Synchrotron-Based Infra-Red Spectroscopic Insights on Thermo-Catalytic Conversion of Cellulosic Feedstock to Levoglucosenone and Furans

Anurag Parihar,† Jitaporn Vongsivivut,‡ and Sankar Bhattacharya*,†

†Department of Chemical Engineering, Monash University, Wellington Road, Clayton 3800, Australia
‡Infrared Microspectroscopy Beamline, Australian Synchrotron, 800 Blackburn Road, Clayton 3168, Australia

Supporting Information

ABSTRACT: Thermo-catalytic conversion of cellulosic feedstock, such as lignocellulose, to platform chemicals offers a renewable alternative to fossil-based chemicals. Mechanistic insights behind thermochemical conversion of lignocellulose would facilitate thermo-catalytic process development for bio-based chemicals. This study employed synchrotron-based Fourier transform infrared (FTIR) microspectroscopy to investigate chemical changes in acid-catalyzed cellulose and lignocellulose and glucose during pyrolysis. Major changes in glucose occurred at 200 °C, where it underwent reactions including ring opening and tautomerization. Acid treatment did not change the molecular structure of cellulose but disrupted the lignocellulose network. The observed synchrotron FTIR spectral features provided evidence for acceleration of catalytic dehydration of cellulose and lignocellulose to levoglucosenone and furans. Catalytic passivation of alkali and alkaline earth metals in lignocellulose was also observed at low acid concentration.

1. INTRODUCTION

Renewable sources for energy and chemicals are gaining favor in the wake of environmental anomalies caused by inordinate usage of fossils. Conversion of lignocellulose to chemicals is one renewable option for gradually replacing fossil-based chemicals and chemical precursors. Producing chemicals from lignocellulose could bolster the economic viability of biorefineries.1 Lignocellulose conversion to chemicals can be achieved through biochemical, chemo-catalytic, and thermochemical routes.2 The thermochemical route, albeit non-selective, offers one step lignocellulose conversion to platform chemicals. The selectivity of this method can be enhanced by employing suitable catalysts into the process.3–5

Understanding the reactions involved in thermochemical conversion of cellulose and lignocellulose is critical to select the most appropriate catalysts for optimal yield and selectivity. There are studies that used acid catalysts (Brønsted and Lewis) to increase the yield of the platform chemicals during thermo-catalytic conversion. Dobele et al. studied the effect of phosphoric acid on the yield of levoglucosan and levoglucosenone during thermochemical conversion.67 The mitigation of inhibitory effects of alkali and alkaline earth metals (AAEMs) by mineral acids has also been investigated.8 In another study, the catalytic effect of sulfuric acid was shown to boost the yield of levoglucosenone9 from lignocellulose. The role of hydrogen chloride as a catalyst and co-reactant for converting lignocellulose to levoglucosenone, levulinic acid, and substituted furans has also been investigated.10,11 Several other studies used sulfated zirconia,12 sulfated titania,13 ZSM-5-based catalyst,14 and solid phosphoric acid3 to convert lignocellulose to chemicals. However, a few studies elaborately investigated the structural and chemical changes that occur in cellulose and lignocellulose treated with acid.

Zheng et al. investigated the chemical changes that occur in the constituents of lignocellulose during torrefaction.15 However, that study does not illustrate the chemical changes that occur in the acid-treated feedstock. Similarly, other studies elucidate the functional group changes in woody16,17 and algal biomass18 during thermochemical conversion but not for the feedstock treated with acid. Mayes et al. used quantum mechanics calculations to illustrate the reaction pathways involved in the thermochemical conversion (pyrolysis) of glucose,19 and Jadhav et al. determined the reaction rates to investigate the intermediates during glucose conversion to furans.20 There is still limited, particularly spectroscopic, information on chemical changes that occur in acid-treated cellulose and lignocellulose which yield more anhydrosugars like levoglucosenone and furans.

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Accordingly, in this study, we used synchrotron Fourier transform microspectroscopy to investigate the changes in functional groups and the molecular structure of raw and acid-treated cellulose and lignocellulose at different temperatures during thermochemical conversion (pyrolysis). The thermal breakdown of glucose and the observed changes in functional groups were studied to gain insights into the mechanism of cellulose and lignocellulose conversion and the formation of platform chemicals (levoglucosenone and furans). Based on the observed spectral features, we have elucidated the reaction pathways that cellulose undergoes during pyrolysis. The mechanism behind the higher yield of levoglucosenone and furans from acid-catalysed cellulose and lignocellulose is also discussed.

