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The pyrolysis mechanism of phenol formaldehyde resin

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ABSTRACT

Fourier transform infrared spectroscopy was used to characterize the structure of phenol formaldehyde (PF) resin pyrolyzed at different temperatures, and pyrolysis gas chromatography mass spectrometry was used to observe the volatiles. A pyrolysis mechanism has been consequently deduced, and several previous ambiguities have been clarified. The occurrence of carbon monoxide and carbon dioxide is attributed to the oxidization of methylene. However, not oxidization, but methylene scission is mainly responsible for the decomposition of PF resin. At the same time, methylene radicals combine with other small molecules and form some volatiles such as ethylene and methanol. With the elevation of heat treatment temperature, PF resin is progressively transformed into amorphous carbon by pyrolysis and polycyclic reactions.

1. Introduction

Pyrolysis is one of the critical processes in the manufacture of carbon or related composites using phenol formaldehyde (PF) resin [1–4]. The pyrolysis reactions convert the resin matrix into amorphous carbon. The potential damage during this process is serious because of the thermal stresses that develop in the composites and the high pressures from the evolution of many gaseous products. Therefore, a good viable process or a suitable thermal modification method is needed to reduce the damage during pyrolysis. Various attempts have been undertaken to realize this aim and uncover the main degradation routes of PF resin [4–9]. Several modified PF resins have been developed, and their thermal stabilities have been well investigated [10–12]. Jackson et al. [6] proposed that pyrolysis occurs as oxidation degradation. Oxygen comes from decomposition products, and oxidation results in the formation of a carbonyl crosslink. In the whole process, no hydrogen gas is evolved as a gas product. By contrast, Ouchi and Honda [7] claimed that hydrogen gas is released early in the pyrolysis stage. According to their suggested mechanism, pyrolysis involves three stages. First, additional crosslink is formed as a result of condensation reactions between functional groups, such as phenol. Second, the crosslinks are gradually scissored with increased temperature, resulting in the evolution of methane, hydrogen, and carbon monoxide. Finally, hydrogen atoms are stripped from the aromatic structure and released as hydrogen gas. A number of other investigations to date are concerned with the characterization of PF resin in pyrolysis [13–16]. However, these studies are mainly focused on some reaction principles of given functional groups, which helps clarify some specific pyrolysis reactions, but not the entire pyrolysis process.

To the best of the authors' knowledge, almost no systematic study on the mechanism of PF resin pyrolysis has been published since 2000. The main reason may be that a mechanism is already widely accepted, wherein the whole pyrolysis process is divided into three stages, such as the formation of additional crosslinks, the scission of crosslinks, and polycyclic aromatization. In recent years, research has been focused on how to improve the thermal stability and efficiency of PF resin. These mechanism studies can well explain some experimental phenomena. However, there are some discrepancies in the mechanism of PF resin pyrolysis, and these differences are not directly correlated with the pyrolytic ambiance (such as air, argon, nitrogen, or vacuum) [5]. For example, Ouchi and Honda [7] failed to interpret the oxygen sources of carbon monoxide and carbon dioxide. Their conclusion that the release of carbon monoxide occurs before that of carbon dioxide does not agree with the experimental results. In the late 1990s, Trick et al. [4] proposed a three-region mechanism. The mechanism divides the

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whole pyrolysis process into three regions, which overlap and involve a relatively complex series of reactions. Each region can be characterized as the dominant type of reaction. However, the mechanism still cannot well explain several phenomena such as the origin of carbon dioxide. Their view that the oxygen of carbon monoxide comes from the condensation of water has not been widely accepted. Clarifying these discrepancies can help in the exploration of a more efficient method of enhancing thermal stability of PF resin. Therefore, further research is necessary to acquire an in-depth understanding of the pyrolysis mechanism and develop a more efficient thermal modification system.

Pyrolysis reactions are very complex, and an elementary reaction often occurs simultaneously with other reactions. No elementary reaction can be determined directly by modern analytical instruments. A mechanism is often deduced either according to the characterizations of the resin residue treated at different temperatures or the volatiles released during pyrolysis. Despite the preliminary attempt of Trick et al. [4], almost no other mechanism is obtained by researching both the resin residue and volatiles. Therefore, some discrepancies in these mechanisms still exist. However, these discrepancies can be clarified, and a real mechanism can be deduced from simultaneously analyzing results from both the resin residues and the released volatiles. In the present paper, Fourier transform infrared spectroscopy (FTIR) is applied to characterize the resin residue, and pyrolysis gas chromatography mass spectrometry (Py-GC–MS) is utilized to examine the volatiles. A reaction mechanism for the pyrolysis of PF resin is proposed based on the analyses of the residual char and evolved volatiles.

