Physicochemical Characterization of Pyrolyzates Produced from Carbonization of Lignocellulosic Biomass in a Batch-type Mechanical Kiln

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Abstract: Physicochemical properties of the pyrolyzates obtained from carbonization of lignocellulosic biomass, such as bamboo, oak, and pine wood, were analyzed. The results revealed that the specific gravity, color values of L* and a*, and degree Brix may be useful factors for quality estimation of these pyrolyzates. The pH and organic acid content correlated poorly because of a complex effect among the various pyrolyzate components. The chemical composition of the pyrolyzates was estimated by gas chromatography. Fifteen of the major pyrolyzate components were identified, of which acetic acid was the major component. The bamboo pyrolyzate contained a higher organic content (4.82 %) than the oak (1.53 %) and pine (0.89 %) wood pyrolyzates. No significant difference was found in the chemical compositions and quantities of the phenolic and neutral compounds of the oak and pine wood pyrolyzates, but the acetic acid content of the oak wood pyrolyzate (1.06 %) was higher than that of the pine wood pyrolyzate (0.40 %).

Keywords: physiochemical properties, pyrolyzates, lignocellulosic biomass, bamboo, oak wood, pine wood

Introduction

Wood carbonization, which can be categorized as conventional pyrolysis, a subclass of the pyrolysis process [1], has been a traditional process in charcoal production [2]. Wood carbonization in an oxygen-free environment leads to gaseous and liquid by-products, such as fuel gas, wood tar, and wood pyrolyzate [3]. Fuel gas can be combusted, thereby generating heat, or used in an engine or turbine for electricity generation [4]. Wood tar provides a sticky liquid fuel that can substitute for fuel oil in any static heating or electricity generation application. In addition, the preparation of tar-based phenol-resin [5] and strongly acidic cation exchange resins from tar blended with phenol has also been studied [6].

Wood pyrolyzates are strongly smoke-flavored liquors obtained as by-products from the charcoal manufacturing process of wood. Wood pyrolyzates are mostly composed of water (80–90 %) and more than 200 species of organic compounds (10–20 %). Wood pyrolyzates, particularly those obtained from oak and pine woods, have been used as agents with some biological effects on microorganisms and plants, for their germination and growth-acceleration effects, and as disinfectants or conditioners of soil [7]. Bamboo has gained increased attention as an alternative crop with multiple uses and benefits. Bamboo pyrolyzate was also found to strongly inhibit the germination and radicle growth of seed plants [8]. Based on such biological effects, these pyrolyzates have been used in agriculture, the food industry, and in environmental fields. In recent years, the Korea Forest Research Institute (KFRI) approved bamboo and wood pyrolyzates for official use in agriculture. This decision has stimulated their extensive utilization over related industries in Korea.

Bamboo (Phyllostachys pubescens), oak (Quercus serrata), and pine (Pinus densiflora) wood pyrolyzates have been used universally in agricultural applications. However, the physiochemical properties of wood and bamboo pyrolyzates have not yet been compared despite their potential for large-scale use. In this study, bamboo and wood pyrolyzates were prepared during the carbonization of bamboo, oak, and pine in a batch-type me-
The pyrolyzates of bamboo (*Phyllostachys pubescens*), oak (*Quercus serrata*), and pine (*Pinus densiflora*) woods were recovered from a cooling device following carbonization with a batch-type mechanical kiln (Figure 1, 800 ∼ 1,000 °C), located at the Korea Forest Research Institute (KFRI).

**Physical Properties**

Physical properties of the pyrolyzates were determined with slight modification of the KFRI guidelines. The pH was calibrated in standard buffer solutions (pH 4.0 and 7.0) and measured using a pH meter (Suntex, SP-701, Taiwan). Specific gravity was measured using a glass hydrometer at 15 ± 0.1 °C. A portion (20 g) of either bamboo or wood pyrolyzate was transferred into a crucible and heated to remove any low-volatility components. The obtained residues were used to calculate the tar content. The L*a*b* color coordinates, lightness (L*), redness (a*), and yellowness (b*), as defined by the Commission Internationale de l’Eclairage (CIE), were measured using a color difference meter (Denshoku, TC-3600, Japan). Degree Brix was measured using a hand refractometer (Atago, N-1E, Japan; Brix range: 0 ∼ 32 %) without dilution.

**Total Organic Acid Content**

Bamboo or wood pyrolyzate was diluted to 1 % (v/v) with ion-exchanged water and titrated using 0.1 N NaOH solution. The total organic acid content was calculated from the volume of the titrated NaOH at pH 8.15, the terminal point of acetic acid, which has been determined to be the major organic acid in the pyrolyzates.

