Preparation of Syringaldehyde from Lignin by Catalytic Oxidation of Perovskite-Type Oxides

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ABSTRACT: The influence of different reaction conditions on the yield of syringaldehyde was studied by using perovskite oxide as the catalyst. The optimal reaction conditions are as follows: 0.60 g of dealkali lignin, 0.60 g of 5 wt % theta ring-loaded LaFe0.2Cu0.8O3 catalyst, 30 mL of 1.0 mol/L NaOH solution, 160 °C reaction temperature, 0.80 MPa O2 pressure, and 2.5 h reaction time. Under these conditions, the highest syringaldehyde yield was 10.00%. The recycling performance of the catalyst was studied. It was found by XRD analysis that the catalyst maintained high catalytic activity after four times of use.

1. INTRODUCTION

Biomass, as a widely existing renewable resource in nature, has been paid more and more attention to because of its properties and efficient utilization. Lignin is one of the three major components of biomass. It is composed of guaiacyl, syringyl, and p-hydroxyphenyl monomers linked by C–O and C–C bonds and has a complex three-dimensional structure.1,2 Lignin molecules contain phenolic hydroxyl, methoxy, and carboxyl groups, which provide a basis for its industrial applications.3 In recent years, the degradation of lignin into small molecular products with high added values has become a research hotspot. Its own benzene ring structure also provides a possibility for the formation of small molecular compounds with broken chains. In the previous study, lignin was degraded into small aromatic products with high added values, such as phenol and aromatic aldehydes, via reduction and oxidation.4–6 As one of the refined products of lignin, syringaldehyde has some unique applications in medicine due to its characteristics.29 In some experiments, syringaldehyde was used as a raw material to prepare dendrimers from alkynes catalyzed by solid copper particles, which greatly improved the oxidation resistance.34 Through the study on the intravenous injection of syringaldehyde in diabetic rats, researchers found that syringaldehyde can increase the glucose consumption in the body of the sick rats and play a role in reducing blood sugar, so syringaldehyde can be used as an auxiliary agent for the treatment of diabetic patients in the future.35 In addition, a study has shown that syringaldehyde can indirectly cut the DNA strand through some mechanism, which is a potential natural resource with anticancer properties.36 Because the yield of syringaldehyde is far lower than those of vanillin and other aldehydes and it is not as nontoxic as vanillin, there are few studies on syringaldehyde.

Perovskite oxides exhibit high activity and stability in the catalytic oxidation of hydrocarbons and have been widely used in biomass catalytic conversion, oxygenated fuel combustion, electrochemistry, and other fields in recent years.17–19,24 It has broad prospects in replacing noble-metal catalysts.7–9 Perovskite oxide is a heterogeneous catalyst with large specific surface area, high catalytic activity, and small environmental pollution.10 It can be separated from the reaction system via a simple centrifuge operation, and when reused, it can still maintain high reactive activity. Because of its excellent properties, most of the existing studies use perovskite catalysts to guide the catalytic reaction.11–13 Ansaloni et al.30 used bioethanol to produce industrial waste as the raw material (steam-exploded lignin derived from wheat straw) and perovskite as the catalyst. The best performance exhibits a lignin dissolution ratio of 53% with 1.3% yield toward aromatic compounds. Banu et al.31 used perovskite as the catalyst to transform bagasse lignin. The results showed that the phenolic product mainly consisted of phenol, guaiacyl, catechol, and syringyl groups; their selectivities were 35.19, 6.18, 10.68, and 14.21%, respectively. Some researchers33 also prepared a series of LaFe1–xMnxO3 and La0.9Sr0.1MnO3 hollow nanospheres for the catalytic conversion of lignin. They have good catalytic performance and can be recycled several times.
LaB1 was selected as the best lignin. On the basis of the study of according to the yield of syringaldehyde, the dealkaline lignin syringaldehyde were selected for further studies. Finally, lignins were compared. Then two lignins with high yields of So, LaNi1−xMxO3 as catalysts, a new type of supported perovskite catalyst with theta ring packing as the carrier was innovatively considered to improve syringaldehyde yield. At the same time, the mass transfer effect of theta ring packing is better, the supported catalyst is easy to separate, and it has corrosion resistance and structural stability, which provides a new method for the industrialization of the lignin scale industry.

