

Research Article

Thermogravimetry-Infrared Spectroscopy Analysis of the Pyrolysis of Willow Leaves, Stems, and Branches

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The pyrolysis of willow samples from various plant positions was analysed using thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR). The results indicate that pyrolysis can be divided into four stages. The first stage from 30 to 120°C involves free evaporation of moisture, with a mass loss of 5%. The second stage from 120 to 200°C involves the pyrolysis of hemicellulose and unstable cellulose, with a mass loss of 4%. The third stage is from 200 to 400°C, with a weight loss of 60%, in which the chemical components of wood thermally decompose and emit heat, carbon dioxide, and so on. In the final stage, which occurs above 400°C, the pyrolysis of lignin and charring of cellulose occur, with a mass loss of 10%. Moreover, in FTIR, the samples exhibit the highest absorbance during the main pyrolysis phase, from which wood vinegar ingredients mainly arise, including CO₂, H₂O, CO, and small amounts of hydrocarbons, alcohols, phenols, acids, esters, and aromatic compounds. Additionally, leaves are decomposed more thoroughly before the main pyrolysis phase, whereas decomposition of branches occurs fullest during this phase. Finally, we put forward some suggestions to support further research on conversion of willow into wood vinegar products.

1. Introduction

The willow tree has some excellent characteristics, such as fast growth, strong transpiration, and high biomass content. Willow not only provides a purification effect to the surrounding environment but also plays an important role as a natural landscape with good ecological effects. The willow wastewater facility (see Supplementary Material available online at <http://dx.doi.org/10.1155/2015/303212>) is a type of cleaning facility with zero discharge. This is the only type of facility that has a positive energy balance over its lifetime. In the zero-discharge wastewater system, willow can effectively absorb organic compounds and heavy metals from wastewater and thereby reduce environmental pollution. Additionally, in three years, willow can produce about 10–20 tons of dry matter per hectare, which can be used as building materials, woodchips, and wood vinegar.

Beside willow, there are a number of other sources of wood vinegar with varied performance characteristics.

The main components of wood vinegar, with the exception of water with a content of 80%–90%, are organic acids, phenols, alcohols, and ketones. Acids are the most typical components of wood vinegar and often account for more than 50% of the organic matter. The composition and component content of wood vinegar can be affected by different preparations, pyrolysis temperatures, and the type of raw materials [1–3]. In agriculture, wood vinegar is used to promote the growth of plants, improve soil fertility, eliminate pests, and so on. In addition, it has a wide range of other uses as a feed additive, deodorant and antibacterial agent. Wood vinegar also is safe for use with livestock [4].

Pyrolysis is a key step in the forest biomass conversion process and in the production of wood vinegar. However, this method lacks reliability when used alone [5]. In this context, TG-FTIR is an accurate and sensitive analytical technique with excellent reproducibility and is widely used in biomass pyrolysis and gasification research to improve the reliability and feasibility of pyrolysis experiments [6–8].

The formation mechanisms of different types of vinegar have been examined and their compositions and applications in agriculture have been reported in some previous studies [9–11]. The fundamental method of wood vinegar collection is thermal decomposition. However, for various applications, methods including standing only, distillation and membrane filtration, and distributing are common nowadays to refine vinegar production. Mao et al. analysed the antibacterial activity and chemical composition of bitter almond shell wood vinegar and concluded that its inhibitory abilities were strongest when the collection temperature was 170–370°C, where phenol and its derivatives are the main chemical components [12]. Using TG infrared (IR) technology, Adebayo et al. determined the composition of the pyrolysis products of *Pennisetum* and studied the pyrolysis mechanism [13]. Zhao et al. also adopted the TG and FTIR techniques to analyse the biomass pyrolysis process [14]. In addition, Liu et al. and Wang et al. studied the pyrolysis of willow at different heating rates and showed that the thermal cracking of wood during pyrolysis can be attributed to the presence of three major components, namely, cellulose, hemicellulose, and lignin [15, 16].