**Gas Chromatography**

The pyrolyzates were analyzed using a Shimadzu GC-17A instrument combined with a flame ionization detector. A CBP 20 silica fused capillary column (25 m × 0.22 mm i.d., 0.25 μm film thickness) was used to separate the components. The GC parameters were as follows: the oven temperature was maintained at 50 °C for 2 min, then raised from 50 to 220 °C at 3 °C/min, and finally maintained at 220 °C for 5 min. The helium gas flow rate was 0.72 mL/min. The split ratio was adjusted to 10. The pyrolyzate components were identified according to the procedure described in a previous report [9]. The pyrolyzates were analyzed quantitatively using acetic acid and phenol as standards, the former for organic acids and phenol as standards, the former for organic acids and neutral compounds and the latter for phenolic compounds.

**Results and Discussion**

**Physical Properties of Crude Bamboo and Wood Pyrolyzates**

Table 1 shows the physical properties of the bamboo,
Table 1. Physicochemical Properties of Bamboo, Oak Wood, and Pine Wood Pyrolyzates

<table>
<thead>
<tr>
<th>Source</th>
<th>pH</th>
<th>S.G</th>
<th>Tar (%)</th>
<th>O.A (%)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>ΔE</th>
<th>°Brix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo</td>
<td>3.45</td>
<td>1.016</td>
<td>0.89</td>
<td>4.37</td>
<td>3.4</td>
<td>6.1</td>
<td>2.2</td>
<td>7.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Oak</td>
<td>4.05</td>
<td>1.004</td>
<td>0.23</td>
<td>1.07</td>
<td>5.7</td>
<td>2.4</td>
<td>3.1</td>
<td>6.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Pine</td>
<td>3.70</td>
<td>1.005</td>
<td>0.33</td>
<td>0.56</td>
<td>6.0</td>
<td>1.1</td>
<td>3.8</td>
<td>7.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

a S.G: specific gravity.
b O.A: organic acids.

Figure 2. Gas chromatogram of the pyrolyzates from (a) bamboo, (b) oak wood, and (c) pine wood.

The color of the pyrolyzates was more systematically investigated using the CIE L*a*b* system values. L*, a*, and b* values represent the lightness, redness, and yellowness, respectively. The L* lightness value decreased with increasing total content of tar and organic acid, suggesting its usefulness as an indicator of the approximate total organic content. The values of a* and b* indicated that the bamboo pyrolyzate is relatively more deeply colored than are the oak and pine wood pyrolyzates. The a* value tended to be affected sensitively by the total organic compound content. From these results, L* and a* values may become useful parameters for monitoring the quality control of bamboo and wood pyrolyzates.

The results indicated that the total content of tar and organic acid, which corresponded almost directly to the total amounts of these pyrolyzate components, may be quantitated using the specific gravity and the L* and a* color values. In addition, the degree Brix may be useful as an indicator of the tar content in bamboo and wood pyrolyzates. However, the pH and organic acid content were correlated poorly because of a complex effect among the various pyrolyzate components.

Chemical Composition of Bamboo and Wood Pyrolyzates

To determine the chemical compositions of the bamboo, oak, and pine wood pyrolyzates, quantitative analysis was conducted using gas chromatography, with reference to a previous report [9]. Acetic acid and phenol were used for quantitative determination of all of the pyrolyzate components because, in fact, it is difficult to quantify all of the pyrolyzates produced from the considerably irregular radical reaction that occurs during the carbonization process. Acetic acid was applied for quantitative analysis of organic acids and neutral compounds, and phenol for that of the phenolic compounds.

The main 15 peaks were identified and analyzed quantitatively (Figure 2, Table 2). Bamboo pyrolyzate showed...
### Table 2. Major Compounds in Bamboo, Oak Wood, and Pine Wood Pyrolyzates

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>RT (min)</th>
<th>Compound</th>
<th>Bamboo</th>
<th>Oak</th>
<th>Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.7</td>
<td>Methanol</td>
<td>0.29</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>15.1</td>
<td>1-Hydroxy-2-propanone</td>
<td>0.34</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>21.2</td>
<td>Acetic acid</td>
<td>2.85</td>
<td>1.06</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>22.0</td>
<td>Furfural</td>
<td>0.14</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>5</td>
<td>25.5</td>
<td>Propionic acid</td>
<td>0.20</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>6</td>
<td>29.0</td>
<td>Dihydro-2(3H)-furanone</td>
<td>0.18</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>30.5</td>
<td>Furfuryl alcohol</td>
<td>0.14</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>8</td>
<td>37.1</td>
<td>2-Hydroxyl-1-methyl-1-cyclopentene-1-one</td>
<td>0.14</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>38.3</td>
<td>Guaiacol</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>39.5</td>
<td>4-Methyl guaiacol</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>42.1</td>
<td>Maltol</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>43.9</td>
<td>Phenol, o-Cresol</td>
<td>0.16</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>13</td>
<td>46.6</td>
<td>p-Cresol</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>14</td>
<td>46.8</td>
<td>m-Cresol</td>
<td>0.16</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>52.7</td>
<td>Syringol</td>
<td>0.10</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>4.82</td>
<td>1.53</td>
<td>0.89</td>
</tr>
</tbody>
</table>

