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Pyrolysis of wood species based on the compositional analysis

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Abstract−Based on the Van Soest method, the components in Chinese fir and fast-growing poplar were quantified, and the fiber present was separated into three fractions: neutral detergent fiber, acid detergent fiber and strong acid detergent fiber. Microstructure of the fibers was investigated by a Fourier transform infrared spectrometry. Cellulose and hemicellulose both represent the characteristics of polysaccharides, while lignin has dissimilar structure. Pyrolysis of fir, poplar and the detergent fibers was carried out on a thermogravimetric analyzer coupled with FTIR spectrometry. After the removal of extractives and soluble minerals, pyrolysis of NDF shows the characteristics of the three main components. Hydrocarbons, aldehydes, ketones, acids, alcohols and others are generated due to the primary pyrolysis of hemicellulose and cellulose in single stages. Phenols and alcohols are the dominant volatiles released from pyrolysis of lignin in two successive stages, respectively.

Key words: Wood, Pyrolysis, TG, FTIR, Component

INTRODUCTION

Biomass energy is regarded as one of the key options to substitute fossil fuels and mitigate greenhouse gas emissions. Wood and other forms of biomass can be used in various ways to provide energy, such as combustion, gasification, pyrolysis, etc. [1]. Biomass fast pyrolysis is a promising and economical process to produce liquid fuels that can be readily stored or transported [2]. Biomass is mainly composed of hemicellulose, cellulose, lignin, minor amounts of other organics, as well as a few minerals, and thus the pyrolysis mechanisms and pathways are quite complex [3]. Generally, the pyrolysis behavior of biomass is studied based on the three main components, cellulose, hemicellulose and lignin, taking the proportions into account. The different components are quantified by a set of extractions with alkaline and acid reagents, each able to remove one component, leaving the others undisturbed. There are many analytical methods, and the Van Soest method is often used according to its accuracy in quantification and high purity of the fractions [4].

The previous works paid much attention to the pyrolysis behavior of model components extracted from biomass and the blends of them. Cellulose, xylan, glucomannan, lignin were the commercial model compounds usually used. The pyrolysis of polysaccharides occurred quickly in narrow temperature ranges, and the weight loss of hemicellulose happened earlier than that of cellulose. The decomposition of lignin was more difficult and occurred in a wide temperature range, achieving high residue yield [5]. It was suggested that the pyrolysis of biomass could be considered as the superposition of the main components [6,7]. Alen et al. [8] investigated the pyrolysis of pine wood and its main components (cellulose, hemicelluloses, and lignin) by Py-GC/MSD, and indicated that wood behaved as the sum of these components in the temperature range of 400-1,000 °C. Kinetic calculations performed by Svenson et al. [9] showed that the three components acted independently during pyrolysis, and the sum in the proportions of birch wood was in good agreement with the data of crude birch wood. Yang et al. [10] also indicated negligible interaction among the pyrolysis of three components by studying that of synthesized samples. The technology of the thermo-gravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR) has been adopted widely considering the advantage of online gas analysis. Bassilakis et al. [11] studied the pyrolysis behavior of biomass and three model compounds on a TG-FTIR system, and reported the product-evolution patterns. Later they used the experimental results to determine kinetic parameters, which were incorporated into a pyrolysis model to predict product yields [12].

Besides the three main components, other organics together with the minerals were ignored in most of the previous studies. The commonly used model compounds were found to be unreliable to evaluate pyrolysis of the whole biomass. During compositional analysis, the detergent fibers obtained were rarely investigated, which contained different components present in the raw biomass. Pyrolysis of these fibers might show the role of each component during the pyrolysis of biomass. The aim of this study is to explore the characteristic pyrolysis behavior of each fiber due to its individual component characteristics, and conclude the contribution of the main components to pyrolysis kinetics and product evolution based on TG-FTIR analysis.