However, there has been little research on the pyrolysis of willow specimens from different parts of the plant. In this study, we have examined the pyrolysis of three types of willow samples collected from different parts of the plant, namely, leaves, stems, and branches, using TG-FTIR [17, 18]. The data reported in this paper is expected to help support further research on the conversion of willow into wood vinegar products.

2. Experimental

2.1. Materials. Selected leaves, stems, and branches from three parts of the willow plant in the zero-discharge wastewater system were used as samples for the experiments. The willow samples were air-dried at 90°C for 24 h. Then, the samples were ground into particles with a 0.1 mm grinder to obtain particle sizes of ≤ 0.1 mm.

The biomass of willow cultivars is known to have good thermophysical compositions and contain cellulose and hemicelluloses, with only small amounts of undesirable components, such as ash, sulfur, and chlorine [19].

2.2. Pyrolysis. The willow samples were first analysed using a PerkinElmer STA6000 TGA instrument to obtain 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 calcination 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⁻¹ was passed through the furnace to ensure an inert atmosphere. The initial temperature of the furnace was set at 30°C. Once the furnace

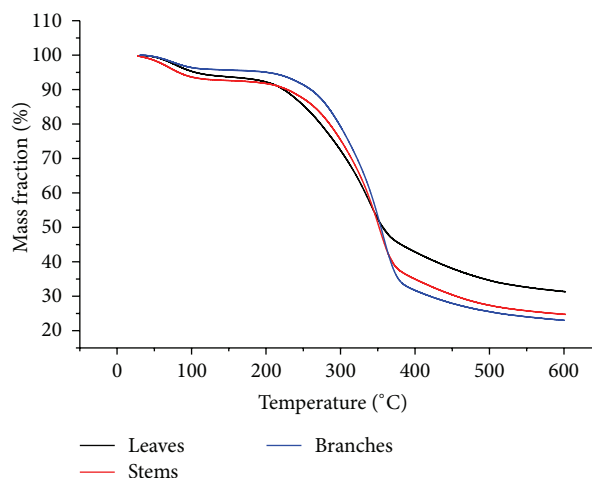


FIGURE 1: TGA curves for the three types of willow samples.

stabilised at 30°C, the sample was heated from 30 to 600°C at a heating rate of 20°C min⁻¹.

2.3. IR Spectroscopy. The decomposition gases generated during pyrolysis were analysed by IR spectroscopy using a PerkinElmer Spectrum 100 FTIR spectrometer. The line 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 the IR frequency range of 4500–600 cm⁻¹.

3. Results and Discussion

3.1. Thermogravimetric Analysis (TGA) and Derivative TGA Curves. The willow samples underwent a series of complex chemical reactions during the pyrolysis process. Figures 1 and 2 are the TGA and derivative TGA curves, respectively, for the three types of willow samples. In the TGA curves, the rate of change of mass was continuously recorded as a function of temperature. The derivative TGA curves were obtained by computing the first derivative of the TGA curves with respect to temperature.

Based on Figure 2, the willow pyrolysis process can be divided into four stages. The first of these stages lasts from 30 to 120°C with the first TGA peak at about 75°C. During this stage, moisture evaporates freely from the willow samples. Moisture evaporation is an endothermic process and the weight loss during the first stage is about 5%. The second stage occurs from 120 to 200°C. During this stage, the pyrolysis of hemicellulose and unstable cellulose occurs and the mass loss is about 4%. The third stage lasts from 200 to 400°C. The maximum pyrolysis rate is achieved in this stage at a temperature of 360°C and the weight loss during the third stage is about 60%. In this temperature range, carbonisation occurs and the various chemical components of wood, such as lignin, hemicellulose, and cellulose, undergo thermal decomposition to emit carbon dioxide,

