Lignin-phenol monomers govern the pyrolytic conversion of natural biomass from lignocellulose to products

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1. Introduction

The annual biomass energy production exceeds the total global energy demand, which is equivalent to eight times global energy consumption [1,2]. China produces billions of tons of agricultural and forestry waste every year, and more than hundreds of millions of tons of unmanageable crop residues are burned in fields, which results in serious air pollution and is a substantial waste of resources [3–7]. The efficient conversion and utilization of this biomass energy could help alleviate the energy shortage. Biomass energy is a clean and sustainable form of energy that has replaced fossil fuels for its efficiency and environmentally friendly properties [8,9]. The development of a biomass energy industry could help address problems relating to energy security and environmental pollution.

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Biomass pyrolysis is a new and effective approach for utilizing biomass energy [10,11]. However, the product yield of biomass pyrolysis is low, and the quality of pyrolysis oil is poor. Moreover, the oil composition is complex, and this requires purification and separation equipment [11], thereby limiting its efficient and large-scale application. This primarily stems from an in-depth understanding of the mechanism of biomass pyrolysis. A comprehensive understanding of the theory of biomass pyrolysis is thus important for the development of biomass energy. Biomass pyrolysis refers to the conversion of biomass into non-condensable gas, liquid bio-oil, and solid carbon residue through thermochemical conversion in the absence of complete oxygen or under extremely low oxygen content [12]. The biomass is primarily composed of a high polymer system interlaced by cellulose, hemicellulose, and lignin [13]. Thus, biomass pyrolysis involves a series of complex chemical transformation processes of polymers in biomass such as cellulose, hemicellulose, and lignin under high-temperature conditions, including the breakage of chemical bonds, polymerization, and isomerization [14].

Lignin is the primary component of biomass; its relative content ranges from 15% to 40%, and it has the highest specific energy...
among all components in biomass [15–18]. Lignin has higher thermal stability compared with cellulose and hemicellulose [19]. The functions of the three polymers in biomass pyrolysis differ. Lignin is the primary source of solid coke, whereas cellulose and hemicellulose can be easily split into gases and liquids [19]. The dry mixing method has shown that the amount of lignin is important for the decomposition of cellulose, and the decomposition interval of levoglucosan has been extended [20,21]. Cellulose and hemicellulose facilitate the formation of liquid products, and lignin pyrolysis can promote the production of phenolic substances. Mixing of a model mixture to simulate the composition of the actual biomass has revealed that the pyrolysis rate of the biomass sample slows as the lignin content in the sample increases and the gas product content decreases [19]. Furthermore, the components of cellulose, hemicellulose, and lignin can interact with one another during biomass pyrolysis. The interaction between the three polymers can promote the formation of biomass carbohydrates, whereas the interaction between cellulose and lignin inhibits the demethoxylation of guaiacol [20].

Thus, the interactions of components during the pyrolysis of biomass determine the distribution and composition of the gas, liquid, and solid-phase products. However, most studies examining the interaction of components during the pyrolysis of biomass have focused on the synthetic biomass materials of model compounds prepared by the dry mixing method [22–27]. By contrast, no studies have clarified the interactions between components and the characteristics of products in the original crosslinking structure of natural biomass. Model compounds and natural biomass differ in several major ways. In natural biomass, there are chemical bonds among the natural components in the original cross-linking structure, such as hydrogen bonds between hemicellulose and cellulose, chemical bonds between glucuronic acid and lignin ester, and ether bonds in hemicellulose. This close crosslinking structure among different components is absent in synthetic biomass model compounds. In addition, the molecular composition and structure of the internal lignin vary among different types of biomass [28,29], which may affect the interaction between lignin and synthetic cellulose during the pyrolysis of natural biomass. Therefore, the study of the interactions between natural biomass components in different types of biomass is important for optimizing the distribution of biomass pyrolysis products, evaluating and predicting the properties of products, and improving energy conversion efficiency.

In this study, the sodium chlorite-acetic acid method was used for the delignification of natural biomass raw materials with different lignin phenolic compounds, including corn straw, apple branch, ginkgo branch, pine branch, biogas residue, and edible fungi residue. This method can retain the original crosslinking structure among biomass components. After treatment with sodium chlorite-acetic acid for different periods, biomass samples differing in total lignin content were obtained from natural biomass. Fixed-bed pyrolysis was then conducted to explore the effect of variation in lignin content at different pyrolysis temperatures on the gas and liquid products during biomass pyrolysis. The results of this study enhance our understanding of the characteristics of pyrolysis products and the interaction among natural biomass components. Generally, our results provide new insights into the interaction of different polymers of natural biomass during pyrolysis that could be used to achieve the high-value utilization of biomass products.

2. Materials and methods

2.1. Selection and pretreatment of biomass

Corn stalk, apple branch, ginkgo branch, pine branch, biogas residue, and edible fungi residue were used as biomass raw materials. The six types of biomass were smashed and granulated, and their diameters were between 50 and 60 mesh. The sodium chlorite-acetic acid method removed part of the lignin among the six types of biomass powder samples. This method has been widely used to prepare holocellulose and does not damage the cellulose structure; it also has little effect on hemicellulose structure. The six types of biomass were treated in triplicate with sodium chlorite and acetic acid for different lengths of time (1, 3, and 5 h) to obtain biomass with different lignin mass fractions. The elements and composition of the obtained biomass are listed in Table 1.