EXPERIMENTAL

1. Compositional Analysis

Van Soest analysis was carried out on a FIWE3 raw fiber determination system, which was manufactured by an Italian company, Velp Scientifica. In the process of Van Soest analysis, biomass was separated progressively into neutral detergent fiber (NDF), acid detergent fiber (ADF) and strong acid detergent fiber (SADF). NDF

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Table 1. Compositional analysis of biomass

Component (wt%) Sample	Soluble minerals & extractives	Hemicellulose	Cellulose	Lignin	Insoluble minerals
Fir (softwood)	7.70	11.94	48.90	31.21	0.25
NDF	/	12.94	52.98	33.81	0.27
ADF	/	/	60.85	38.84	0.31
SADF	/	/	/	99.21	0.79
Poplar (hardwood)	2.94	19.06	60.70	14.80	2.50
NDF	/	19.64	62.54	15.25	2.57
ADF	/	/	77.82	18.97	3.21
SADF	/	/	/	85.55	14.45

mainly consists of hemicellulose, cellulose, lignin and insoluble minerals, while ADF is composed of cellulose, lignin and insoluble minerals. And there are only lignin and insoluble minerals in SADF. Table 1 shows the composition of Chinese Fir and fast-growing poplar, as well as their detergent fibers based on the difference calculation. Fir contains much more extractives and lignin than poplar, while the contents of polysaccharides including hemicellulose and cellulose are relatively lower. Poplar contains more insoluble minerals than fir, which will influence the pyrolysis behavior of the detergent fibers.

2. FTIR Spectroscopy

The detergent fibers of fir and poplar were analyzed with a Nicolet NETXUS 670 FTIR apparatus to study their microstructures. The pretreatment was carried out by tabletting the mixture of each sample and KBr (where KBr has a proportion of 0.5-1 wt%) into a very thin film with a diameter of 5 mm. The resolution of the FTIR was set in 4 cm^{-1} and each spectrum was composed of 120 scans. Here the mercury cadmium telluride detector was used to fit the spectrum scope of 400-4,000 cm^{-1}.

3. TG-FTIR Experiment

A Mettler-Toledo TGA/SDTA851e thermo-balance, coupled with Nicolet NETXUS 670 FTIR by using a Teflon tube, was used to study the pyrolysis behavior of the samples, referring to fir, poplar and their detergent fibers. The experiments were done at a linear heating rate of 20 K/min from the ambient to 1,073 K, at a steady nitrogen flow of 30 ml/min. The weight of samples was kept at about 5 mg and volatiles released during pyrolysis would be swept into FTIR gas cell quickly by pure nitrogen. The Teflon tube and FTIR gas cell were already preheated to 453 K before each experiment. The deuterated triglycine sulfate pyroelectric detector was adopted for its rapid response and low noise. The spectrum scope was located in the range of 400-4,000 cm^{-1} and the resolution factor was selected to be 1 cm^{-1}.

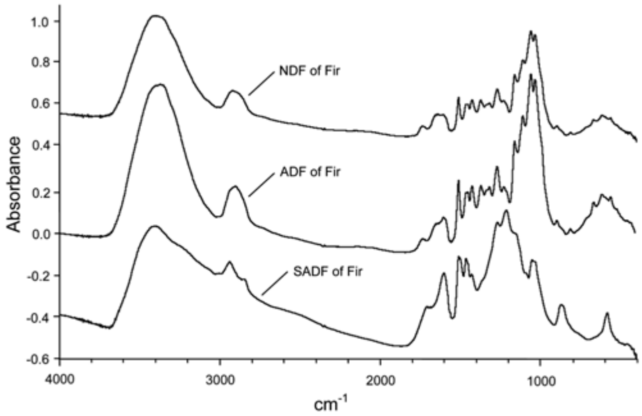

Fig. 1. FTIR spectra of the three detergent fibers from fir.