2. RESULTS AND DISCUSSION

2.1. Functional Group Changes in Cellulose on Acid Treatment. Figure 1a presents the synchrotron FTIR spectra of microcrystalline cellulose and acid-treated cellulose taken at ambient temperature. The acid treatment resulted in minor changes in the functional group vibrations of cellulose that are shown in Figure 1b. The peak at 1370 cm$^{-1}$ (C–H vibration) shifted to 1360 cm$^{-1}$ for cellulose treated with 0.1 M and higher concentration of acid. Similarly, the peak at 1340 cm$^{-1}$ (O–H vibration) shifted to 1330 cm$^{-1}$. The shift of these two peaks could be due to the breakage of inter- and intra-chain hydrogen bonds depicted as dotted lines in Figure 1c. The treatment of cellulose with high concentration of acid (≥0.1 M) cleaved the hydrogen bond but did not cleave the covalent bonds inside the cellulose. The presence of peaks at 1100 and 900 cm$^{-1}$ (ring vibrations) implies that the acid treatment of cellulose did not cleave any bond in the ring structure. Table 1 shows the assignment of the peaks found in the synchrotron FTIR spectra.$^{21−23}$

2.2. Changes in Functional Groups Observed during Pyrolysis of Cellulose and Acid-Treated Cellulose. Figure 2 shows the synchrotron FTIR spectra of cellulose and changes in functional groups observed for cellulose during pyrolysis. The peaks presented at ∼3400, 1330, and 1200 cm$^{-1}$ correspond to O–H stretching vibrations. The C–H stretch is represented by the peaks at 2900, 1430, 1370, and 1280 cm$^{-1}$. The peaks at 1230, 1060, and 1030 cm$^{-1}$ are attributed to C–O vibrations, while the peak at 1160 cm$^{-1}$ is attributed to the C–O–C stretching mode. The ring valence vibrations led to the peaks at 1110 and 895 cm$^{-1}$.

The in situ monitoring of changes in the molecular structure of cellulose was performed at different temperatures from 30 to 500 °C. The peak at 1640 cm$^{-1}$ corresponds to adsorbed water molecules and this bound water started to disappear at 100 °C as the cellulose particles were heated. The depolymerization of cellulose was observed to commence at 250 °C. The peaks at 1320 cm$^{-1}$ (C–H stretch) and 1230 cm$^{-1}$ (C–O stretch) started to diminish at 250 °C and disappeared at 300 °C. The depolymerization was followed by dehydrogenation reactions at 350 °C. The appearance of peak at 1690 cm$^{-1}$ suggested the presence of compounds with C=O groups, which could be furans and other anhydrosugars. With further increase in temperature, the peaks at 1160 cm$^{-1}$ (C=O–C) and 1100 cm$^{-1}$ (glucose ring vibration) disappeared. The breakage of the C–O–C bond and disappearance of glucose ring vibration suggested that the disruption of the cellulose structure occurred at 400 °C. At this temperature, there was also an additional peak at 1590 cm$^{-1}$ attributed to the aromatic skeletal vibration and C=O stretch.$^{15,22}$ The aromatic vibration, in particular, represents molecular evidence for the existence of carbonization of cellulose and formation of a benzene ring.$^{24}$ Additionally, the presence of the peak at 1690 cm$^{-1}$ (C=O) at 400 °C implies the presence of carbonyl compounds. These compounds undergo further fragmentation, decarboxylation, and decarbonylation to liberate light gases$^{25}$ which can be observed through the decreasing intensity of this peak at higher temperatures. Based on the synchrotron FTIR spectral data, it could be concluded that cellulose pyrolysis starts with the loss of adsorbed water, followed by depolymerization and subsequently a dehydrogenation reaction that results in the formation of furans and anhydrosugars. A further increase in temperature results in a series of simultaneous reactions including fragmentation, carbonization,
and re-polymerization that lead to char formation and liberation of light gases.