2.2. Determination of the total lignin content in biomass

The lignin mass fraction of biomass before and after treatment was determined by heating acid detergent. First, the plant samples were passed through a 2-mm sieve, and 1.0 g of biomass samples was accurately weighed in a beaker. Next, 100 mL of hot acid solution (2% hexadecyl trimethylammonium bromide solution) was added. The samples were then covered with a condensing ball and quickly heated to a boil. The samples were continuously heated and digested for 60 min. When the heating and digestion were complete, the solution was added to the sintered glass filter crucible and then vacuumed with an air pump. After suction and filtration, the sample residue was rinsed with a glass rod, and then the crucible wall and sample residue were washed repeatedly with hot water. After three to five washes, the sample residue was cleaned two times with acetone solution (approximately 40 mL). The filter crucible was then transferred to the fume hood. When the acetone in the filter crucible was completely volatilized, the crucible was baked in an electric thermostat (105 °C) for 4 h and then cooled in a dryer. The dried sample residue was placed in a 50-mL beaker, and 12 mol L−1 sulfuric acid was added to soak the sample at 20–25 °C for 3 h. The solution was then poured into the filtering crucible, and the acid was removed using a vacuum. The residue samples were then washed repeatedly with hot water until the pH of the solution was neutral. The residue samples were baked in an oven (105 °C) for 4 h, cooled in a dryer to room temperature, and finally weighed. The weight of the residue sample, obtained through the procedure described above, was the weight of the total lignin in the biomass sample. The detailed results are shown in Table 1.

2.3. Analysis of lignin phenolic monomer compounds in biomass

Alkaline CuO oxidation was used to extract lignin phenolic monomer compounds from biomass. First, 4 g of the ground samples was added to the digestion tank, and then 1,000 mg of CuO, 100 mg of (NH4)2Fe(SO4)2, and 15 mL of NaOH solution (2 mol L−1) were added. The sample was stirred evenly, and the air in the loess solution was blown out with nitrogen for approximately 5–10 min. Then, 10 mL of 6 N HCl solution was added to the digestion tank, and then 1,000 mg of CuO, 100 mg of (NH4)2Fe(SO4)2, and 15 mL of NaOH solution were added. Next, the supernatant was poured to the centrifuge tube, and the remaining sample residue was rinsed with 10 mL of deionized water. The suspension was left to stand for 4 min and then added to the previously obtained suspension, then centrifuged. Next, the supernatant was poured into another centrifuge tube, and 5.5 N sulfuric acid solution was added to ensure that the pH of the solution was approximately 1. The solution was then placed in the dark for 1 h. Twenty-five milliliters of ethyl acetate was used to conduct two extractions, and then the three organic phase solutions were pooled. Approximately 1.0 g of anhydrous sodium sulfate was added to remove the residual water. After the solution was rotary evaporated, the concentrate was cleaned two times with acetone solution (approximately 40 mL). The filter crucible was then transferred to the fume hood. When the acetone in the filter crucible was completely volatilized, the crucible was baked in an electric thermostat (105 °C) for 4 h and then cooled in a dryer. The dried sample residue was placed in a 50-mL beaker, and 12 mol L−1 sulfuric acid was added to soak the sample at 20–25 °C for 3 h. The solution was then poured into the filtering crucible, and the acid was removed using a vacuum. The residue samples were then washed repeatedly with hot water until the pH of the solution was neutral. The residue samples were baked in an oven (105 °C) for 4 h, cooled in a dryer to room temperature, and finally weighed. The weight of the residue sample, obtained through the procedure described above, was the weight of the total lignin in the biomass sample. The detailed results are shown in Table 1.

Table 1. Composition of the obtained biomass are listed in Table 1.

| Biomass Type | Lignin Mass Fraction | Carbohydrates | Phenolic Compounds |
|--------------|----------------------|---------------|-------------------|
| Corn stalk   | 0.23                 | 0.65          | 0.12              |
| Apple branch | 0.25                 | 0.60          | 0.15              |
| Ginkgo branch| 0.27                 | 0.62          | 0.16              |
| Pine branch  | 0.24                 | 0.64          | 0.14              |
| Biogas residues | 0.26              | 0.63          | 0.15              |
| Edible fungi | 0.28                 | 0.61          | 0.17              |
transferred to a 2-ml cell culture flask with dichloromethane, blown with dry nitrogen to approximately 50 μL, and finally stored in a refrigerator.

Fifty microliters of salinization reagent, 10 μL of pyridine, and 0.5 mL of dichloromethane were added to the cell culture flask, which contained lignin phenolic monomer compound concentrate before computer analysis. The solution was placed in an oven at 70 °C for 2 h of derivatization. Computer analysis was performed on an Agilent 7890 gas chromatograph equipped with a flame ionization detector using an HP5 capillary column, which had a column length of 30 m, an inner diameter of 0.32 mm, and a film thickness of 0.25 μm; the carrier gas was helium with a purity of >99.999%. The carrier gas flow rate was 1.5 mL min⁻¹, and the sample injection split ratio was 1:50. For the heating program, the temperature was increased from 100 °C to 270 °C at a rate of 4 °C min⁻¹, and the temperature was further increased from 270 °C to 300 °C at a rate of 15 °C min⁻¹ and maintained for 10 min. The temperature of the injector and detector was kept at 300 °C. The content of lignin phenolic monomer compounds was quantified by an external standard, and the relative deviation in the content of lignin compounds was less than 5% through parallel sample experiments. The target lignin phenolic monomers in the present study included cinnamyl phenols (p-coumaric acid, ferulic acid), syringyl phenols (syringaldehyde, acetylsyringone, syringic acid), and vanillyl phenols (vanillin, acetovanillone, vanillic acid).

