



Evolution of functional groups and pore structure during cotton and corn stalks torrefaction and its correlation with hydrophobicity



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HIGHLIGHTS

- The broken of O–H bond and C–O bond in primary alcohol groups occurs preferentially.
- Until 230 °C, hydroxyl removal and generation of micropore are due to dehydration.
- Formation of carboxyl or conjugated ketone and reconstruction of pore occur followed.
- Hydrophobicity may have a highly linear correlation with hydroxyl and micropore.

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ABSTRACT

The evolution of physicochemical structure of two stalks during torrefaction and its correlation with the hydrophobicity were investigated. Two-dimensional perturbation correlation infrared spectroscopy was used to study the evolution of functional groups. The pore structure of torrefied stalks was analyzed based on the isothermal adsorption of N₂ and CO₂. During torrefaction, the removal of hydroxyl groups on the holocellulose resulted in dehydration and formation of carboxyl and conjugated ketone. The breaking of O–H bond and C–O bond in primary alcohol groups occurs preferentially for cotton stalk and corn stalk, respectively. Due to the modification of structure, the macropores diminished while more micropores formed. Equilibrium moisture content decreased significantly when torrefaction temperature increased, suggesting that hydrophobicity is improved by torrefaction. Meanwhile, the removal of hydroxyl and the formation of micropores had highly linear correlation with the formation of hydrophobicity. The result will be beneficial for better understanding of the mechanism of torrefaction and formation of hydrophobicity.

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1. Introduction

Biomass is an efficient, clean, and renewable energy source with near-zero emission of CO₂ and low pollutants emission [1]. However, the low bulk density, high moisture content, degradation during storage, and low energy density of biomass are critical challenges in using biomass as feedstock of combustion, gasification or pyrolysis [2,3]. Torrefaction, a thermal treatment carried out at the relatively low temperature ranging from 225 °C to 300 °C, may ameliorate these problems and enhance fuel properties of solid

biomass [4–6]. In the past several years, biomass torrefaction related to different types of biomass feedstock [7–12], operating condition [13–16], and the effect on the subsequent conversation [8,17–20], was intensively researched.

Meanwhile, to deeply understand the mechanism of torrefaction, the evolving structures during torrefaction have also been characterized. Based on FTIR and solid ¹³C NMR analysis of torrefied corncobs, Zheng et al. [21] further confirmed that different transformation of the polymers would occur in agricultural straws similar to the torrefied wood [22] and the formation of cross-linking during cellulose torrefaction affected the bio-oil quality. Chang et al. [23] analyzed the torrefied sprucewood and bagasse using FTIR and XRD, and suggested that thermal decomposition of hemicellulose predominated over lignin decomposition and the cross-linking of cellulose in torrefaction. Several other FTIR analyses on different types of biomass [10,24–27] also confirmed that (1) hemicellulose is initially degraded by mild torrefaction at

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low temperature (<250 °C) while cellulose and lignin are degraded by severe torrefaction at high temperature (>250 °C) and (2) the increasing intensity of C—O—C band demonstrates that cross-linking reaction occurs during torrefaction.

However, conventional FTIR is mainly used to describe the interaction between the infrared beam and the sample, it is difficult to show the information on the significant peak overlaps, especially the fingerprint part, and it is difficult for the mechanistic assessments [28]. Recently, the generalized two-dimensional perturbation correlation infrared spectroscopy (2D-PCIS), put up by Noda, etc. was supposed to understand the evolution of chemical function groups of solid materials [29]. Harvey et al. [28] reported the application of 2D-PCIS on biochar formation process. It revealed that the primary reactions controlling biochar properties contain the defragmenting of lignocellulose H-bonding network and emethylenation/demethylation, oxidation, or dehydroxylation/dehydrogenation of lignocellulose fragments. In this study, the 2D-PCIS was introduced to the structure analysis of torrefied biomass, a deep understand of torrefaction mechanism would be obtained.

Not only the chemical structure changed during torrefaction for biomass, but also the physical structure, especially the pore structure, would be changed. However, in the previous works, the evolution of pore structure of torrefied biomass is rarely reported, which is not conducive to further understand the torrefaction mechanism. On the other hand, the changing of torrefied biomass during torrefaction is also reflected by the evolution of other properties such as the hydrophobic property. The hydrophobic property of torrefied biomass was determined by the chemical and physical structure [26,30–32].

Therefore, in this study, the 2D-PCIS was used to investigate the evolution of chemical structure of two agriculture straws during torrefaction, and the pore properties including the surface area, pore volume and pore size distribution, were analyzed. To understand deeply the formation mechanism of hydrophobic property, a quantitative correlation between these physicochemical structures and the hydrophobicity is calculated.