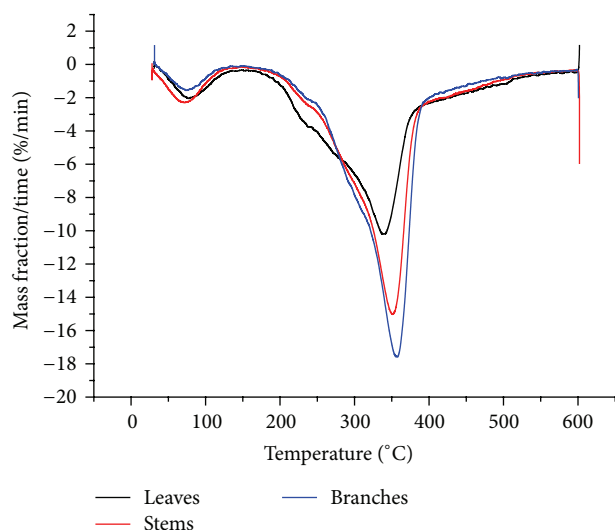


FIGURE 2: Derivative TGA curves for the three types of willow samples.

carbon monoxide, methane, methanol, wood tar, and so forth, while simultaneously emitting heat. Finally, the fourth stage of pyrolysis occurs between 400 and 600°C. During this stage, pyrolysis of lignin and charring of cellulose take place. This final phase is exothermic and the mass loss is about 10%.

It is evident from Figure 1 that the trends in the TGA curves for the three samples are similar. The curves of the stems and branches lie close to each other; however, there is a significant difference compared with that of the leaves. This indicates that different parts of the willow plant exhibit significantly different behaviour during the third and fourth stages. In addition, branches exhibit smaller mass loss rates below 360°C and larger ones above 360°C. This observation may be accounted for by thermal decomposition during the third stage of the chemical components of wood, such as lignin, hemicellulose, and cellulose, which are more abundant in branches, to emit heat, carbon dioxide, carbon monoxide, methane, methanol, wood tar, and so forth. Next, with increasing time and temperature, the branches of willow release more heat, as a result of which the willow particles are completely decomposed. Lignin, hemicellulose, cellulose, and other chemical components in the particles produce more carbon dioxide, carbon monoxide, methane, methanol, wood tar, and so forth, as the extent of thermal decomposition increases. Therefore, the mass loss increases above 360°C.

The differential scanning calorimetry (DSC) curves for the three types of willow samples are shown in Figure 3. DSC is a reliable thermal analysis technique. The vertical axis of the curve is the amount of heat per unit time and the horizontal axis represents the temperature. The area under the curve is proportional to the change in the heat. From Figure 3, it is evident that the willow branches, which have the curve with the highest peak at 75°C, absorb the most heat from 30 to 75°C. The large endothermic peak at about 75°C is mainly a result of the volatilisation of water present in the willow

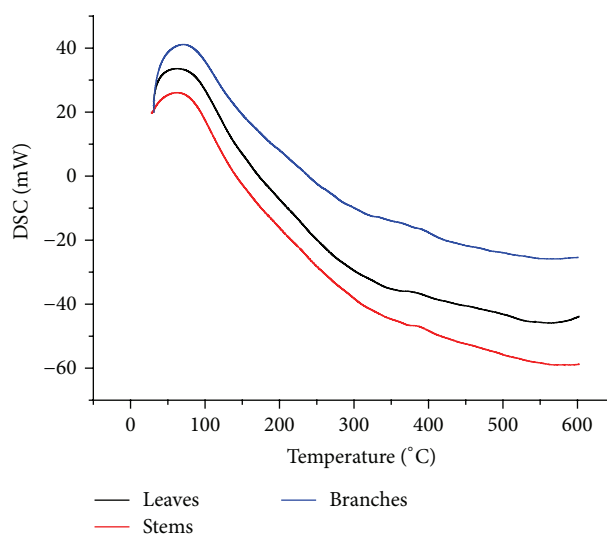


FIGURE 3: DSC curves for the three types of willow samples.

wood flour and the absorption of the heat emitted during endothermic heat volatilisation. Moreover, the DSC curve corresponding to the willow leaves is more similar to that of stems than that of the branches. The endothermic peak is mainly caused by the thermal decomposition of cellulose at about 370°C.

