Transformation of lignocellulosic biomass during torrefaction

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\textbf{A B S T R A C T}

In this study, the effect of torrefaction on the chemical and structural transformation of lignocellulosic biomass was investigated using complementary analytical tools. It was observed that the acid-insoluble fraction was increased from approximately 30 to 38% and the methoxyl content was decreased to about half after torrefaction at 330 °C for 2.5 min. These results highlight the formation of condensed structures along with lignin transformation via demethoxylation. Solid-state NMR spectroscopy indicated that upon torrefaction the aromaticity increased from about 36 to 60%. For the sample torrefied at 330 °C, the non-protonated aromatic carbon fraction was found to be about 60% of total aromatic carbons, indicating the formation of large aromatic clusters. Complementary analyses used in this study are proposed as a suitable approach for the elucidation of chemical and structural transformation of biomass during thermal treatment.

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1. Introduction

Torrefaction is a relatively mild thermochemical process that uses low temperature (200–300 °C) and inert gas atmosphere to produce homogeneous solid fuels with higher hydropobicity and lower oxygen content relative to the feed biomass. The main fiber cell-wall components (cellulose, hemicelluloses, and lignin) present in the biomass undergo different chemical transformations because of their distinct chemical and thermal reactivity during torrefaction [1]. It has been reported that compared to cellulose and lignin fractions, most of the hemicelluloses degrade into volatile components at low torrefaction temperatures [2,3]. Due to the fuel value of torrefied biomass, it has been used as replacement of coal, in co-combustion with other fuels, and in the production of pellets or briquettes [4,5]. Recently, torrefaction has renewed interest as thermochemical processes are further investigated for the production of solid fuels from different raw materials and under optimized conditions.

The evaluation of torrefied biomass as an enhanced solid fuel is mandatory prior to any application and therefore several methods have been applied within the fields of wood and fuel sciences and industries. Common analyses include wet-chemistry methods for identifying wood composition (cellulose, hemicellulose, and lignin) in lignocellulosic biomass [6–8], and proximate/ultimate analyses (volatile matter, fixed carbon, ash content, and elemental CHN). These methods have also been generally applied in coal assays [9,10]. In addition, the amount of energy required for grinding [11,12], mass/energy balances [9,13,14], hydrophobicity [14,15], and combustion analyses [6,16] have been used to evaluate processability as solid fuels.

Furthermore, there have been constant attempts to investigate the fundamental mechanism of the thermal alteration of lignocellulosic biomass. Spectroscopic analyses such as FTIR or NMR are usually employed for analyzing chars from biomass. For example, FTIR can indicate relative changes in spectrum and assess changes in functional groups and chemical bonding in solid samples [17,18]. Solid-state NMR spectroscopy is a powerful tool for structural analysis of solid biomass. For example, \textsuperscript{13}C CP/MAS (cross polarization/magic angle spinning) NMR spectroscopy has been applied to thermally modified biomass [19] to indicate the increased crystallinity of treated samples. This observation has been ascribed to the thermal degradation of less ordered domains rich in hemicelluloses and amorphous cellulose.

The cleavage of β-O-4 linkages and condensation of lignin structures have been suggested after comparison of the spectra from untreated and thermally-treated spruce samples. Sharma and co-workers used \textsuperscript{13}C CP/MAS NMR to show the loss of lignin substructure and increased aromaticity of pyrolyzed lignin, which was transformed to char-like structures from biomass [18]. Recently, it was shown that more quantitative analyses of biochar are possible by using direct polarization and magic angle spinning (DP/MAS) \textsuperscript{13}C NMR [20,21]; as a consequence, biomass models for fused aromatic ring cluster have been proposed. The techniques discussed above have been generally used for studying biochar, which is highly

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homogeneous, but rarely applied to torrefied biomass which is a more complex and heterogeneous material in its composition. In fact, despite its reported use since early 1980s, details about the thermal and chemical transformations that occur during torrefaction are still not well understood.

In this study, we characterized torrefied biomass by combining different chemical and structural approaches. Conventional methods were used to quantify the compositional changes of biomass fractions undergoing thermal transformation. In addition, we applied complementary methods to gain information on structural alteration. This included changes in methoxyl functional groups and spectroscopic fingerprints obtained by solid-state DP/MAS NMR spectroscopy. From these observations, it was possible to reveal the principal chemical changes that occurred in lignocellulosic biomass during torrefaction and to shed new light to further related applications.