2. RESULTS AND DISCUSSION

2.1. Gel Permeation Chromatography (GPC) Analysis of Different Lignin Species. The relationship between the average molecular weight in GPC chromatogram and the response intensity of the detector is shown in Figure 1 and Table 1. Cross-linked lignin (CLL) is calculated by using the peak value at 1500/1600 in Fourier transform infrared (FT-IR) data. It can be seen that the corresponding intensity of dealkali lignin is similar to that of industrial lignin, and the polydispersity coefficient is close in value. However, the average molecular weight of dealkali lignin is slightly higher, and the ash content is lower. From Figure 2A, the yield of syringaldehyde is also higher. When the molecular weight distribution of lignin samples is basically the same, the higher the ash content is, the lower the yield of syringaldehyde is. Sodium lignosulfonate was prepared from wheat straw and Masson’s pine. However, the shape of molecular weight distribution is similar, which may be due to the same extraction method. The yield of syringaldehyde from wheat straw is slightly higher than that from woody Pinus massoniana because of the larger average molecular weight and polydispersity coefficient of wheat straw than those from woody P. massoniana.

2.2. Effect of Cu Doping on Syringaldehyde Yield. As shown in Table 2, syringaldehyde yields catalyzed by different Cu-doped catalysts are different. When the catalyst is not added, the syringaldehyde yield is only 0.96%. Under the catalysis of LaFeO3, syringaldehyde yield is increased to 1.80%. With increasing Cu doping amount on the perovskite B position, syringaldehyde yield is increased. When the doping amount of Cu reaches 0.8, syringaldehyde yield is the highest. When LaFe1−xCu2xO3 is used as a catalyst, the yield is 4.38%. Meanwhile, when LaNi0.2Cu0.8O3 is used as a catalyst, the yield is 4.00%. Therefore, the addition of the Cu element improves the catalytic performance of perovskite oxide. Increasing the

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Table 1. Physical Parameters of Different Lignin Samples

| Lignin sample          | Lignin content (%) | Water content (%) | Glucose content (%) | Xylose content (%) | Sulfur (%) | Ash (%) | Mw (kD) | CLL (%) |
|------------------------|--------------------|-------------------|--------------------|-------------------|------------|---------|---------|---------|
| Dealkaline lignin (DL) | 87.97              | 2.35              | 1.24               | 0.93              | 1.42       | 2817    | 0.97    |
| Industrial lignin (IL) | 86.33              | 3.22              | 1.37               | 0.55              | 4.01       | 2674    | 0.99    |
| Wheat straw lignosulfonic acid sodium (WSL) | 81.32            | 1.56              | 1.10               | 2.12              | 7.12       | 2683    | 0.97    |
| Masson’s pine sodium lignin sulfonate (MPL) | 78.57            | 2.21              | 2.29               | 3.35              | 8.33       | 2560    | 0.96    |

Figure 1. Molecular weight distribution of lignin samples.

Figure 2. Effect of catalyst/lignin ratio (g/g) on syringaldehyde yield (LaFe1−xCu2xO3 as catalyst, liquid/lignin at 50:1 (v/w), 30 mL 1 mol/L NaOH, 0.8 MPa O2, 160 °C, 2 h). (A) Effect of different catalyst dosages on syringaldehyde yield from different lignins; (B) effects of catalyst dosage on lignin conversion and SY yield.
content of Cu in the catalyst can increase the oxygen content of perovskite oxides, enhance the activity of the catalyst, and increase the yield of syringaldehyde. When the content of Cu is higher, the specific surface area of the catalyst is larger, which makes the catalyst have more active sites, thus improving the catalytic performance of perovskite oxides.

2.3. Effect of the Amount of Catalyst on Syringaldehyde Yield. As shown in Figure 2A, when the amount of catalyst is increased, the yields of syringaldehyde in all lignin samples are increased. Compared with industrial lignin, wheat straw, and Masson’s pine, dealkaline lignin can obtain higher yield of syringaldehyde under the same reaction conditions. Taking dealkaline lignin as an example, the yield of syringaldehyde is only 2.51% when the catalyst/lignin (g/g) is 1:50; when the ratio is increased to 1:20, the yield of syringaldehyde increases to 4.38%; when the ratio is further increased to 1:10, the yield of syringaldehyde decreases to 4.19%. The yields of syringaldehyde from the other three lignins also show the same trend. Compared with dealkaline lignin and industrial lignin, the syringaldehyde yields of sodium lignosulfonate and Masson’s pine are lower than that of the sodium lignosulfonate under the same reaction conditions. The reason may be due to the fact that WSL and MPL contain the sulfur element. During the reaction, the sulfur element may be adsorbed on the surface of metal catalysts in a reversible or irreversible state. The active sites of the catalysts are affected by electronic or shielding effects, and thus, the catalytic effect of the catalysts is affected. 20, 21

