

WANG Qingwen, LI Jian, LI Shujun

## Fire-retardant mechanism of fire-retardant FRW by FTIR

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**Abstract** The structures of the solid state products formed by the partial combustion of Korean pine wood treated with fire-retardant FRW were analyzed by microscopic FTIR. The volatile pyrolytic products of basswood (*Tilia amurensis*) specimens treated with FRW and its components guanidurea phosphate and boric acid were analyzed by GC-FTIR. The pyrolytic and charring process, the effects of fire-retardant, and the structural characteristics of the pyrolytic products were discussed. It was concluded that upon heating and by the catalysis of FRW and its decomposition products reactions of wood took place successively, namely the dehydration of polysaccharide, the elimination of acetic acid from hemicellulose, the degradation of polysaccharide, the degradation of lignin, the polymerization of the pyrolytic products of wood, reactions of oxygen-element-elimination of aliphatic polymers and the structural change of the latter to form aromatic structures, and charring. The pyrolysis process of wood was altered and the yield of volatile pyrolytic products was decreased by FRW treatment.

**Keywords** wood, fire-retardant FRW, fire-retardant mechanism, FTIR, GC-FTIR

### 1 Introduction

It was very difficult to analyze black charcoal samples with FTIR. Recently, the technical progress of instruments used for analysis solved this problem. For instance, Gabor (1998) and Kazayawoko et al. (1997) analyzed wood charcoal powder with FTIR equipped with diffuse reflectance accessory. In this paper, the structures of the solid-state products formed by the limited combustion of Korean pine wood

treated with fire-retardant FRW were analyzed by microscopic FTIR (Wu, 1994a; Wang et al., 2000), and the processes of wood pyrolysis and charcoal formation were studied.

In order to reveal the fire-retardant mechanism of fire retardants, the effect of a fire retardant on wood pyrolysis and the relationship between wood pyrolytic products and temperature must be studied firstly. Usually, GC analysis of pyrolytic products combined with other structural analysis instruments can be used. However, because of the complexity in components and structures of wood, no reliable identification of the main components released from wood pyrolysis by existing analysis methods such as GC-MS, which is powerful for analyzing compounds, has been obtained. In contrast, with GC-FTIR coupling technique (Wu, 1994b), the structure of some known compounds can be identified. Meanwhile, their main function groups can be determined so that unknown compounds or undetermined fine chemical structures can be classified, which is very valuable. In this paper, the volatile pyrolytic products from basswood (*Tilia amurensis*) control specimens under several special temperatures were analyzed by GC. In order to reduce the work for experiments and spectra analysis, certain temperatures were set to obtain more information and more typical components of products. In order to simplify the spectra, analysis filter paper, in which the main component is cellulose, was used as a polysaccharide specimen; isothermal pyrolysis was carried out under the same conditions as wood treated with FRW. The main components were guanidurea phosphate (GUP) and boric acid. Their volatile products were collected and analyzed with GC-FTIR.

### 2 Materials and methods

#### 2.1 Microscopic FTIR spectra

##### 2.1.1 Preparation of specimens

The specimens, with dimensions 100 mm (L)×100 mm (T)×10 mm (R), were prepared from a Korean pine solid

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WANG Qingwen (✉), LI Jian, LI Shujun  
Research Institute of Wood Science and Technology,  
Northeast Forestry University,  
Harbin 150040, China  
E-mail: qwwang@public.hr.hl.cn

wood in which the retention of FRW was 10% (w/w). The specimen was radiated for 2 min on an area of 100 mm×100 mm (tangential section) by a cone calorimeter operated with a power of 50 kW/cm<sup>2</sup> and the surface temperature of the specimen was up to 780°C so that the specimen partially burned and carbonized. The thickness of charcoal was about half of the specimen. After cooling, the specimen was taken apart along the radial section, and new carbonized and non-carbonized surfaces were exposed. The surfaces were smoothed with a special knife and their oxidized parts of about 0.5 mm in thickness were removed. Then the specimens were used to obtain spectra with microscopic FTIR.