2. Materials and methods

2.1. Sample production

Loblolly pine chips (about 15 mm × 6 mm) containing bark were obtained from a local wood product industry and were torrefied using a pilot-scale torrefaction unit (about 1 ton/day capacity), which was installed in North Carolina State University (Lake Wheeler Road Field Laboratory, Raleigh, NC). Three torrefied samples with different treatment temperatures (270, 300, and 330 °C) and residence time of 2.5 min were prepared and named as lightly (TA), moderately (TB), and severely (TC) torrefied biomass. Untorrefied biomass is indicated as “Raw” biomass for short. The weight loss of biomass during torrefaction was estimated using a linear correlation ($R^2 = 0.997$) between the weight loss and the atomic O/C ratio, developed from lab-scale experiments with a tube furnace. The correlation was measured within the temperature range of 200–500 °C with seven data points. All samples were milled to 40–60 mesh using a Willey mill, and stored in an air-tightened plastic bag at 4 °C before further analyses.

2.2. Ultimate and proximate analysis, heating value measurement

Carbon, hydrogen, and nitrogen content in the samples were analyzed by using PerkinElmer 2400 Series II Elemental Analyzer (PerkinElmer, Waltham, MA). Oxygen content was calculated by subtraction of the ash and the CHN content from the total. Proximate analysis was conducted according to ASTM standard method D5142-09 [22] with the following adaptations. For ash determination, the leftover solid after volatile matter determination from the standard method was heated to 750 °C for 6 h without cover under atmospheric condition, then cooled in a desiccator to minimize moisture absorption, and weighed to determine the ash content. Both ultimate and proximate analyses were performed at least by duplicate. Heating values were measured using 1341 Oxygen Bomb Calorimeter (Parr Instrument Company, Moline, IL). About 10 mg of sample was loaded into the apparatus and combusted under oxygen atmosphere and the temperature rise recorded at 1-min intervals to calculate the higher heating value (HHV) for each sample.

2.3. Compositional analysis

Structural carbohydrates – cellulose and hemicelluloses – were measured by HPLC sugar analysis after two-step acid hydrolysis [8]. Acid soluble/insoluble lignin content was measured using a modified Klason lignin analysis [23]. Based on the calculated weight loss and compositional analysis of the torrefied biomass, the extent of mass reduction for glucan, other polysaccharides, and acid-insoluble residue from the Klason lignin method was determined.

2.4. Thermogravimetric analysis (TGA)

The thermal behaviors of the samples (about 10 mg of milled wood per run) were investigated using a TGA Q500 (TA Instruments, New Castle, DE). The heating program consisted on a 5 min hold at 30 °C, ramp up to 900 °C at a heating rate of 10 °C/min, and then the weight difference was recorded as a function of temperature profile. Nitrogen was used as purging gas at a flow rate of 100 mL/min.

2.5. FTIR spectroscopy

FTIR analyses were performed with a Nexus 470 instrument (Thermo Scientific, Waltham, MA) using potassium bromide (KBr) pellets with 1% (w/w) dried samples. Each spectrum was recorded after 64 scans in the wavenumber range from 4000 to 650 cm⁻¹. Background spectra were collected before every measurement. KBr was oven-dried before making the pellets to reduce interferences from water.

2.6. Quantification of methoxyl groups

Methoxyl group content was measured by the GC quantification method [24]. Briefly, 20 mg of milled and dried samples were dispersed in 5 mL 57% hydroiodic acid at 130 °C for 30 min with frequent agitation. Following, 10 mL of n-pentane was added with a known concentration of an internal standard, ethyl iodide. After dissolution of the generated methyl iodide in the pentane solvent, the liquid was analyzed in a gas chromatograph instrument (Hewlett Packard HP 5890, Agilent Technologies) equipped with a flame ionization detector, using with DB-WAX column (40 m × 0.18 mm i.d. × 0.3 μm; Agilent Technologies Inc., CA, USA). Temperature for the injector and detector was set to 110 and 150 °C, respectively. Oven temperature was isothermal at 80 °C, and total run time was 7 min.

