Advance Journal of Food Science and Technology 10(10): 807-813, 2016
DOI: 10.19026/ajfst.10.2266
ISSN: 2042-4868; e-ISSN: 2042-4876
© 2016 Maxwell Scientific Publication Corp.
Submitted: August 10, 2015 Accepted: September 3, 2015 Published: April 05, 2016

Research Article

Pyrolysis Process and Infrared Analysis of *Platycladus orientalis* in Different Particle Sizes by TG-FTIR

[1]Li Xue, [1]Luan Yaning, [2]Wang Yue, [3]Sun Yingkun, [1]Liu Zhen and [1]Sun Zihan
[1]Beijing Forestry University, Beijing 100083, China
[2]Shandong Normal University, Shandong 250358, China
[3]Qingdao Agricultural University, Shandong 266109, China

Abstract: Analysis on pyrolysis and Infrared process by TG-FTIR using *Platycladus orientalis* in different particle size. The results show that *Platycladus orientalis* pyrolysis process can be divided into four stages: the first stage from 30 to120°C, which most caused by water molecules adsorpted on the surface of *Platycladus orientalis* samples during thermal desorption, free water and bound water evaporate in this stage, with a mass loss of 5%. The second stage from 120 to170°C involves the pyrolysis of hemicelluloses and unstable cellulose, with a mass loss of 4%. The third stage from 200 to 400°C. Maximum pyrolysis rate is about achieved in this stage at 365°C, weight loss of this stage is about 50%, due to the thermal decomposition of cellulose, including dehydration, depolymerization and decomposition of anhydroglucose unit. In the final stage, which occurs beyond 430°C, the pyrolysis of lignin and charring of cellulose occur. In the three-dimensional IR spectrum, the *Platycladus orientalis* samples exhibit higher absorbance at 200, 525, 830, 1100 and 1420 sec during thermal decomposition. The smaller particle size can be decomposing more thoroughly and rapidly. The particle size of *Platycladus orientalis* samples which less than 0 mm has a smaller influence on the thermal decomposition. Wood vinegar is formed from the pyrolysis stage until the charring stage.

Keywords: Particle size, *Platycladus orientalis*, pyrolysis, TG-FTIR

INTRODUCTION

Platycladus orientalis has many characteristics, such as likes light, drought resistance and cold resistance and has no strict requirements about soil. It is also planting as a forestation in drought south slope and tree species in garden. Wood can be make into construction and furniture, leaves and branches can be used as medicines, including its activities of constringency, haemostasia, diuretic, strengthening stomach, Detoxification and Dissipation Blood Stasis Formula; seed has the efficacy of tranquilization and strengthening with tonics. The use of *Platycladus orientalis* is wide. Using *Platycladus orientalis* as raw material has a lot of advantages consists of low cost, simple, easy to operate, pollution-free and so on.

Platycladus orientalis is also an important source of wood vinegar. Wood vinegar has a complex composition and typically consists of organic acids, aldehydes, ketones, alcohols, phenols and derivatives and other organic compounds (Zhou *et al*., 2007, 2012; Hu *et al*., 2014). In agriculture, wood vinegar is used to promote the growth of plants, improve soil fertility and eliminate pests and so on. In addition, it has a wide range of other uses such as a feed additive, deodorant and antibacterial agent. Wood vinegar is safe for use with livestock as well (Ping *et al*., 2009; Shi and Du, 2003).

Pyrolysis is a key step in the forest biomass conversion process and in the production of wood vinegar. However, it lacks reliability when used alone. In this context, Thermo-Gravimetric-Fourier Transform Infrared spectroscopy (TG-FTIR), which is an accurate and sensitive analytical technique with excellent reproducibility, is widely used in the biomass pyrolysis and gasification research and improves the reliability and feasibility of pyrolysis experiments (Ren *et al*., 2012). Particle grinding a key step in the biomass conversion process (Ni *et al*., 2011; Luo *et al*., 2012). There has been little research on the pyrolysis of *Platycladus orientalis* in different particle size. This study based on some previous studies, by taking *Platycladus orientalis* as the research object, using DSC-FTIR as the auxiliary, mainly studies the different of *Platycladus orientalis* pyrolysis process and IR Spectra. The data reported in this study is expected to help support further research on the conversion of *Platycladus orientalis* into wood vinegar products.