2. Experimental

A commercial PF with a thermoset property was provided by the Tianjin Daying Resin Company (trade number 213). The viscosity of the resin was measured between 0.8 and 1.53 Pa s using a rotary viscosimeter at 20 °C. The solid content was 80 ± 3 wt% and the content of free phenol was less than 21wt%.

Some cured samples were treated at different temperatures ranging from 350 to 750 °C, which was controlled by a PTC-2 Intelligent Temperature Control instrument. Each sample was heat-treated at a heating rate of 2 °C·min^{-1}, and then kept at a given temperature for 2 h. Using the KBr mull technique, the FTIR spectra of the samples with the same amount were obtained using a 750 FTIR (Nicolet, USA). Spectra were obtained between 4000 and 400 cm^{-1}. Specific spectral peaks were identified and assigned to functional groups present in the pyrolyzing resin matrix.

A QP2010 GC–MS system was used to identify the pyrolysis volatiles using a PY-2020s pyrolysis device (Shimadzu, Japan). When the pyrolysis device was heated at a given temperature such as 450, 550, 650, and 750 °C and maintained stability, the cured sample about 5 mg was introduced and pyrolyzed. Their corresponding volatiles were separated in a 30 m quartz capillary column with a diameter of 3 mm and then analyzed by MS. The temperature of the column was increased from 40 to 260 °C at a rate of 10 °C min^{-1}, and kept at 260 °C for 10 min. Helium was used as the carrier gas.

3. Results

3.1. Infrared spectroscopy measurements

The FTIR spectra obtained from each sample are shown in Fig. 1. Following recognized peak identifications of the infrared spectra of organic compounds [4,5,17–21], functional groups corresponding to the major peaks of the spectra were identified and are listed in Table 1.

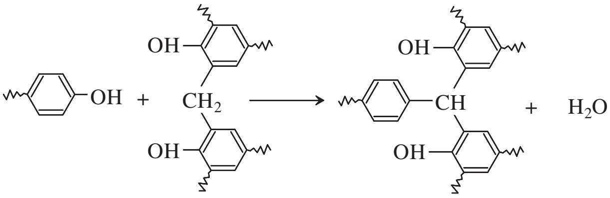
3.2. Py-GC–MS measurements

The GC of the volatiles from PF resin pyrolyzed at different temperatures is shown in Fig. 2. Their identifications by MS are listed in Table 2.

4. Discussion

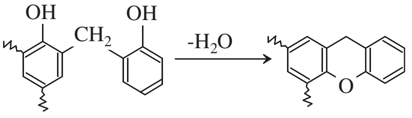
4.1. The reactions involved phenolic hydroxy

From the FTIR spectra of Fig.1, a broad peak at 3440 cm^{-1}, assigned to the stretching vibration of phenolic hydroxy, is found to become weaker with increased heat treatment temperature. At 650 °C, the peak broadens and becomes obscure. This change is similar to that of methylene, which has two stretching modes at 2910 and 2850 cm^{-1} as well as a bending pattern at 1458 cm^{-1}. Both series of peaks are ambiguous at 650 °C. All these characters indicate that phenolic hydroxy may react with methylene, or a condensation reaction takes place between phenolic hydroxyls, or phenolic hydroxy is stripped off and generates a hydroxy radical. As to the reaction between phenolic hydroxy and methylene, a widely accepted proposal is expressed as follows [4,5,7]:



(1)

In the case of the condensation reaction between phenolic hydroxyls, it can be verified by the volatiles such as xanthenes (No. 18, 22 and 23 in Table 2). This reaction can be expressed as Reaction (2). In fact, the peak at 1205 cm^{-1} is attributed to the stretch vibration of alkyl-phenol C—O. This can also infer the existence of above reaction.