Table 2. The main functional groups of the three detergent fibers

Wave number (cm^{-1})	Functional groups
3,000-3,600	O-H stretching
2,850-2,970	C-H_n stretching
1,700-1,765	C=O vibrations
1,509, 1,601	aromatic rings
1,430-1,470	-O-CH_3
1,429	C-H bending
1,400-1,440	O-H bending
1,317-1,375	C-H bending
1,260-1,270	C-O-C stretching
1,210-1,230	aromatic phenyl C-O stretching
1,035, 1,058, 1,110, 1,161	C-O stretching and deformations
897	β-bonds in heterogeneous region
400-700	C-C stretching

RESULTS AND DISCUSSION

1. Chemical Structure of the Detergent Fibers

The FTIR spectra of the three detergent fibers from fir are shown in Fig. 1. The typical functional groups are listed in Table 2. The oxygen-containing functional groups are observed in the three fibers, such as OH (3,000-3,600 cm^{-1}), C=O (1,700-1,765 cm^{-1}), C-O-C (1,260-1,270 cm^{-1}), and C-O-(H) (-1,210 cm^{-1}). However, the three detergent fibers show different FTIR structures due to their compositions. The spectra of NDF and ADF are quite similar, while apparent differences are shown in that of SADF, especially in the finger print region (667-1,830 cm^{-1}). It is indicated that cellulose and hemicellulose have similar functional groups, both representing the characteristics of polysaccharides. The bands related to the pyranoid ring stretching (1,035, 1,058, 1,110, 1,161 cm^{-1}) appear in the spectra of both NDF and ADF. Asymmetric shrinkage of the characteristic bond C-O-C (1,260-1,270 cm^{-1}) of pyranoid ring, symmetric and asymmetric stretching vibration of aliphatic C-H (2,850-

2,970 cm^{-1}), symmetric and asymmetric bending of C-H (1,429, 1,317-1,375 cm^{-1}) are also observed. However, the absorbance of C=O vibrations (1,700-1,765 cm^{-1}) in the spectra of NDF should be higher, related to the carboxyl groups of uronic acid in the hemicellulose [13]. Several major absorption bands in the spectrum of SADF represent the typical structure of lignin. The characteristic bands located in 1,429, 1,464, 1,509 and 1,601 cm^{-1} indicate the existence of aromatic rings and C-H bonds. The absorption band in 1,430-1,470 cm^{-1} shows that lignin might be rich in methoxyl-O-CH$_3$ groups. Moreover, the bands in the region of 1,210-1,230 cm^{-1} indicate the appearance of aromatic phenyl C-O.

2. Thermogravimetric Analysis

The TG/DTG curves of fir and poplar, as well as their detergent fiber pyrolysis at the heating rate of 20 K/min are presented in Fig. 2 and Fig. 3. It is indicated that the pyrolysis behavior of raw fir and poplar samples varies considerably. However, after the removal of soluble minerals and extractives, pyrolysis of NDFs behaves quite similarly, which represents the characteristics of the three main components. The slight distinctions are attributed to the different proportions of the components. It was proposed that the extractives decomposed in the same temperature range as the main components [14]. Comparing the curves of raw biomass and NDF, the presence of minerals affects the pyrolysis behavior significantly. Taking fir as an example, the minerals advance the pyrolysis obviously and greatly promote the residue yield. Due to the presence of hemicellulose in NDF, the pyrolysis occurs earlier and achieves higher residue yield in contrast with that of ADF. A slight shoulder appears in the DTG curve of NDF from poplar, attributed to the relatively higher content of hemicellulose.

Assuming all components are undergoing pyrolysis individually, the pyrolysis behavior of the main components could be deduced according to the TGA curves of biomass and its detergent fibers. It was proposed that the weight-loss curve for hemicellulose could be obtained by subtracting the TG curve of acid-washed wood from the TG curve of water-washed wood [15]. The results for hemicellulose would be more reliable when taking the influence of extractives (that absent in NDF) into account. Based on the composition of each fiber as shown in Table 1, the TG/DTG curves of hemicellulose and cellulose pyrolysis are obtained by difference calculation according to those of NDF and ADF, ADF and SADF, respectively