Dealkaline lignin with high syringaldehyde yield is selected as the raw material. As shown in Figure 2B, when the catalyst is not added, the conversion of lignin is only 20.10%, and the yield of syringaldehyde is very little, only 0.96%. After adding the catalyst, the lignin conversion rate and the syringaldehyde yield are significantly increased. The lignin conversion rate is 35.26% and syringaldehyde yield is 2.51% when the mass ratio is 1:50. Compared with the reaction without the catalyst, lignin conversion and syringaldehyde yield are increased by 43.85 and 61.75%, respectively. After further increasing the amount of catalyst, the conversion rate of lignin increases further. When the ratio of catalyst/lignin is 1:20, the lignin conversion rate is the highest, reaching 84.97%. With the increase of catalyst dosage (when the ratio is greater than 1:20), the conversion of lignin is increased, while the yield of syringaldehyde is decreased. The reason may be due to the fact that, with the increase in the amount of catalyst, the contact chance between catalyst and lignin is increased, more

| catalyst               | syringaldehyde yield (%) |
|------------------------|--------------------------|
| LaFe0.2Cu0.8O3         | 4.38 ± 0.09              |
| LaFe0.4Cu0.6O3         | 3.56 ± 0.11              |
| LaFe0.8Cu0.2O3         | 2.00 ± 0.07              |
| LaFeCu0.1O3            | 1.80 ± 0.06              |
| LaNi0.2Cu0.8O3         | 4.00 ± 0.20              |
| LaNi0.6Cu0.4O3         | 3.28 ± 0.24              |
| LaNi0.8Cu0.2O3         | 1.69 ± 0.16              |
| LaNiCu0.1O3            | 1.16 ± 0.11              |

"Dealkali lignin as raw material, liquid/lignin at 50:1 (v/w), catalyst/lignin at (g/g) at 1:20, 30 mL 1 mol/L NaOH, 0.8 MPa O2, 160 °C, 2 h.

Figure 3. Effect of different reaction conditions on syringaldehyde yield. (A) Effects of alkali concentration on SY yield; (B) effects of reaction time on SY yield; (C) effects of O2 pressure on SY yield; (D) effects of temperature on SY yield.
lignin is broken, and the conversion of lignin is increased. While the catalyst promotes the formation of syringaldehyde, it also further catalyzes the oxidation of aldehydes to form carboxylic acid or other by-products, resulting in a decrease in the yield of syringaldehyde. Therefore, choosing the appropriate amount of catalyst plays a key role in the catalytic conversion process. When the ratio is 1:20, the lignin conversion rate is higher, and the syringaldehyde is not further catalyzed to be oxidized to carboxylic acid. Therefore, a follow-up study on the catalyst/lignin ratio (g/g) under the condition of 1:20 is performed.

2.4. Effect of Different Reaction Conditions on Syringaldehyde Yield. As shown in Figure 3A (LaFe_{0.2}Cu_{0.8}O_{3} as catalyst, liquid/lignin at 50:1 (v/w), 30 mL NaOH, 0.8 MPa O₂, 160 °C, 2.5 h), when dealkaline lignin is used as the raw material, the alkali concentration increases from 0.5 to 1 mol/L, and the yield of syringaldehyde increases from 3.46 to 6.31%. When industrial lignin is used as the raw material, the alkali concentration increases from 0.5 to 1 mol/L, and the yield of syringaldehyde increases upward trend. The highest yields are 5.28 and 4.60% at 2.5 h. When the reaction time is 3 h, the yield of syringaldehyde decreases. This may be due to the further oxidation of syringaldehyde to acid under the catalysis of oxygen oxidation and perovskite oxides. Therefore, when the reaction time is controlled at 2.5 h, a higher yield can be obtained and further oxidation of the product can be prevented.

