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ORIGINAL RESEARCH ARTICLE

Comparison of the pyrolysis properties of corn straw fermentation residue and phenolic resin

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ABSTRACT

The regularity and variability of the composition distribution of the pyrolysis products of corn stover fermentation residue and phenolic resin with the pyrolysis temperature were investigated by thermogravimetry (TG) and lyser-gas/mass spectrometer (Py-GC/MS). The results show that toluene, phenol and methyl phenol are the main common components of the two systems, 2,3-dihydrobenzofuran, alkoxy compounds and a small amount of carboxylic acid are the unique components in the pyrolysis products of corn straw fermentation residue, while dimethyl phenol, 9H-xanthene and other components in the phenolic. This is a reflection of the differences in the composition and structure of the two raw materials.

Keywords: Corn Straw Fermentation Residue; Phenolic Resin; Pyrolysis; Py-GC/MS

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1. Introduction

With the increasing shortage of fossil fuels and the growing problems of environmental pollution and greenhouse effect caused by long-term applications, the utilization of biomass by pyrolysis has received widespread attention[1,2]. The biomass pyrolysis process is significantly affected by the treatment process, reaction conditions, and material sources, especially the structure of lignin-rich biomass fractions from different sources varies greatly, so the study of pyrolysis for different sources of biomass and its various single-component model compounds is an important part of biomass thermal conversion research[3-7]. The main industrial sources of lignin-rich biomass include paper black liquor and lignocellulosic fermentation residue, etc. This type of biomass waste is widely available but has not been effectively utilized, so the research on high-value thermal conversion and utilization of lignin-rich biomass is of great value.

Phenolic resin is the main component of the circuit board, the use of pyrolysis technology to treat waste circuit boards is conducive to the realization of energy (gas, coke) recovery at the same time can be obtained high-value chemical materials (phenolic oil). Therefore, it is of great value to study the pyrolysis characteristics of phenolic resins that are the main components of the circuit board. The composition of pyrolysis products and their pyrolysis kinetics of phenolic resins have been reported[8,9], but there is a lack of research on the composition distribution of pyrolysis products and their pyrolysis mechanism at different temperatures of phenolic resins. Lignin and phenolic resin are both polymers of phenolic base units. In this paper, the regularity and variability of the distribution of the main products of the pyrolysis of corn stover fermentation residue (lignin enriched by the fermentation of cellulose and hemicellulose into alcohol fuel) and phenolic resin with the pyrolysis temperature were investigated by thermogravimetric analyzer (TG) and lyser-gas/mass spectrometer (Py-GC/MS) in order to provide a reference for the analysis of the pyrolysis mechanism of phenol-based unit polymers and the optimization of the pyrolysis process conditions.

2. Raw materials and experimental methods

2.1 Experimental raw materials

The phenolic resin used in the experiments was purchased from phenolic resin 2123 powder produced by Boshan Resin Factory in Zibo, Shandong Province, and the lignin-rich biomass was corn straw fermentation residue provided by Henan Tianguan Group.

2.2 Experimental instruments and methods

The thermogravimetric analyzer used was a German NETZSCH integrated thermal analyzer STA449F3 with a balance sensitivity of 0.1 μg and a sample loading capacity of 9 mg. Thermal transformation conditions: nitrogen atmosphere 50 mL/min, initial temperature 30 ℃, final temperature 900 ℃, temperature increase rate 30 ℃/min.

The pyrolysis products were analyzed online using a Py-GC/MS analyzer (Model: CDS5200 Pyrolyzer-Trace GC/ISQ MS) and operated in Trap mode, in which the pyrolysis products generated in the pyrolysis probe were first trapped by a sorption trap (Trap) at 40 ℃, and then resolved at 300 ℃. The resolved volatile fraction was transported by carrier gas to the gas chromatography/mass spectrometry (GC/MS) system at 300 ℃ for online analysis of the composition. GC/MS conditions: initial temperature of 40 ℃ for 3 min, followed by 6 ℃/min to 100 ℃ for 1 min, then 6 ℃/min to 180 ℃ for 2 min, then 6 ℃/min to 240 ℃ for 5 min, and finally 6 ℃/min to 280 ℃ for 1 min. The temperature was raised to 280 ℃ for 1 min. The ion source temperature is 250 ℃, the EI source is 70 eV, and the mass-to-charge ratio (M/Z) ranges from 2 to 500.