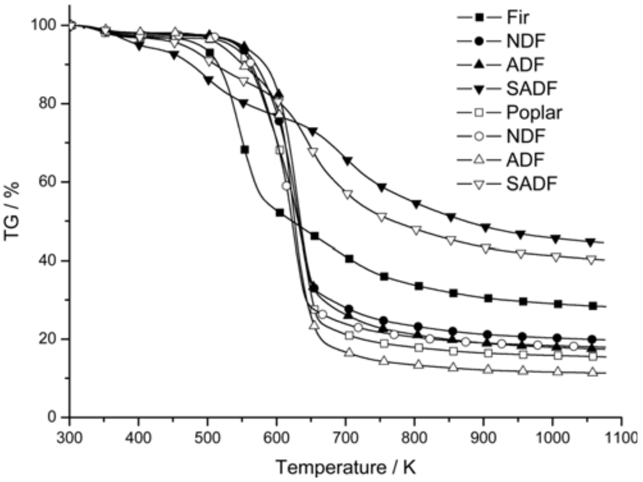

Fig. 2. TG plots of fir, poplar and their detergent fibers pyrolysis (20 K/min).

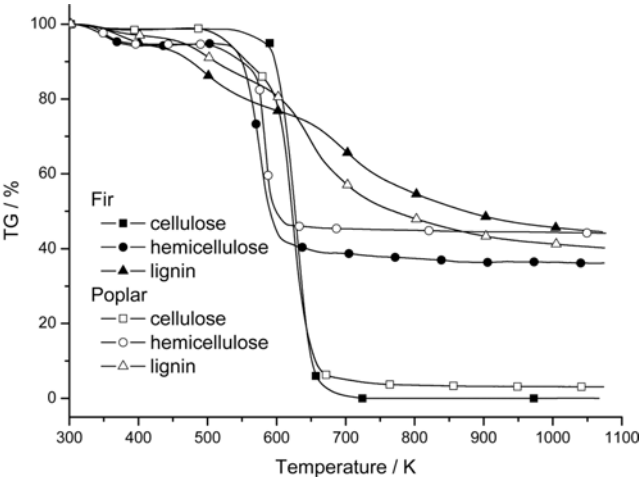

Fig. 4. TG plots of the main components obtained by difference calculation.

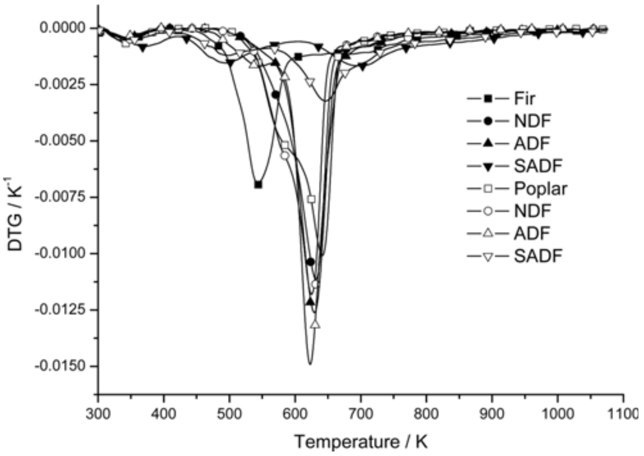

Fig. 3. DTG plots of fir, poplar and their detergent fibers pyrolysis (20 K/min).

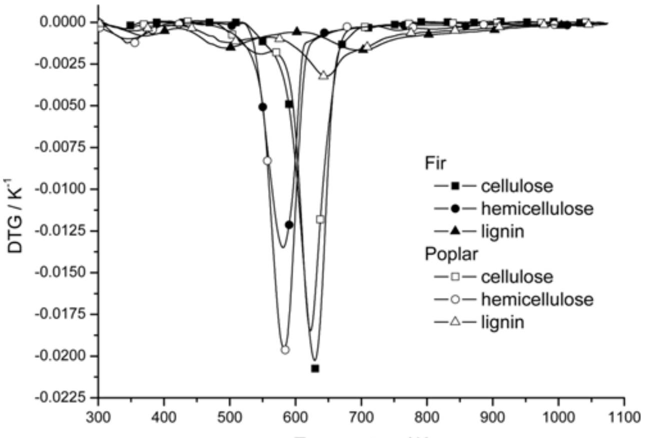

Fig. 5. DTG plots of the main components obtained by difference calculation.

