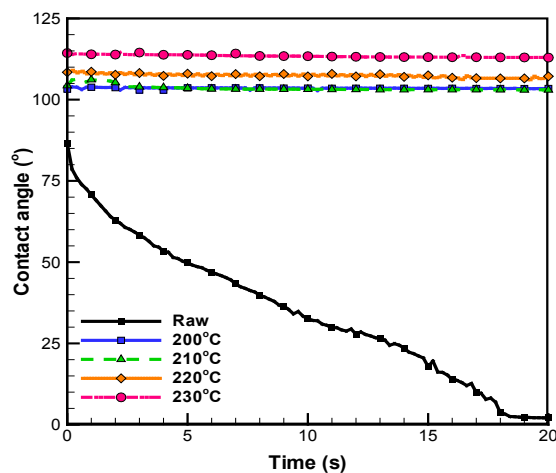


Fig. 2. Profiles of contact angle on the surface of raw and torrefied biomass

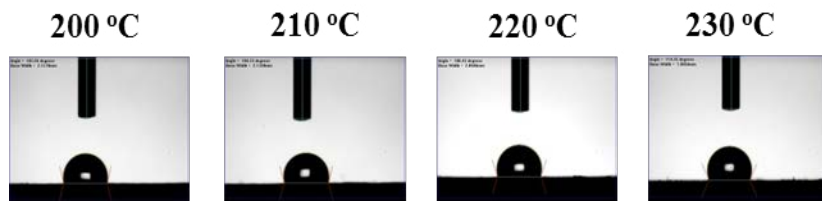


Fig. 3. Diagram of contact angle on the surface of torrefied biomass at different conditions

4. Conclusions

The torrefaction of fir (*Abies pectinata*) has been carried out at 200–230 °C under low pressure (200 hPa) to produce high homogenous torrefied wood in this study. The results point out that the EMCs of torrefied wood are decreased significantly while torrefaction temperature is increased, and it is in the range of 2.34–3.60 %. On the other hand, the solid yield of 200 °C torrefied wood is 96.18% (around 3.8 wt% of mass loss), which is implied a very light degradation of biomass. However, the reduction of EMC is reached up to 34 %, and it could be owing to release of extractives condensed inside the wood pores to prevent the water contact the wood surface directly. For the determination of contact angle on wood surface, the contact angles of all the torrefied samples in the present study are higher than 90° (in the range of 103–113 °), and it is increased with torrefaction temperature, indicating the reduction of wettability (or increase of hydrophobicity).

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