2.7. Solid-state NMR

The solid-state magic angle spinning (MAS) NMR spectra were acquired with a Varian 3.2 mm MAS probe, on a Varian Inova 500 spectrometer. A spinning speed of 7 kHz and a contact time of 1 ms were used for cross-polarization (CP) MAS NMR experiments. In order to remove spinning sidebands, the four-pulse total suppression of sidebands (TOSS) was applied before detection, and 1,000–2,000 FID (free induction decay) signals were accumulated with an acquisition delay of 2 s. For the direct-polarization (DP) MAS experiments, the sample was spun at a higher frequency of 14 kHz and the TOSS pulse sequence was not used. A dephasing time of 68 μs was used for dipolar dephasing experiments to determine the non-protonated aromatic carbon fraction [20,21]. For the quantitative DP NMR experiments, 1,000–2,000 FIDs were collected with a long acquisition delay of 60 s. The 90° pulse-lengths for $^1$H and $^{13}$C were 3.0 μs and 2.7 μs, respectively. The two-pulse phase-modulated (TPPM) decoupling scheme was employed with radio-frequency field strength of 80 kHz. Quantitative spectral analysis was performed by integrating the assigned area of DP NMR spectra and fractionating into three major categories – carboxyl, aromatic, and alkyl carbon fractions [20]. Quantification for corresponding non-protonated aromatic carbon fraction was carried out in the same manner using DP NMR spectra with dipolar dephasing.
3. Results and discussion

3.1. Proximate and ultimate analysis

The basic compositional analysis of the feedstock material and the torrefied biomass is presented in Table 1. Thermal breakdown and release of volatile matter is expected to be mainly from the carbohydrate fractions, especially hemicelluloses, the content of which decreased from approximately 85 to 60% after the most severe torrefaction condition at 330 °C (TC). Due to the degradation of volatilized matter, residual ash was accumulated after torrefaction at increased levels (from TA to TC). In addition, the content of fixed carbon increased with the severity of the torrefaction conditions. Ultimate analysis data showed large reductions in oxygen content after torrefaction. High oxygen content is a distinctive characteristic of biomass compared to that of other fuels. The significant decrease of oxygen content can be explained by dehydration reaction, which generates water vapor as a product. Furthermore, the loss of volatile organic products and their release as gases (mostly of CO and CO2) were also responsible for the decrease of oxygen in the solid phase. The amount of hydrogen also decreased along with the loss of volatile/gaseous products and water. Due to the loss of oxygen and hydrogen, the carbon content experienced a relatively important increase, from approximately 51 to 66%, equivalent to a change in atomic O/C ratio from 0.63 to 0.31 after torrefaction. This substantial changes in elemental analysis showed that the torrefied biomass becomes close to lignite on the Van Krevelen diagram [6,25], and its heating value is also comparable with that of lignite [16,26].

3.2. Compositional analysis

In this study, the compositional changes were monitored by quantification of each component, as indicated in Table 2. The fraction of each component in the untorrefied as well as the torrefied samples are presented based on 100 g of the initial biomass. Compared to the untorrefied biomass (Raw), the content of glucans and other carbohydrates in the highly-torrefied sample (TC) were reduced by approximately 74 and 97%, respectively. It has been widely accepted that the carbohydrate fraction, especially hemicelluloses, are more easily degraded by thermal treatment. By comparing the untorrefied biomass with that after a light torrefaction (TA), there is evidence that hemicellulose degraded more rapidly than cellulose.

The amount of the solid residues after acid hydrolysis, expressed as Kason lignin, increased with torrefaction. In the Kason lignin analysis, highly-concentrated sulfuric acid (72%) swells the carbohydrate structure, and the dilute acid hydrolysis at high temperature that follows degrades glycosidic bonds of the carbohydrates, converting them into monomeric sugars and leaving an acid-insoluble fraction as Kason lignin. If the solid residue after the acid hydrolysis represents the actual lignin content in the biomass, the amount of residues in the torrefied samples should decrease or become close to the initial amount, compared to that from untorrefied material. It was observed that the amount of acid-insoluble residue increased from approximately 30 to 38 g for the Raw and TC samples, respectively (Table 2). This observation might indicate the formation of condensed structures into thermally degraded/modified products. As the severity of torrefaction increases, the heat energy may induce the formation of acid-resistant linkages between products, e.g. carbon–carbon bonds, resulting in an increased amount of acid-insoluble residue. For example, Pastorova and coworkers reported that, when a microcrystalline cellulose (Avicel) was pretreated under inert atmosphere for 2.5 h at 270 °C, it showed 40% of weight loss, and only 13% of glucose can be recovered from the char by sulfuric acid hydrolysis. And, over 290 °C glucose recovery was below 3% [27]. This implies that the loss of glycosidic bonds in cellulose structure and the formation of acid-resistant condensed solid products, induced by thermal treatment. Hence, it is expected that a close correlation exists between the amount of residue and the formation of condensed structures during torrefaction.