(Fig. 4 and Fig. 5). SADF contains little acid-insoluble ash and mainly consists of lignin, and thus its pyrolysis behavior could roughly represent that of lignin.

As shown in Fig. 4 and Fig. 5, hemicellulose starts to decompose at about 500 K and cellulose at about 550 K, both intensively with sharp DTG peaks [5,16]. The pyrolysis of cellulose generates mainly volatiles, and more char is yielded from hemicellulose pyrolysis. In comparison, the pyrolysis of lignin occurs in a wide temperature range with flat DTG peaks, and contributes the greatest in char yield. It begins to decompose at a lower temperature but quite slowly. Both ADF and NDF contain a considerable amount of cellulose and hemicellulose, and thus undergo pyrolysis at higher temperatures than lignin, as well as SADF, which is indicated in Fig. 2. Due to the unneglectable content of insoluble minerals present in poplar fibers, pyrolysis of the three main components in poplar begins earlier and achieves higher char yield, especially the pyrolysis of SADF is influenced greatly.

3. FTIR Analysis of Gas Evolution for Poplar Pyrolysis

Compared with fir, poplar contains fewer minerals, extractives and lignin, while more cellulose and hemicellulose. Here the gas evolution during pyrolysis of poplar and its detergent fibers are studied in detail, in order to conclude the products generated from three main components. The evolved gas profiles at the heating rate of 20 K/min are shown in Fig. 6, which are consistent with the corresponding DTG curves shown in Fig. 3. Pyrolysis of SADF could be roughly regarded as that of lignin in poplar, progressing in two successive stages. Due to the higher lignin content in ADF than in raw poplar, an apex appears in the early stage, showing characteristics of lignin pyrolysis. The products generated in the main pyrolysis stage of ADF are primarily from cellulose, secondly lignin. Pyrolysis products of NDF are contributed by the three main components together. The pyrolysis characteristics of hemicellulose could be observed in the profile of NDF, compared with that of ADF.

Fig. 5 shows that the maximum weight loss rates for hemicellulose and cellulose pyrolysis appear at about 583 K and 624 K, respectively. Assuming all components are undergoing pyrolysis individually, the gas evolved from hemicellulose is analyzed by comparing the FTIR spectra of NDF and ADF pyrolysis at 583 K, while for cellulose based on those of ADF and SADF pyrolysis at 624 K. The maximum volatile release occurs at 500 K and 650 K in the two pyrolysis stages of lignin, respectively. Figs. 7-9 display the spectra mentioned above. Water (3,500-3,964 and 1,300-1,800 cm^{-1}), carbon dioxide (2,217-2,391 and 586-726 cm^{-1}) and carbon monoxide (2,112 and 2,180 cm^{-1}) are released out as small molecular gases during the pyrolysis of three detergent fibers. Special attention is paid to the formation of large molecular volatiles.

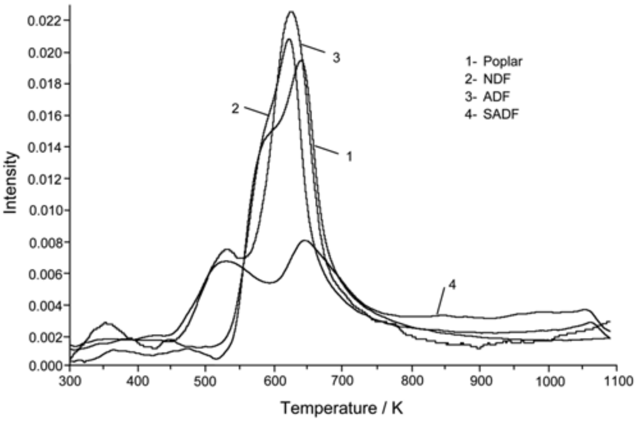

Fig. 6. Evolved gas profiles during pyrolysis of poplar and its detergent fibers (20 K/min).