### Table 3. Chemical Compositions of Bamboo, Oak Wood, and Pine Wood Pyrolyzates

<table>
<thead>
<tr>
<th>Component</th>
<th>Bamboo</th>
<th>Oak</th>
<th>Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic acids</td>
<td>3.05</td>
<td>1.12</td>
<td>0.45</td>
</tr>
<tr>
<td>Phenolics</td>
<td>0.53</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>Neutral compounds</td>
<td>1.24</td>
<td>0.25</td>
<td>0.29</td>
</tr>
</tbody>
</table>

a higher content of organic compounds (2.85 %) than did the oak (1.06 %) and pine (0.40 %) wood pyrolyzates. The pyrolyzate components were classified into organic acids, phenolics, and neutral compounds (Table 3). The organic acid contents were 3.05 % (bamboo), 1.12% (oak), and 0.45 % (pine). The organic acids contained acetic acid and propionic acid. Particularly, acetic acid was recognized as the major component among the organic compounds in the pyrolyzates, comprising 59 % (bamboo), 69 % (oak), and 45 % (pine). The organic acids contained acetic acid and propionic acid. Particularly, acetic acid was recognized as the major component among the organic compounds in the pyrolyzates, comprising 59 % (bamboo), 69 % (oak), and 45 % (pine). Phenolic compounds contained pyrolytic products having the basic aromatic structures of lignin, i.e., guaiacol, 4-methylguaiacol, phenol, cresols (o-, m-, and p-isomers), and syringol. The contents of the phenolic compounds, which were the major components of tar, were 0.53 % (bamboo), 0.16 % (oak) and 0.15 % (pine). The contents of the phenolic compounds were similar in the two wood pyrolyzates, but 3.5-fold lower than that of the bamboo pyrolyzate. Most of the neutral compounds were considered to be the following pyrolyzates formed during the pyrolysis process of carbohydrate, accompanied by dehydration: methanol, 1-hydroxy-2-propanone, furfural, dihydro-2(3H)-furanone, furfuryl alcohol, and 2-hydroxy-1-methyl-1-cyclopentene-1-one. The chemical compositions and quantities of the phenolic and neutral compounds of oak and pine wood pyrolyzates were very similar, but the acetic acid content of the oak wood pyrolyzate (1.06 %) was higher than that of the pine wood pyrolyzate (0.40 %), indicating the richer presence of acetyl groups in hemicellulose.

### Pyrosynthesis Route of Pyrolyzate Components

The main components of bamboo and wood pyrolyzates were identified by comparison with standards; some were confirmed from their 1) mass fragmentation patterns, 2) retention times (RT) dependent on steric hindrance in isomeric compounds, 3) regular RT intervals depending on carbon number for similarly classified compounds under isothermal temperature conditions, and 4) possibility as pyrolyzates, which can be derived from polysaccharides and lignin, the major chemical components of wood. The pyrolyzate components are composed of products arising, basically, from the thermal degradation of wood carbohydrate and lignin, such as furan and pyran derivatives, aldehydes, ketones, acids, and phenolic compounds with certain isomeric positions [12-14].

The pyrolysis mechanism of cellulose involves an initiation reaction associated with a dramatic reduction in the degree of polymerization of the cellulose [15]. At temperatures below 300 °C, anhydrocellulose is produced through a slow dehydration reaction, whereas at temperatures above 300 °C, rapid depolymerization or unzippering results in the formation of levoglucosan. The anhydrocellulose and levoglucosan further decompose to form char, permanent gases, and other volatiles during the secondary reactions [16].