### 2.1.2 Determination of FTIR microarea spectra

There are mainly two parts in the instrument used for microscopic FTIR studies. One is an FTIR spectrophotometer and the other is an IR microscope such as Inspect IR. In fact, Inspect IR is a highly sensitive detecting system that collects data from a microarea (micron). This system comprises an optical microscope, a highly sensitive MCT detector that is cooled by liquid nitrogen, CCD video camera, a high brightness visible lamp-house, and a visible light/infrared light switch from the mainframe. Inspect IR has the functions of an ordinary optical microscope. When visible light is used, a microscopic image can be seen on the computer screen by a special software named  $\mu$ -View and the detection point can then be located. When infrared light is used, the system can collect FTIR spectra data.

Inspect IR detects the reflected infrared ray from the surface of the specimen; so the surface should be smoothed to reduce diffusion and enhance reflection. The diameter of the point that is detected by Inspect IR is 100  $\mu$ m. On the smooth surface, the points were selected every 0.5 mm, with the carbonized side (0 mm) as the starting point, to determine FTIR spectra.

## 2.2 GC-FTIR analysis

### 2.2.1 Experimental materials and main instruments

Experimental materials were basswood (*Tilia amurensis*) control specimen (UZ), basswood treated with boric (BZ, retention 3.49%), basswood treated with GUP (GZ, retention 10%), basswood treated with FRW (FZ, retention 10%), and filter paper (PA).

The main instruments used in this study were Magna 560 E.S.P FTIR spectrometer, GC-FTIR interface, HP6890 GC, HP-5 quartz capillary column (non-polar, 30 m×0.32 mm), pyrolysis oven that was controlled between 80–600°C and precision  $\pm$ 1%, and a heating chamber of  $\phi$ 20 mm×50 mm (length).

### 2.2.2 Preparation of specimens for GC-FTIR

The curved bottom of a thin U-formed glass tube (13 mm in height), whose inner diameter was 3 mm, was heated with alcohol burner till its inner diameter shrunk to 1 mm. The two sides at the position of 7 mm from the bottom were bent into 75° and 135° angles, respectively. Wood and filter paper were ground into 20 to 40 meshes and put into the glass tube to 20 mm in height from the side at an angle of 135°. Highly pure nitrogen was introduced from this side at 60 mL per minute. After half an hour, the glass tube was heated up to about 110°C over the heating chamber of the pyrolysis oven and maintained for 10 min in order to replace oxygen. The glass tube was then put into the heating chamber, which had been set to a certain temperature, to pyrolyze the sample. The outlet (75° angle) was put into a covered conical test tube to its bottom, in which there was 1.5 mL ether and acetone mixture. The volatile pyrolytic products from the wood sample were absorbed. This process ended within 10 min. After concentration by mild warming, the solution was analyzed using GC-FTIR.

### 2.2.3 GC-FTIR analysis conditions

Two phases of heating were used for GC analysis. The initial temperature was 70°C, which was maintained for 7 min, and then up to 150°C at a heating rate of 20°C per minute, maintained for 2 min. In the second phase, the system was heated up to 210°C in 20°C per minute and maintained for 15 min. The injector temperature was 280°C, and the temperature of the FID detector (connected after FTIR interface) was 280°C. The carrier gas He (constant volume mode) was introduced at 1.6 mL per minute.

