



# Evaluation of the structure and fuel properties of lignocelluloses through carbon dioxide torrefaction



Ming-Fei Li <sup>a,\*</sup>, Le-Xuan Chen <sup>a</sup>, Xun Li <sup>a</sup>, Chang-Zhou Chen <sup>a</sup>, Yi-Chao Lai <sup>a</sup>, Xiao Xiao <sup>a,b</sup>, Yu-Ying Wu <sup>a,\*</sup>

<sup>a</sup> Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China

<sup>b</sup> School of Engineering, Brown University, Providence, Rhode Island 02912, USA

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## ABSTRACT

Two typical lignocelluloses, pine and poplar, were torrefied in a tubular reactor under carbon dioxide medium at temperatures ranging from 220 to 340 °C. The effect of torrefaction temperature on the structure and properties of the chars obtained was investigated to evaluate their fuel applications. As the temperature raised from 220 to 340 °C, the mass yield decreased from 96.7% to 48.7% for pine, and from 97.1% to 43.8% for poplar. The higher heating value of the torrefied pine increased to 25.6 MJ/kg for the sample torrefied at 340 °C. An increase in reaction temperature resulted in a decrease in the contents of cellulose and hemicelluloses but notable increase of the content of lignin, especially for the sample subjected to the strongest torrefaction. The variation of C, H, and O contents of the samples after torrefaction suggested that a high temperature promoted the dehydration and deacetylation reactions. Thermal analysis indicated that the combustion activity of the sample was improved to a level of lignite after torrefaction. The hydrophobicity of lignocelluloses was notably increased with increased torrefaction severity, suggesting the prepared samples are good feedstocks for further processing.

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## 1. Introduction

The huge consumption of fossil fuels in worldwide has led to increased research on the non-conventional sources for energy uses. Among the existing resources, lignocelluloses are widely available, carbon-neutral and renewable. The major chemical compositions of lignocelluloses are cellulose, hemicelluloses, lignin, organic extractives and ash. Cellulose is a linear polysaccharide composed of  $\beta$ -D-glucopyranose units linked by  $\beta$  (1 → 4) glycosidic bonds [1,2]. Hemicelluloses are branched mixtures of different polymerized monosaccharides, such as xylose, glucose, mannose, galactose, arabinose as well as glucuronic and galacturonic acids. Lignin is a branched phenolic polymer consisting of irregularly arrayed hydroxyl- and methoxyl-substituted phenylpropane units. These components show great potentials in the conversion into various products regarding their chemical structure [1,2]. The chemical formulas of cellulose, hemicelluloses, and lignin are summarized as  $(C_6H_{10}O_5)_m$ ,  $(C_5H_8O_4)_n$ , and  $[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_x$ , respectively [3]. It has been determined that lignin shows the highest higher heating value (HHV) among the components (cellulose, hemicelluloses and lignin) [3]. Due to the differences of the

structure, cellulose, hemicelluloses, and lignin show different thermal degradation characteristics. For instance, the thermal decomposition temperatures of cellulose, hemicelluloses, and lignin are approximately 315–400, 220–315, and 160–900 °C, respectively [4]. As compared to fossil fuels, lignocelluloses are characterized by high moisture content, hydrophilic nature, heterogeneous and uneven composition, as well as low higher heating value and energy density [5,6]. To overcome these disadvantages, lignocelluloses need to be treated to enhance the quality for the purpose of highly efficient energy conversion [7].

Among these technologies, torrefaction is a thermochemical decomposition process to treat lignocelluloses at elevated temperatures of 200–350 °C in oxygen-constrained conditions [8]. During the process, lignocellulose is thermally activated and decomposed without oxidation reactions. By varying the reaction parameters: temperature, pressure, and time, the predominant products of gas, liquid and solid can be obtained at different proportions. Most oxygen compounds are removed from the raw material, and the enrichment of carbon leads to the increment of the higher heating value. After torrefaction, the solid char showed increased higher heating value [9]. The rigid structure of the cell wall becomes brittle, yielding a product with improved grindability, thus the cost and energy consumption for grinding are reduced [10]. After torrefaction, the sample becomes easier to transport, store and handle for end-use purposes [9,11]. The utilization of lignocellulose thus

\* Corresponding authors.

E-mail addresses: [limingfei@bjfu.edu.cn](mailto:limingfei@bjfu.edu.cn) (M.-F. Li), [yu-yingwu@bjfu.edu.cn](mailto:yu-yingwu@bjfu.edu.cn) (Y.-Y. Wu).

becomes notably convenient after torrefaction, which substantially improves the volumes of lignocellulose for the replacement of coal as well as a candidate for fuel gasification process. It has been reported by Fisher et al. [12] that torrefaction was considered to be a promising pretreatment approach prior to combustion. The good features of torrefied biomass has been confirmed by Asadullah et al. [13] when comparing to coal. Starfelt et al. [14] found that the torrefied lignocelluloses exhibited characteristics similar to coal, and the process can be integrated with an existing heat and power plant. Acharjee et al. [15] reported that the equilibrium moisture content (EMC) of the torrefied lignocellulose was much lower than that of the raw material when the samples were analyzed at the relative humidities of 11–97% and 30 °C.