3. Results and discussion

3.1 Thermogravimetric analysis

The results of thermogravimetric analysis of corn straw fermentation residue and phenolic resin are shown in **Figure 1**. It can be seen from the TG and DTG curves in the figure, phenolic resin has three pyrolysis weightlessness peaks. The first weightlessness peak (170–210 ℃) should be related to the precipitation of free phenol in phenolic resin, the second weightlessness peak (380–480 ℃) and the third weightlessness peak (500–680 ℃) should be caused by the fracture of methylene bridge bonds in polymers. Chen *et al.*[10] concluded that the methylene in phenolic resins was depyrogenated in two stages. The temperature range from 350 to 450 ℃ is mainly for the decomposition of part of the o-o-methylene and o-para-methylene, and 400 to 620 ℃ is for the decomposition of the para-para-methylene. The two methylene pyrolysis temperature intervals here are higher than the results of Chen *et al.* and should be related to the differences in the pyrolysis heating rate, carrier gas velocity, heat and mass transfer, polymer composition and physicochemical properties of the two systems. There are two weightlessness stages occurred in the pyrolysis of corn straw fermentation residue. The first stage (200–570 ℃) has a large temperature span of pyrolysis weight loss, high weight loss and low starting pyrolysis temperature, which should be attributed to the pyrolysis of organic matter mixture. The second stage (630–720 ℃) weightlessness starts at a high starting temperature, low weight loss and narrow temperature range. It should be the decomposition of carbonate inorganic ash in corn straw fermentation residue. In comparison, the composition of phenolic resin is similar in structure and the thermal stability is high, so the starting temperature of pyrolysis is relatively high. However, the composition of corn straw fermentation residue is complex, among which there are many carboxyl functional groups that are easy to decompose. At the same time, a small amount of cellulose, hemicellulose and other components contained in the fermentation slag are not fully consumed, which also lowers the initial pyrolysis temperature of corn straw fermentation slag, and the inorganic ash may also play a catalytic role in promoting the pyrolysis of organic matter.

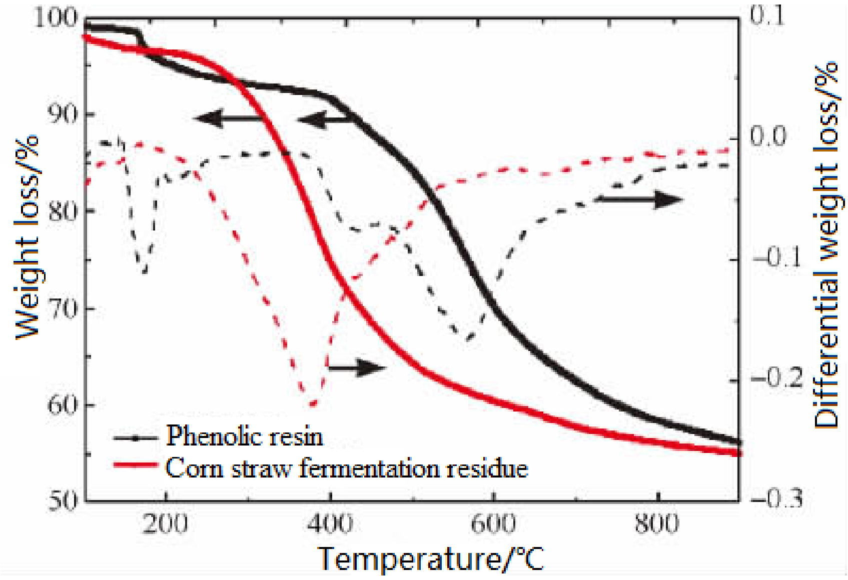

Figure 1. Comparison of thermogravimetric analysis of corn straw fermentation residue and phenolic resin.

3.2 Py-GC/MS analysis

Through the online analysis of pyrolysis products of phenolic resin and corn straw fermentation residue at different temperatures through Py-GC/MS, the results show that the pyrolysis product composition of phenolic resin is relatively concentrated, mainly composed of toluene, phenol, methyl phenol, dimethylphenol and other alkyl phenol components while the composition of corn stover fermentation residue pyrolysis products is more complex, and the main products cover a variety of components such as small molecule acids, alkyl phenols and alkoxyphenols.