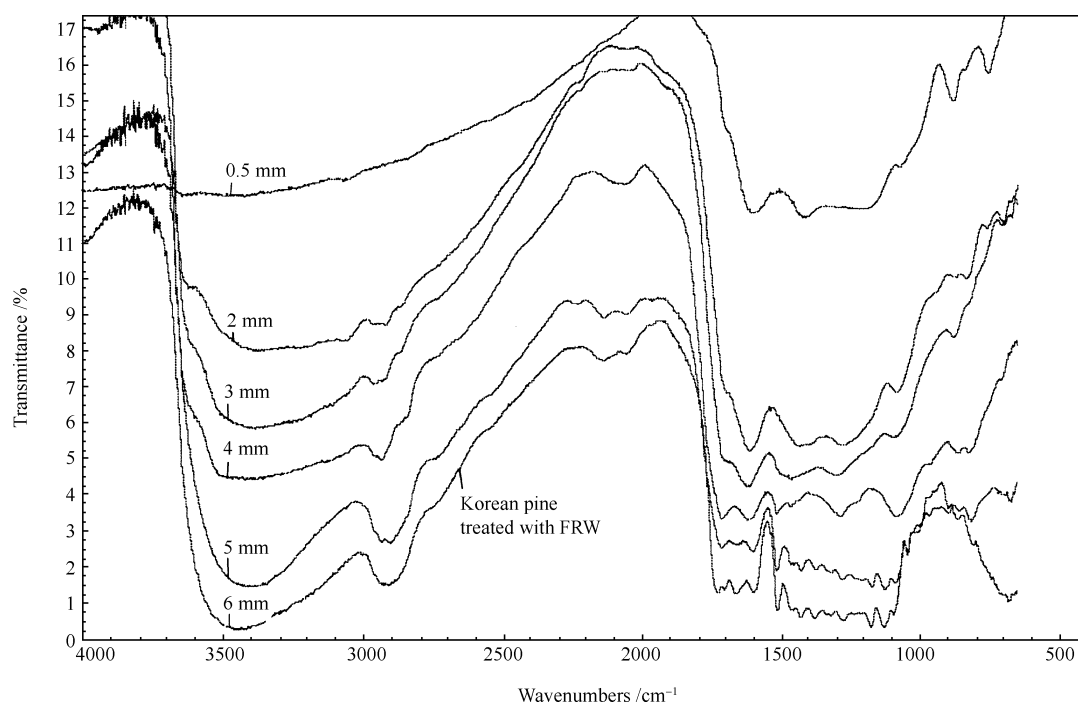
FTIR analysis conditions: The temperature of both light tube and transportation line was 220°C. The resolution was set to 8 cm<sup>-1</sup>. Samples were scanned 8 times except for the background, which was done 150 times.

## 3 Results and discussion

### 3.1 Microscopic FTIR spectra

#### 3.1.1 Microscopic FTIR spectra of solid-state pyrolytic products from Korean pine wood treated with FRW and its absorption peaks assignment

Some FTIR spectra of solid-state pyrolytic products from Korean pine wood treated with FRW are shown in Fig. 1. The FTIR spectrum of solid-state pyrolytic products from untreated Korean pine wood is the same as the spectra shown in Fig. 1, except that there is no GUP characteristic peak at 1,700 cm<sup>-1</sup> in the former (Wang, 2000). Therefore, the basic information of wood and its solid-state pyrolytic products is shown in these spectra, but the FTIR signal of



**Fig. 1** Microscopic FTIR spectra of the solid phase pyrolytic products of Korean pine wood treated with FRW

fire-retardant pyrolytic products is hidden by the strong signals of wood and its pyrolytic products.

The absorption curves in Fig. 1 were obtained by scanning at points 0.5, 2, 3, 4, and 5 mm from the carbonized surface, respectively, and one is the microarea FTIR spectrum of Korean pine wood treated with FRW (6 mm). Their absorption peaks assignment is as follows:

3,650–3,200  $\text{cm}^{-1}$ , O—H stretch vibration; 3,080–3,020  $\text{cm}^{-1}$ , C—H stretch vibration (benzene ring); 2,980–2,820  $\text{cm}^{-1}$ , C—H stretch vibration (aliphatic compounds);  $\sim 1740 \text{ cm}^{-1}$ , C=O stretch vibration (acetyl et al., hemicellulose characteristic);  $\sim 1,700 \text{ cm}^{-1}$ , the special absorption peak of the main component GUP of FRW (no this peak for wood and its components);  $\sim 1,650 \text{ cm}^{-1}$ , C=O stretch vibration (aromatic aldehyde and ketone, lignin characteristic);  $\sim 1,600 \text{ cm}^{-1}$ , benzene ring stretch vibration;  $\sim 1,275 \text{ cm}^{-1}$ , C—O—C stretch vibration (aromatic ether, lignin characteristic);  $\sim 1,175 \text{ cm}^{-1}$ ,  $\sim 1,132 \text{ cm}^{-1}$ , C—O stretch vibration (aliphatic ether, aldehyde, hydroxyl and so on).