3.2. Pyrolysis and IR Analysis of Willow Samples Collected from Different Stalk Positions. A large absorbance value implies that the gas being analysed has a high concentration. From Figures 4(a), 5(a), and 6(a), it is observed that the willow samples exhibit high absorbance values at 200, 525, 830, 1100, and 1420 s during the thermal decomposition process, implying that the willow sample decomposes more severely at these points of time.

Figure 4(a) shows the three-dimensional IR spectrum of willow leaves. The characteristic absorption peaks of some functional groups can be known from the FTIR analysis of previous reports as mentioned above [11–15]. In Figure 4(b), which is the FTIR spectrum acquired at 200 s, peaks corresponding to gaseous and liquid water molecules can be seen at 3500–3950 cm^{-1} and 3400–3500 cm^{-1} , respectively. This corresponds to the TG-DTG curve peak at about 75°C, which is regarded as the water loss phase. Moreover, a characteristic carbon dioxide peak appears in the 2200–2400 cm^{-1} range, which may be caused by the decomposition of hemicellulose with poor thermal stability. The peak at 2820–2930 cm^{-1} corresponding to the C–H stretching vibration and the peak at 2800 cm^{-1} attributed to methane are also produced by hemicellulose. In addition, the peak at 3356–3600 cm^{-1} corresponds to the O–H stretching vibration, which confirms the appearance of alcohols. In Figure 4(c), the FTIR spectrum acquired at 525 s shows an increase of the characteristic carbon dioxide peak compared with that of Figure 4(b), which is due to the glass transition stage of pyrolysis. At the same time, the absorbance of alcohols and phenolic compounds near 3000 cm^{-1} also increases.