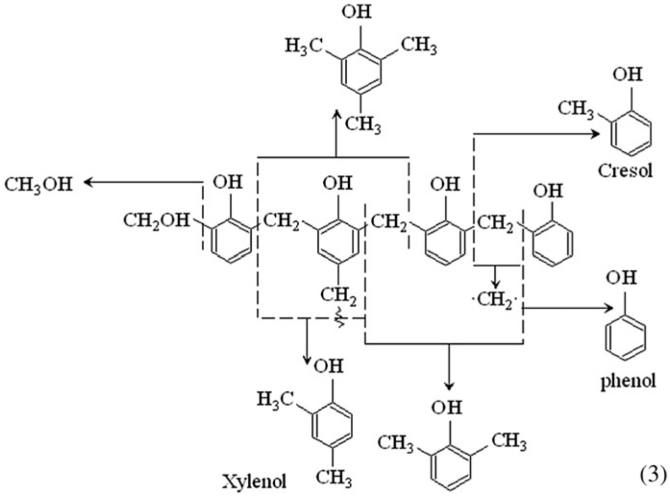
(2)

Concerning the strip off the phenolic hydroxyl, it is possible and its production hydroxyl radical provides an oxidative atmosphere for methylene which will be discussed in Section 4.2.

According to the above analysis, phenolic hydroxy is active in pyrolysis, but there is no direct relationship on the decomposition of PF resin. In contrast, its reaction with methylene forms an additional crosslink in polymer chain backbone at initial pyrolysis stage, which may strengthen the thermal stability.

4.2. The reactions involved methylene

Besides reacting with phenolic hydroxyl, methylene can also be oxidized or scissored out of polymer chain backbone. According to the results of Fig. 2, phenol and its methyl derivatives are the main volatiles when PF resin is pyrolyzed at 450 °C. This means some methylenes are scissored as the pyrolysis reactions proceed. The corresponding reaction pathway is expressed as follows:



(3)

Table 1
Peak identifications of the FTIR spectra of PF resin heat-treated at different temperatures.

Band position (cm^{-1})	Assignment
3440	Phenolic OH stretch
3005	Aromatic CH stretch
2910	Aliphatic CH_2 asymmetric stretch
2850	Aliphatic CH_2 symmetric stretch
1607	C—C aromatic ring stretch
1510	Semicircle ring stretch
1458	Aliphatic (o—p) CH_2 scissor bend
1327	CH_3 deformation
1257	Phenolic OH in-plane deformation
1205	Alkyl-phenol C—O stretch
1135	Alkyl-phenol C—O stretch
1092	Aromatic C—H in-plane deformation (1,2,4)
1077	polycyclic aromatic ring deformation
876	Aromatic C—H wag (1,2,4,6)
815	Out-of-plane ring deformation (1,2,4)
754	Out-of-plane ring deformation (1,2,6)

This finding agrees well with the results of most studies [4,13,14,22], except for the formation of methylene radical [13]. The analysis result suggests that phenol and its methyl derivatives are always the majority volatiles whenever PF resin is pyrolyzed at 450, 550, 650 or 750 °C. Therefore, it can be inferred that metylene scission results in the damage of polymer chain backbone. Undoubtly, metylene scission is mainly responsible for the decompositon of PF resin.