To understand the effect of acid on these reactions, the in situ synchrotron FTIR measurement was performed on acid-treated cellulose. Figure 3a shows synchrotron FTIR spectra of cellulose treated with 0.05 M HCl observed at different temperatures, suggesting that the onset of depolymerization occurred at 250 °C at which the peaks at 1320 cm$^{-1}$ (CH stretch) and 1230 cm$^{-1}$ (C−O stretch) started to diminish. The acid treatment accelerated the dehydration reaction as evidenced by the strong intensity of C−O vibrational modes at 1710 and 1650 cm$^{-1}$ at 350 °C, compared to that of cellulose without acid treatment. In addition, the peaks found in the range of 1560−1510 cm$^{-1}$ (i.e. aromatic skeletal vibrations) shown in Figure 3b, indicate the onset of carbonization of cellulose at 350 °C. The early onset of aromatization is caused by the acceleration of dehydration reactions as a result of acid treatment. The fragmentation of these carbonyl compounds produced smaller organic oxygenated molecules, supported by an increase in the intensity of the peaks at 1700 and 1590 cm$^{-1}$ at 400 °C. Such molecular evidence also agrees well with the appearance of the vibrations around 1430 cm$^{-1}$, corresponding to C−O−H bending modes. The disappearance of C−O−C and C−O vibrations confirms the breakage of the chain structure that led to the formation of smaller organic molecules. With further rise in temperature, light gases were evolved and the intensity of the peaks 1700 and 1590 cm$^{-1}$ increased before they eventually diminished at 550 °C.

Figure 4a–c illustrate synchrotron FTIR spectra of cellulose treated with higher concentration of acid. The spectral changes observed for cellulose treated with 2 and 4 M acid are shown in Supporting Information Figures S1 and S2, respectively. Higher concentration of acid was found to accelerate dehydration and charring reactions. The vibration of the C==O bond started to appear at 300 °C during thermal breakdown of cellulose, which was treated with ≥0.5 M acid. Figure 5 highlights the early appearance of C==O vibration for cellulose treated with 0.5 M acid. Peaks representing other functional groups, including C−O, C−H, and O−H, started to diminish at lower temperature (from 350 °C and lower) for cellulose treated with higher concentration of acid (greater than 0.5 M). This implies that increasing the concentration of acid accelerates the fragmentation and scission reactions.

Accordingly, based on the synchrotron FTIR results, in this study, it was observed that pyrolysis of cellulose began with

| wavenumber (cm$^{-1}$) | assignment                                                      |
|------------------------|-----------------------------------------------------------------|
| 3400−3300              | OH stretch                                                      |
| 2900                   | CH stretch                                                      |
| 2400−2300              | CO$_2$                                                          |
| 1750−1690              | C==O                                                            |
| 1640                   | adsorbed water                                                  |
| 1610−1590              | aromatic skeletal vibration + C==O                              |
| 1560−1505              | aromatic skeletal vibration                                      |
| 1430                   | CH$_2$ C−O−H                                                    |
| 1370                   | CH                                                              |
| 1340−1330              | OH                                                              |
| 1320                   | CH$_2$ wagging                                                  |
| 1280                   | CH                                                              |
| 1230                   | C−C + C−O + C==O                                               |
| 1200                   | OH                                                              |
| 1160−1140              | C−O−C                                                          |
| 1110                   | glucose ring stretch; ring vibration                            |
| 1060                   | C−O                                                            |
| 1030                   | C−O                                                            |
| 900                    | ring vibration                                                  |

Table 1. Peak Assignment for Cellulose$^{21−23}$
depolymerization (at 250 °C), followed by dehydration (from 350 °C). The dehydration reactions resulted in the formation of anhydrosugars and a further increase in temperature led to breakage of bonds that produce smaller organic molecules and light gases. This observation is in good agreement with the previous literature.25 The aromatization of cellulose was observed to occur at higher temperatures (400 °C onwards) which is consistent with previously published results.26 Treating cellulose with high concentration acid accelerated the dehydration reaction, resulting in the formation of carbonyl compounds at a lower temperature (300 °C). The accelerated dehydration also results in the higher yield of platform chemicals (e.g. anhydrosugars like levoglucosenone and furans) at low temperature similar to those observed in the earlier study.27 It is evident from the FTIR spectra that higher concentration of acid also resulted in fragmentation and scission of organics at a lower temperature (350 °C) and early aromatization of cellulose. Shafizadeh and Fu28 detected glucose in cellulose pyrolysis and there is a possibility of formation of cellulose pyrolytic products via a transient glucose form.29 Hence, after investigating cellulose pyrolysis and obtaining insights on the different types of associated reactions, we investigated cellulose dehydration in detail through the changes in spectral features obtained during glucose pyrolysis.