Due to the simplicity of SADF in composition, the FTIR spectra are analyzed first. The presence of insoluble minerals does not affect the chemical reaction pathways [17]. Thus, the volatiles generated from lignin pyrolysis are not altered. As shown in Fig. 9, at 500 K, in the first pyrolysis stage the most significant band is O-H at 1,300-1,400 cm^{-1}, corresponding to the main presence of alcohols and phenols. Methanol is identified as the most important alcohol according to the characteristic bands at 2,710-3,140 and 960-1,085 cm^{-1}, but relatively weaker compared with that of phenols. When pyrolysis progresses into the second stage, for example at 650 K, the release of phenols is less violent. The strong absorption band at 2,850-3,200 cm^{-1} shows the existence of hydrocarbons, especially methane. According to the intense characteristic band at 960-1,085 cm^{-1}, methanol is released out continuously in a considerable amount, contributed by the methoxy substituents in the lignin structure.

Fig. 8 compares the FTIR spectra of gas released out at 624 K during ADF and SADF pyrolysis, showing the volatiles originat-

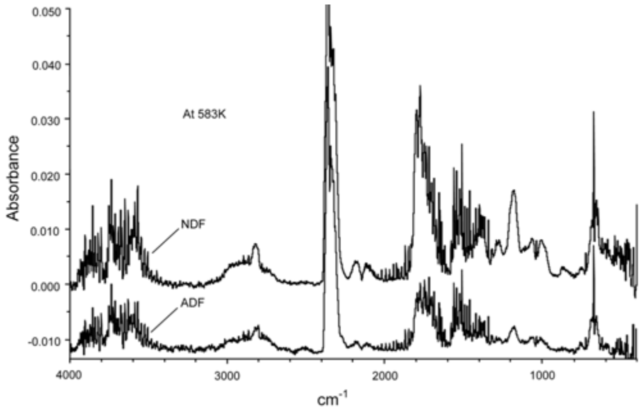

Fig. 7. FTIR spectra of gas released out at 583 K during NDF and ADF pyrolysis.

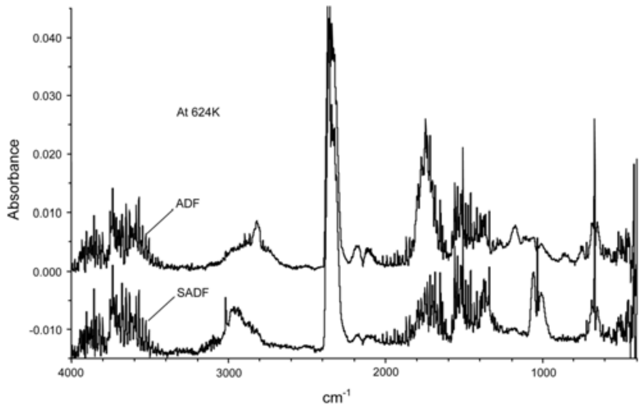

Fig. 8. FTIR spectra of gas released out at 624 K during ADF and SADF pyrolysis.

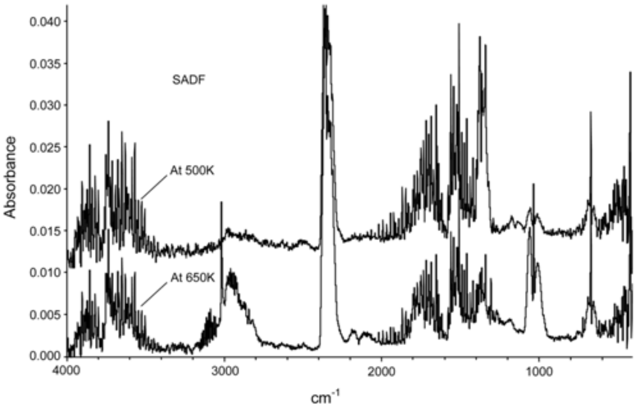

Fig. 9. FTIR spectra of gas released out at 500 K and 650 K during SADF pyrolysis.

ing from cellulose. The spectral regions of 2,700-3,200 cm^{-1} in the spectrum of ADF pyrolysis represent C-H stretching, and show the formation of hydrocarbons, formaldehyde, acetaldehyde and others [18]. The strong absorption bands appearing at 1,600-1,850 cm^{-1} represent the flexible vibration of C=O double bond, corresponding to various aldehydes and ketones [13]. A band appears at 900-1,500 cm^{-1} due to the in-plane flexure vibration of C-H and the skeletal vibration of C-O and C-C, showing the formation of carboxylic acids, alcohols and others. Levoglucosan with an absorption band at 1,183 cm^{-1} and glycoaldehyde at 860 cm^{-1} are also observed [18].