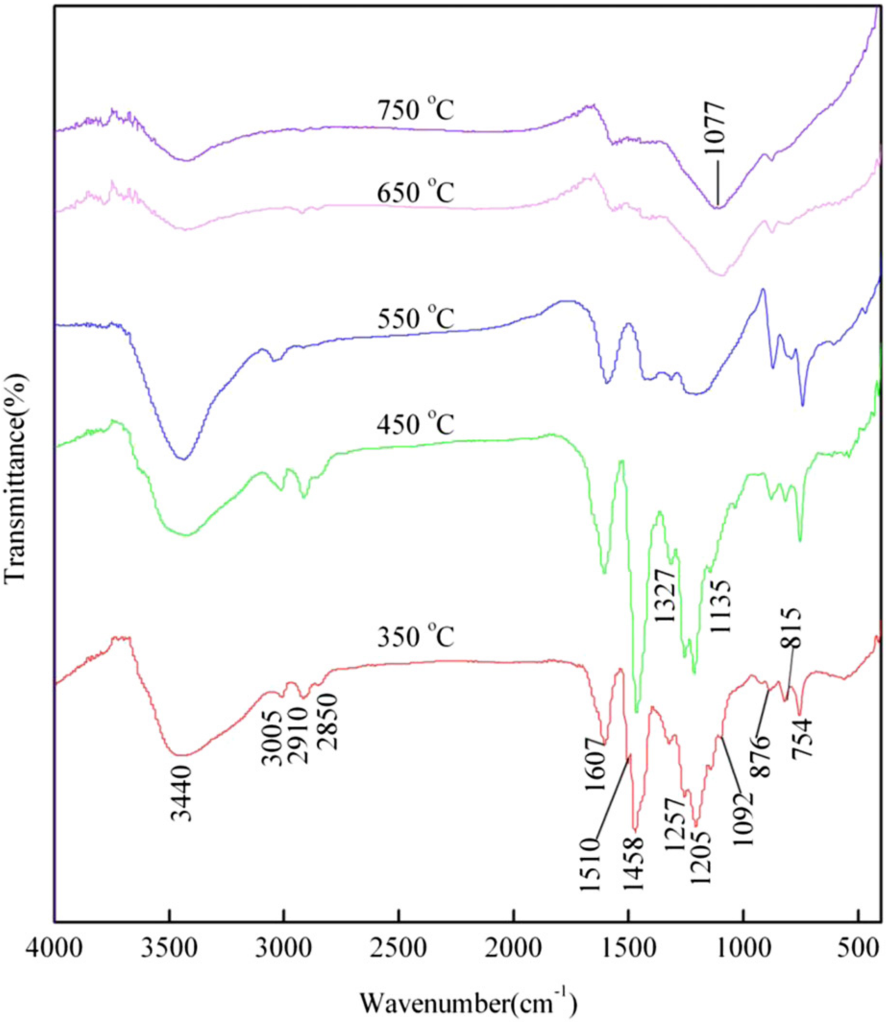


Fig. 1. FTIR spectra of PF resin heat-treated at 350–750 °C.

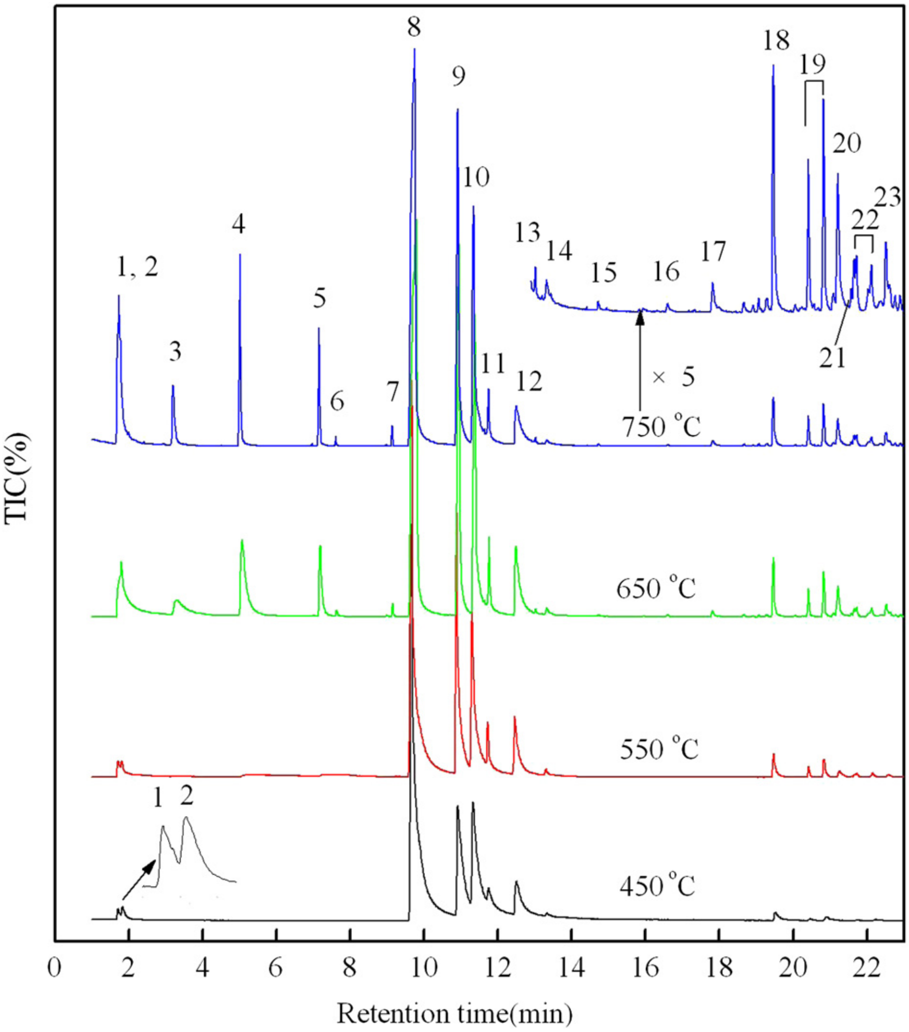
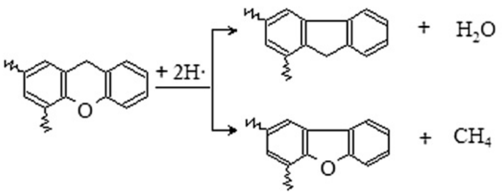