### 2.4. Biomass pyrolysis

In this study, a temperature-controllable tubular heating furnace was used for the pyrolysis of biomass. This furnace was equipped with a quartz tube reactor (50 mm in diameter and 650 mm in total length), electric furnace, temperature controller, condensing system, filter, desiccator, gas analyzer, and gas supply system (Fig. 1). During testing, the body of the furnace was first heated to the set temperature, which was 400 °C and 750 °C. In addition, high-purity N₂ with a 1000 mL min⁻¹ flow rate was used to purge the quartz tube for over 10 min to ensure the air in the tube reactor was completely discharged. Afterwards, the flow rate of N₂ was adjusted to 400 mL min⁻¹.

Approximately 2 g of biomass powder samples was placed into the sample tray, and then the tray was pushed into the central reaction zone. The volatile gas phase components produced during the test were collected after being condensed by the ice–water mixture. The non-condensable gas was filtered with absorbent cotton, dried with a mixture of anhydrous calcium chloride and color-changing silica gel, and then collected into an airbag. After complete pyrolysis for 20 min, the quartz tube reactor was removed and cooled to room temperature under continuous nitrogen purge. The bio-oil in the condensing tube was collected with 3 mL of pure acetone. The mass of solid and liquid products during pyrolysis was obtained according to the mass of the sample tray and condensing tube before and after pyrolysis.

### 2.5. Composition analysis of pyrolysis gas

The non-condensate gas produced during pyrolysis was quantitatively analyzed by four-channel micro gas chromatography, with Ar and He as the carrier gas in the heat conduction detector. The pyrolytic gas was collected by the airbag and carried into the chromatographic columns by the carrier gas. There were three chromatographic columns: A, B, and C. Column A was a 5A molecular sieve, and the column temperature was 110 °C for the detection of N₂, H₂, O₂, CH₄, and CO. Column B was Plot U, and the temperature was set at 105 °C. Column B was used to detect CO₂, C₂H₆, C₂H₅OH, and C₂H₅OH. Column C was used for the detection of CO₂, Ar, and CO. For the quantitative analysis of pyrolysis gas, standard gas was used to calibrate the system. The standard gas consisted of H₂ (9.83%), CO (20.7%), CH₄ (9.89%), CO₂ (20.1%), C₂H₅OH (0.49%), C₂H₆ (0.5%), C₂H₅OH (0.5%), and N₂ (37.99%). The gas product yield during pyrolysis was calculated based on the volume content of N₂ and pyrolysis gas components in the mixture and the volume of carrier gas (N₂) in the experiment.

### 2.6. Composition analysis of pyrolysis liquid products

The composition of liquid bio-oil produced during pyrolysis was detected by an Agilent 7890 gas chromatograph. A splitless injector

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**Table 1**

| Treat time (h) | Biomass          | Lignin (%) | Volatile (%) | Ash (%) | C (%)  | H (%)  | N (%) |
|---------------|------------------|------------|--------------|---------|--------|--------|-------|
| 5             | Corn stalk       | 4.83       | 83.4         | 0.91    | 44.3   | 5.43   | 0.21  |
|               | Apple branch     | 6.05       | 80.9         | 0.94    | 47.4   | 5.27   | 0.20  |
|               | Ginkgo branch    | 5.71       | 82.6         | 0.90    | 43.0   | 5.10   | 0.20  |
|               | Pine branch      | 5.69       | 85.9         | 0.86    | 46.1   | 5.86   | 0.23  |
|               | Biogas residue   | 4.95       | 80.9         | 0.84    | 43.9   | 5.43   | 0.21  |
|               | Edible fungi residue | 4.17   | 79.1         | 0.83    | 41.6   | 5.86   | 0.22  |
| 3             | Corn stalk       | 15.6       | 80.4         | 1.10    | 47.9   | 5.82   | 0.42  |
|               | Apple branch     | 14.9       | 79.6         | 1.03    | 45.2   | 6.17   | 0.39  |
|               | Ginkgo branch    | 14.5       | 79.6         | 1.08    | 43.3   | 5.59   | 0.42  |
|               | Pine branch      | 13.3       | 84.4         | 1.11    | 45.2   | 5.53   | 0.40  |
|               | Biogas residue   | 15.3       | 83.6         | 1.10    | 43.3   | 6.17   | 0.42  |
|               | Edible fungi residue | 16.0   | 80.4         | 1.04    | 45.1   | 6.17   | 0.44  |
| 1             | Corn stalk       | 26.7       | 78.3         | 1.04    | 49.3   | 6.14   | 0.46  |
|               | Apple branch     | 25.6       | 80.6         | 1.04    | 48.8   | 5.89   | 0.44  |
|               | Ginkgo branch    | 27.4       | 76.7         | 0.96    | 52.3   | 6.57   | 0.49  |
|               | Pine branch      | 23.2       | 82.2         | 1.08    | 49.8   | 5.96   | 0.48  |
|               | Biogas residue   | 24.4       | 78.3         | 1.04    | 49.3   | 6.39   | 0.45  |
|               | Edible fungi residue | 22.4   | 75.0         | 1.03    | 46.3   | 5.71   | 0.46  |
| 0             | Corn stalk       | 35.5       | 77.5         | 0.75    | 52.4   | 6.21   | 0.68  |
|               | Apple branch     | 36.5       | 75.2         | 0.71    | 50.3   | 6.40   | 0.73  |
|               | Ginkgo branch    | 34.5       | 75.2         | 0.67    | 48.7   | 6.52   | 0.67  |
|               | Pine branch      | 37.2       | 78.3         | 0.74    | 49.3   | 6.52   | 0.63  |
|               | Biogas residue   | 33.4       | 77.8         | 0.74    | 55.0   | 6.52   | 0.65  |
|               | Edible fungi residue | 31.6   | 74.0         | 0.70    | 55.5   | 6.40   | 0.71  |
A, quartz tube reactor. B, furnace heater. C, thermal insulating layer. D, ceramic crucible. E, temperature controller. F, thermal sensor. G, pressure gauge. H, condensing system. I, filter. J, desiccator. K, gas analyzer.

was used, and the temperature was held at 250 °C. The initial column temperature was kept at 50 °C for 3 min, increased to 250 °C at a speed of 20 °C min⁻¹, and then kept at this temperature for 18 min. The scan range was 30–500 mass-to-charge ratio, and the solvent delay time was 4.5 min. The electron bombardment capacity of the electron ionization source was 70 eV. The concentration of the compounds was determined by an external standard method.