Fig. 7 shows the FTIR spectra of gas released out at 583 K during NDF and ADF pyrolysis, which are quite similar. Acids, alcohols, aldehydes, ketones and phenols are all formed as the main volatile products. Due to the similar polysaccharide structure of cellulose and hemicellulose, the contribution of hemicellulose to the volatiles generated is not quite clear. By spectral subtraction to remove the interfering bands, 2-furaldehyde (2,770-2,865 and 965-1,435 cm^{-1}) is identified as a prominent product of hemicellulose pyrolysis.

According to the widely applied Lambert-Beer Law, the absorbance at a specific wavenumber is linearly dependent on gas concentration [19]. As analyzed above, a characteristic band in which a peak appears indicates the presence of a specific chemical species. Thus, the variation of peak area in the whole pyrolysis process can reflect the tendency of product yield of the specific volatiles. The evolution peaks of most large molecular volatiles, such as hydrocarbons, aldehydes, ketones, acids, alcohols and others, all appear due to the primary pyrolysis of hemicellulose and cellulose, which process in single pyrolysis stage. However, the status is more complex for lignin. Fig. 10 shows the specific FTIR profiles of volatiles evolved from SADF pyrolysis, which behave dissimilarly in two successive stages. At lower temperature, phenols are generated in a large amount, while the formation of alcohols such as methanol is rather weak. At higher temperature, only a small amount of phenols is released. They might undergo further secondary reactions with the increase of temperature [20]. A considerable amount of alcohols as methanol etc. are generated in this stage, close to the pyrolysis temperature of cellulose. Accordingly, methanol might achieve a maximum yield at about 650 K.

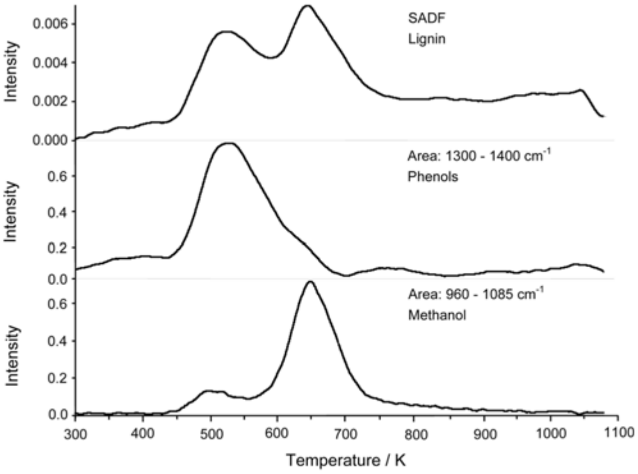

Fig. 10. Specific FTIR profiles of volatiles evolved from SADF pyrolysis.

CONCLUSIONS

To explore the characteristic pyrolysis behavior of biomass components, compositional analysis based on the Van Soest method was done on Chinese fir and fast-growing poplar. The samples were separated progressively into NDF, ADF and SADF, which had different compositions. FTIR spectra show that cellulose and hemicellulose have similar functional groups, both representing the characteristics of polysaccharides, while the microstructure of lignin is quite different. TGA analysis shows that the presence of minerals affects the pyrolysis behavior significantly. Pyrolysis of NDFs behaves quite similarly, which represents the characteristics of the three main components. Pyrolysis of SADF could be roughly regarded as that of lignin, progressing in quite a wide temperature range. Water, carbon dioxide and carbon monoxide are released out as small molecular gases during the pyrolysis of three components. Hydrocarbons, aldehydes, ketones, acids, alcohols and others are generated due to the primary pyrolysis of hemicellulose and cellulose, which process in single pyrolysis stages. Phenols and alcohols are the dominant volatiles released from pyrolysis of lignin in two successive stages, respectively.

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