Corresponding Author: Luan Yaning, College of Forestry, Beijing Forestry University, Beijing 100083, China
This work is licensed under a Creative Commons Attribution 4.0 International License (URL: http://creativecommons.org/licenses/by/4.0/).

MATERIALS AND METHODS

Materials: Before the experiment make the *Platycladus orientalis* dried and ground it with a grinder, then screened 0.1, 1 and 2 mm *Platycladus orientalis* as samples, respectively.

Methods:

Pyrolysis: The *Platycladus orientalis* samples were first analysed using a PerkinElmer STA6000 TG A instrument to get baseline data. To reduce the impact of heat and mass transfer, as well as temperature gradients inside the material during the pyrolysis process, about 10 mg of the sample was placed in a crucible made of alumina. Prior to collecting the baseline data, the sample in the crucible was subjected to high temperature calcinations at about 1300°C, to reduce the impact of other impurity components on the TGA curves. Nitrogen (99.99%) at a flow rate of 30 mL/min was passed through the furnace to ensure an inert atmosphere. The initial temperature of the furnace was set at 30°C. Once the furnace stabilized at 30°C, the sample was heated from 30 to 600°C at a heating rate of 20°C/min.

IR spectroscopy: The decomposition gases generated during pyrolysis were analysed by IR spectroscopy using a PerkinElmer spectrum 100 FTIR spectrometer. The pipe connecting the TGA unit with the IR spectrometer was insulated to ensure that all the gases produced during pyrolysis entered the IR spectrometer. The compositions of the pyrolysis gases were analysed in real time in an IR frequency range of 4500-600/cm.

RESULTS AND DISCUSSION

Analysis of the Thermo Gravimetric Analysis (TGA) and Differential Thermo Gravimetric curves (DTG): The *Platycladus orientalis* samples underwent a series of complex chemical reactions during the pyrolysis process. The derivative TGA curves were obtained by computing the first derivative of the TGA curves with respect to temperature. The rate of change of mass was continuously recorded as a function of temperature. We can see from 0.1, 1.0 and 2.0 mm, respectively particle sizes in Thermo Gravimetric Analysis (TGA) and Differential Thermogravimetric curves (DTG) of *Platycladus orientalis* samples (Fig. 1 and 2), It is evident from Fig. 1 that the TGA curves for the *Platycladus orientalis* in different particle size lie close to each other, but 0.1 mm particle size can be decomposed more rapidly.

The pyrolysis process could be divided into four stages: the first stage was from 30 to 120°C, which most caused by water molecules adsorpted on the surface of *Platycladus orientalis* samples during thermal desorption, free water and bound water evaporate in this stage, with a mass loss of 4%. The second stage from 130 to180°C involves the pyrolysis of hemicelluloses and unstable cellulose, with a mass loss of 4%. The third stage from 200 to 400°C. Maximum pyrolysis rate is about achieved in this stage at 365°C, weight loss of this stage is about 50%, due to the thermal decomposition of cellulose, including dehydration, depolymerization and decomposition of anhydroglucose unit. The fourth stage was above 430°C, the pyrolysis of lignin and charring of cellulose occurs.

