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# Hygroscopic transformation of woody biomass torrefaction for carbon storage

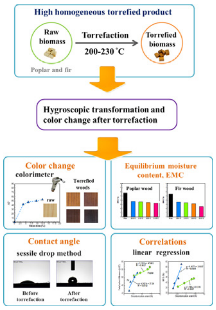
Wei-Hsin Chen[a,b,*], Bo-Jhih Lin[a,c], Baptiste Colin[c], Jo-Shu Chang[b,d,*], Anélie Pétrissans[c], Xiaotao Bi[e], Mathieu Pétrissans[c]

[a] Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan
[b] Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 701, Taiwan
[c] Université de Lorraine, Inra, LERMaB, F88000 Epinal, France
[d] Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan
[e] Department of Chemical and Biological Engineering, University of British Columbia, Vancouver V6T 1Z3, Canada

## HIGHLIGHTS

- Color change and hygroscopic transformation of poplar and fir from torrefaction are analyzed.
- Total color difference linearly increases with increasing mass loss or torrefaction severity.
- Hygroscopic transformation of biomass is evaluated by equilibrium moisture content (EMC) and contact angle.
- Hygroscopicity reduction extent (HRE) can reach up to 57.39% at 230 °C.
- Carbon, hydrogen, and oxygen removals from torrefaction can be predicted by color change and HRE.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Biochar is a potential medium for carbon storage, so its production and storage have been considered as is a crucial route to effectively achieve negative $CO_2$ emissions. Meanwhile, torrefaction is a thermochemical conversion process for producing biochar. Biochar is featured by its hydrophobicity, which makes it different from its parent biomass with hygroscopicity and is conducive to material storage. To evaluate the hygroscopic transformation of biomass from torrefaction, two woody biomass materials of poplar (hardwood) and fir (softwood) are torrefied at temperatures of 200–230 °C, and the variations of color, equilibrium moisture content, and contact angle of raw and torrefied samples are examined. The results indicate that the total color difference of torrefied woods increases linearly with increasing mass loss. The hygroscopicity reduction extent in torrefied fir is higher than in torrefied poplar, and can be increased by up to 57.39% at 230 °C. The tests of the contact angle suggest that the hygroscopicity of the raw woods is evidently exhibited, whereas the angles of the torrefied woods are in the range of 94–113°, showing their hydrophobic surfaces ($> 90°$). The decarbonization, dehydrogenation, and deoxygenation phenomena of the biomass during torrefaction are also analyzed. It is found that the three indexes can be correlated well by the total color difference and hygroscopicity reduction

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* Corresponding authors at: Department of Aeronautics and Astronautics; Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan.

*E-mail addresses:* chenwh@mail.ncku.edu.tw, weihsinchen@gmail.com (W.-H. Chen), changjs@mail.ncku.edu.tw (J.-S. Chang).

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extent. A comprehensive study on the improvement of hydrophobicity of produced biochar has been performed, which clearly shows the potential of carbon storage and negative $CO_2$ emissions by biochar.

## 1. Introduction

The sustainability of fuel resources and environment is an issue that is of considerable concern in the world currently. Considering global warming, it is desired to reach the target to "bend down" the greenhouse gas (GHG) emission curve by 2020 [1]. Another goal after Paris Agreement is to limit the global average temperature increment less than 2 °C [2]. The development of biofuels is regarded as an effective countermeasure to reduce fossil fuel consumption and $CO_2$ emissions [3]. Compared with fossil fuels, biofuels have the following advantages: (1) they can be easily obtained and converted from biomass which is characterized by the short life cycle; (2) their combustion is based on the carbon-dioxide cycle (carbon neutral); and (3) they are sustainable and more environment friendly [4].

Biomass is an abundant and available bioresource, and can be supplied from agricultures, forests, industries, and lignocellulosic residues [5]. By means of the thermochemical methods, biomass can be converted into different types of biofuels such as biochar, bio-oil, bioethanol, biodiesel, and syngas [6]. Biochar is a promising alternative fuel to replace coal which generates highest $CO_2$ emissions during combustion when compared with oil and natural gas [7]. It has been pointed out that biochar could reduce net GHG emissions when it was co-fired with coal in power plants [8]. Meanwhile, biochar is a potential material to stably store and fix carbon in soil for negative carbon emissions [9]. While biochar plays a role as a long-term sink for atmospheric $CO_2$ in carbon sequestration process, $CO_2$ emissions could be reduced by up to 84% [10].