### 3.1.2 Pyrolysis processing of Korean pine wood treated with FRW

When Korean pine wood treated with FRW was heated, it was pyrolyzed and carbonized from its surface to the inner part step by step. Therefore, the pyrolysis process can be followed and analyzed along the sequence from the inner part to the surface by analyzing microscopic FTIR spectra individually.

According to the results of TGA and DTA (Wang, 2004a),

the main component GUP of FRW started to degrade at  $184^\circ\text{C}$ . Korean pine wood treated with FRW obviously pyrolyzed and dehydrated at  $190^\circ\text{C}$ , and started to degrade at  $250^\circ\text{C}$ . Hypothetically, (1) their temperatures change linearly from the surface to the inner part when the specimens burn; (2) the surface temperature of Korean pine wood treated with FRW is  $780^\circ\text{C}$  when the specimens burn (which is the radiation temperature of the cone calorimeter, heat released by burning, and heat lost by radiation were neglected); (3) because the characteristic peak of GUP disappeared in the spectrum of 5 mm in Fig. 1 and according to its appearance and its FTIR spectrum, it is deduced that this part of the specimen had dehydrated though it was not obviously degraded. The temperature might be between 190 and  $250^\circ\text{C}$ . It was estimated and supposed to be  $220^\circ\text{C}$ , according to hypothesis 1. The pyrolysis temperatures of other points were estimated as follows:  $720^\circ\text{C}$  to 0.5 mm,  $550^\circ\text{C}$  to 2 mm,  $440^\circ\text{C}$  to 3 mm,  $320^\circ\text{C}$  to 4 mm,  $220^\circ\text{C}$  to 5 mm, and  $100^\circ\text{C}$  to 6 mm.

When the pyrolysis temperature was under  $100^\circ\text{C}$  (more than 6 mm from the carbonized surface), it was seen that the color of the specimen was the same as that of the specimen that was not radiated and there was no difference between their FTIR spectra, which means there was no obvious chemical change. When the pyrolysis temperature was up to  $220^\circ\text{C}$ , wood color turned into brown, acetyl groups disappeared, and the absorptions of O—H and C—O (C—OH and saturated C—O—C) declined. In other words, stripping off acetyl groups, dehydrating, and decomposing reactions had occurred. When the pyrolysis temperature was up to and under  $320^\circ\text{C}$ , wood color almost turned to black, and

the absorptions of O—H and saturated C—O—C (indican bond) declined largely. The absorption of saturated C—H declined obviously, which means the dehydration was almost completed and carbohydrates had pyrolyzed. When the pyrolysis temperature was up to 440°C, wood color completely turned to black, and the absorptions of saturated C—H declined largely. The absorptions of aromatic C=O and ether bond declined largely, which means the carbohydrate pyrolysis was almost completed and lignin started to degrade. Before the pyrolysis temperature reached 550°C, the absorptions of saturated C—H and aromatic C=O declined largely. Meanwhile, absorption peaks of aromatic C—H appeared, which means that aromatization had started and more oxygen atoms were eliminated from the system. When the temperature was up to 720°C, the spectrum belonged to typical charcoal. There were absorption peaks of aromatic C—H, but those of aliphatic C—H had disappeared.

According to the results mentioned earlier and the theoretical analysis, the pyrolysis process of Korean pine wood treated with FRW can be outlined as follows:

1) Acetyl groups were stripped off from hemicellulose and carbohydrates dehydrated under heat radiation. Acid was a catalyst for these two reactions (especially to the later), so it was concluded that FRW and its acidic pyrolytic products were catalysts to these processes. This has been proven by relative studies (Wang et al., 2004).