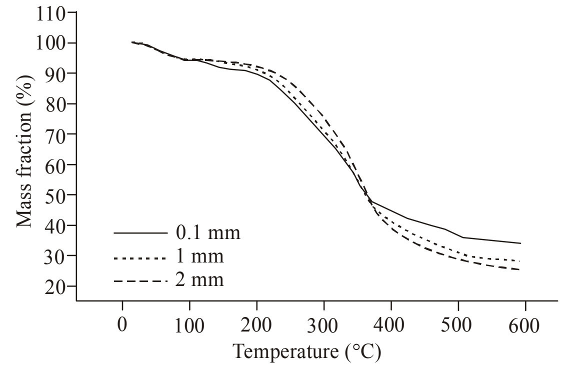

Fig. 1: TGA curves for the three types of *Platycladus orientalis* samples

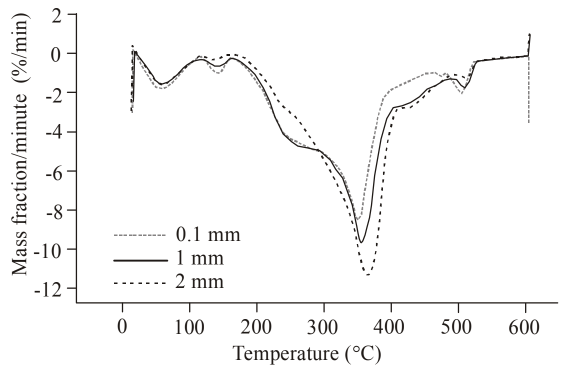

Fig. 2: DTG curves for the three types of *Platycladus orientalis* samples

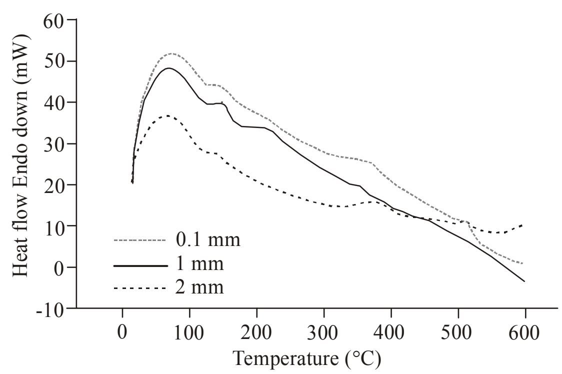

Fig. 3: DSC curves for the three types of *Platycladus orientalis* samples

The Differential Scanning Calorimetric (DSC) curvesis under program control temperature, measuring the difference between losing a technology power and temperature dependence of the substance and reference material. The Differential Scanning Calorimetric (DSC) samples are shown in Fig. 3. From the figure, it is