The phenolic structure of lignin and conjugated structure of benzene ring have higher reactivity with O₂. O₂ plays an oxidant role in the catalytic transformation of lignin. In the normal state, O₂ is a substance with weak oxidation. Therefore, it is necessary to use alkali as the catalyst in the oxidative degradation of lignin. Alkali ionizes phenolic hydroxyl groups on lignin structural units and then forms aldehydes under the oxidation of oxygen and catalysis of catalysts. The effect of oxygen on the syringaldehyde yield is shown in Figure 3C. The figure shows that the reaction does not occur when O₂ is not filled, and the formation of aldehydes is not detected. The O₂ pressure is gradually raised from 0.2 to 0.80 MPa, and the syringaldehyde yield is increased from 1.78 to 5.28% with dealkaline lignin as the raw material. However, the high O₂ concentration can cause the syringaldehyde yield to decrease because high O₂ pressure and O₂ solubility will promote the ring opening reaction and form a small molecular substance, such as succinic acid, acrylic acid, and other carboxylic acids. Thus, 0.80 MPa is the most appropriate O₂ pressure.

Table 3. Yields of Other Products under Different Reaction Conditions

| alkali concentration (mol/L) | time (h) | O₂ (MPa) | temperature (°C) | p-hydroxybenzaldehyde yield (%) | vanillin yield (%) | syringic acid (%) |
|-----------------------------|----------|----------|------------------|-------------------------------|-------------------|------------------|
| 0.5                         | 2.5      | 0.8      | 160              | 1.23 ± 0.22                   | 5.33 ± 0.56       | 0.44 ± 0.07      |
| 1.0                         | 2.5      | 0.8      | 160              | 1.35 ± 0.15                   | 6.16 ± 0.47       | 0.42 ± 0.07      |
| 1.5                         | 2.5      | 0.8      | 160              | 1.32 ± 0.12                   | 6.32 ± 0.64       | 0.33 ± 0.08      |
| 2.0                         | 2.5      | 0.8      | 160              | 1.29 ± 0.21                   | 6.34 ± 0.52       | 0.30 ± 0.02      |
| 2.5                         | 2.5      | 0.8      | 160              | 1.27 ± 0.11                   | 5.12 ± 0.44       | 0.27 ± 0.03      |
| 3.0                         | 2.5      | 0.8      | 160              | 1.23 ± 0.34                   | 4.93 ± 0.52       | 0.22 ± 0.07      |
| 1.0                         | 0.5      | 0.8      | 160              | 0.52 ± 0.14                   | 4.34 ± 0.44       | 0.24 ± 0.08      |
| 1.0                         | 1.0      | 0.8      | 160              | 0.94 ± 0.52                   | 4.27 ± 0.23       | 0.25 ± 0.02      |
| 1.0                         | 1.5      | 0.8      | 160              | 1.17 ± 0.11                   | 4.35 ± 0.52       | 0.34 ± 0.03      |
| 1.0                         | 2.0      | 0.8      | 160              | 1.33 ± 0.13                   | 6.44 ± 0.61       | 0.37 ± 0.01      |
| 1.0                         | 2.5      | 0.8      | 160              | 1.37 ± 0.53                   | 6.21 ± 0.59       | 0.41 ± 0.03      |
| 1.0                         | 3.0      | 0.8      | 160              | 1.37 ± 0.14                   | 6.33 ± 0.47       | 0.47 ± 0.04      |
| 1.0                         | 2.5      | 0.4      | 160              | 0.94 ± 0.21                   | 4.37 ± 0.36       | 0.22 ± 0.08      |
| 1.0                         | 2.0      | 0.6      | 160              | 1.24 ± 0.17                   | 5.11 ± 0.58       | 0.21 ± 0.07      |
| 1.0                         | 2.5      | 0.8      | 160              | 1.32 ± 0.21                   | 5.36 ± 0.46       | 0.37 ± 0.06      |
| 1.0                         | 2.5      | 1.0      | 160              | 1.34 ± 0.30                   | 6.18 ± 0.44       | 0.41 ± 0.07      |
| 1.0                         | 2.5      | 1.2      | 160              | 1.30 ± 0.22                   | 5.22 ± 0.85       | 0.52 ± 0.04      |
| 1.0                         | 2.5      | 0.8      | 100              | 1.28 ± 0.11                   | 4.14 ± 0.75       | 0.55 ± 0.03      |
| 1.0                         | 2.5      | 0.8      | 120              | 1.12 ± 0.12                   | 4.16 ± 0.49       | 0.51 ± 0.05      |
| 1.0                         | 2.5      | 0.8      | 140              | 1.27 ± 0.15                   | 5.43 ± 0.85       | 0.47 ± 0.04      |
| 1.0                         | 2.5      | 0.8      | 160              | 1.31 ± 0.19                   | 5.77 ± 0.72       | 0.45 ± 0.08      |
| 1.0                         | 2.5      | 0.8      | 180              | 1.36 ± 0.14                   | 6.15 ± 0.74       | 0.44 ± 0.04      |
| 1.0                         | 2.5      | 0.8      | 180              | 1.41 ± 0.14                   | 6.09 ± 0.22       | 0.46 ± 0.03      |