2) With temperature increasing and with increasing time, under the catalysis of FRW degradation products, carbohydrates degraded. Some groups and segments were eliminated in the form of water and oxo-organic compounds of low molecular weight. Unsaturated products polymerized into large molecular substances in the condensed state. In the second phase of carbohydrate degradation, lignin started to degrade and eliminated low molecular oxo-organic compounds. Compared with control specimens, because of the catalysis of FRW decomposition products, the pyrolytic products of wood treated with FRW were low in calorimetry. There was concrete proof for this in the study of fire retardance mechanism, in which CO<sub>2</sub> yield was reduced when wood was treated with FRW (Wang et al., 2002, 2004b).

3) Aromatization occurred in the pyrolytic products of carbohydrate. Lignin pyrolyzed, degraded, and polymerized. Some oxo-groups were eliminated.

4) Wood charcoal was formed through pyrolytic products aromatization.

Wood pyrolysis is a very complicated chemical process. Not only are there many chemical reactions affected by temperature, other concomitant, and substance and heat transfer state in the typical phases mentioned but also these typical phases and their reaction time and space are not completely separated from but interact with each other. Besides this, the complexity also drives most researchers to think that pyrolysis reaction follows statistics rules, that is, macromolecules split randomly. Although there are such complexities, the present experimental results mentioned above showed that carbonization proceeds in sequence

when wood burns. The charcoal yield from wood treated with FRW is more than that of the control. It can be deduced that, some treatment with chemicals can change the process of wood pyrolysis and degradation. The more the carbon products formed, the less the heat released from the burning process. This is very helpful in fire retardance.

## 3.2 GC-FTIR analysis of isothermal pyrolytic products from wood treated with FRW

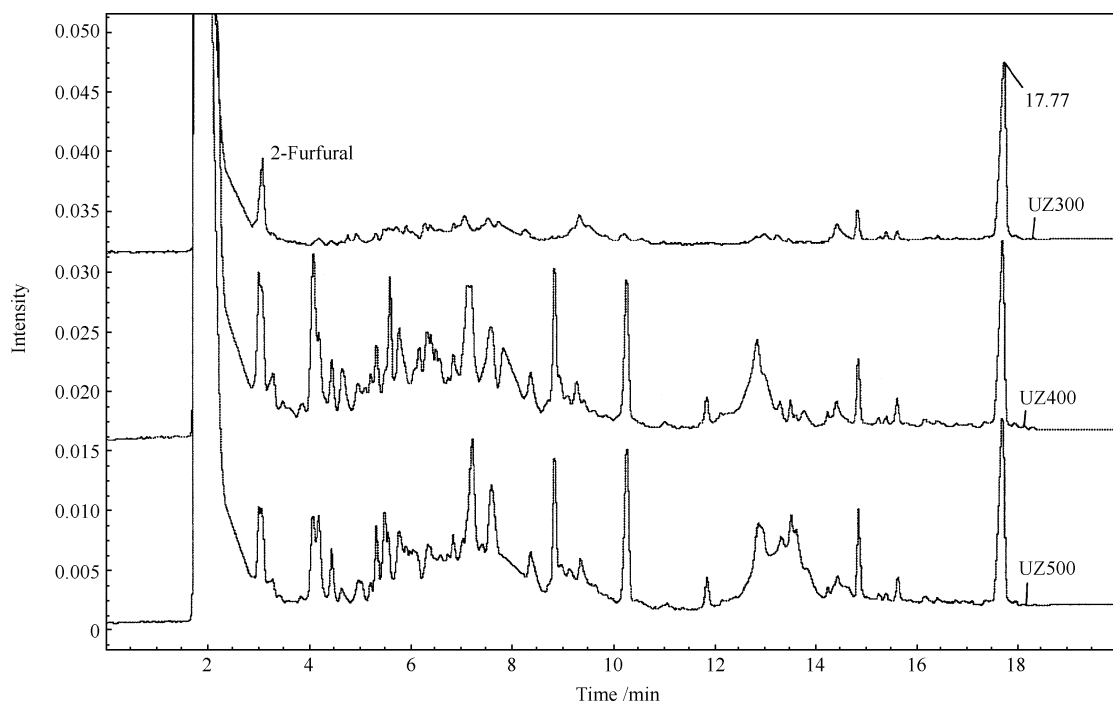
### 3.2.1 Preferable pyrolysis temperature

Basswood control specimens pyrolyzed under 300, 400, and 500°C. Their volatile products were analyzed by GC and the spectra are shown in Fig. 2. When pyrolysis occurred below 500°C, the most complicated components were formed and the most abundant information was available. this temperature was set as the preferable pyrolysis temperature and it was difficult to control the heating chamber if the temperature was higher.