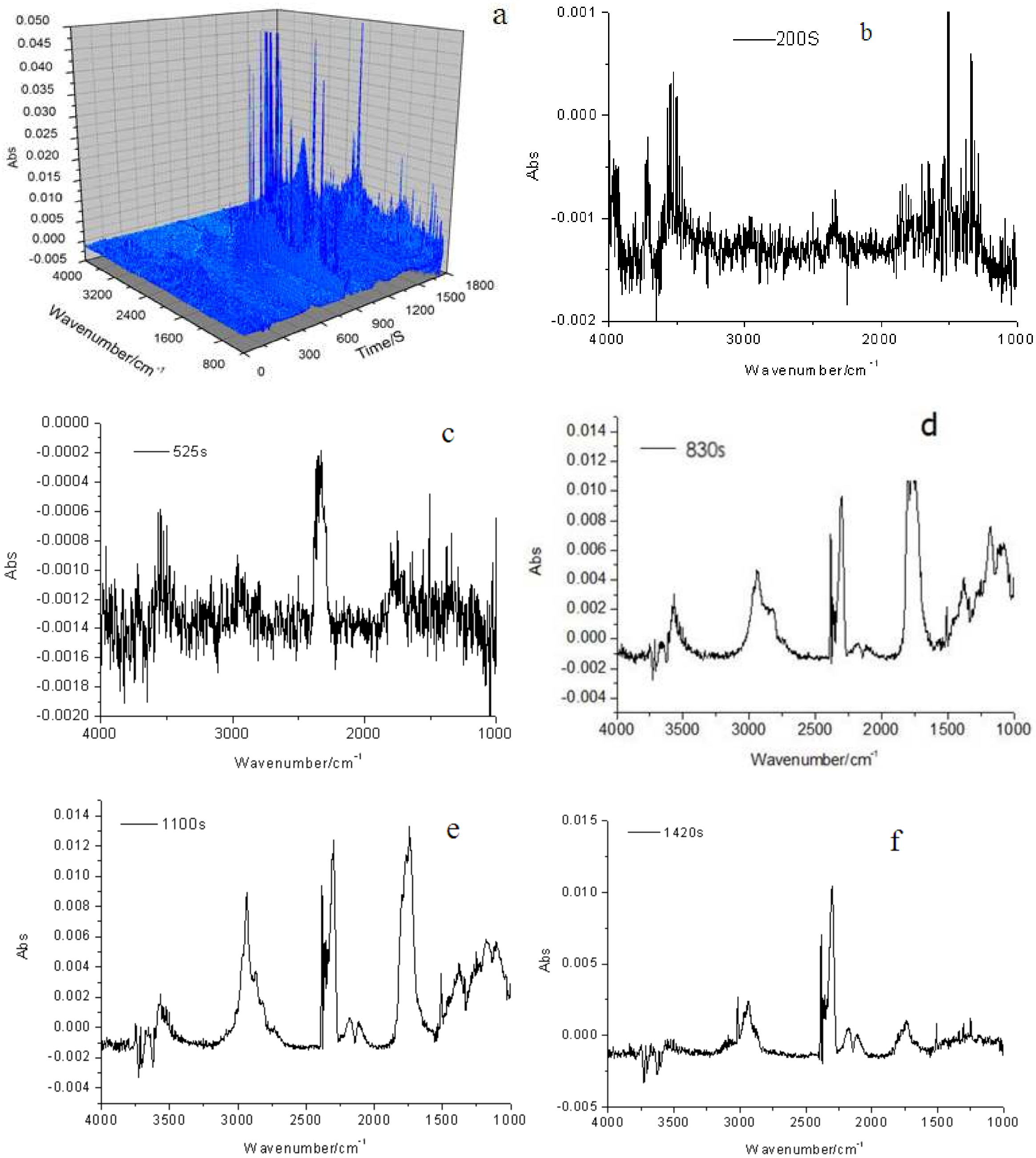

Fig. 4: The FT-IR spectra of *Platycladus orientalis* in the particle size of 0.1 mm and different time; (a): Three-dimensional IR spectrum; (b): 200 sec; (c): 525 sec; (d): 830 sec; (e): 1100 sec; (f): 1420 sec

curves for the three types of *Platycladus orientalis* evident that the 0.1 mm *Platycladus orientalis* at about 68.44°C reaches large endothermic peak, The temperature of three particle size endothermic peak is basically identical. The difference is the larger the particle size leads to the more heat absorption and the higher the endothermic peak, the weak endothermic peak is mainly caused by the thermal decomposition of cellulose and hemicellulose at about 500°C.

Infrared spectrum analysis of different particle size *Platycladus orientalis* samples: From the three-dimensional IR spectrum, it is observed that the *Platycladus orientalis* samples has high absorbance at 200, 525, 830, 1100 and 1420 sec, respectively during the thermal decomposition process, implying that the *Platycladus orientalis* samples decomposed more completely at these points of time. Based on the thermal IR spectra, the decomposition of the *Platycladus orientalis* particles can be divided into four stages, namely water loss, unstable degradation of hemi cellulose and cellulose, decomposition of cellulose and lignin and charring. Figure 4a shows the three-dimensional IR spectrum of 0.1 mm *Platycladus* *orientalis* samples. Figure 4b, which is the three-dimensional IR spectrum acquired at 200 sec peaks corresponding to gaseous water molecules and liquid molecules can be seen at 3500-3950 and 3400-3500/cm, respectively. This corresponds to the TG-DTG (differential thermal gravity) curve peak at about 80°C, which is regarded as the water loss phase. Figure 4c, which is the three-dimensional IR spectrum acquired at 525 sec, a characteristic carbon dioxide peak appears in the 2200-2400/cm range and therefore, this spectrum corresponds to the glass transition stage of pyrolysis. In general, hemi cellulose begins to soften at about 200°C. The softening of hemi cellulose is accompanied by the evolution of small amounts of low molecular weight volatile gases. Carbon dioxide is generated, owing to the thermal instability of cellulose and partial cellulose decomposition.