Fig. 2. Py-GC spectra of PF resin pyrolyzed from 450 to 750 °C.

Table 2
List of volatiles of PF resin identified by MS.

No	Volatiles species	Molecular weight
1	Carbon dioxide	44
2	Carbon monoxide	28
3	Benzene	78
4	Toluene	92
5	o-Xylene	106
6	p-Xylene	106
7	Mesitylene	120
8	Phenol	94
9	o-Cresol	108
10	p-Cresol	108
11	2,6-Dimethylphenol	122
12	2,4-Dimethylphenol	122
13	Naphthalene	128
14	2,4,6-Trimethyphenol	136
15	2-Methylnaphthalene	142
16	Diphenylmethane	168
17	3-Methylbiphenyl	168
18	Xanthene	182
19	1,2-Dimethyl naphtho[2,1-b]furan	196
20	Anthracene	178
21	Methanone	209
22	Dimethyl-9H-Xanthene	210
23	Trimethyl-9H-Xanthene	224

Additionally, a similar scission reaction can also be evolved as follows:

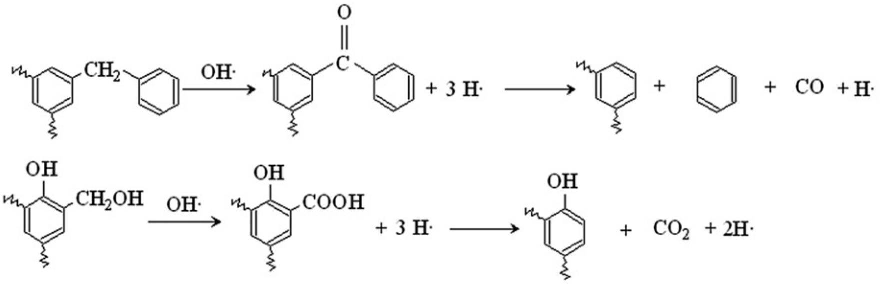


(4)

This reaction is accompanied by a continuous release of water and methane. Sobera and Trick had drawn a similar conclusion [3,4]. Volatiles including naphthalene, 3-methylbiphenyl, and anthracene (No.13, 17 and 20 in Table 2) also indicate the occurrence of these reactions.

It should be pointed out that some volatiles such as benzene and its methyl derivatives have been released at temperature above 650 °C. These volatiles propose that some phenolic hydroxyls are apparently stripped off, and hydroxyl radicals are generated correspondingly. It is consistent with the inference in Section 4.1. Given the relatively high activation, hydroxyl radical, as an oxidizing agent, reacts with methylene- and hydroxymethyl-evolved the structures of carbonyl and the carboxyl. The reaction can be confirmed with the presence of products such as methanone (No. 21 in Table 2). However, there are almost no carboxyl compounds in the pyrolysis products, which can be explained by the difference in thermal stability. The carboxyl, located at the terminal chain, is debonded upon the formation of carbon dioxide at high temperatures. The carbonyl, located between aromatic rings, has a higher stability for the conjugation effect. It is not removed until the temperature is sufficiently high and carbon monoxide is released. Therefore, carbon dioxide evolves before carbon monoxide. This inference is expressed as Reaction (5) and agrees well with the experimental data of Li [16]. With regard to the release of carbon monoxide and carbon dioxide, Jackson and Fitzer had made similar judgments [6,23].