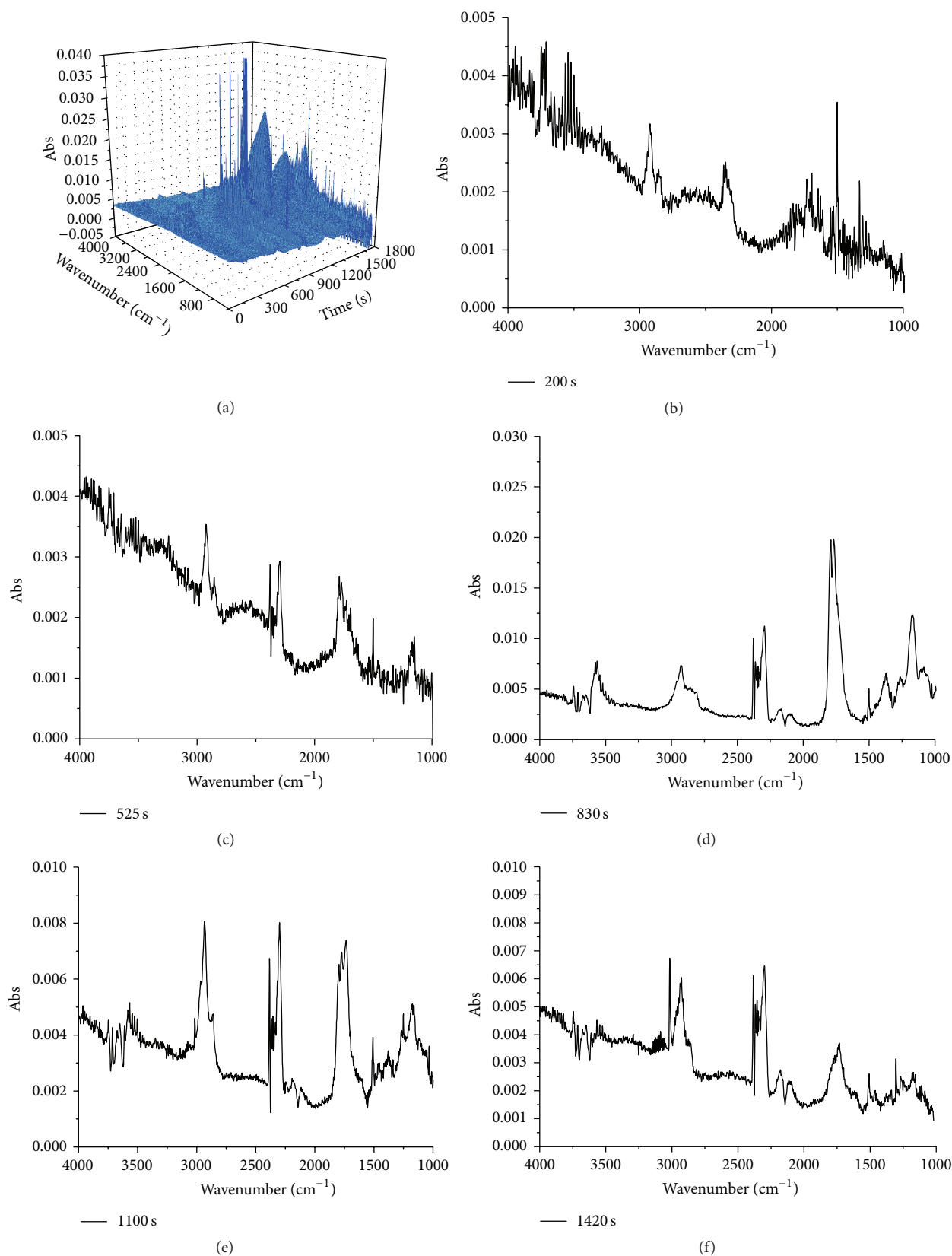


FIGURE 4: FTIR spectra of willow leaves at different times. (a) Three-dimensional IR spectrum of willow leaves and IR spectra obtained at (b) 200 s, (c) 525 s, (d) 830 s, (e) 1100 s, and (f) 1420 s.

The broad peak in the range of $1680\text{--}1700\text{ cm}^{-1}$ corresponds to $\text{C}=\text{O}$, representing the presence of ketone and aldehyde functional groups. Furthermore, the peak at $2820\text{--}2960\text{ cm}^{-1}$ is strengthened, which may be caused by the $\text{C}\text{--}\text{H}$ stretching vibration of aromatic compounds. We believe that the spectra in Figure 4(c) indicate the softening of hemicellulose accompanied by the evolution of small amounts of low molecular weight volatile gases and partial cellulose decomposition at a temperature of about 200°C . From Figures 4(d) and 4(e), the rates of decomposition are observed to be much higher at 830 and 1100 s, which correspond to decomposition temperatures of about 280 and 390°C , respectively, referring to Figure 2. In these spectra, it is clear that the peak observed at $1200\text{--}1300\text{ cm}^{-1}$ corresponds to carboxylic acid groups, the peak at $1000\text{--}1100\text{ cm}^{-1}$ corresponds to ethanol, and the peak at 3000 cm^{-1} is attributed to methanol. Moreover, the peak at $1000\text{--}1500\text{ cm}^{-1}$ originates from the vibration of the benzene ring, the peak at 1370 cm^{-1} corresponds to $\text{C}\text{--}\text{O}$, and the peak at 1743 cm^{-1} represents $\text{C}=\text{O}$. Further, the peak at 2800 cm^{-1} attributed to methane is obvious. Therefore, we can conclude that gases containing hydrocarbons, aldehydes, ketones, phenols, alcohols, carboxylic acids, and other small molecules are generated during the third stage. From Figure 4(f), we can determine that the temperature corresponding to the production of methane is about 500°C . At this temperature, the pyrolysis process enters the carbonisation stage, and $\text{C}\text{--}\text{H}$, $\text{C}\text{--}\text{O}$, and $\text{C}=\text{O}$ bonds are broken down to produce methane, carbon dioxide, carbon monoxide, and other gases and small phenolic molecules [20].