The peaks detected within RT of ca. 37.1 min were considered to be compounds mainly derived from the pyrolysis of polysaccharides, such as cellulose and hemicellulose (Figure 2). Methanol arises from the breakdown of methyl esters and/or ethers from the decomposition of pectin-like plant materials, and also from methoxyl groups of uronic acid and partly from the methoxyl group of lignin basic units [17]. Acetic acid is formed from the thermal decomposition of all three main wood components and also from the elimination of acetyl groups originally linked to the xylose units [18]. Quantitatively, 1-hydroxy-2-propanone was present in high concentrations in the pyrolyzate liquid products. This alcohol is partly esterified by acetic acid. In conventional slow pyrolysis, this alcohol is not found in such great quantities because of its low stability. The typical five-membered ring compounds, such as furans, cyclopent-
anones, and furanones, were observed from the pyrolyzates. The furans and cyclic ketones may be cyclization products of dicarbonyl intermediates formed by aldol condensation reaction of low-molecular-mass compounds formed as degradation products during the initial stages of thermal degradation [19]. The furan derivatives are formed by scission of the cellulose chain as water initializes the opening of the pyranose ring [20] (Figure 3). Furfural is formed by the dehydration of the xylose unit. Furans and furanones of the five-membered ring compounds distill rapidly from the pyrolysis zone rather than degrade due to their particularly thermally stable aromatic nature. Thus, in many studies, these furans and furanones have been observed as major components derived from polysaccharides. In the pyrolysis of polysaccharides, five-membered-ring furans are formed preferentially, rather than six-membered-ring pyrans [21]. This phenomenon explains the presence of many five-membered-ring compounds in the bamboo and wood pyrolyzates.

Lignin, one of the major biomass constituents (typically 15 ~ 30% by weight of wood), is a macromolecule having a complex, three-dimensional structure consisting of alkylphenols such as guaiacyl-, syringyl-, and p-hydroxyphenyl units. Phenolics are derived from lignin by cracking of the phenyl propane units of the macromolecular lattice [18].

Amen-Chen and coworkers proposed that the dehydration reaction of aliphatic hydroxyl groups linked to β- and γ-carbon atoms yields compounds possessing alkyl or vinyl groups [22] (Figure 4). Some of the alkenes formed by dehydration are hydrogenated to form aliphatic bonds and are then removed from the reaction zone as volatile species. It is found that ether linkages, mainly α- or β-O-4 bonds, are readily broken during the initial pyrolysis stage. β-Ether cleavage takes place in parallel to the appearance of water by dehydration of the aliphatic HO- groups in the α-position. Elimination of carbonyl entities in the alkyl side chain in the form of low-molecular-weight compounds, like HCHO, or gases, such as CO, may also occur during wood thermal degradation. Methoxyl groups are thermally stable and resistant to cleavage, even at a pyrolysis temperature of 335 °C. Demethylation of methoxyl groups in guaiacyl and syringyl units occurs at ca. 450 °C (Figure 5), while the alkyl chains decompose at ca. 600 °C. Therefore, the alkyl chain is more resistant to thermal degradation than is the C-OCH₃ bond. The evolution of methoxyl radicals is also detected at almost the same temperatures as the methyl radicals.

Lignin undergoes a variety of thermal modification and decomposition stages, such as dehydration, cleavage of ether linkages, hydrogenation of alkenes, elimination of carbonyl entities, demethylation, and demethoxylation. Particularly, the pyrolyzates of lignin in the high temperature range, between 450~600 °C, may also undergo thermal modification of methoxyl groups to form hydroxyl groups, simultaneous with the demethoxylation-
to-alkylation reaction and the positional rearrangement of methoxyl groups. The pyrolyzates derived from the guaiacyl-type lignin unit produce guaiacol, acetoguaiacol, methylguaiacols, ethylguaiacols, acetoaniline, eugenol, isoeugenols, 4-propylguaiacol, and vanillin, although not all of these analogues were found. Guaiacol undergoes scission of the methoxyl group at the aromatic ring to produce pyrocatechol, cresols, methylpyrocatechol, phenol, and methylguaiacol [23]. The secondary decomposition of guaiacols into catechols occurs during the carbonization process at high temperature. However, the absence of catechols was assumed to have resulted from their participation in the formation of charcoal or from a certain condensation reaction with other phenolics or aldehydes in the pyrolyzate liquor. Phenol is produced through CH$_3$-O bond scission and further H abstraction from an anisole molecule; it is also produced from guaiacol via a catechol intermediate. On the basis of C-O linkage scission, the secondary pyrolysis of syringol has been known to occur via reaction pathways similar to those of guaiacol [23]. The thermolysis of syringol conducted at increasing temperatures increases the yields of formation of guaiacol, phenol, and o-cresol [23].

Conclusions

Lignocellulosic pyrolyzates were produced from the carbonization of bamboo, oak, and pine wood in a batch-type mechanical kiln. The physicochemical properties and chemical compositions of these pyrolyzates were characterized. Three sets of physical properties (specific gravity, degree Brix, and CIE L*a*b* system values), were evaluated as being useful parameters for estimating the approximate chemical compositions of bamboo, oak, and pine wood pyrolyzates. Quantitative and qualitative analyses of these pyrolyzates determined that acetic acid was the major component, with the bamboo pyrolyzate showing a higher organic content (4.82 %) than either the oak (1.53 %) or pine (0.89 %) wood pyrolyzate. A pyrosynthetic route was proposed for the generation of these pyrolyzates.

References