Figures 4d and e, we can see that the rate of decomposition is higher at 830 and 1100 sec, which correspond to decomposition temperatures of about 310 and 390°C, respectively. The peak at 2820-2930/cm represents the C-H stretching vibration. And the peak at 1743/cm represents C = O, which indicates the C-H stretching and bending vibrations. The peak at 600-1500/cm originates from the vibration of the benzene ring, whereas the peak at 1370/cm corresponds to CO. During pyrolysis, gases containing hydrocarbons,

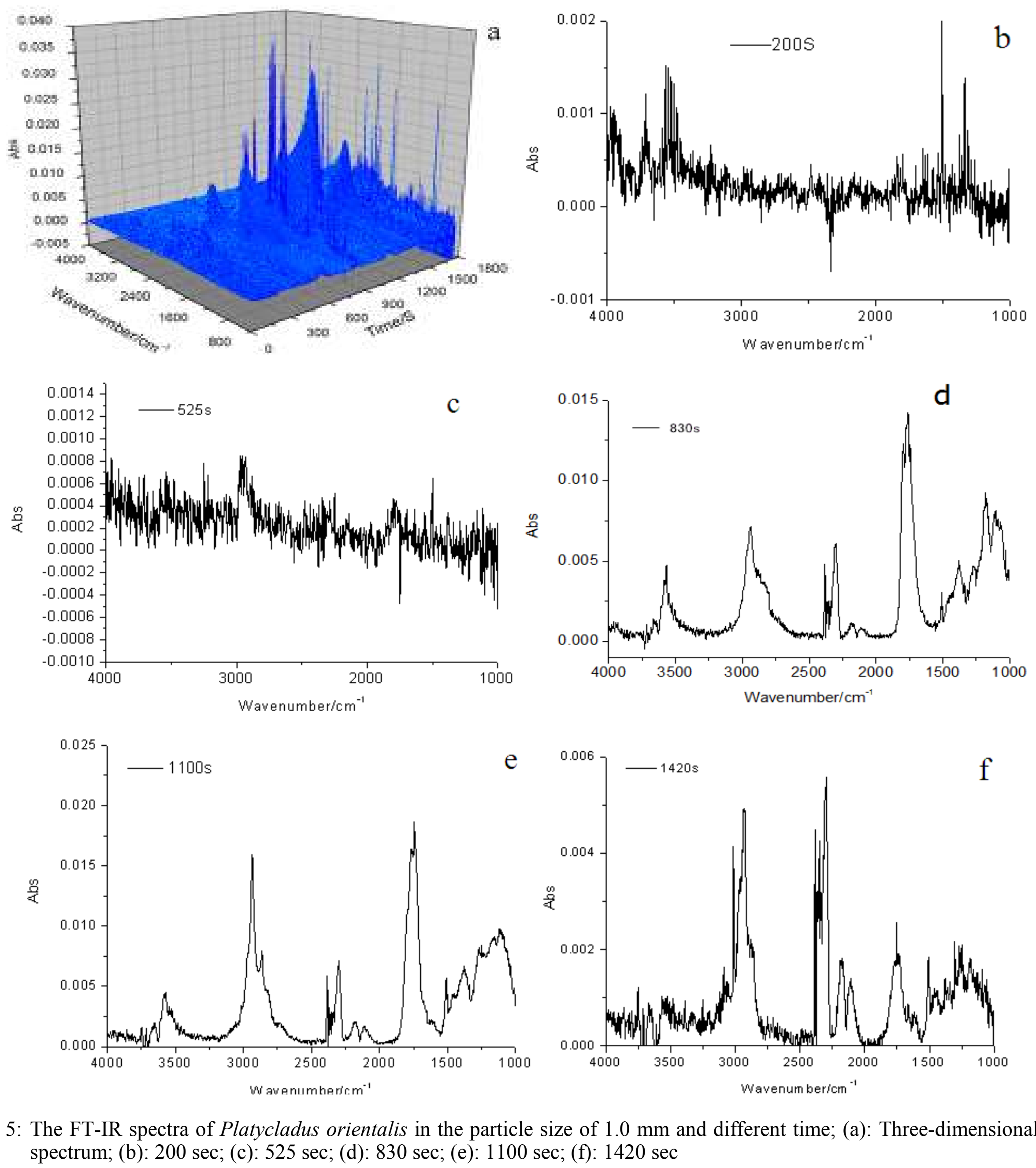

Fig. 5: The FT-IR spectra of *Platycladus orientalis* in the particle size of 1.0 mm and different time; (a): Three-dimensional IR spectrum; (b): 200 sec; (c): 525 sec; (d): 830 sec; (e): 1100 sec; (f): 1420 sec