2.3. Functional Group Changes during Pyrolysis of Glucose. Figure 6a,b depicts the synchrotron FTIR spectra of glucose. As described in Table 2, the synchrotron FTIR spectra of glucose present peaks associated to O−H groups (3400−3300, 1365, 1350, 1220, and 1200 cm−1), C−H stretches (2950−2890, 1430, 1406, and 1300 cm−1), C−O vibration (1100, 1080, and 1030 cm−1), and C−O−C stretches (1150 cm−1).

Changes in functional groups of glucose during thermal breakdown are presented in Figure 7a−c. There was no change in the functional groups until 100 °C (shown in Supporting Information Figure S3). The O−H stretching vibration between 3400 and 3300 cm−1 became noisy at 150 °C, with new peaks found at 1460, 1270, and 1120 cm−1. Figure 8 shows the difference between the synchrotron FTIR spectra of α-glucose and β-fructose. The peaks at 1460 and 1270 cm−1 are characteristic of fructose and are absent in the spectra of glucose. The appearance of these peaks during thermal breakdown of glucose is indicative of the commencement of isomerization of glucose.

The major changes in the glucose structure were observed at 200 °C. First, the peaks at 1370, 1230, and 1200 cm−1 vanished due to loss of O−H groups. Next, the vibrations for the C−H group (1430 cm−1) and C−O group (1100−
1010 cm\(^{-1}\)) also disappeared. Finally, there was disappearance of the C–H vibrational mode at 2910 cm\(^{-1}\). The loss of these functional groups could be due to dehydration reactions at higher temperature.\(^{19,29}\) The peak at 1140 cm\(^{-1}\) (C–O–C vibration) is indicative of dehydration, which led to the formation of levoglucosan. There are peaks associated to C\(\equiv\)O vibrations as well at 200 °C, which could be due to ring opening and keto–enol tautomerization\(^{20}\) that lead to the formation of furans. All the aforementioned reactions are not necessarily sequential but likely to be very fast competing reactions resulting in different products. The vibration for carbonyl compounds (\(\sim 1700\) cm\(^{-1}\)) at a higher temperature (from 250 °C) could arise from aldehydes, ketones, and organic acids. Furthermore, the peak around 1590 cm\(^{-1}\) found at temperatures between 350 and 500 °C (Figure 7b,c) could be the consequence of condensation products that led to the formation of compounds with C\(\equiv\)O groups and aromatics. Scission of other bonds, such as C\(\equiv\)O–C and C–O, also occurred at higher temperatures, suggesting fragmentation.

**Figure 6.** (a) Synchrotron FTIR spectrum of D-glucose. (b) Functional groups presented in the synchrotron FTIR spectrum of D-glucose.

**Table 2. Peak Assignment for D-Glucose\(^{21−23}\)**

| Wavenumber (cm\(^{-1}\)) | Assignment                  |
|---------------------------|-----------------------------|
| 3400–3300                 | OH                         |
| 2950–2890                 | CH                         |
| 2400–2300                 | CO\(_2\)                    |
| 1750–1690                 | C\(=\)O                    |
| 1460–1450                 | CH                         |
| 1430–1420                 | CH or C–O–H                |
| 1406                      | CH                         |
| 1380–1360                 | CH                         |
| 1350–1300                 | OH                         |
| 1280                      | CH                         |
| 1270–1240                 | C–O                        |
| 1220–1200                 | OH                         |
| 1160–1140                 | C–O–C                      |
| 1110–1100                 | ring vibration             |
| 1080–990                  | C–O                        |