2.7. Calculations and statistical analysis

Data for low-carbon-number hydrocarbon compounds were not provided because of their low pyrolysis yield. The rates of change of biomass pyrolysis products with the lignin mass fraction were calculated based on the changes in the percentage of pyrolysis products under the highest lignin mass fraction relative to the lowest lignin mass fraction. The univariate relationships between the content of biomass lignin-phenol monomers and rates of change of biomass pyrolysis products with the lignin mass fraction were evaluated using ordinary least squares regression. A stepwise multiple regression method was performed to assess the effect of lignin-phenol monomers on the rates of change of biomass pyrolysis products with the lignin mass fraction. Both linear analysis and stepwise multiple regression were conducted using SPSS 20.0 (SPSS, Inc.), and the results of these analyses were considered significant at \( P < 0.05 \).

3. Results and discussion

3.1. Distribution characteristics of the pyrolysis gas, liquid, and solid-phase products of biomass

The pyrolysis gas, liquid, and solid-phase products distribution of biomass samples changed as the lignin content increased, but the patterns of change varied with pyrolysis temperature (Fig. 2). When the pyrolysis temperature was 400 °C, the solid yields of the pyrolysis products of the six biomass samples increased significantly as the lignin content in the samples increased; the production of liquid and gas products decreased, and the yield of gas products was low. These findings indicate that the amount of lignin that decomposed was less than the amount of hemicellulose and cellulose that decomposed at 400 °C [19]. The yield of solid-phase coke, which was determined by lignin, increased as the lignin content increased, whereas the yield of gas and liquid products decreased.

When the pyrolysis temperature was increased to 750 °C, the solid yield decreased significantly compared with that at 400 °C. However, the solid yield did not change significantly as the lignin content in the samples increased, which is in contrast to results obtained by the mixing model mixture method [30]. These findings indicate that lignin and holocellulose in the original crosslinking structure of biomass interacted during pyrolysis, resulting in an equal solid-phase coke yield via the high synthetic cellulose and lignin content. The distribution of pyrolysis products was improved at 750 °C compared with 400 °C, and the overall yield of gas products was increased; the yield of gas products decreased as the lignin content increased at 700 °C, which was the same pattern observed at 400 °C. The pattern of variation in liquid yield at 750 °C was opposite that at 400 °C; specifically, the liquid yield was slightly increased as the lignin content increased. When the pyrolysis temperature was 750 °C, holocellulose was completely broken down. The yield of liquid bio-oil did not decrease as the lignin content increased, indicating a strong interaction between lignin and synthetic cellulose in the original crosslinked structure of biomass that promoted carbonization via the high holocellulose content and oil formation via the high lignin content.

![Fig. 1. Temperature-controllable tubular heating furnace for the pyrolysis of biomass.](image)

![Fig. 2. The pyrolysis gas, liquid, and solid-phase products distribution as the lignin content of natural biomass increased at pyrolysis temperatures of 400 °C (a) and 750 °C (b). The ranges of the horizontal and vertical lines indicate the 90th percentiles of the lignin content and pyrolysis product yield, respectively. The intersection of the horizontal and vertical lines corresponds to the average lignin content and pyrolysis product yield.](image)
3.2. Composition characteristics of gas products

Changes in the main components of gas products after the pyrolysis of biomass samples differing in lignin content are shown in Fig. 3. As the lignin content increased, the pattern of variation in the gas products was the same among the six biomass samples, but the range of variation differed (Fig. 3). This result mainly stemmed from differences in the lignin content and composition among the six selected biomass samples [31].

The main components of the gas products included H2, CH4, CO, and CO2. When the pyrolysis temperature was 400 °C, the pyrolysis gas products of biomass samples were primarily CO2, CH4, and CO, and the H2 content was relatively low. As the lignin content of the samples increased, the CH4 content in the pyrolysis gas products of the biomass samples increased rapidly, and the relative content of CO2 decreased rapidly. CH4 was primarily derived from the fracture of methoxy phenylpropane in lignin, whereas CO2 was derived from the oxidation of the hydroxyl group and the decarboxylic acid reaction of holocellulose [32], which results in a significant increase in the CH4 content in gas products and a rapid decrease in the CO2 content as the lignin content increased and the synthetic cellulose content increased. Compared with CH4 and CO2, the relative content of CO in the pyrolysis gas products of ginkgo and pine tree branches increased rapidly as the lignin content of the biomass increased, whereas the relative content of CO in the pyrolysis gas products of biogas slurry and mushroom residue increased more gradually; this variation was related to the characteristics of the different biomass raw materials. Numerous studies of the biomass pyrolysis mechanism have determined the sources of CO to be decarboxylation, gas-phase interaction, and gas–solid interaction between lignin and holocellulose during pyrolysis.

When the pyrolysis temperature was increased to 750 °C, the content of H2 in the pyrolysis gas products of biomass samples was high, and it decreased as the lignin content in the samples increased. Variation in CO2, CO, and CH4 content at 750 °C was consistent with that at 400 °C. The H2 in the gas product was obtained from the dehydrogenation and polycondensation of aromatic hydrocarbons [37]. As the pyrolysis temperature increased, lignin was further decomposed, dehydrogenation and polycondensation were intensified, and the production of H2 was significantly increased. However, when the pyrolysis temperature was 750 °C, aromatic compounds increased as the lignin content in biomass samples increased, whereas the H2 content decreased [Fig. 3], which was inconsistent with results obtained from the mixing model mixture method [30]. This inconsistency might stem from the material differences between natural biomass and mixed-mode biomass.