3.2.1 The main common components of the pyrolysis products of the two raw materials

Toluene, phenol, o-methylphenol and p-methylphenol are the main common components of the two raw material pyrolysis products, but the content of each component varies with temperature, as shown in **Figure 2**.

The content of toluene obtained by pyrolysis of corn straw fermentation residue increases slowly and monotonously with the increase of pyrolysis temperature from 400 °C, while toluene obtained from pyrolysis of phenolic resin only appears after higher than 600 °C, and the content increases rapidly with temperature and exceeds the content of toluene in corn straw fermentation residue pyrolysis products after 700 °C.

It is difficult to completely separate the peaks of phenol and o-methylphenol, and because the content of o-methylphenol in the fermentation residue pyrolysis product system is low and only exists as a shoulder peak on the side of the main phenol peak, it is difficult to discuss the content of both independently. Therefore, the combined peaks of phenol and o-methylphenol are compared here as the sum of the contents. The sum of this content in the system of corn straw fermentation residue pyrolysis products showed a fast and then slow increase with the increase of pyrolysis temperature, while it decreased with the increase of temperature in the system of phenolic resin pyrolysis, which was a sharp contrast between the two.

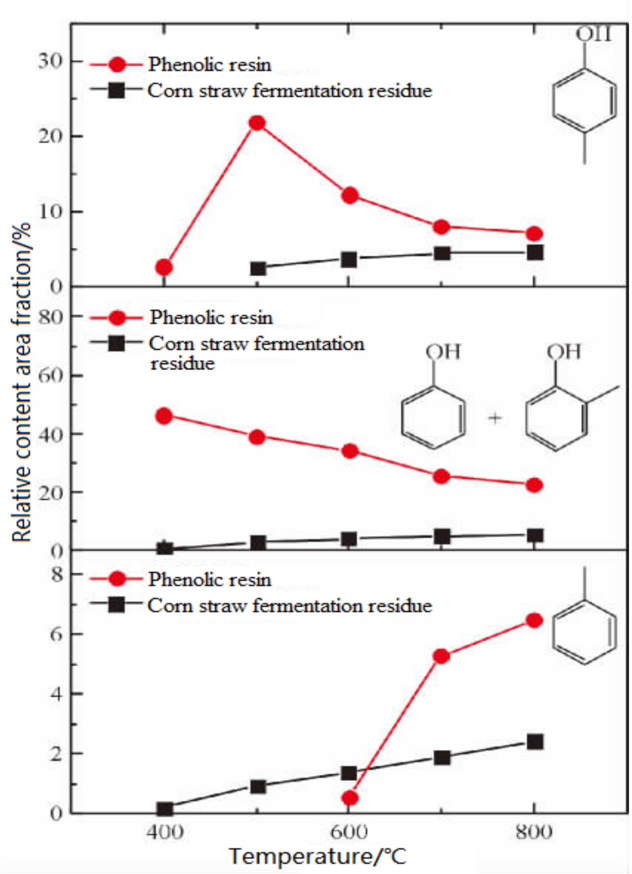

Figure 2. Temperature dependence of the content of the main common components in the pyrolysis products of corn straw fermentation residue and phenolic resin.

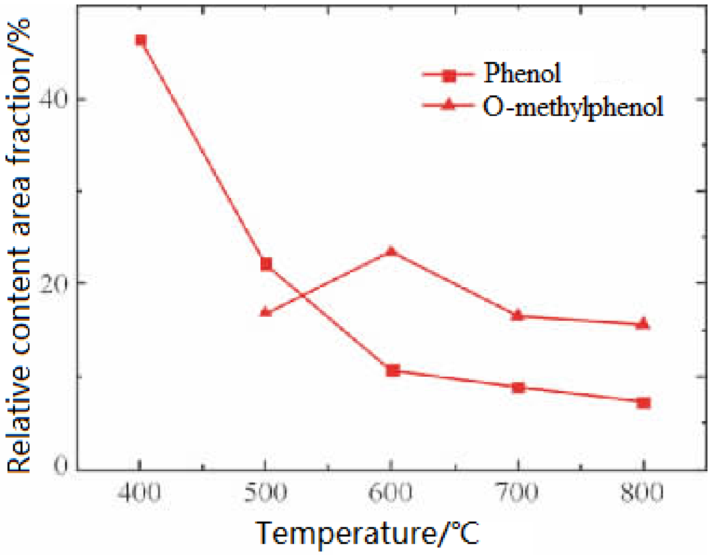

Figure 3. Temperature dependence of phenol and o-methylphenol content in phenolic resin pyrolysis systems.