A mechanism that PF resin decomposed for oxidation is hereby proposed based on the existence of carbon monoxide and carbon dioxide. The oxidative atmosphere comes from hydroxyl radicals [6]. However, the authors' previous study [24] has indicated that the drastic pyrolytic reactions occur at approximately 531 °C. At this time, the polymer chain backbone of the PF resin has already been damaged. While the resin pyrolyzes at 550 or 650 °C, the release amount of phenol molecules and their methyl derivatives is much more than that of benzene and its methyl derivatives (Fig. 2). This can be explained the resin decomposed mainly from the methylene scission, or else the release proportion of benzene and its methyl derivatives would have been triggered because of the stripping of hydroxyl radicals. Therefore, the methylene scission, and not the oxidation, is mainly responsible for the degradation of



(5)

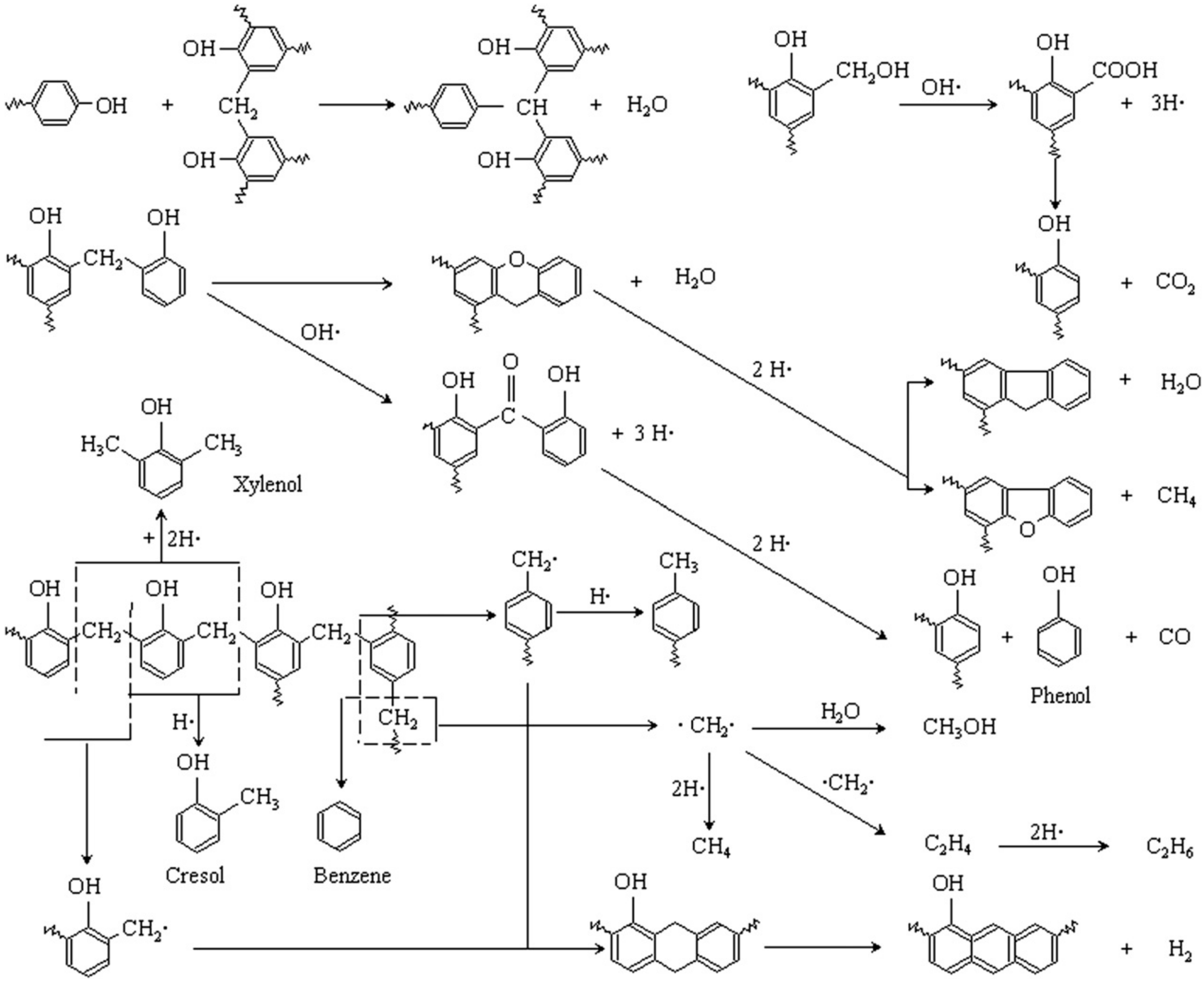


Fig. 3. Schematic of the main pyrolysis route of PF resin.