As evidenced from Figures 4, 5, and 6, the IR spectra obtained for the three types of willow samples are substantially similar. The IR spectra of the three types of willow materials at 200, 525, 830, 1100, and 1420 s indicate that vigorous thermal decomposition occurs at these times and gases are continuously generated. Overall, the absorbance of the willow stems is lower than that of the leaves. The stems and branches also exhibit higher absorbance at 830 and 1100 s because more gas is produced at these two times during the pyrolysis process. However, the absorbance of the stems and leaves is lower than that of the branches at 830 s but higher than that of the branches at 1100 s. This may be attributed to the different chemical components of the three samples. Further, for the different stalk positions, there are differences in the time at which more gas is produced. The amount of gas generated decreases over the course of the IR spectrum scanning process, and, consequently, acids, alcohols, aldehydes, phenols, and so forth, in addition to some gases, can be detected. The presence of these substances indicates that cellulose, hemicellulose, and lignin decompose, which produces heat.

Above all, it can be seen that monitoring the pyrolysis process via IR spectroscopy enables verification of the steps that occur during the process and the products generated. Moreover, the pyrolysis products mainly consist of CO_2 , H_2O , and CO , as well as a small amount of hydrocarbons, alcohols, phenols, acids, esters, and aromatic compounds. Based on the thermal IR spectra, the decomposition of the willow particles can be divided into four stages, namely, water

loss, degradation of hemicellulose and unstable cellulose, decomposition of cellulose and lignin, and charring. Wood vinegar is formed from the main pyrolysis stage until the charring stage. The analysis results are consistent with those of Biagini et al. and Pétrissans et al. [21, 22].

4. Conclusions

From the DTG and DSC plots, it can be concluded that the primary pyrolysis stage for the three types of willow samples occurs in the $200\text{--}400^\circ\text{C}$ range. However, the peak in the TG curve for the willow branches is more pronounced than those for the willow stems and leaves, indicating that the willow branches decompose more evenly and thoroughly compared with the other two samples. Therefore, the actual rate of heating in large particles is below the values set in the heating rate experiments [17].

Thermal decomposition of the willow particles occurs in four stages, namely, water loss, hemicellulose and unstable cellulose decomposition, decomposition of cellulose and lignin, and charring. These stages reflect the formation of wood vinegar. From the three-dimensional IR spectra, willow particles are found to exhibit higher absorbance during thermal decomposition at 200, 525, 830, 1100, and 1420 s. The thermal IR spectroscopy results suggest that the formation of wood vinegar, including CO_2 , H_2O , CO , and small amounts of hydrocarbons, alcohols, phenols, acids, esters, and aromatic compounds, occurs mainly from the main pyrolysis stage until the charring stage.

According to the qualitative results of these experiments, we put forward some suggestions to improve conversion of willow into wood vinegar products.