3.3. Thermogravimetric analysis

Fig. 1 shows the thermograms of torrefied woods. One distinct difference from the weight loss curves is that the char amount, which is defined as the % residue left in the TGA pan after analysis, was substantially increased with the severity of torrefaction, from Raw to TC samples. The opposite trend was observed for the volatile matters released during the heating process, consistent with the proximate data discussed previously. No significant differences in peak temperatures were observed from the derivative thermogravimetry (DTG) curves. Thermal degradation of cellulose generally occurred between 300 and 400 °C in TGA [28]. It was reported that the DTG peak of cellulose can be shifted by structural changes of cellulose quantifiable by the crystallinity index, crystallite size, and degree of polymerization [29]. Hence, the almost identical peak position between the samples might indicate that the structural characteristic of cellulose fraction was preserved even after the torrefaction condition for TC sample that resulted in a degraded material with half its original weight. Other features observed in the DTG curves are the small and wide bumps placed around 200 °C (“a” in Fig. 1) just before the major DTG peak, and the shoulder at 340–350 °C (“b” in Fig. 1) on the major DTG peak. The former might be ascribed to thermal degradation of low-molecular weight, volatile products. These products were likely to be released as gases during treatment, but considerable amounts are expected to remain in the residual solid by re-condensation and/or entrapment. The shoulder at 340–350 °C (“b”) observed in the DTG of the untorrefied sample has been reported from the degradation of hemicelluloses in lignocellulosic biomass [30,31]. Hemicelluloses are less thermally stable than cellulose, since they are more susceptible to hydrolysis and dehydration reactions [32]. Due to the degradation of hemicellulose, DTG curves of TA and TB samples showed shoulders smaller than those of the Raw sample. In the thermogram for TC, identification is less clear, which is ascribed to the more limited presence of hemicellulose in this fraction, as indicated in the compositional analyses (Table 2). In addition, the relative difference between the DTG peak area reflects the changes of the carbohydrates fractions in the torrefied wood – smaller peaks as the severity of torrefaction is increased.

3.4. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was used to investigate the changes in chemical structure after torrefaction (Fig. 2). The spectra of Raw, TA, and TB samples were similar, but the spectrum collected for TC sample was distinguishable. The peak around 1740 cm⁻¹ (“a” in Fig. 2) corresponds to carbonyl group in samples [33,34], and that for TC might be due to the removal of ester group in hemicellulose which is caused by decacylation during thermal treatment [35]. It has been also reported that the reduction of the intensity of the peak at 1740 cm⁻¹ was observed during the hydrothermal treatment of wood samples [36]. The peak at 1700 cm⁻¹ (“b”), together with the peak at 1600 (left peak of (“c”), were for C=O and C=C stretching vibrations, which can be from ketones, aldehydes, esters, carboxyl groups, and aromatic structures [37–39]. The increased intensity of this peak indicates that the degradation of carbohydrates and the relative increase of lignin result in more intense C=O absorptions (1700 cm⁻¹) as the severity of torrefaction increases (from Raw to TC). The substantial intensity increase at 1600 and
Table 1
Proximate/ultimate analysis and heating values of the untorrefied (Raw) and torrefied biomass (TA, TB, and TC). a

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis, %</th>
<th>Ultimate analysis, %</th>
<th>O/C Ratio</th>
<th>Heating Value (HHV)c, MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCb</td>
<td>VMb</td>
<td>FCb</td>
<td>Ash</td>
</tr>
<tr>
<td>Raw</td>
<td>7.69</td>
<td>84.6</td>
<td>14.8</td>
<td>0.6</td>
</tr>
<tr>
<td>TA</td>
<td>6.32</td>
<td>78.6</td>
<td>20.8</td>
<td>0.6</td>
</tr>
<tr>
<td>TB</td>
<td>5.43</td>
<td>76.4</td>
<td>22.8</td>
<td>0.8</td>
</tr>
<tr>
<td>TC</td>
<td>4.03</td>
<td>59.9</td>
<td>38.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Lignite</td>
<td>36.1</td>
<td>41.5</td>
<td>43.1</td>
<td>15.4</td>
</tr>
</tbody>
</table>

a Proximate and ultimate analyses data were presented as a dry basis.
b MC – moisture content (% as received); VM – volatile matter; FC – fixed carbon.
c Higher heating values: dry-basis (wet-basis).
d Values for North Dakota Beulah-Zap lignite [26].