The syringaldehyde yields are only 0.69 and 0.56% at 100 °C, and the syringaldehyde yields increase to 2.12 and 2.00%, respectively, when the temperature is increased to 120 °C. When the temperature is further increased to 140 °C, the syringaldehyde yields are 3.50 and 3.21%. At 160 °C, the syringaldehyde yields are 5.28 and 3.71%. When the reaction is carried out at 180 °C, the syringaldehyde yields are decreased to 2.94 and 2.46%. Therefore, increasing the reaction temperature can promote the reaction process and increase...
syringaldehyde yield. However, very high temperature will lead to secondary polymerization. This phenomenon is similar to the effect of temperature on syringaldehyde yield in the ionic liquid system. The lignin conversion system reaches the best temperature of 160 °C. The yields of other products in the reaction are shown in Table 3. It can be seen from Table 3 that the change trends of vanillin and p-hydroxybenzaldehyde under different reaction conditions are similar to that of syringaldehyde. As a follow-up product of syringaldehyde, the yield of syringic acid increased with the increase of O2 pressure.

### 2.5. Recycling Efficiency of the Catalyst.

Figure 4B shows an XRD diagram of LaFe0.2Cu0.8O3 before and after repeated use four times. It can be seen that the structure of perovskite has no obvious change. Perovskite still has high structural stability. The experimental results of the catalyst reused four times are shown in Figure 4B. It can be seen that LaFe0.2Cu0.8O3 still has good catalytic performance after four times of use. The conversion of lignin and the yield of syringaldehyde were 4.73 and 62.11%, respectively, after three reuses, which were similar to the results of the first reuse, indicating that perovskite oxides had high catalytic activity and structural stability in the reaction system.

### 2.6. Effect of Supported Catalyst Dosage on the Yield of Syringaldehyde.

On the basis of the quality of LaFe0.2Cu0.8O3 in the catalyst, the catalyst/lignin ratios (g/g) are 1:50, 1:20, and 1:10. The results show that, when the content of active components is the same, the syringaldehyde yield from the catalyst loaded on the theta ring is significantly higher than that of the unsupported catalyst (Figure 4B). When the catalyst/lignin (g/g) is 1:50, the yield of syringaldehyde obtained by the unsupported catalyst is 3.18%. The yield of syringaldehyde after 5 wt % theta ring-supported LaFe0.2Cu0.8O3 catalyzed the dealkalization of lignin was 5.28%. The yield of syringaldehyde catalyzed by 10 wt % theta ring-supported LaFe0.2Cu0.8O3 was 5.62%. With the increase in LaFe0.2Cu0.8O3 dosage, syringaldehyde yield also increases. When the ratio of catalyst to lignin (g/g) is 1:20, the yield of syringaldehyde catalyzed by a 5 wt % theta ring is 10.00%, and that of syringaldehyde supported by a 10 wt % theta ring is 7.91%. When the amount of LaFe0.2Cu0.8O3 is further increased, syringaldehyde yield is decreased. Therefore, the catalyst/lignin ratio (g/g) of 1:20 is beneficial to syringaldehyde formation. When the amount of active ingredient is the same, the presence of the carrier increases the specific surface area of the catalyst. Moreover, the 5 wt % loaded theta ring has larger load space than that of the 10 wt % theta ring. Thus, the catalytic effect of the 5 wt % theta ring is better than that of the 10 wt % theta ring.