The combined peak of phenol and o-methylphenol in the phenolic resin system due to the high content of o-methylphenol, the combined peak of phenol and o-methylphenol each independent peak tip obvious, through the integration of the split peak can obtain the independent relationship between the two changes with temperature. From **Figure 3**, it can be seen that the content of phenol in the pyrolysis system of phenolic resin decreases monotonically with the increase of temperature, while o-methylphenol changes greatly with the increase of temperature. The high phenol content of phenolic resin at low temperature should be related to the excessive phenol monomers that are not fully reacted in the polymer, which is consistent with the first weightlessness peak of phenolic resin in thermogravimetric analysis. With the increase of pyrolysis temperature, the physical volatile phenol content in phenolic resin decreases and the share of phenol produced by pyrolysis increases. The net result of elongation is that the content of phenol decreases with the increase of temperature.

The content of p-methylphenol obtained by pyrolysis of phenolic resin is similar to that of o-methylphenol, which changes greatly with the increase of pyrolysis temperature. Methylphenol is the basic structural unit of phenolic resin polymer. The release of methylene phenol from polymer fracture and disintegration at high temperatures is the basis for the formation of methylene phenol, while the chance of secondary reactions at higher temperatures increases and the content of methylene phenol decreases as a result. In the pyrolysis products of corn straw fermentation residue, the p-methylphenol content increased with temperature in a similar pattern as the sum of phenol and o-methylphenol content described above, which is also a result of the enhanced secondary reaction of alkyl phenols at high temperatures. Gong *et al.*[11] investigated the composition distribution of high-temperature conversion products and speculated on the possible conversion pathways using methyl phenol as a model compound. The results showed that methyl phenol may undergo a series of reactions such as demethylation, dehydroxylation, isomerization, cleavage, reforming and polymerization to obtain aromatics, phenols, thick-ringed hydrocarbons, benzofurans and small-molecule hydrocarbons.