aldehydes, ketones, phenols, alcohols, carboxylic acids and other small molecules are generated. The peak at 1200-1300/cm corresponds to the carboxylic acid molecule, whereas the peaks at 1000-1100 and 3000/cm are attributed to ethanol and methanol, respectively. Further, the peak at 2800/cm is attributed to the methane molecule (Wang *et al*., 2008, 2005). Figure 4f, we can calculate that the temperature corresponding to the production of methane is about 500°C. At this temperature, the pyrolysis process enters the carbonization stage and CH, CO and C = O was broken down to produce methane, carbon dioxide, carbon monoxide and other gases. Fewer small-molecules produced and gas absorbance decreased when experiment closed too late.

As evidences from Fig. 5 and 6, the IR spectra obtained for the 1.0 and 2.0 mm particle size of *Platycladus orientalis* samples are substantially similar.

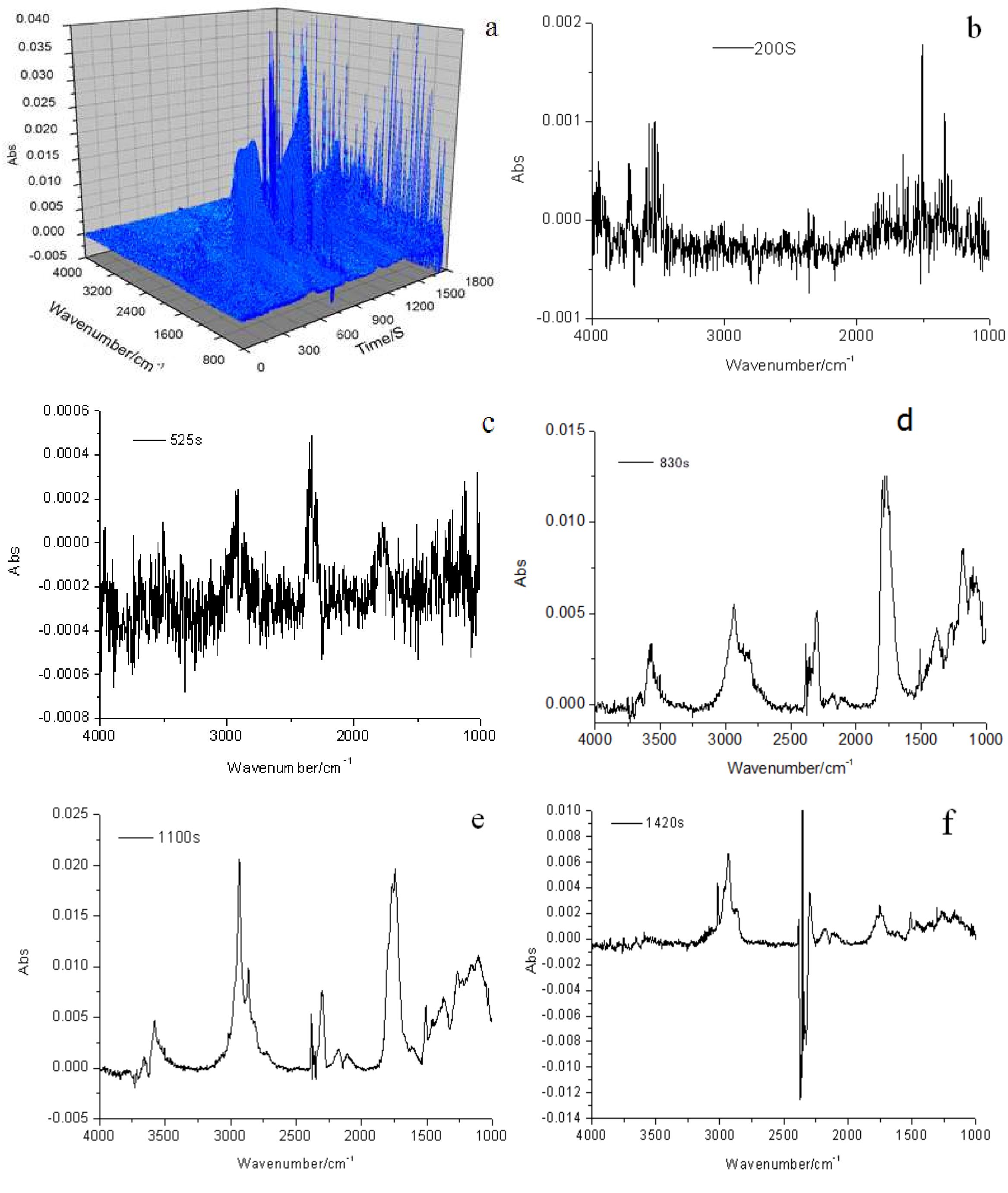

Fig. 6: The FT-IR spectra of *Platycladus orientalis* in the particle size of 2.0 mm and different time; (a): Three-dimensional IR spectrum; (b): 200 sec; (c): 525 sec; (d): 830 sec; (e): 1100 sec; (f): 1420 sec

There are little differences between different particle sizes. The IR spectra of the three types of *Platycladus orientalis* samples at 200, 525, 830, 1100 and 1420 sec, respectively indicate that vigorous thermal decomposition occurs at these times and gases are continuously generated. Overall, the absorbance of 1.0 mm particle size is lower than that of the 2.0 mm particle size. The 1.0 and 2.0 mm also exhibit higher absorbance at 830 and 1100 sec. However, the absorbance of the 1.0 and 2.0 mm are lower than that of the 1.0 mm at 830 sec, but higher than that of the 1.0 mm at 1100 sec.

CONCLUSION