3.3. Composition characteristics of liquid products

After the hydrogen bonds in cellulose are broken at high temperature, it is directly degraded and converted into amorphous levoglucosan (LG). Direct degradation results in the formation of aliphatic compounds with even carbon numbers, and these compounds are further transformed to form small molecules of aldehydes, ketones, and CO. Aldehydes and ketones include formaldehyde, acetaldehyde, aceton, pyruvaldehyde, acetol, and 5-hydroxymethyl furfural. The amorphous LG converted from cellulose results in the opening of the ring to form CO, formaldehyde, acetaldehyde, glyceraldehyde, pyruvaldehyde, propanoic acid, furfural, and furfuryl alcohol [38]. Thus, LG and anhydro sugar in liquid bio-oil were the pyrolysis products of cellulose in biomass. Small molecular oxygen-containing compounds such as acetic acid and furfural are typical pyrolysis products of hemicellulose [19,20]. The overall patterns of change for most pyrolysis liquid compounds as the lignin content of natural biomass increased were similar between low-temperature pyrolysis and high-temperature pyrolysis, but the magnitude of the changes differed (Fig. 4). As the lignin content in biomass samples increased, the LG content of cellulose increased, and the LG content was inversely proportional to the cellulose content in biomass. During biomass pyrolysis, lignin contributed to the formation of LG in the pyrolysis products via the electronic structure of the hydrocarbon group and π system, which was formed through conjugation of LG of the holocellulose molten phase; the lignin decomposition of guaiacol aromatic compounds can enhance the thermal stability of sinistral glucan [39]. As the lignin content in biomass samples increased, the content of aromatic compounds increased, which increased the LG content and modified the electronic structure of the hydrocarbon group and π system. Compared with LG, another typical product of cellulose DDG decreased slightly as the lignin content increased. The interaction between cellulose and hemicellulose promoted the dehydration reaction of oligosaccharides. However, as the lignin content increased, cellulose and hemicellulose content decreased, which inhibited the dehydration reaction; this finding explained the decrease in DDG.
In liquid products, small molecular oxygen-containing compounds such as acetic acid, hydroxy-acetone, and furfuryl alcohol decreased gradually as the lignin content increased (Fig. 4), but the content of CO$_2$ in gas products decreased gradually as the lignin content increased (Fig. 3). Given that lignin can inhibit the decarboxylation reaction during pyrolysis [32], CO$_2$ in gas products can be reduced from the dehydration of cellulose. Furthermore, the volatile components of lignin are conducive to forming acid and ketone compounds in the gas phase during the pyrolysis of cellulose and hemicellulose. Complexes are formed by the carboxyl of hemicellulose and dehydrated sugars and remain in the molten phase [40]. Therefore, when the lignin content in biomass is low, the dehydrated sugar generated by the pyrolysis of holocellulose results in secondary decomposition, and the two-to-four-carbon molecular fragments containing carboxyl or carbonyl do not undergo further decarboxylation or decarboxylic reactions but instead react to generate the furan structure. This process can lead to a gradual decrease in acid, ketone, and furan compounds in liquid products, and CH$_4$ and CO in gas products gradually increase as the lignin content in biomass increases.

The pyrolysis process of lignin mainly involves the breaking of aryl ether bonds, methoxy ether bonds, and part of the aliphatic carbon-carbon bonds, but not all of the bonds are broken. Part of the aromatic ether bonds and aliphatic carbon-carbon bonds result in the formation of phenol free radicals, quinone free radicals, phenols, aromatic aldehydes, and aromatic alkenes after breaking, and the end aliphatic carbon-carbon bonds are broken to produce formaldehyde [41]. Thus, phenols such as guaiacol (GL) and cycloketones are typical products of lignin. Phenols in liquid bio-oil are important pyrolytic products, and changes in their content reflect the effect of holocellulose on lignin pyrolysis. Typical phenolic products in lignin pyrolysis primarily include GL and its substituted derivatives; substituted groups such as esters, acids, alcohols, hydroxyl groups, and carboxyl groups exist on the hydro-para position in the structure of GL, such as HMA, EMP, vanillin, phenol, and alkylphenol (Fig. 4). As the lignin content increased, the guaiacyl-substituted derivatives were generated by the breaking of bonds of aliphatic ether and aryl alkyl ether in lignin increased, whereas the content of GL, the primary pyrolysis product of lignin, decreased. This finding might stem from the increase in the content of holocellulose, which promoted the removal of aliphatic substituents of lignin and inhibited the dimethoxy reaction of GL and led to a decrease in the content of GL in liquid products and an increase in the content of phenols with methoxy groups [22].

### 3.4. Effect of biomass lignin-phenol monomers on the pyrolysis products of biomass

The rate of change in biomass pyrolysis products with the lignin mass fraction can indicate the degree to which the lignin gradient affects the distribution of products during pyrolysis. Stepwise regression analysis was performed to assess the effect of biomass lignin monomer compounds on the changing rate of biomass pyrolysis products with the lignin mass fraction. Cinnamyl phenol monomers, including p-coumaric acid and ferulic acid, increased the rate of change in the lignin mass fraction, which affected the distribution of biomass pyrolysis gas, liquid, and solid-phase products, as well as the composition of gas and liquid-phase products under low-temperature (400 °C) pyrolysis (Fig. 5). Cinnamyl phenol monomers (p-coumaric acid, ferulic acid) and syringyl (syringaldheyde, acetylxyregine, syringic acid) and vanillyl phenol monomers (vanillin, acetovanillone, vanillic acid) increased the rate of change of lignin pyrolysis products with the lignin mass fraction at high temperatures (750 °C) (Fig. 6). These results indicate that the lignin monomer compounds in biomass affect the interaction of components during pyrolysis to different degrees, and the specific mechanism is closely related to the pyrolysis temperature.

