



A Thermogravimetric study of the characteristics of pyrolysis of cellulose isolated from selected biomass



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HIGHLIGHTS

- Pyrolysis characteristics of cellulose from various biomass resources was studied.
- Isolated and reference celluloses showed similar chemical structure.
- Isolated and reference celluloses showed different crystallinity, crystallite size.
- Structural differences of cellulose strongly affected their pyrolysis behavior.

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ABSTRACT

Utilisation of biomass by means of pyrolysis is of practical interest for the production and use of biofuels at small and flexible scales. Biomass consists of three major components, namely, cellulose, hemicellulose and lignin and their contents vary from feedstock to feedstock. Understanding the pyrolysis behaviour of each component and their interactions holds a key to understanding the complex biomass pyrolysis process. This study was aimed to compare the pyrolysis characteristics of cellulose from various biomass resources, namely pine wood, poplar wood and wheat straw, and pure cellulose samples acquired from Sigma Aldrich and Avicel. Cellulose samples were isolated from the raw biomass samples using a well-established cellulose isolation technique. Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD) and scanning electron microscope (SEM) were applied to characterise the surface functional groups, the crystallinity and the morphologies of the samples. The pyrolysis experiments were performed using a thermogravimetric analyser (TGA) in nitrogen at 10 K min^{-1} heating rate from room temperature to the final temperature of 823 K. The FTIR, XRD and SEM results indicated that cellulose can be successfully isolated from the raw biomass samples via the chemical treatment used. The cellulose samples isolated from the selected biomass had lower crystallinity and smaller crystallite compared to the reference cellulose. The cellulose isolated from pine wood, poplar wood and wheat straw showed similar pyrolysis characteristics but differed significantly from the reference celluloses. The temperature corresponding to the maximum weight loss rate of the isolated cellulose samples was ca 5–18 K lower than that of the reference celluloses and exhibited a large flat shoulder in the temperature range of 475–575 K.

1. Introduction

The processing of biomass resources, such as forestry by-products, agricultural residues, and non-food energy crops, for renewable electricity and fuels has been recognised as a feasible means of reducing CO₂ emissions and combating global climate change. Pyrolysis is considered a promising technology to utilise biomass. Pyrolysis gas and liquid can be used for combined heat and power (CHP) generation [1]. The solid residual, also known as biochar, can be used as fuel [2], a soil conditioner [3], feedstock for activated carbon manufacturing, and adsorbent [4]. Biomass mainly consists of three components, namely

cellulose, hemicellulose and lignin, and their contents vary from feedstock to feedstock. Due to the complexity and variability of biomass, understanding the pyrolysis behaviour of individual components and their interactions during pyrolysis would be beneficial for the development and optimisation of biomass pyrolysis technology [5–7], especially in predicting the product distribution. The ultimate goal is, for a given biomass, its pyrolysis behaviour can be predicted by knowing the content and structure of its individual components (cellulose, hemicellulose and lignin).

Pyrolysis behaviour of cellulose has been a subject of study in a number of literature reports, as it is the most abundant building

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Table 1
A summary of the characteristics of samples used in the present study.

Samples	Proximate analysis (wt% d.b. ¹)			Ultimate analysis (wt%, d.a.f. ²)					Wax Content (wt % _o , d.b.)	Klason lignin (wt % _o , d.w.f. ⁴)	Crystallinity index (%)	Apparent crystallite size (nm)
	Volatiles	Fixedcarbon	Ash	N	C	H	S	O ³				
PN0	87.3	12.1	0.6	0.13	49.84	6.26	0.00	43.76	2.72	n/a	44.2	3.78
PN1	85.7	14.0	0.3	0.17	49.57	6.22	0.00	44.04	n/a	21.25	48.4	3.95
PN2	76.2	21.0	2.7	0.11	45.37	6.65	0.00	47.86	n/a	0	60.4	4.42
PN3	80.7	17.6	1.7	0.14	44.58	6.64	0.00	48.65	n/a	n/a	70.8	4.65
PP0	90.71	8.84	0.45	0.17	49.64	6.20	0.00	44.00	2.53	n/a	44.5	3.81
PP1	84.73	14.95	0.32	0.20	48.91	6.20	0.00	44.69	n/a	20.89	48.1	3.92
PP2	83.21	14.34	2.45	0.11	46.80	6.02	0.00	47.06	n/a	0	60.5	4.39
PP3	83.45	14.75	1.80	0.10	44.58	6.31	0.00	49.01	n/a	n/a	70.8	4.68
WS0	72.1	24.7	3.2	1.69	48.08	6.65	0.07	43.50	6.78	n/a	28.0	3.58
WS1	80.4	15.8	3.8	1.84	48.12	6.55	0.09	43.39	n/a	18.23	28.3	3.72
WS2	80.6	16.8	2.6	0.14	45.62	6.39	0.00	47.84	n/a	0	42.0	3.89
WS3	80.2	17.8	2.0	0.13	44.95	6.59	0.00	48.34	n/a	n/a	55.6	4.04
RC-S	82.2	17.7	0.1	0.08	45.09	6.26	0.00	48.57	n/a	n/a	79.8	6.24
RC-A	81.9	18.0	0.1	0.11	44.39	6.27	0.00	49.22	n/a	n/a	80.4	6.39