**Figure 7.** (a) Changes in spectral features observed for glucose started at 150 °C. (b) Synchrotron FTIR spectra observed during thermal breakdown of D-glucose between 300 and 400 °C. (c) Synchrotron FTIR spectra observed during thermal breakdown of D-glucose between 450 and 550 °C.
reactions, which produced lower molecular weight compounds. Decarboxylation was also evident at higher temperature according to the peaks at 2400 cm$^{-1}$ that correspond to gas phase CO$_2$ vibration. According to the observed synchrotron FTIR spectral data, the breakdown of the glucose proceeded via dehydration, ring opening, and isomerization that result in the formation of furans. Dehydration reactions produce levoglucosan, and lower molecular weight compounds are formed as a result of fragmentation reactions. Decarboxylation liberates light gases during glucose pyrolysis. Figure 9, in particular, presents the proposed mechanism for glucose pyrolysis based on the results from this study, which also provides further insights into cellulose pyrolysis. The effect of acid on these reactions when cellulose is present with other biomass constituents, hemicellulose and lignin, is described in the next section.

2.4. In Situ Functional Group Changes in Acid-Treated Lignocellulose (Woody Biomass). A lignocellulosic network consists of cellulose, hemicellulose, and lignin. It also contains AAEM ions that are known to interact with cellulose and influence the pyrolysis process. The effect of different concentrations of acid treatment on the molecular structure of biomass was studied using the synchrotron FTIR microspectroscopy technique and is shown in comparison to that of raw biomass in Figure 10. The spectra revealed vibrations from the major constituents of biomass, including cellulose, hemicellulose, and lignin. The O–H vibrations associated to cellulose, hemicellulose, and lignin, are reflected...
by the peaks at 3350, 1335, and 1320 cm$^{-1}$. The peaks at 2900, 1450, and 1370 cm$^{-1}$ represent the C–H stretches. The C=O stretches between 1730 and 1590 cm$^{-1}$ were originated from both holocellulose and lignin. The skeletal vibration of aromatic rings produced peaks at 1590, 1560, 1540, and 1505 cm$^{-1}$. The C–O–C stretching modes, on the other hand, resulted in the peak at 1160 cm$^{-1}$, while the C–O stretches yielded peaks at 1060 and 1030 cm$^{-1}$. The peaks at 1100 and 900 cm$^{-1}$, in particular, are indicative of ring stretches of the glucose unit. These ring stretches likely arose from cellulose and hemicellulose structures. Table 3 outlines the assignment of peaks observed in the spectra of biomass.

Table 3. Peak Assignment for Biomass$^{21–23}$

| wavenumber (cm$^{-1}$) | assignment |
|------------------------|------------|
| 3500–3300              | OH         |
| 2900–2800              | CH         |
| 2400–2300              | CO$_2$     |
| 1730–1650              | C=O        |
| 1590                   | aromatic skeletal vibration + C=O |
| 1560–1505              | aromatic skeletal vibrations |
| 1450                   | CH         |
| 1430–1400              | aromatic + CH |
| 1370                   | CH         |
| 1335–1320              | OH         |
| 1270                   | G ring + C=O |
| 1230                   | C–C and C–O |
| 1160–1140              | C–O–C     |
| 1110–1100              | ring vibration |
| 1060–1030              | C–O        |

It was found that pre-treatment of biomass with a concentration of up to 1 M did not have any effect on the functional groups. However, at $\geq$2 M concentration of acid, the peaks at 1730 and 1590–1500 cm$^{-1}$ started to diminish. These vibrations originate mainly from hemicellulose and lignin. Treatment of biomass with 2 M and higher acid concentration was observed to disrupt the lignocellulosic network by dissolving hemicellulose and lignin. In fact, treatment of biomass with acid is known to remove hemicellulose and lignin. Figure 11a–e shows the effect of acid pre-treatment on the thermal breakdown profile of biomass. Changes in spectral features observed for raw biomass during thermal breakdown are presented in Supporting Information Figure S4. Similar changes are reported and discussed in detail elsewhere in the literature.17