Lignin monomers vary in their effects on thermal stability. Cinnamyl phenol monomers are the easiest to degrade, followed by syringyl phenol monomers and vanillyl phenol monomers [42]. This difference in thermal stability among lignin monomers was attributed to the higher degree of cross-linking between the vanillyl phenol monomers. However, this difference might also be related to the presence of different lignin monomers in different plant tissues. In wood tissue, the intermediate layer of the secondary wall is relatively rich in syringyl phenol monomers, whereas the outer and inner layers of the secondary wall primarily contain vanillyl and p-hydroxy phenol monomers [43]. Given that the middle layer of the secondary wall can be more easily oxidized than other cell wall structures, the syringyl phenol monomers are preferentially destroyed compared with the vanillyl phenol...
monomers during lignin pyrolysis [44–46]. Lignin monomers also vary in their resistance to degradation [47], which stems from their different matrix types (plant types, plant tissues, and plant cells). At low temperatures, vanillyl phenol monomers are easily oxidized and decomposed, which might be responsible for their major contribution to the rates of change of biomass pyrolysis products with the lignin mass fraction. At high temperature, the lignin monomers of vanillyl phenol monomers also began to be oxidized and decomposed, which explains the large contribution they made to the rate of change of biomass pyrolysis products with the lignin mass fraction.

3.5. Prospects and implications

Biomass resources mainly include crop stalks, agricultural product processing residues, forestry wood residues, poultry and livestock manure, municipal solid waste, organic wastewater, and product processing residues, forestry wood residues, poultry and livestock manure, municipal solid waste, organic wastewater, and processing residues, forestry wood residues, poultry and livestock manure, municipal solid waste, organic wastewater, and processing residues. Available resources of crop straw and forest wood residues are 170 million tons and 200 million tons equivalent of standard coal in China, respectively. Total biomass resource reserves are equivalent to 460 million tons of standard coal in China.

but the amount used is only 22 million tons of standard coal equivalent. Thus, biomass resources in China are not utilized to the extent that they could be.

Compared with traditional fossil energy, biomass energy has obvious advantages in terms of energy sources, costs, and environmental pollution. First, biomass is derived from the photosynthesis of plants and is a renewable resource. Second, because of the low content of sulfur, nitrogen, and ash in biomass energy, the emissions of soot, SO₂, and nitrogen oxides are lower; thus, biomass is a clean energy source. Third, biomass energy is storable because it can be converted into storable solid, liquid, and gaseous fuels using modern technology. The results of our study provide insight into how the value of biomass could be maximized and its disadvantages minimized through pyrolysis.

The main components of lignocellulosic biomass are cellulose, hemicellulose, and lignin. Our results showed that the lignin-phenol monomers had significant effects on the interaction between lignin and holocellulose and thus on the product distributions during the pyrolysis of natural biomass. This indicated that the type of lignin monomers in biomass can affect the utilization potential of biomass resources by affecting the characteristics of
pyrolysis. The type and content of lignin monomers vary among plants. Vanillyl phenol monomers occur in all vascular plants and are the only lignin-like compounds found in the woody tissues of gymnosperms [31,48]. Although trace amounts of syringyl phenol monomers occur in the non-woody tissues of gymnosperms, they are mostly products of angiosperms and can be found in woody and non-woody tissues [31,49]. Cinnamyl phenol monomers have only been found in the non-woody tissues of angiosperms and gymnosperms [31]. The formation of pyrolysis products can be controlled by the pyrolysis temperature depending on the type of biomass to achieve its high-value utilization. Although the sodium chlorite-acetic method does not damage the structure of cellulose and hemicellulose, it does alter the structure of lignin to a certain extent. Additional studies are needed to characterize variation in lignin structure after sodium chlorite-acetic pretreatment to reveal the effect of the lignin content on biomass pyrolysis.

Only the effect of the lignin gradient on biomass pyrolysis products under pure pyrolysis was explored in our study. Given that biomass is a low-quality hydrocarbon resource, the quality of the product directly used as a raw material for pyrolysis is usually poor. The addition of suitable catalysts and proper pre-treatment aid the preparation of target biomass pyrolysis products and are key links in the industrial chain for generating high-quality products by biomass pyrolysis. There is thus a need for future research to examine how the lignin gradient affects the pyrolysis products of biomass through the addition of catalysts and the use of pre-treatments such as drying, crushing, torrefaction, and acid treatment. High-value pyrolysis products can be prepared after optimizing the use of biomass and pyrolysis conditions. However, advanced separation devices following biomass pyrolysis are required to separate different products from the pyrolysis process to improve their utilization, including coolers, gas-liquid separators, tar tanks, and lye pools.