In general, pyrolysis of wood includes thermal decomposition of cellulose, hemicellulose and lignin (Wang *et al*., 2008). The *Platycladus orientalis* pyrolysis process can be divided into four stages. The second stage was slow, owing to the thermal instability of cellulose and partial cellulose decomposition. As temperature increased, this spectrum corresponds to the glass transition stage of pyrolysis (Ping *et al*., 2009; Shi and Du, 2003). The differences of different particle sizes is that the absorbance of the 1.0 and 2.0 mm lead to the obvious endothermic peak, implying that the smaller particle size leads to the more violent decomposition. In the final stage, the pyrolysis of lignin and charring of cellulose occur, From the TG and DTG curves, the weight of *Platycladus orientalis* simples has no obvious changes (Zhang and Zhang, 2013). From the DSC curves, the absorbance of the 1.0 and 2.0 mm lead to the higher the endothermic peak and the lower decomposition, the 0.1 mm *Platycladus orientalis* at about 68.44°C reaches large endothermic peak, which most caused by water molecules volatile during thermal desorption (Liao *et al*., 2002), During pyrolysis, gases containing carbon monoxide, carbondioxide water and other alkanes are generated. From the three-dimensional IR spectrum, it is observed that the *Platycladus orientalis* samples has high absorbance at 200, 525, 830, 1100 and 1420 sec, respectively during the thermal decomposition process, implying that the *Platycladus orientalis* samples decomposed more completely at these points of time. Absorbance refers to the difference between the intensity of the incident light before it passes through the gas product and the intensity of light transmitted through the gas products. A large change in absorbance implies a high concentration of the gas being analyzed. A characteristic carbon dioxide peak appears in the 2200-2400/cm range (Wang *et al*., 2008, 2006), the pyrolysis process enters the carbonization stage and CH, CO and C = O are broken down to produce methane, carbon dioxide, carbon monoxide and other gases and small molecules of phenols (Liao *et al*., 2002; Zhang and Zhang, 2013).