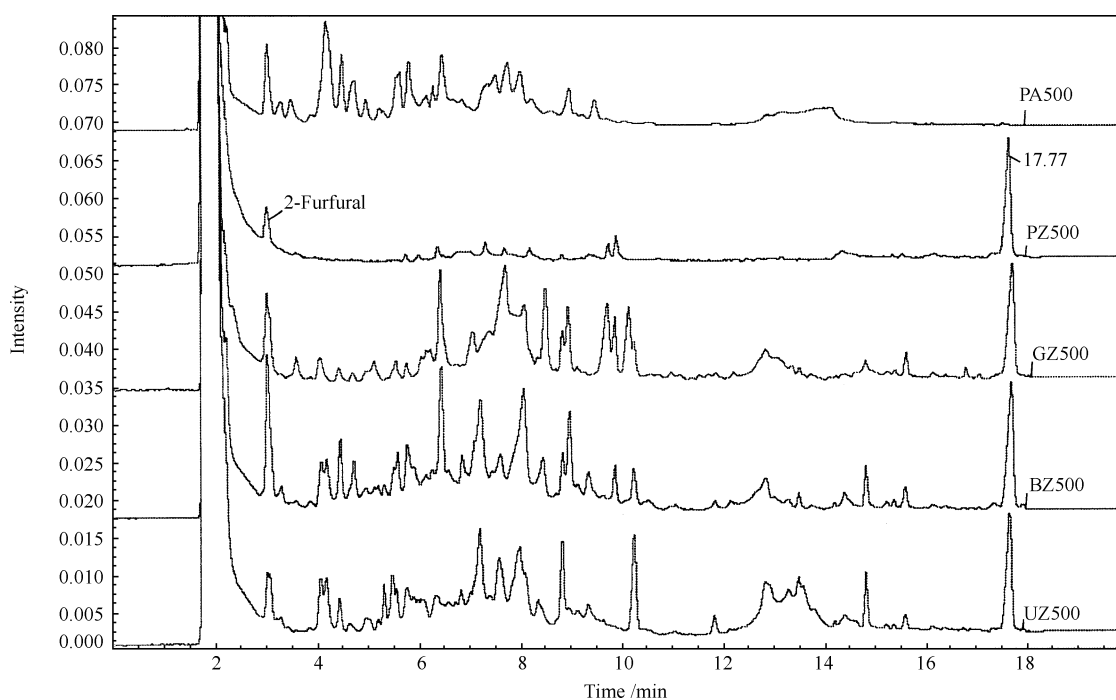
### 3.2.2 GC analysis results and discussion

The GC spectra of volatile products from UZ, BZ, GZ, FZ, and PA pyrolysis below 500°C are shown in Fig. 3. The peak with retention time 17.77 min belonged to the aliphatic acid extract from basswood. It was used as a control peak. For the peaks with different retention times in the same spectrum, their relative quantity can be made sure according to their height, and for the peaks in different spectra with the same retention time their relative mass can be compared quantitatively because of the same coordinates, the same height of control peaks, and similar components. The peak of acetic acid was not identified in the figure because acetic acid formed is high in quantity and cannot be separated from the solvent.