- (1) For willow materials with the same particle size, when the collecting temperature is below 200°C , we can acquire more active ingredient from willow leaves, whereas when the temperature is above 200°C , branches should be chosen.
- (2) With an increase of temperature, more types of ingredients arise. It is suggested to collect willow wood vinegar over different temperature ranges to obtain targeted components for various purposes more efficiently and effectively.
- (3) In the preparation of rough wood vinegar, the amount of organic content obtained directly through pyrolysis is small. Therefore, it is necessary to optimize equipment and improve purification during the refining process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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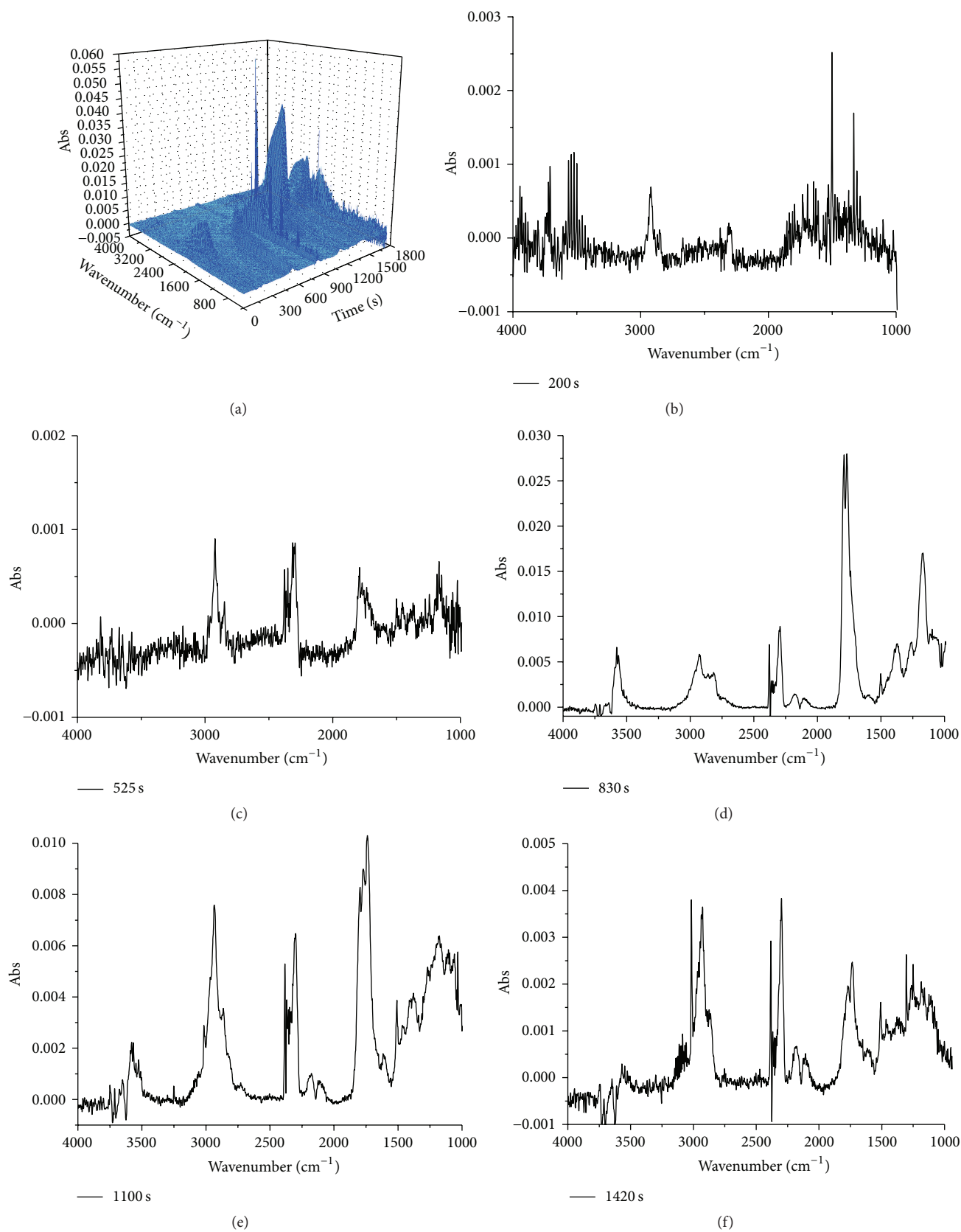


FIGURE 5: FTIR spectra of willow stems at different times. (a) Three-dimensional IR spectrum and IR spectra obtained at (b) 200 s, (c) 525 s, (d) 830 s, (e) 1100 s, and (f) 1420 s.