There are still some differences between different particle sizes during IR spectrum process: The 1.0 and 2.0 mm also exhibit higher absorbance at 830 and 1100 sec. However, the absorbance of the 1.0 and 2.0 mm are lower than that of the 1.0 mm at 830 sec, but higher than that of the 1.0 mm at 1100 sec. A large change in implies a high concentration of the gas being analyzed. This may be the larger the particle size leads to the slower particles decomposition. The absorbance of the 1.0 mm, there are some differences from points of time in which more gas produced. Fewer small-molecules produced and gas absorbance decreased when close to late. During pyrolysis, gases containing hydrocarbons, aldehydes, ketones, phenols, alcohols, carboxylic acids and other small molecules are generated owing to the thermal decomposition of cellulose, hemicellulose and lignin. Based on the above analysis, it may be concluded that wood vinegar formation occurs from the main pyrolysis stage until the charring stage. The analysis results are consistent with those of precious studies. It can be seen that the application of infrared spectrum verifies pyrolysis. Above all, wood vinegar is formed from the main pyrolysis stage until the charring stage.

ACKNOWLEDGMENT

This study was supported by the Fundamental Research Funds for the Central Universities (No. YX2013-09).

REFERENCES

Hu, R.R., Y.Q. Su and M.Q. Zhu, 2014. Research on antimicrobial and antioxidant activities of pyroligneousacids of Eucommiaul-moides branch dealing with different refined methods [J]. J. North West Forestry Univ., 29(2): 139-143.

Liao, Y.F., S.R. Wang, Z.Y. Luo *et al*., 2002. Research on cellu-lose pyrolysis kinetics [J]. J. Zhe Jiang Univ., 36(2): 171-176.

Luo, X.T., Z.Q. Wang, J.L. Wu and J.H. Wu, 2012. Study on the pyrolysis mechanism of polyethylene, polystyrene, and polyvinyl chloride by TGA-FTIR. J. Fuel Chem. Technol., 40(9): 1147-1152.

Ni, Q.Y., Y.L. Wu, M.D. Yang *et al*., 2011. Study on pyrolysis process of bischofitecrystallization by TG-FTIR [J]. Spectrosc. Spect. Anal., 31(7): 1747-1751.

Ping, A., G.T. Yang and X.J. Yu, 2009. Study on the wood vinegar in agricultural production [J]. J. Integr. Agric., 25(19): 244-247.

Ren, X.Y., H.S. Du, W.L. Wang *et al*., 2012. Study on gas-phase evolution law and pyrolysis of larchwood [J]. Spectrosc. Spect. Anal., 32(04): 944-948.

Shi, Y.Z. and X.G. Du, 2003. Study on the bamboo vinegar in agricultural production [J]. J. Integr. Agric., 19(03): 108-109.

Wang, S.R., Q. Liu, Y. Zheng *et al*., 2006. Mechanism study of biomass pyrolysis by thermo-gravimetric analysis coupled with infrared spectroscopy [J]. J. Eng. Thermo-phys., 27(2): 351-353.

Wang, W., Y.X. Lan and M. Li, 2008. Pyrolysis of pine sawdust by TG-FTIR analysis [J]. J. Agro-Environ. Sci., 27(1): 380-384.

Wang, W.P., Z.Y. Xue, F.X. Zhu, H. Qian and C.Z. Wu, 2005. Study on the bamboo vinegar in agricultural production [J]. J. Agric. Sci. Technol., 7(6): 53-55.

Zhang, X.M. and Y.Y. Zhang, 2013. Pyrolysis of pine sawdust by TG-FTIR analysis [J]. Renew. Energ., 31(9): 74-77.

Zhou, L., E.C. Jiang, Q. Zhang *et al*., 2007. Study on the wood vinegar in agricultural production [J]. Renew. Energ., 25(4): 56-60.

Zhou, L., F.J. Li and E.C. Jiang, 2012. Analysis of wood vinegar during the pyrolysis of cotton stalk by TG-FTIR [J]. Renew. Energ., 30(11): 74-77.