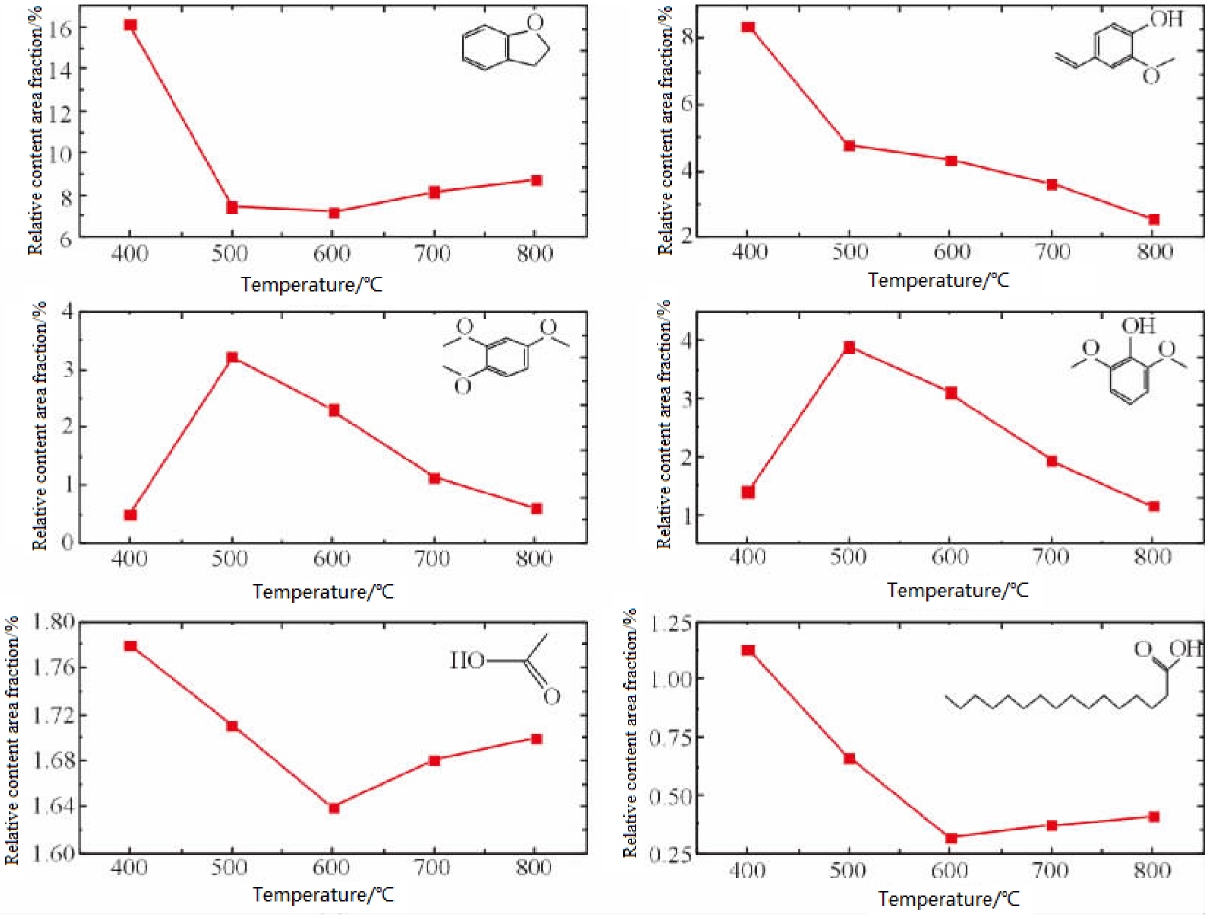

Figure 4. Temperature dependence of the content of other major components in the pyrolysis products of corn straw fermentation residue.

3.2.2 Other main components in the pyrolysis products of corn straw fermentation residue

Alkoxy compounds, 2,3-dihydrobenzofuran and carboxylic acids were only found in the pyrolysis products of corn straw fermentation residue. **Figure 4** shows that the content of 2,3-dihydrobenzofuran is the highest in pyrolysis products, followed by 2-methoxy-4-vinylphenol. The content of both is significant at low temperature, and then decreases rapidly with the increase of pyrolysis temperature. The content of 2,3-dihydrobenzofuran increases slightly with the further increase of pyrolysis temperature. The content of 2-methoxy-4-vinylphenol decreased monotonically with the increase of pyrolysis temperature. The high content at low temperature reflects that the two products may be the main components of the original structure of fermentation residue and belong to the primary pyrolysis products released from the original structure by high temperature pyrolysis. The secondary reaction probability of primary pyrolysis products increases with the increase of pyrolysis temperature, leading to the decrease of primary product content and diversification of product composition. The content of 2,3-dihydrobenzofuran increased at higher pyrolysis temperature, which may be caused by the secondary conversion products of other components at higher pyrolysis temperature.

2,6-dimethoxyphenol and 1,2,4-trimethoxybenzene are typical alkoxy compounds whose content varies greatly with increasing pyrolysis temperature, corresponding to a maximum of 500 °C. Significant alkoxy compound product composition, reflecting the structure information of the alkoxy aromatic ring component of corn straw fermentation residue, its content increases with the increase of pyrolysis temperature at low temperatures, and should be contributed by the original structure of the fermentation residue due to the release of the constituent components by pyrolysis, and the rapid decrease of its content at higher pyrolysis temperatures should be caused by its secondary conversion. Compared with the pattern of increasing alkyl phenol content with increasing pyrolysis temperature shown in **Figure 2**, it can be seen that alkoxyphenols have a more active reactivity than alkyl phenols, i.e. alkoxy is more susceptible to thermal breakage than alkyl, leading to a decrease in alkoxy compounds at high temperatures.

The content of acetic acid and hexadecanoic acid in corn straw fermentation residue is much lower than that of phenols, and the minimal value appears at 600 °C with the increase of pyrolysis temperature. The production of acetic acid should be obtained by the conversion of the remaining cellulose and (or) hemicellulose in the fermentation residue that has not been completely consumed, and the production of hexadecanic acid should be contributed by the fat component in the fermentation residue.