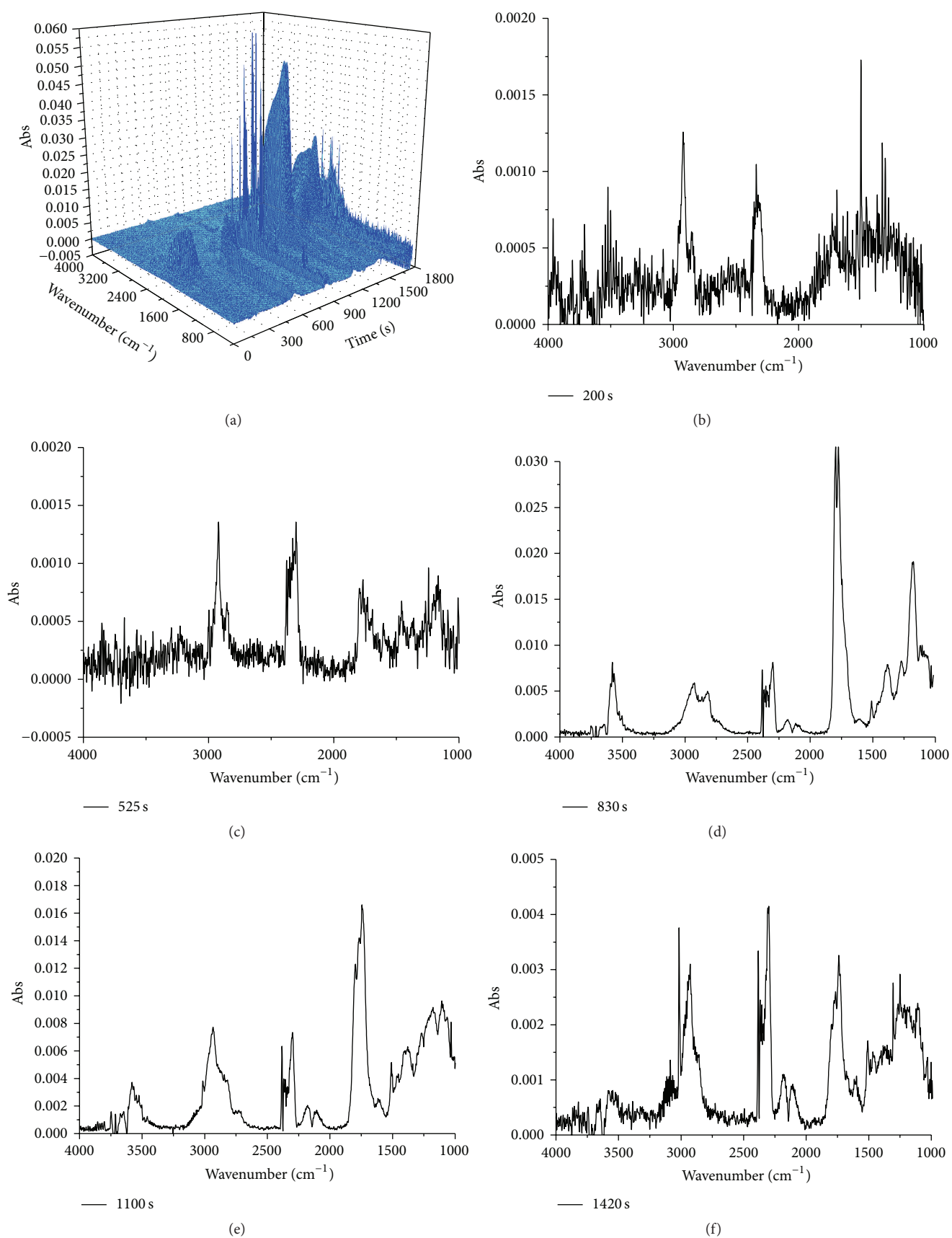


FIGURE 6: FTIR spectra of willow branches at different times. (a) Three-dimensional IR spectrum and IR spectra obtained at (b) 200 s, (c) 525 s, (d) 830 s, (e) 1100 s, and (f) 1420 s.

the National Forestry Bureau (no. 2012-39). The authors would like to thank Editage [<http://online.editage.cn/>] for English language editing.

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