Note: 1. dry basis; 2. dry ash free basis; 3. oxygen content was calculated by difference; 4. dry and wax free basis.

component of biomass with well-known chemical structure [5–13]. However, commercial microcrystalline cellulose samples isolated from high cellulose content biomass via hydrolysis process were often employed in the work reported in the literature. Common laboratory filter papers as cellulose substitutes were also used in the literature studies of cellulose pyrolysis [8,11,14]. However, cellulose exists in crystalline and amorphous form and crystallinity of cellulose may have a significant impact on the thermal decomposition behaviour [15]. Therefore, using such microcrystalline cellulose and regenerated filter paper cellulose for experimentation, which is obviously very different from the actual physical arrangement of the cellulose in a real biomass, would only provide partial information on this subject. Wang et al. [16] used ball-milling to alter the crystallinity of the raw microcrystalline cellulose. After ball-milling the raw cellulose for 24 h, the crystallinity of the treated cellulose dropped significantly compared with the raw sample. The reduction in the crystallinity of the sample induced a shift of ca. 4 °C of the differential thermogravimetric curve towards lower temperature range. They also reported that the composition of pyrolysis liquids were different for the samples before and after being milled. The raw microcrystalline cellulose with higher crystallinity gave higher yields of anhydrosugars while the sample after being milled yielded more furanic compounds. Poletto et al. [17] and Wang et al. [18] found that the pyrolysis process was governed by a diffusion controlled mechanism under certain conditions in which the thermal diffusion was affected by the well-packed cellulose chains in the wood. Thus, the structural differences in the cellulose chain arrangement can affect the thermal decomposition behaviour of cellulose. However, the cellulose structure also varies with the raw biomass from which the cellulose is extracted. To the author's best knowledge, no previous work has attempted to isolate cellulose from real biomass samples and compare their pyrolysis behaviour.

The present work was aimed to examine and compare the pyrolysis characteristics of cellulose samples with different crystallinity. A chemical treatment method commonly used for nanocellulose isolation was adapted and used [19–23] to isolate the cellulose samples from real biomass feedstocks. Two commercial cellulose samples widely reported in the literature were acquired and employed as reference materials.

2. Experimental

2.1. Material

Three raw biomass materials, namely pine wood, poplar wood and wheat straw, were selected to represent samples from forestry residual and agriculture waste, covering both woody and herbal biomass for the present study. The as-received samples were first milled to a particle

size fraction of less than 310 μm. The details of the cellulose isolation procedures can be found elsewhere [19,24]. In brief, wax was first removed from the raw biomass using Soxhlet solvent extraction with a 2:1 (v/v) mixture of toluene/ethanol as the solvent for 6 h. Lignin in the sample was then removed by soaking the dried de-waxed sample in a 1.0 M NaClO₂ solution at 343 K until the products became white. Finally, the sample was treated in a 6 wt% KOH solution at room temperature overnight and then at the same concentration at 80 °C for 2 h in order to leach hemicellulose. The isolated cellulose was first dried at 323 K and 100 kPa and then fed through the cutting mill with a 310 μm screen to break the large agglomerates formed during the chemical treatments. The technique used in the present study does not affect the native cellulose structure according to the work reported in the literature [25–27]. The Klason lignin contents of the raw, de-waxed, de-lignified samples were measured following the standard procedure reported in [28]. Two widely used reference cellulose samples sourced from Sigma Aldrich and Avicel were included for comparison. For convenience, the pine wood, poplar wood, wheat straw, reference cellulose (Sigma) and reference cellulose (Avicel) were denoted as “PN”, “PP”, “WS”, “RC-S” and “RC-A”, respectively. The raw and treated biomass samples were abbreviated following the biomass name and numbers 0 to 3. For instance, PN0, PN1, PN2 and PN3 stand for raw, de-waxed, de-lignified pine wood and cellulose isolated from pine wood, respectively. The proximate and ultimate analysis, wax and Klason lignin content results of the various samples are shown in Table 1.

2.2. Experimental

The surface functional groups of the raw, intermediate and final samples, as listed in Table 1, were characterised using Fourier transform infrared spectroscopy (FTIR) (Thermo fisher Nicolet 6700) with iTR sample accessory and each sample was scanned in absorption mode in the range of 4000–650 cm⁻¹. The X-ray diffraction (XRD) analysis was performed using the Panalytical Empyrean X-ray diffractometer. The accelerating voltage and current were 40 kV and 40 mA, respectively. The X-ray diffraction traces were monitored using a diffractometer with copper Kα radiation at 5–40°/2θ at a scan rate of 4° min⁻¹. The sample crystallinity index (CI) and apparent crystallite size (L) were determined using the Segal method (Eq. (1)) [23,29] and Scherrer method (Eq. (2)) [29,30], respectively, and the results are also shown in Table 1.

$$CI = \frac{I_{200} - I_{AM}}{I_{200}} \times 100\% \quad (1)$$

where I_{200} is the peak height of the 200 crystallographic plane and I_{AM} is the intensity of the amorphous phase (2θ at ca. 18.5°) [23,29].

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