Lower concentration of acid (up to 0.1 M) was observed to stabilize certain functional groups of biomass up to 500 °C. The O–H (≈3400 cm$^{-1}$) and C–H (≈2900 cm$^{-1}$) functional groups in the raw biomass substantially diminished at a temperature higher than 400 °C (see Supporting Information Figure S4) but were observed after 400 °C in the acid-treated biomass at 0.05 and 0.1 M acid concentration (Figure 11a,b). The stabilization of C–O vibration (at 1060 and 1030 cm$^{-1}$) was also observed. The evolution of CO$_2$ was evident at temperatures above 400 °C for the biomass treated with 0.05 and 0.1 M hydrochloric acid. A loss of C=O vibrations above 400 °C was also observed. The treatment with low concentration of acid favored the decarboxylation reaction. However, the stabilization of other functional groups suggested that it delayed the fragmentation and polycondensation reactions. No significant effect on dehydration reactions was observed. The peak at 880 cm$^{-1}$ (≡C–H) indicated that dehydration reactions occurred at higher temperatures, but the catalytic effect of acid on dehydration was not observed. This could be due to the neutralization of acid by ash and AAEMs in biomass.32 The AAEM ions are known to have a positive effect on char formation during biomass pyrolysis.30,33 The passivation of ash and metal ions by the acid resulted in delay of fragmentation and polycondensation reactions responsible for char formation.

Biomass treated with 0.5 M acid concentration exhibited minor differences with rising temperature during thermal breakdown. The peaks associated with O–H functional groups (at 3400 and 1320 cm$^{-1}$) started to disappear after 350 °C (Figure 12). The higher concentration of acid could not only passivate the ash and metal ions but also catalyze the dehydration reaction. The diminishing intensity of C=O vibrations (1730–1650 cm$^{-1}$) at a temperature higher than 350 °C indicated the onset of decarboxylation reactions. The onset of the disappearance of the peaks representing C–H vibrations (1460–1430 and 1370 cm$^{-1}$) was found at temperatures lower than 350 °C. The effect was found to be very significant at higher acid concentrations (>1 M). The biomass treated with higher concentration of acid (>1 M) underwent depolymerization and dehydration reactions very quickly. The majority of the functional group vibrations disappeared from 400 °C (Figure 11e). The high acid concentration also accelerated the char-producing polycondensation reaction as evidenced by the peaks at 1560 cm$^{-1}$ (aromatic skeletal vibrations) and 1590 cm$^{-1}$ (aromatic ring conjugated with C=O group). At 4 M acid concentration, these bonds underwent scission and decarboxylation reactions, which resulted in the loss of almost all the functional groups in biomass at 400 °C (see Supporting Information Figure S5).

Thus, low concentration of acid treatment was found to passivate the ash content and stabilize certain functional groups during the thermal breakdown. On the other hand, higher concentration of acid was observed to accelerate reactions, including scission and fragmentation. Our synchrotron FTIR microspectroscopy study suggested that the acid treatment exhibited a catalytic effect during the thermal breakdown and also accelerated the reactions required for the formation of platform chemicals as well as the reactions that led to char formation. The acceleration of the dehydration reaction in acid-treated biomass results in higher yields of platform chemicals, such as levoglucosenone and furans, which were obtained even at low temperatures in the previous studies.7,9,34

3. CONCLUSIONS

In this study, synchrotron FTIR microspectroscopy was used to (i) investigate the effect of acid treatment on the molecular structure of cellulose and biomass and (ii) determine the changes in the functional groups of glucose, acid-treated cellulose, and biomass samples during thermochemical conversion. The results obtained from the synchrotron FTIR spectroscopy study provided molecular evidence for the proposed mechanism behind the conversion of biomass to platform chemicals like levoglucosenone and furans.

Based on the observed synchrotron FTIR spectral features, cellulose did not undergo significant structural changes upon acid treatment, confirming that all the functional groups of cellulose were intact even for those treated with 4 M hydrochloric acid. However, the lignin and hemicellulose
components of the lignocellulose network were found to be dissolved when the biomass was treated with hydrochloric acid stronger than 2 M. This was supported by the disappearance of the vibrations characteristic to hemicellulose and lignin typically presented at ∼1740 cm⁻¹ and within the 1590–1505 cm⁻¹ spectral range.