Table 2
Compositional analysis of the untorrefied (Raw) and torrefied biomass (TA, TB, and TC). The values were calculated based on 100 g of untorrefied biomass.

<table>
<thead>
<tr>
<th></th>
<th>Chemical composition, g</th>
<th>% Compositional change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glucan b</td>
<td>Other carb., b</td>
</tr>
<tr>
<td></td>
<td>Glucan b</td>
<td>Other carb., b</td>
</tr>
<tr>
<td>Weight loss after torrefaction a, g</td>
<td>36.1</td>
<td>18.7</td>
</tr>
<tr>
<td>Raw</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>16.4</td>
<td>28.8</td>
</tr>
<tr>
<td>TB</td>
<td>24.4</td>
<td>24.2</td>
</tr>
<tr>
<td>TC</td>
<td>48.5</td>
<td>9.3</td>
</tr>
</tbody>
</table>

a Weight loss was estimated based on linear correlation with atomic O/C ratio from lab-scale experiments.
b Glucan & other carbohydrates were calculated based on the monosaccharide amount obtained from HPLC.
c Residue is the insoluble solid after two-step acid hydrolysis (Klason lignin method).

1511 cm⁻¹ (“c”), as well as at 1268 cm⁻¹ (“d”), can be ascribed to aromatic skeletal vibrations and guaiacyl ring with C–O stretch, and it implies an increase of aromatic fraction by thermal modification. In addition, the peak at 1600 cm⁻¹ (“e”) could also indicate that in torrefied biomass more condensed guaiacyl units are present relative to etherified ones [33]. This supports the assumption that thermal treatment induces the cleavage of ether bond in lignin (mainly, β-O-4 structure) and the condensation of lignin by linking carbons directly (e.g., 5–5 coupling). The increasing peak shoulder at about 1221 cm⁻¹ (“f”) corresponds to more condensed guaiacyl units. The increased intensity of FTIR signal from aromatic and condensed structure is in good agreement with the compositional data presented before, which showed larger amounts of acid-insoluble residues in TC sample. The assigned bands around 1030–1060 cm⁻¹ (“g”) with highest intensities correspond to aliphatic C–O–C and C–OH in alcohol, which is mainly from cellulose in the samples [37,39]. In this range, TC sample showed lower absorbance, indicating the loss of the carbohydrate fractions.

3.5. Quantification of methoxyl group content by gas chromatography

From the previous discussion, it can be suggested that the lignin fraction is thermally modified during the torrefaction process by way of cleavage of ary1 ether linkages (e.g., β-O-4) and condensation-like reactions. The β-O-4 linkage has an important role in the polymeric lignin structure. Compared to softwoods, hardwoods have a higher β-O-4 content, and lower condensed structures. This is due to the fact that hardwood lignin contains more syringyl units, carrying two methoxyl groups. This implies
that the free C5 position is important in the production of condensed lignin structures. In this study, it was assumed that thermal condensation of lignin is accompanied by the loss of methoxyl groups, and thus it is possible to quantify the extent of lignin modification by measuring the extent of demethylation. Lignin in softwood, such as loblolly pine, contains primarily guaiacyl (3-methoxy-4-hydroxyphenyl) structures. Thermal modification of lignocellulosic biomass can induce the cleavage of aryl-ether bond, like the linkage between phenylpropane unit and methoxyl group. Demethylation of lignin can generate additional reactive sites and lead to more condensed lignin during the thermal modification process [40].