4. Conclusions

Lignin in the original crosslinked structure of natural biomass strongly interacted with holocellulose under high-temperature pyrolysis, which increased the generation of solid-phase coke via the high content of holocellulose and gaseous volatiles via the high content of lignin. When the pyrolysis temperature was 750°C, the interaction between lignin and holocellulose in biomass promoted the generation of CO and inhibited the generation of CO2. The content of H2 in the gas products of the biomass decreased as the lignin content increased because the interaction between synthetic cellulose and lignin inhibited the dehydrogenation and condensation of aromatic rings, which led to a decrease in H2 production. The associated lignin in biomass could promote the pyrolysis of cellulose to produce a large amount of LG and inhibit the decomposition of LG, which improved its preservation. The presence of holocellulose in biomass can inhibit the dimethoxy reaction of the lignin monomer guaiacyl, promote the dealkylation of phenylpropane, and increase the formation of more phenolic compounds. Lignin monomers varied in their effects on the interaction among components during pyrolysis. Cinnamyl-phenol monomers increased the rate of change of biomass pyrolysis products with the mass fraction of lignin under low-temperature pyrolysis (400°C). However, under high-temperature (750°C) pyrolysis, cinnamyl-phenol monomers (p-coumaric acid, ferulic acid), as well as syringyl (syringaldehyde, acetosyringone, syringic acid) and vanillyl phenol–monomers (vanillin, acetovanillone, vanillic acid), were detected. Overall, our work provides new insights into the interaction mechanism of the components in the original cross-linking structure of biomass and the characteristics of the products formed. The results of our study could be used to facilitate the development of approaches that permit the modification of the pyrolysis of various types of biomass to improve the preparation of high-grade gaseous and liquid fuels.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M. Balat, G. Ayar, Biomass energy in the world, use of biomass and potential trends, Energy Sources 27 (2005) 931–940.
[2] M. Balat, Global status of biomass energy use, Energy Sources, Part A Recovery, Util. Environ. Eff. 31 (2009) 1160–1175.
[3] D.I. Mausel, J.A. Logan, D.J. Jacob, B.E. Anderson, D.R. Blake, J.D. Bradow, B. Heikes, G.W. Sachse, H. Singh, B. Talbot, Photochemistry in biomass burning plumes and implications for tropospheric ozone over the tropical South Atlantic, J. Geophys. Res. Atmos. 103 (1998) 8401–8423.
[4] G. Cao, X. Zhang, F. Zheng, Inventory of black carbon and organic carbon emissions from China, Atmos. Environ. 40 (2006) 6516–6527.
[5] X. Yan, T. Ohara, H. Akimoto, Bottom-up estimate of biomass burning in mainland China, Atmos. Environ. Times 40 (2006) 5262–5273.
[6] S. Yang, H. He, S. Lu, D. Chen, J. Zhu, Quantification of crop residue burning in the field and its influence on ambient air quality in Suqian, China, Atmos. Environ. Times 42 (2008) 1961–1969.
[7] H. Zhang, X. Ye, T. Cheng, T. Yang, X. Yang, L. Wang, R. Zhang, A laboratory study of agricultural crop residue combustion in China: emission factors and emission inventory, Atmos. Environ. 42 (2008) 8432–8441.
[8] H. Chen, B. Xie, J. Ma, Y. Chen, NOx emission of biodiesel compared to diesel: higher or lower? Appl. Therm. Eng. 137 (2018) 584–593.
[9] J.H. Ng, K.J. Chow, K.Y. Wong, C.T. Chong, Exergy-based analysis of diesel engine when fuelled with fossil diesel and Palm Methyl Ester (PME), IOP Conf. Ser. Earth Environ. Sci. 288 (2019), 012127.
[10] A. Debdouzi, A. El Amarti, E. Colaco, M.J. Blesa, L.H. Hajaj, The effect of rate field on yields and compositions of oil products from espalto pyrolysis, Int. J. Energy Res. 30 (2006) 1243–1250.
[11] M. Shariatzadeh, M. Sadeqzadeh, M. Guo, T.N. Borhani, N.M. Konda, M.C. Garcia, L. Wang, J. Hallett, N. Shah, The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: a review of the state of art and future research directions, Prog. Energ. Combust. 71 (2019) 1–80.
[12] S.V. Pisupati, A.H. Tchlapa, thermochemical processing of biomass, Adv. Bioproc. Technol. Cham: Springer (2015) 277–314.
[13] A.Y. Bridgewater, G.V.C. Peacock, Fast pyrolysis processes for biomass, Renew. Sustain. Energy Rev. 4 (2000) 1–73.
[14] S. Yaman, Pyrolysis of biomass to produce fuels and chemical feedstocks, Energy Convers. Manag. 45 (2004) 651–671.
[15] M.P. Pandey, C.S. Kim, Lignin depolymerization and conversion: a review of thermochemical methods, Chem. Eng. Technol. 34 (2011) 29–41.
[16] S.H. Ghaffar, M. Fan, Structural analysis for lignin characteristics in biomass straw, Biomass Bioenergy 57 (2012) 264–279.
[17] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan, C.E. Wyman, Lignin valorization: improving lignin processing in the bioeconomy, Science 344 (2014) 1246843.
[18] C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Catalytic transformation of lignin for the production of chemicals and fuels, Chem. Rev. 115 (2015) 11559–11624.
[19] K. Ravendran, A. Ganesh, K.C. Khilar, Pyrolysis characteristics of biomass and biomass components, Fuel 75 (1996) 987–998.
[20] S. Wang, X. Guo, K. Wang, Z. Luo, Influence of the interaction of components on pyrolysis behavior, J. Anal. Appl. Pyrol. 91 (2011) 183–189.
[21] H. Zhou, C. Wu, A. Meng, Y. Zhang, P.T. Williams, Effect of interactions of biomass constituents on polycyclic aromatic hydrocarbons (PAH) formation during fast pyrolysis, J. Anal. Appl. Pyrol. 110 (2014) 264–269.
[22] T. Hosou, H. Kawamoto,Pyrolysis behaviors of wood and its constituent polymers at gasification temperature, J. Anal. Appl. Pyrol. 78 (2007) 328–336.
[23] G. Van Oost, M. Hrabovský, V. Kopecký, M. Konrad, M. Hlina, T. Kavka, Pyrolysis/gasification of biomass for synthetic fuel production using a hybrid
gas–water stabilized plasma torch, Vacuum 83 (2008) 209–212.