To date, biochar has been produced and utilized for several thousand years and is well known as charcoal (when produced from woody biomass). The applications of biochar are very multiple, ranging from energy production [10], building and furniture materials [11], bio-adsorbent for wastewater treatment to soil amendments [12]. Torrefaction is a mild pyrolysis process where biomass is thermally degraded in an inert atmosphere at temperatures of 200–300 °C to produce biochar (torrefied biomass), and can be categorized into light, mild, and severe torrefaction with corresponding temperature ranges of approximately 200–235, 235–275, and 275–300 °C, respectively [13]. Torrefaction is regarded as a pretreatment method to improve the physical, chemical, and biochemical properties of raw biomass [7]. In addition, biochar produced from torrefaction has been proposed as a suitable feedstock for co-combustion, gasification, and thermochemical fuel production [14].

Raw biomass is a hygroscopic material in nature, attributing to the cell wall polymers containing hydroxyl (−OH) groups. The groups absorb moisture into the walls and hold water molecules through hydrogen bonding [6]. This high hygroscopic nature results in biomass being characterized by low calorific value, low dimensional stability, and poor durability [6,15]. These drawbacks also give rise to poor conversion efficiency of biomass, thereby limiting its utilization as fuels and causing high costs for biomass collection, storage, and transportation [16]. After biomass undergoes torrefaction, the produced biochar possesses lower moisture content and higher calorific value. These changes are mainly due to the removal of −OH functional groups during torrefaction. As a result, the hygroscopicity of pretreated biomass is obviously lowered [17], and biochar's resistance to microbial degradation is intensified [18], rendering easier and cheaper handling and storage of torrefied biomass. The biochar with longer durability implies, in turn, that the ability of carbon sequestration is enhanced.

The equilibrium moisture content (EMC) is a common indicator to evaluate the hygroscopicity of biomass. The EMC of torrefied biomass varies from 1 to 6%, depending on torrefaction severity. Torrefied biomass has showed its feature of high hydrophobicity [19]. Strandberg et al. [20] examined the EMC of untreated and torrefied spruce woods at 20 °C along with 65% relative humidity, and pointed out that the EMC of the torrefied wood was decreased by 50% or more when compared to the EMC of the raw wood. Chen et al. [21] conducted the torrefaction of cotton stalk at different temperatures, and indicated that the EMC decreased obviously with increasing torrefaction temperature. The EMC of the raw material was 10.8% at 25 °C along with 50% relative humidity, whereas the EMC values of the cotton stalk torrefied at 220, 250, and 280 °C were 7.1, 5.6, and 4.3%, respectively. Kambo and Dutta [22] produced biochars via torrefaction and hydrothermal carbonization. Their results indicated that the EMC values of biochars were in the range of 3.52–7.54%, and were all lower than their parent biomass. Mei et al. [23] used a pilot scale rotary kiln to torrefy cedarwood in flue gas and $N_2$. The EMC value of torrefied cedarwood was reduced by approximately 12–43% when compared with untreated cedarwood. Moreover, compared with $N_2$ torrefaction, the biomass torrefied in the flue gas had a lower EMC value, presumably owing to the oxidation reactions which obviously destroyed biomass structure.

The literature reviewed above has provided some of impressive results concerning the EMC of torrefied biomass. Nevertheless, some crucial information in the variation of hygroscopicity from torrefaction remains insufficient. For example, the contact angle is also a crucial measure to response the change of biomass hygroscopicity from torrefaction. But very few studies examined the contact angle of torrefied biomass. In addition, another important physical quantity accompanied by torrefaction is the color change of biomass. With increasing the torrefaction severity, biomass has a trend to become darker. It has been underlined that there was a strong correlation between the EMC and color change when biomass was thermally treated [24]. The improvement in the hydrophobicity of biomass is a pivotal consequence from torrefaction, which will play an important role for biochar production and carbon sequestration, thereby achieving the development of negative $CO_2$ emission technologies (NETs). For this reason, a comprehensive study on the hygroscopic behavior of biomass undergoing torrefaction is carried out in this study where the color change, EMC, and contact angle of torrefied woods are simultaneously considered. The observed phenomena of color change and hygroscopic transformation will be discussed. Furthermore, the correlations between element removals and color change and hygroscopic transformation will be established. In industry, the developed correlations can give a simple tool to produce biochar in accordance with the requirement of hydrophobicity, element removals, or color change, thereby providing a useful insight into the development of NETs.

## 2. Experimental methodology

### 2.1. Material preparation and torrefaction

Two common European wood species with the dimensions of 60 cm × 17 cm × 2.2 cm were adopted in this study; they were poplar (*Populus nigra*) and fir (*Abies pectinata*). Before torrefaction, the wood boards were dried at 103 °C in an oven until mass stabilization. In order to obtain torrefied wood boards with uniform surface and interior, light torrefaction rather than mild and severe torrefaction which would cause intense destroy on the biomass surface [25], was carried out. Another advantage of light torrefaction was that the obtained results were able to provide useful insights into the application of wood treatment for producing sustainable biochar materials [26]. The light