The spectra in Fig. 3 were compared with each other. Some conclusions were drawn as follows: (1) When the basswood treated with FRW (FZ) pyrolyzed, its volatile products were less than those of UZ and other specimens in quantity. Its composition was very different from that of other specimens, which means the pyrolysis process of FZ is different from that of other specimens. (2) When the basswood treated boric acid (BZ) pyrolyzed, its volatile products were similar to that of UZ in quantity and composition, which means boric acid affected the pyrolysis reaction of wood, but not much. (3) Comparing the PA spectrum with the UZ one, it was deduced that volatile pyrolytic products from wood, especially the low-boiling-point substances, were from polysaccharide pyrolysis and degradation. (4) The pyrolytic products of wood treated with GUP (GZ) were very different from those of UZ. Low-boiling-point substances (their retention times were 3 to 7 min) were less, which means the reaction of polysaccharide degrading into low-molecular-weight substance was restrained.



**Fig. 2** GC spectra of the volatile products formed in the pyrolysis of basswood at different temperatures



**Fig. 3** GC spectra of the volatile products formed in the pyrolysis of UZ, BZ, GZ, FZ and PA at 500°C

In addition, according to Fig. 3, 2-furfural was formed largely when wood pyrolyzed under a low temperature (300°C). According to the experimental data, acetic acid yield, which was determined under a low column temperature,

was affected little by temperature within the set temperature range (300–500°C). Therefore, it was concluded that the pyrolysis of hemicellulose took place firstly. This is consistent with the results of the study of micro FTIR.

### 3.2.3 GC-FTIR analysis result and discussion

FTIR detector was used to obtain GC spectra in Figs. 2 and 3. By using a highly sensitive detector (FID), the experimental result indicated that there were more than 140 components in FZ500. However, most of them were too less to get discernable FTIR spectra.

(1) Identification of volatile pyrolytic products from basswood treated with FRW

The spectra of some products from basswood treated with FRW (FZ500) are shown in Fig. 4. Ten simple products from FZ500 were identified by GC-FTIR and the type of other products with unknown fine structures was deduced as follows:

(i) There were ten simple products such as carbon dioxide, aldehyde, acetic acid, 2-furfural, 2-acetyl furan, propanoic acid, formamide, ethylamide, 2-methoxyl phenol, and 2,5-bimethoxyl phenol. Among them, amide was formed by ammonia, which was from GUP degradation, reacting with carboxylic acid from wood pyrolysis. It could not be detected in the pyrolytic products from control.

(ii) The structure type of unknown products from FZ500 pyrolysis

All the unknown components that were large in quantity were carbonyl compounds. Most of them contained hydroxy or ether bond groups. Some unknown compounds contained unsaturated double bonds and hydrogen atoms linked with unsaturated carbon atoms, except for carbonyl groups.

(2) The pyrolysis reaction of wood treated with FRW

With the structure and property characters of cellulose, hemicellulose, and lignin, which are main components of wood, the GC-FTIR results of FZ, GZ, BZ, UZ, and PA were compared and analyzed. The following conclusion can be drawn. (i) According to Fig. 4, when basswood treated with FRW pyrolyzed, carbohydrates (hemicellulose and cellulose) dehydrated. Unsaturated compounds with C=C group and carbonyl compounds were produced. Multihydroxyl compounds dehydrated and isomerized into carbonyl ones. (ii) Hemicellulose stripped off acetyl groups, which changed into acetic acid. (iii) Carbohydrates degraded into unsaturated low-molecular-weight substances. (iv) Lignin pyrolyzed and some phenolic compounds were produced.