It is observed that the methoxyl content in torrefied biomass decreased with the severity of torrefaction, based on the mass of feedstock (Table 3). Consequently, the amount of unmodified lignin–lignin with one methoxyl group, which was calculated based on the decrement of methoxyl content in samples compared to the initial amount in the Raw – also decreased. By subtracting the unmodified lignin fraction from the total residue after acid hydrolysis, the amount of thermally-modified compounds can be determined. Some fraction of the total mass of the thermally-modified solids is from residual lignin. This fraction of residual lignin can be referred to as “modified lignin”, in which the demethoxylated lignin units are interlinked by more condensed bonding, such as 5–5 biphenoxy linkages.

However, the changes of condensed structure of lignin might not be enough to explain the substantial increase (by 27% in weight) of acid-insoluble residues after torrefaction, from 30.1 to 38.2 g in TC sample. It is expected that a considerable portion of the acid-insoluble residue could originate from the carbohydrate fractions in the lignocellulosic biomass. For example, acid-resistant condensed structure of carbohydrates and their complexes with reactive lignin as well as degraded carbohydrates are likely.

3.6. NMR spectroscopy

Combined with the indirect methods to estimate the degree of thermal transformation of lignin using functional group analysis, solid-state NMR spectroscopy was employed to obtain more detailed structural information from samples of torrefied biomass. First, the solid-state $^{13}$C CP/MAS NMR spectra were obtained from the untorrefied (Raw) and torrefied biomass (Fig. 3). The NMR spectrum of a pyrolysis char, which is from fast pyrolysis of loblolly pine at 500 °C [41], was also acquired as a reference for highly aromatic solids after thermal treatment. One large and wide peak at 125 ppm (“a” in Fig. 3) is apparent, corresponding to aryl carbons. In contrast to the sharp peak for carbohydrates at 105 ppm (“b” (Fig. 3, Raw to TC) present in all samples, it is noticeable that the broad peak at around 125 ppm (“c”) for aromatic carbon and the small peak at 140–150 ppm (“c”) from lignin [42,43] were substantially increased upon torrefaction. The decrease in the NMR signal intensity for aliphatic carbons in the carbohydrates – 72–75 ppm (“d”) for C2/C3/C5 and 105 ppm (“b”) for C1 in cellulose [19] – clearly suggests relatively high decomposition of the carbohydrates after the heat treatment. In addition, a small shoulder at 102 ppm (“e”) from hemicellulose [19] diminishes in TC sample (in Fig. 3). One interesting observation is the presence of the peaks for C4 and C6 of ordered (crystalline) cellulose at 89 and 65 ppm (“f”), and disordered (amorphous) cellulose at 84 and 62 ppm (“g”) [19,44,45]. For the Raw sample, the sharp peak corresponding to ordered cellulose is less intense than that of disordered cellulose. In the NMR spectra of TA and TB (Fig. 3d and e), the signal for disordered fraction (“g”)

![Fig. 2. FTIR spectra between 650 and 1850 cm$^{-1}$ range for untorrefied (Raw) and torrefied biomass (TA, TB, and TC).](image)

Table 3

Methoxyl (MeO) content analysis of the untorrefied (Raw) and torrefied biomass (TA, TB, and TC). The weight values were calculated based on 100 g of untorrefied biomass.

<table>
<thead>
<tr>
<th>Residue</th>
<th>MeO content, g</th>
<th>% relative decrease in MeO content</th>
<th>Unmodified lignin*, g</th>
<th>Modified lignin + acid-insoluble carbohydrates, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>30.1</td>
<td>5.00</td>
<td></td>
<td>30.1</td>
</tr>
<tr>
<td>TA</td>
<td>34.3</td>
<td>3.93</td>
<td>21.4</td>
<td>23.6</td>
</tr>
<tr>
<td>TB</td>
<td>36.4</td>
<td>3.72</td>
<td>25.6</td>
<td>22.3</td>
</tr>
<tr>
<td>TC</td>
<td>38.2</td>
<td>2.45</td>
<td>51.0</td>
<td>14.7</td>
</tr>
</tbody>
</table>

* Unmodified lignin in a torrefied sample = initial amount of unmodified lignin in raw material × (MeO content in torrefied wood/MeO content in raw material).
becomes smaller, compared to that from ordered structure ("F"). This observation might be explained by the selective degradation of disordered cellulose fractions during low-severity torrefaction. In TC sample, however, there is a small sharp peak at 84 ppm without corresponding peak for less-crystalline cellulose at 62 ppm, which might indicate unidentified structural changes in the carbohydrate fraction. The peak at 56 ppm ("h") corresponds to methoxyl groups in lignin, indicating the relative increase in signal due to the degradation of the carbohydrates fraction. In methoxyl group content analysis, it was observed that the amount of methoxyl group was decreasing, because the content is calculated based on the initial mass of feedstock, with consideration of weight loss during torrefaction process. From the NMR spectra, however, it is noted that the signal from methoxyl group at 56 ppm was increased. It is because carbohydrates were depleted and lignin fraction became dominant, resulting in a higher signal for methoxyl group for torrefied biomass.