2. Materials and methods

2.1. Sample preparation and torrefaction

Cotton stalk and corn stalk were collected locally and naturally dried after being reaped. Straws samples were then stored in a storage room with good ventilation. The results of the fiber analysis and the ultimate analysis of raw, dry feedstock are presented in Table 1. The content of cellulose in cotton stalk is up to 53.57%, which is higher than that of corn stalk. On the other hand, corn stalk had higher content of hemicellulose (up to 40.44%), about twice of cotton stalk. The ultimate analysis shows that both these two stalks have high O content and low C content, although the contents of cellulose, hemicellulose and lignin of these two stalks are significantly different.

Torrefaction was carried out with a fixed bed comprising a vertical tube (I.D.: 38 mm and H: 600 mm), an electrical furnace, a gas condensing system, and an incondensable gas collection and analysis system. After the tube was pre-heated to selected

temperatures (200 °C, 230 °C, 260 °C and 290 °C), the sample (5 g, particle size: 2–3 cm) was quickly put into the center of the reactor and kept for 30 min. Pure N₂ (99.99%) was purged continuously to maintain an inert atmosphere and the flow rate was set at 1000 ml/min. The solid products were then cooled to ambient temperature. Each trial was repeated three times, and the subsequent analysis was based on the mixed products from these repeated experiments.

2.2. Characterization of physicochemical structure

2.2.1. 2D-PCIS

The infrared spectrum of the samples between 4000 cm⁻¹ and 400 cm⁻¹ was recorded using a VERTEX 70 spectrometer (Bruker, Germany). Each spectrum was the result of 120 accumulated scans with 4 cm⁻¹ resolution, and the apodization function was the Happ-Genzel type. To prepare the pellet, approximately 0.7 mg of dried solid sample and 70 mg KBr (Merck, spectroscopy grade) were mixed, and the resulting mixture was pressed successively at pressures of 5 tons/cm² for 5 min and 10 tons/cm² for 5 min under vacuum.

Noda et al. [29] put forward the mathematical procedure and numerical computation of the 2D-PCIS spectroscopy in detail. A basic concept of 2D-PCIS spectroscopy is described below [28]. Firstly, consider a perturbation-induced change of the spectral intensity $y(w, t)$ observed during an interval of external variable t between T_{\min} and T_{\max} , where w and T are wavenumber and perturbation of temperature, respectively. The change is expressed as follows:

$$\tilde{y}(w, t) = \begin{cases} y(w, t) - \bar{y}(w) & \text{for } T_{\min} \leq t \leq T_{\max} \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

where $\bar{y}(w)$ is the stationary or averaged spectrum defined by:

$$\bar{y}(w) = \frac{1}{T_{\max} - T_{\min}} \int_{T_{\min}}^{T_{\max}} y(w, t) dt \quad (2)$$

Secondly, the 2D correlation spectrum $X(w_1, w_2)$ is expressed as:

$$X(w_1, w_2) = \langle \tilde{y}(w_1, t) \cdot \tilde{y}(w_2, t) \rangle \quad (3)$$

where $X(w_1, w_2)$ represents the functional comparison of spectral intensity variations $\tilde{y}(w, t)$ measured at different wavenumbers, w_1 and w_2 , during a fixed interval of the external temperature. The symbol $\langle \rangle$ denotes the correlation function designed to compare the dependence of changes of spectral intensity, $\tilde{y}(w, t)$, at w_1 and w_2 on temperature. Noda et al. [29] adopt a simple convention to treat $X(w_1, w_2)$ as a complex number function:

$$X(w_1, w_2) = \Phi(w_1, w_2) + i\Psi(w_1, w_2) \quad (4)$$

where $\Phi(w_1, w_2)$ and $\Psi(w_1, w_2)$ denote synchronous and asynchronous 2D correlation intensity, respectively. The synchronous 2D correlation intensity $\Phi(w_1, w_2)$ represents the overall similarity (in-phase or coincidental) between intensity changes in w_1 and w_2 when the external temperature T increases from T_{\min} to T_{\max} . On the other hand, the asynchronous 2D correlation intensity $\Psi(w_1, w_2)$ is regarded as a measure of dissimilarity (out-of-phase or sequential) of the changes of spectral intensity in w_1 and w_2 on T .

Table 1
The properties of the samples.

Sample	Chemical composition (d, wt.%)			Ultimate analysis (d, wt.%)					
	Hemicellulose	Cellulose	Lignin	Other	C	H	N	S	O
Cotton stalk	20.98	53.57	17.21	8.24	47.43	6.65	1.21	0.36	39.54
Cornstalk	40.44	34.6	7.79	17.17	44.94	6.54	1.28	0.34	38.22

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