### 3. CONCLUSIONS

In this paper, the process of catalytic conversion of lignin to syringaldehyde is studied by using perovskite oxide as the catalyst. The results show that the optimum reaction conditions are as follows: lignin 0.60 g, 5 wt % theta ring-supported LaFe0.2Cu0.8O3 catalyst 0.60 g, 1 mol/L NaOH 30 mL, temperature 160 °C, reaction time 2.5 h, and highest syringaldehyde yield 10.00%. The catalyst still has high catalytic activity after four cycles. Using the supported catalyst, syringaldehyde has higher yield and good recycling efficiency, which provides a new method for the industrialization of the lignin scale industry.

### 4. MATERIALS AND METHODS

#### 4.1. Experimental Materials.

Industrial lignin (IL), wheat straw lignosulfonic acid sodium (WSL), Masson’s pine sodium lignin sulfonate (MPL), and dealkaline lignin (DL) were bought from Beijing Coronway Science and Technology Co., Ltd. Perovskite-type oxide LaBxCu0.8O3 (B = Fe, Ni; X is the mole fraction) was synthesized by the citric acid complexation method as described in the previous study.

#### 4.2. Single Factor Optimization.

The conditions were as follows: solid/liquid ratio 1:50 (w/v), lignin 0.60 g, catalyst/lignin (g/g) 1:50–1:2, 0.5–3.0 mol NaOH solution 30 mL, oxygen 0.2–1.2 MPa, reaction temperature 100–180 °C, reaction time 0–4 h. After the reaction, the catalyst was separated by centrifugation at 3000 rpm speed and reused after washing and drying. After determining the pH value of the supernatant, the pH value was adjusted to 2–3 and unreacted lignin was precipitated. After centrifugation, the supernatant was extracted with 30 mL of ethyl acetate. After filtration using the 0.45 μm membrane, the peak area of syringaldehyde in the extraction phase was determined by HPLC, and then using the standard curve, the yield of syringaldehyde was calculated.
4.3. Analytical Methods. 4.3.1. Product Analysis. Analyses of the transformation products (HPLC Agilent Technologies 1200 Series) were performed using a DAD detector (detection wavelength, 210 nm) with a C18 column (3.9 mm × 150 mm) as the chromatographic column. The mobile phase was methanol/water = 43:57 (v/v), the flow rate was 0.6 mL/min, the detector temperature was 35 °C, and the injection volume was 1 μL.15 The following formula was used to calculate syringaldehyde yield:

\[ Y_{SY} = \frac{m_{SY}}{m_{lignin}} \times 100 = \frac{C_{SY} \times V_{EA}}{m_{lignin}} \times 100 \] (1)

where \( m_{lignin} \) is the dry weight of lignin (g), \( V_{EA} \) is ethyl acetate volume (mL), \( C_{SY} \) is the syringaldehyde concentration (mg/mL).

4.3.2. XRD Analysis. Characterization of perovskite oxides was performed via X-ray diffraction (XRD) pattern analysis. The Cu Kα source was adopted, the current was 20 mA, the tube voltage was 36 kV, the scanning angle was 20°–80°, and the scanning rate was 4°/min.

4.3.3. GPC Analysis. The lignin sample (100 mg) was dissolved in 2% NaOH solution and diluted 10 times in 0.1 mol/L NaAc solution. After filtration with the pore size of 0.45 μm, the molecular weight was determined by GPC. The GPC analysis was carried out with an Agilent1260 series equipped with RID and diode array detector (DAD). The chromatographic column was a TSKgel G-3000PWxl (300 × 7.8 mm). The mobile phase was 0.1 M NaAc with a flow rate of 0.6 mL/min. The temperature of the column temperature box was 35 °C, as described in the previous study.16 The differential distribution of molecular weight \( W(\log M) \) was used to determine the polymer mass content in a certain molecular weight range and correspond to the intercept of the ordinate corresponding to a certain range of abscissa on the cumulative molecular weight distribution map. To a certain extent, the ordinate represents the normalized mass ratio. Therefore, the y axis is dimensionless.

4.3.4. FT-IR Analysis. The lignin sample (0.002 g) was mixed with KBr in the agate mortar in the proportion of (lignin/KBr = 1:100 w/w). The functional groups of lignin were measured by an FT-IR-600 plus spectrometer (JASCO Corp., Tokyo, Japan). The average scanning time was 32, the scanning wavelength range was 400 to 4000 cm⁻¹, and the resolution was 1 cm⁻¹. Cross-linked lignin (CLL) was calculated by using the peak value at 1500/1600 in FT-IR data.

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Notes
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