3.2.3 Other major components in the pyrolysis products of phenolic resin

Dimethylphenol (sum of 2,4-dimethylphenol and 2,6-dimethylphenol content), 1,2-dimethylnaphthalene [2,1-b] furan, dimethylbenzophenone, 9H-oxanthracene and other components in the phenolic resin pyrolysate content is much higher than its content in straw fermentation residue. As can be seen from **Figure 5**, the content of dimethylphenol and 1,2-dimethylnaphthalene [2,1-b] furan appears as a significant extreme value at 600 °C with the increase of temperature. The content of 9H-xanthene first increased rapidly with increasing temperature and then was basically stable, while the content of dimethylbenzophenone showed a monotonic trend of increasing rapidly and then slowly with increasing temperature.

Phenolic resin pyrolysis is composed of the primary cracking process of the original structure and the complex secondary reactions such as re-cracking, polymerization and condensation of the primary cracking products. Among them, the primary cleavage product is closely related to the structure of the raw material, and the generation and simple secondary transformation path of the primary cleavage product are speculated here by the raw material structure and the main product composition, as shown in **Figure 6** (taking the linear structure phenolic resin as an example). O-methylphenol is obtained when the polymer chain undergoes thermal bond breaking so that one side of the methylene group on both sides of the phenol is broken off while the other side is retained. Phenol can be produced when the methylene on both sides of the phenol is broken; when both sides of the methylene are retained, 2,6-dimethylphenol is obtained; when the bond break occurs on both sides of the phenol connected by a methylene bridge, the 9H-xanthene can be obtained by dehydration cyclization between two phenols through hydroxyl condensation; toluene may be derived from the separation of hydroxyl groups in the methylphenol structure; benzene may be produced either as a product of phenol dehydroxylation or from toluene demethylation. Other thick ring structure products should be related to the deep cleavage of primary cleavage products and the polymerization process between secondary products. Similarly, p-methyl phenol and 2,4-dimethylphenol can be produced when a methylene bridge is present in the phenolic hydroxyl group counterpart in the structure of the phenolic resin.

It should be noted that the two systems listed herein have common or other major components, not only these or absolutely do not exist in another system, for example, benzene is also a common component of the two systems, dimethylphenol is also present in the fermentation residue pyrolysis products, but because of its low content, so it is not discussed one by one. In comparison, phenolic resin pyrolysis solution has higher aromatic and alkyl phenol content and lower oxygen content, which makes it more suitable for liquid fuels after refining. In contrast, the alkoxyphenol content of corn stover fermentation residue pyrolysis products is significant and the component composition is complex at high temperature, but the composition of low temperature pyrolysis products is simple and the 2,3-dihydrobenzofuran content is significant, so low temperature pyrolysis products are beneficial for the separation of high value components.