[24] N. Dahmen, E. Dinjus, T. Kolb, U. Arnold, H. Leibold, R. Stahl, State of the art of the bioliquefaction process for synthetic biofuels production, Environ. Prog. Sustain. 31 (2012) 176–181.

[25] P. Giudicianni, G. Cardone, G. Sorrentino, R. Ragucci, Hemicellulose, cellulose and lignin interactions on Arundo donax steam assisted pyrolysis, J. Anal. Appl. Pyrol. 110 (2014) 138–146.

[26] D.N. Vienescu, J. Wang, A. Le Gresley, J.D. Nixon, A life cycle assessment of options for producing synthetic fuel via pyrolysis, Bioresour. Technol. 249 (2018) 626–634.

[27] M. Tripathi, J.N. Sahu, P. Ganesan, Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review, Renew. Sustain. Energy Rev. 38 (2014) 594–608.

[28] A. Lourenço, J. Rencoret, C. Chemetova, J. Gominho, A. Gutierrez, J.C. del Rio, A. Demirbas, Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels, Energy Explor. Exploit. 29 (2002) 105–111.

[29] A. Lourenço, J. Rencoret, C. Chemetova, J. Gominho, A. Gutierrez, J.C. del Rio, A. Demirbas, Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels, Energy Explor. Exploit. 29 (2002) 105–111.

[30] A. Lourenço, J. Rencoret, C. Chemetova, J. Gominho, A. Gutierrez, J.C. del Rio, A. Demirbas, Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels, Energy Explor. Exploit. 29 (2002) 105–111.

[31] J.I. Hedges, R.A. Blanchette, J.I. Hedges, Fungal degradation of wood

[32] J.I. Hedges, D.C. Mann, The characterization of plant tissues by their lignin oxidation products, Geochim. Cosmochim. Acta 43 (1979) 3985.

[33] K. Ruel, F. Barnoud, Degradation of wood by microorganisms, in: T. Hiouchi (Ed.), Biosynthesis and Biodegradation of Wood Components, Academic Press, Inc., London, 1985.

[34] J.I. Hedges, G.L. Cowie, J.R. Ertel, R.J. Barbour, P.G. Hatcher, Degradation of carbohydrates and lignins in buried woods, Geochim. Cosmochim. Acta 49 (1985) 701–711.

[35] J.I. Hedges, R.A. Blanchette, K. Weliky, A.H. Devol. Effects of fungal degrada-

dation on the CuO oxidation products of lignin: a controlled laboratory study, Geochim. Cosmochim. Acta 52 (1988) 2717–2726.

[36] G.E. Machinet, I. Bertrand, Y. Barrière, B. Chabbert, S. Recous, Impact of plant cell wall network on biodegradation in soil: role of lignin composition and phenolic acids in roots from 16 maize genotypes, Soil Biol. Biochem. 43 (2011) 1544–1552.

[37] E.K. Thomas, L. Gao, D. MacDonald, Y. Huang, A Quantitative and Qualitative Comparison of Aquatic and Terrestrial Plant Lignin Phenols: Critical Information for Paleoecological Reconstructions, American Geophysical Union, 2009 fall meeting (abstract #B33C-0404).

[38] M.A. Go

[39] K. Ruel, F. Barnoud, Degradation of wood by microorganisms, in: T. Hiouchi (Ed.), Biosynthesis and Biodegradation of Wood Components, Academic Press, Inc., London, 1985.

[40] J.I. Hedges, G.L. Cowie, J.R. Ertel, R.J. Barbour, P.G. Hatcher, Degradation of carbohydrates and lignins in buried woods, Geochim. Cosmochim. Acta 49 (1985) 701–711.

[41] J.I. Hedges, R.A. Blanchette, K. Weliky, A.H. Devol. Effects of fungal degrada-
dation on the CuO oxidation products of lignin: a controlled laboratory study, Geochim. Cosmochim. Acta 52 (1988) 2717–2726.

[42] G.E. Machinet, I. Bertrand, Y. Barrière, B. Chabbert, S. Recous, Impact of plant cell wall network on biodegradation in soil: role of lignin composition and phenolic acids in roots from 16 maize genotypes, Soil Biol. Biochem. 43 (2011) 1544–1552.

[43] E.K. Thomas, L. Gao, D. MacDonald, Y. Huang, A Quantitative and Qualitative Comparison of Aquatic and Terrestrial Plant Lignin Phenols: Critical Information for Paleoecological Reconstructions, American Geophysical Union, 2009 fall meeting (abstract #B33C-0404).

[44] M.A. Go

[45] J.I. Hedges, G.L. Cowie, J.R. Ertel, R.J. Barbour, P.G. Hatcher, Degradation of carbohydrates and lignins in buried woods, Geochim. Cosmochim. Acta 49 (1985) 701–711.

[46] J.I. Hedges, R.A. Blanchette, K. Weliky, A.H. Devol. Effects of fungal degrada-
dation on the CuO oxidation products of lignin: a controlled laboratory study, Geochim. Cosmochim. Acta 52 (1988) 2717–2726.

[47] G.E. Machinet, I. Bertrand, Y. Barrière, B. Chabbert, S. Recous, Impact of plant cell wall network on biodegradation in soil: role of lignin composition and phenolic acids in roots from 16 maize genotypes, Soil Biol. Biochem. 43 (2011) 1544–1552.

[48] E.K. Thomas, L. Gao, D. MacDonald, Y. Huang, A Quantitative and Qualitative Comparison of Aquatic and Terrestrial Plant Lignin Phenols: Critical Information for Paleoecological Reconstructions, American Geophysical Union, 2009 fall meeting (abstract #B33C-0404).

[49] M.A. Go