Changes in spectral features observed for glucose indicated specific functional groups associated with various reactions that lead to the formation of platform chemicals during thermal conversion of cellulose and biomass. The thermal breakdown of glucose proceeded through several parallel reactions. The dehydration and isomerization reactions were observed at 150
0.5 g of biomass was suspended in 50 mL of aqueous HCl at different concentrations. Biomass was stirred for 20 h and subsequently centrifuged at 4000 rpm for 10 min. The supernatant was decanted and the pelleted biomass was dried at 60 °C for 48 h followed by final drying at 105 °C for 24 h. Cellulose was also treated with 0.05–4 M of aqueous HCl. To obtain pre-treated cellulose, it was first stirred in desired concentration of aqueous HCl for 5 h. After stirring, the suspension was centrifuged at 4000 rpm for 10 min. The supernatant was decanted and the cellulose pellet was dried at 60 °C for 12 h and then at 105 °C for 24 h.

4.2. Synchrotron-Based Infra-Red Spectroscopy. The changes in functional groups in raw biomass, cellulose, glucose, fructose, pre-treated biomass, and cellulose samples were investigated using synchrotron FTIR microspectroscopy at the infrared microspectroscopy (IRM) beamline, Australian Synchrotron (Victoria, Australia). The unique advantages of the synchrotron FTIR technique are due to the superior characteristics of high photon flux and diffraction-limited spatial resolution, allowing spatially resolved chemical “mapping” measurement of materials to be performed at a lateral resolution between 3 and 10 μm (depending on wavelength). Using the synchrotron FTIR microspectroscopy technique, good quality spectra at a high signal-to-noise ratio can be obtained from very fine particles, which are typically produced as a result of thermal breakdown.

The synchrotron FTIR measurement was performed in the transmission mode using a Bruker Vertex 80v spectrometer coupled with a Hyperion 2000 FTIR microscope and a liquid nitrogen-cooled narrow-band mercury cadmium telluride detector. The synchrotron IR beam was focused to a spot size of ∼16 μm using a 15× objective (NA = 0.4) suitable for the setup of the temperature-controlled Linkam stage. The acquisition parameters were 4 cm⁻¹ spectral resolution and 128 co-added scans. Blackman-Harris 3-term apodization, power-spectrum phase correction, and zero-filling factor of 2 were set as default acquisition parameters using OPUS 7.2 software suite (Bruker). At each temperature, background spectra were acquired from sample-free areas inside the barium fluoride (BaF₂) window used as an IR transparent substrate, once before conducting sample measurement.

4.3. Temperature-Controlled Linkam Stage. The in situ investigation of changes in functional groups during thermal breakdown of the sample was facilitated using a temperature-controlled Linkam stage (FTIR600 Infra Red stage, Linkam Scientific Instruments, Tadworth, UK). The sample stage offered heating rates of up to 150 °C/min and linear cooling rates of 0.01–100 °C/min. In this study, the stage was heated up to 550 °C and was cooled down using liquid nitrogen to prepare it for the next run cycle. The sample was placed on the sample stage located at the centre of its gas tight chamber maintained at atmospheric pressure. The chamber was nitrogen purged at a flow rate of 4 mL/min. Barium fluoride (BaF₂) windows were used with the Linkam stage as they provide a broad IR transmission range (4000–800 cm⁻¹) and can withstand high temperatures.

4.4. Data Acquisition and Analysis. The particles were squashed inside a compression cell to produce sufficiently thin pieces of samples suitable for operation in the transmission mode. The samples were placed and dispersed evenly on a BaF₂ window. After that, the samples on the BaF₂ window were transferred to the Linkam stage. The particles, from which synchrotron FTIR spectra were acquired, were carefully selected and were determined by acquiring spectra at ambient...
temperature (30 °C). Thereafter, the particles were heated at a rate of 150 °C/min (for biomass and cellulose) and 10 °C/min (for glucose and fructose) from 70 to 100 °C and finally at 550 °C. The spectra were acquired at 50 °C intervals.

The collected spectral data were processed using OPUS 7.2 software (Bruker). Spectral processing consisted of baseline correction using the rubber band method, followed by normalization of spectra using the min–max method. The peak assignment was based on cited literature.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03681.

Synchrotron FTIR spectra for thermal breakdown of cellulose treated with 2 M acid and 4 M acid; thermal breakdown on glucose; thermal breakdown of biomass; and thermal breakdown of biomass treated with 4 M acid (PDF).

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: sankar.bhattacharya@monash.edu.

**ORCID**

Sankar Bhattacharya: 0000-0002-7590-6814

**Notes**

The authors declare no competing financial interest.

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