The effect of residence temperature on the properties of various lignocelluloses has been widely documented by using nitrogen as the torrefaction medium. However, although a large amount of research has been conducted on the torrefaction of lignocelluloses, there is a little literature regarding the influence of non-inert gases on the degradation of lignocelluloses as well as the torrefied products. Given the fact that carbon dioxide is one of the emission gases derived from the combustion of lignocelluloses, the recycle of carbon dioxide for the thermal degradation of lignocellulose can improve the integrated efficiency of the whole process. Carbon dioxide is considered to be an alternative for nitrogen to be used as a torrefaction medium. Carbon dioxide has a higher molecular weight and higher specific heat as compared to nitrogen [7]. When carbon dioxide is used for torrefaction, the heat transfer mechanism and diffusion of the product gases are different from the torrefaction under nitrogen, thus producing products with different properties. Thermogravimetric analysis (TGA) of woody biomass indicated increased amount of mass loss as torrefaction was conducted in carbon dioxide than nitrogen, and the derivative thermogravimetric analysis (DTA) showed a drop of the peak rate for hemicelluloses and cellulose mass loss when torrefied in carbon dioxide [16]. It has also been reported that, when lignocellulose was torrefied in a carbon dioxide medium, more mass loss occurred and the char obtained showed better grindability properties than it was treated in nitrogen [17]. Mei et al. [18] investigated the torrefaction of cedar wood in fuel gas containing 10 vol.% CO<sub>2</sub>, 6 vol.% O<sub>2</sub>, and 84 vol.% N<sub>2</sub>, and found that the fuel gas showed larger influence on the grindability of the chars compared to those obtained under nitrogen atmosphere.

Therefore, more information on the torrefaction of lignocelluloses remains to be investigated. Carbon dioxide, as a waste gas resulted from the combustion of fossil and lignocelluloses, is considered to be anthropogenic greenhouse gas producing global warming effect. Carbon dioxide is available from exhaust boiler thus is a potential medium for torrefaction as compared to nitrogen, since specific equipment is needed to obtain a high concentration of nitrogen. In this study, to achieve the effective utilization of carbon dioxide, two samples, pine and poplar, were torrefied under carbon dioxide. *Pinus bungeana* Zucc. ex Endl. is a native softwood species having great potentials in the field of energy in China, and *Populus tomentosa* is a fast-growing hardwood widely planted in China to prevent wind erosion and control desertification, which has considerable economical and ecological functions. In the present study, torrefaction of typical lignocelluloses, pine and poplar, was conducted in a tubular reactor under carbon dioxide medium, and the effect of torrefaction temperature on the structure and properties of the chars obtained was studied, which was meaningful for the evaluating the energy intensity during the process. The characterization of the properties of the char regarding to chemical component, function groups, crystallinity, moisture absorption capacity, and combustion behavior, was intended to provide a deep insight into the torrefaction of lignocellulose under carbon dioxide medium.

## 2. Materials and methods

### 2.1. Materials

The materials studied were pine (*Pinus bungeana* Zucc. ex Endl.) and poplar (*Populus tomentosa*). The samples were ground and sieved to obtain the fractions with sizes between 0.18 and 0.85 mm to provide homogeneous preparations for the experiments, and then they were stored in sealed containers before use.

### 2.2. Torrefaction procedure

A well-insulated batch type facility (SK-G08123 K reactor, manufactured by Tianjin Zhonghuan Experimental Furnace Co. Ltd., China) was used for torrefaction. A batch of 10 g dried sample was loaded into the reactor and then was closed to maintain the desired temperature and atmosphere within the reactor. Carbon dioxide with a flow rate of 100 mL/min was plunged into the reactor to maintain an inert environment during the torrefaction process. A 2.5 kW electrical heater was then turned on to heat the sample at a heating rate of 5 °C/min, a K-type thermocouple was connected to the heater to monitor the temperature and control the heat supply. The sample was heated from room temperature to the desired temperature (220, 260, 300, and 340 °C) and kept for 30 min and then the heating was stopped and the reactor was cooled to a temperature below 80 °C. The torrefaction experiments were conducted in triplicate. The temperature profile during the whole process was recorded as shown in Fig. 1. The severity factor (S) was used to evaluate the effect of temperature and time, which is meaningful for the comparison with other data. The calculation was conducted by Eq. (1):

$$S = \log R_0 = \log(R_{\text{heating}} + R_{\text{cooling}}) \\ = \log \left[ \int_0^{t_{\text{Max}}} \frac{T(t) - T_{\text{Ref}}}{\omega} dt + \int_{t_{\text{Max}}}^{t_{\text{F}}} \frac{T'(t) - T_{\text{Ref}}}{\omega} dt \right] \quad (1)$$

where  $t_{\text{Max}}$  and  $t_{\text{F}}$  represent the times at maximum heating temperature and at the whole heating–cooling process,  $T(t)$  and  $T'(t)$  represent the temperatures during the heating and cooling process, and  $\omega$  and  $T_{\text{Ref}}$  correspond to 14.75 °C and 100 °C, respectively, based on the data in literature [19]. The resulting char products were stored in sealed containers before analysis. The char products were named as following “Sample name-Process temperature”. That is, PI-R and PO-R represent the untreated pine and poplar; PI-220, PI-260, PI-300, and PI-340 represent the chars obtained by torrefaction of pine at 220, 260, 300 and 340 °C, whereas PO-220, PO-260, PO-300, and PO-340 represent the chars produced by torrefaction of poplar at 220, 260, 300, and 340 °C, respectively.

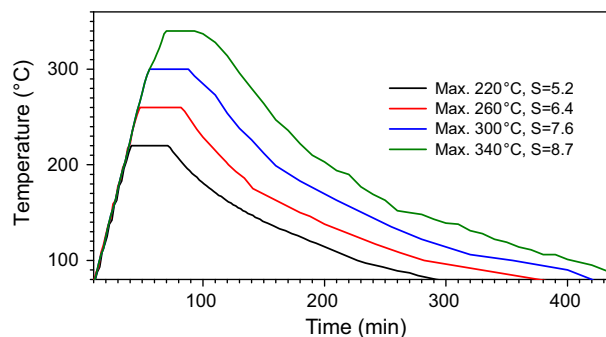


Fig. 1. Temperature profile of lignocellulose torrefaction in carbon dioxide.

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