PF resin. It should be noted that the oxidation has an important effect on the pyrolysis pathway such as the evolution of carbon monoxide and carbon dioxide.

In summary, methylene scission destories the backbone of PF resin chain, and it is mainly resposible for the decomposition of PF resin. On the other hand, some methylenes are oxidized in pyrolysis, but the oxidation does not destroy the backbone of the resin directly which is not the main reason for the decomposition of the resin.

4.3. *Some other reactions in pyrolysis*

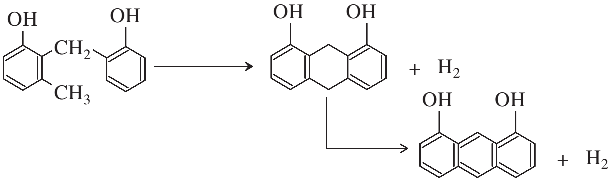
In contrast to the conclusions of other previous studies, the formation of methylene radical is established in the present research. Although there is no apparent experimental data, the formation of methylene radical can successfully interpret the evolution of several small-molecule volatiles, such as methanol, ethylene (Reaction (6)). The occurrence of these small-molecule volatiles has been also verified in various studies [4,6,7]. In fact, the formation of methylene radical is also acceptable because of the randomness of scission positions.

$$\cdot CH_2\cdot + H_2O = CH_3OH$$

$$\cdot CH_2\cdot + 2H\cdot = CH_4$$

$$\cdot CH_2\cdot + \cdot CH_2\cdot = C_2H_4 \qquad (6)$$

It should be noted that not all methylenes are scissored. For example, methylene can also keep a relatively high thermal stability through polycyclic reactions such as Reaction (7). With regard to Reaction (7), it can be verified by the products of xanthene and other polycyclic aromatic hydrocarbons in Table 2. At the same time, the character of FTIR peaks at ranges from 1510 to 754 cm^{-1} become more and more indistinct. Correspondingly, samples heat-treated at 650 and 750 °C, show a broad peak at 1077 cm^{-1} which is associated with a polycyclic aromatic ring. The peak also indicates the occurrence of many polyaromatic reactions when PF resin is treated at temperature above 750 °C. By this way, PF resin is gradually converted to amorphous carbon.



(7)

4.4. *A pyrolysis mechanism of PF resin*

From the analysis of the FTIR spectra and Py-GC—MS, methylene and phenolic hydroxy are active groups in pyrolysis of PF resin. The existence of methylene scission and methylene oxidation is verified. However, not oxidation but scission of memethylene is mainly responsible for the decomposition of PF resin. In the whole pyrolysis pocess, an additional crosslink is firstly formed between methylene and phenolic hydroxyl. Second, some methylene are scissored, thereby generating some volatiles including phenol and its methyl derivatives. Third, some phenolic hydroxyls are stripped off with the formation of hydroxyl radical. Hydroxyl radicals react with methylene and hydroxymethyl, leading to the release of carbon dioxide and carbon monoxide. Finally, the resin is gradually transformed into amorphous carbon by polycylic reactions including those of polyaromatics. Combination of Reactions (1)—(7), the entire pyrolysis pathway can be summarized as follows (Fig. 3):

5. Conclusions

FTIR was used to characterize the residue structure of PF resin, and Py-GC—MS was used to observe the volatiles. From the characterization of both the resin residue and volatiles, a pyrolysis mechanism has been deduced. The main conclusion can be expressed as follows:

(1) Methylene is active and its scission is mainly responsible for the pyrolysis of PF resin. First, an additional crosslink is formed between methylene and phenolic hydroxyl. Second, some methylene molecules are scissored, thereby generating some volatiles including phenol and its methyl derivatives.
(2) Hydroxyl radicals provide an oxidative atmosphere for methylene, the oxidization of methylene results in the formation of carbon monoxide and carbon dioxide. However, oxidation has no direct relationship with the scissor of polymer chain backbone and is not the main reason for the decomposition of PF resin.
(3) The resin is gradually transformed into amorphous carbon by polycylic reactions.

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