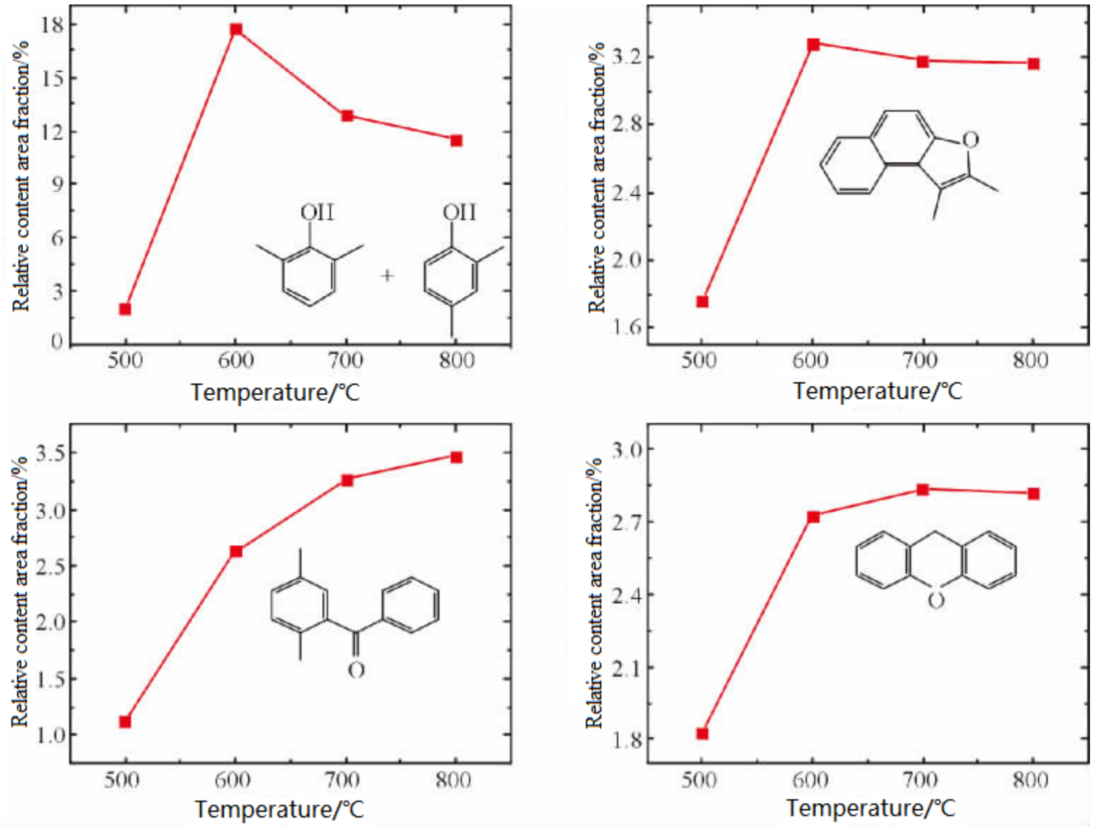

Figure 5. Temperature dependence of the content of other major components in the pyrolysis products of phenolic resins.

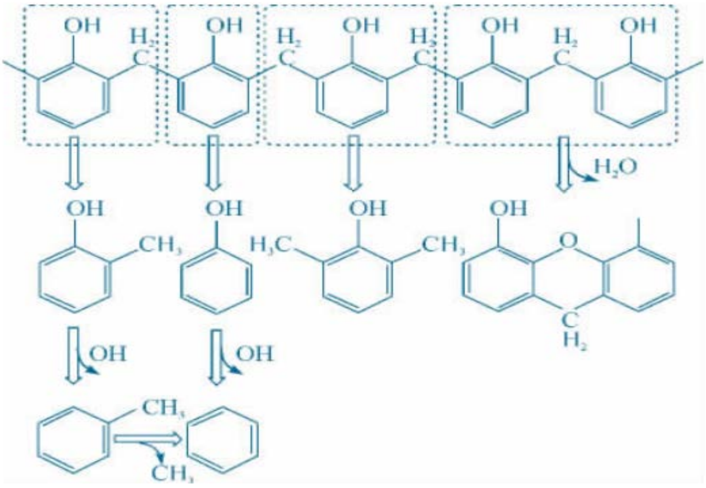

Figure 6. Generation of primary cracking products and simple secondary conversion pathways of phenolic resins.

4. Conclusion

The thermogravimetric and Py-GC /MS analysis were performed to compare the pyrolysis properties and product composition of phenolic resins with corn straw fermentation residue as a function of temperature. The results showed that the initial pyrolysis temperature of corn straw fermentation residue was low, while the thermal stability and pyrolysis starting temperature of phenolic resin were higher. The composition of phenolic resin pyrolysis products is more concentrated, mainly composed of toluene, phenol, methylphenol, dimethylphenol and other alkylphenols and their derivatives, while the composition of the pyrolysis products of corn straw fermentation residue is relatively dispersed, and the main products cover small molecule acids, alkylphenols, alkoxy compounds, 2,3-dihydrobenzofuran and other components. Among them, toluene, phenol and methylphenol are the main common components of the two systems, 2,3-dihydrobenzofuran, alkoxy compounds and a small amount of carboxylic acid are the unique components of the pyrolysis products of corn straw fermentation residue, while dimethylphenol, 9H-oxanthene, 1,2-dimethylnaphthalene [2,1-b] furan, dimethylbenzophenone have significant content in the pyrolysis product of phenolic resin, which is the difference in the composition and structure of the two raw materials. Comparatively speaking, the phenolic resin pyrolysis solution is more suitable for liquid fuel use after refining, while the low-temperature pyrolysis product of corn straw fermentation residue is beneficial for the separation of high-value components.

Conflict of interest

The authors declared no conflict of interest.

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