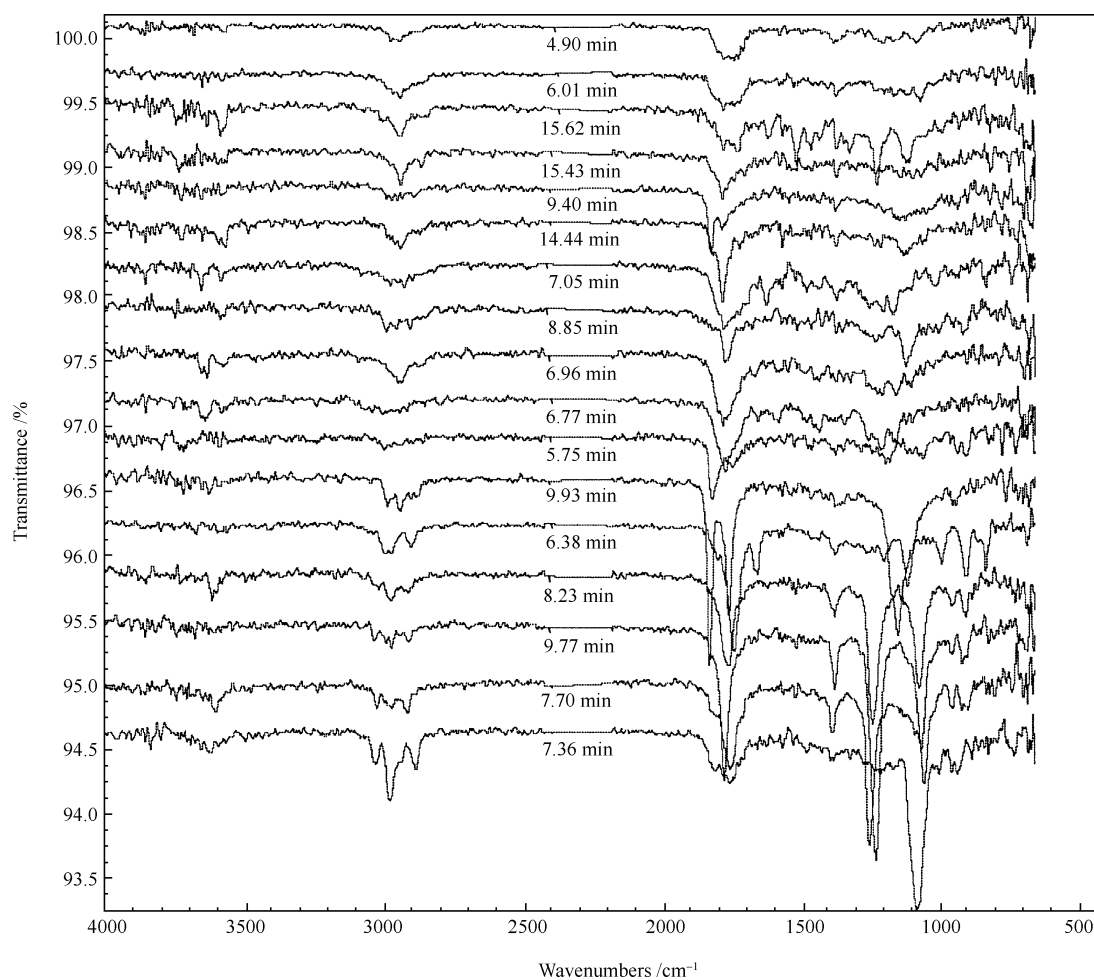


Fig. 4 FTIR spectra of some of the volatile products formed in the pyrolysis of FZ at 500°C

According to Fig. 4, there are strong noise and water peaks in all the spectra. The main reason was that these components are much less in quantity for the FTIR detector to detect. It was difficult to analyze such spectra. The fine structure of pyrolytic products should be identified by GC-MS in the near future.

#### 4 Conclusions

When wood treated with FRW was heated, with temperature increasing, under the catalysis of FRW and its decomposition products, wood turned into charcoal through dehydration of polysaccharides, stripping off of acetyl groups by hemicellulose, degradation of polysaccharides, degradation of lignin, polymerization of pyrolytic products, elimination of oxygen atoms by aliphatic polymers, and formation of aromatic structures.

In the pyrolytic products of wood treated with FRW, ten volatile low-molecular-weight substances such as carbon dioxide, acetaldehyde, acetic acid, 2-furfural, 2-acetyl furan, propanoic acid, formamide, ethylamide, 2-methoxyl phenol, and 2,5-bimethoxyl phenol were detected. Other components with unknown fine structures, which were more in quantity, were identified and were characterized as carbonyl compounds. Most of the unidentified compounds had hydroxyl groups, C—O—C, or C=C bonds.

FRW changed the process of wood pyrolysis. Volatile products obviously declined. This is the main reason that FRW can reduce the heat released from burning of wood.

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