The CP/MAS NMR technique has been widely used to measure carbon functionality and aromaticity in chars and other aromatic materials. However, it has been shown that the non-protonated carbon fraction in the aromatic structures is underestimated by CP/MAS due to the slow magnetization transfer from proton to remote carbon [20, 46, 47]. To overcome this limitation, solid-state $^{13}$C DP/MAS NMR technique was employed for quantitative structural analyses of the thermally-treated biomass. Spectra from this technique showed some different aspects (Fig. 4), compared to those of CP/MAS NMR. The intensity assigned to aromatic fractions increased substantially with the increased torrefaction severity from Raw to TC, which might be not apparent from the CP/MAS NMR spectra. The corresponding dipolar dephasing NMR spectra is also presented in Fig. 4 to allow selectively detection of non-protonated aromatic carbons in the total aromatic structures [20, 48]. With this dipolar dephasing technique, it is possible to attenuate the signal from protonated carbons, resulting in the identification of non-protonated carbons. Based on this protocol, aromatic carbon fraction can be quantified as the total aromatic carbon fraction consists of aromatic C–O, aromatic C–H, and non-protonated aromatic carbon. Thus, the combined DP/MAS and dephasing NMR spectra were used to quantify total carbon fractions in the torrefied biomass (Table 4).

The amount of calculated total aromatic carbon is found to be very close to that obtained from compositional data after acid-insoluble residue content, except for sample TC (30.1, 41.0, 48.1, and 74.2% for untorrefied, TA, TB, and TC, respectively). This might imply that (1) the aromatic carbon fraction in woody biomass as measured by $^{13}$C DP/MAS NMR indicates the acid-insoluble residue content in thermally-treated samples to a certain severity of treatment, and (2) formation of non-aromatic acid-insoluble carbon structures takes place in TC sample. The presence of complex condensed aromatic structure in torrefied loblolly pine has been recently reported [49]. Based on these quantitative analyses, it might be possible that the condensed solid products, which were generated at the early stage of torrefaction (TA and TB), were mainly aromatic in their structure; however, beyond some point of treatment, the formation of non-aromatic condensed structure became dominant. High aromaticity of extensively treated biomass, like biochar, is likely achieved by rearrangement of non-aromatic products and/or selective degradation of the non-aromatic fractions, as well as the remaining carbohydrates at the temperature range beyond typical torrefaction processes. In addition, the increased aromaticity of torrefied biomass might correspond to observations about their higher hydrophobicity [14,15].

The DP/MAS NMR with recoupled dipolar dephasing also presents important characteristics of torrefied biomass. In Table 4, it was observed that the fraction of total aromatics and non-protonated carbon increases, while the protonated carbon/aromatic C–O fraction decreased. This corresponds with the $^{13}$C DP/MAS NMR works on pyrolysis/gasification biochars [20,21].
As the aromatic ring cluster increases, the portion for non-protonated carbons inside the cluster increases on a relative basis, compared to that of the protonated carbons/aromatic C=O along the edge of cluster ring. Therefore, the fraction of non-protonated carbon can be used to assess the size of aromatic cluster. In summary, the solid-state NMR studies suggest that during torrefaction of lignocellulosic biomass not only the amount of aromatic carbons rises, but also the size of the aromatic ring clusters.

4. Conclusions

The chemical and structural changes that take place during torrefaction of biomass were elucidated by using a series of complementary methods. Torrefaction induced the formation of acid-insoluble residues by the formation of condensed aromatic structures. The increased aromaticity and amount of non-protonated aromatic carbon were quantified by solid-state NMR experiments, indicating larger aromatic clusters in TC. This study on the chemical and structural changes in biomass during torrefaction presents a unique opportunity to reveal the complex and heterogeneous thermal transformation of torrefied biomass using complementary tools, including recently introduced $^{13}$C DP/MAS NMR analysis.

References
