ARTICLE

# Elucidation of the Thermal Deterioration Mechanism of Bio-oil Pyrolyzed from Rice Husk Using Fourier Transform Infrared Spectroscopy

Fang Xu,[†] Yu Xu,[†,‡] Rui Lu,[†] Guo-Ping Sheng,*,[†] and Han-Qing Yu[†]

[†]Department of Chemistry and [‡]Anhui Key Lab for Biomass Clean Energy, University of Science and Technology of China, Hefei, 230026, China

**ABSTRACT:** In this study, the rationale for exploring the thermal deterioration mechanism of the bio-oil pyrolyzed from rice husk is established. This is based on identification of the unstable intermediates in the thermal deterioration process. Fourier transform infrared (FTIR) spectroscopy was used to monitor such a thermal deterioration process of bio-oil samples in thermal treatment and/or during long-term storage at ambient temperatures of $20-30$ °C. Terminal olefins, as a key intermediate, so-called "signature", were identified qualitatively by using FTIR spectroscopy. A band shift observed at 880 cm$^{-1}$, which was assigned to the C—H out-of-plane deformation vibration of terminal olefins, indicates the start-up of the bio-oil thermal deterioration. A two-step pathway was proposed to describe the thermal deterioration process of bio-oil. This study suggests that the status of bio-oil could be rapidly monitored by the FTIR method.

**KEYWORDS:** Bio-oil, rice husk, thermal deterioration, FTIR, polymerization, mechanism

## ■ INTRODUCTION

The need for clean sources of energy is receiving growing interest because of declining petroleum resources, increased demand for petroleum, and environmental concerns about fossil fuels.[1−3] Studies are being conducted worldwide to develop new technologies for energy generation from renewable resources.[2−4] Today, the conversion of biomass into bio-oils using fast pyrolysis technologies is one of the most promising alternatives under study to convert biomass into useful products, for example, organic acids, alcohols, phenols, etc., and energy.[3] Agricultural residues, such as rice husks, rice stalks, wheat stalks, corn stalks, cotton stalks, etc., are typical biomass feedstocks for bio-oil production.[5−9] As compared with other biomass materials, rice husk has some favorable physical properties, for example, small particle size and high density for fast pyrolysis. The particle size of rice husk is sufficiently small for direct pyrolysis without complex pretreatment. A series of studies have been conducted on fast pyrolysis of rice husks,[5,6] which are favorable feedstocks for pyrolysis.

The chemical composition of bio-oils is very complex, and it is mainly composed of complex organic mixtures, such as organic acids, alcohols, aldehydes, phenols, etc. It is well-known that bio-oil is highly acidic and viscous and thermally and kinetically unstable.[10,11] For fuel application, bio-oil has to be preheated prior to its combustion to lower its viscosity and improve its atomization. The difficulties encountered in bio-oil processing and handling are attributed mainly to the great variability of their properties, such as the low thermal stability and the colloidal nature. Difficulties such as filter and nozzle plugging at low feeding temperature, jamming and sticking of the injection system after stopping operation, or an agglomeration of structures in recirculation systems are among the problems encountered in bio-oil combustion tests.[4,5,12,13]

The properties of bio-oil can be altered significantly at elevated temperatures and/or long-term ambient storage. The viscosity increases significantly, and eventually, phase-separation takes place. The water content increases, and the higher heating value (HHV) would decrease quickly. All of these show that the quality of bio-oil degrades significantly after storage and affects its further utilization. Therefore, it has become necessary to better understand their behavior changes at elevated temperatures and/or long-term storage at ambient temperatures. A substantial amount of work has been done regarding the thermal deterioration of bio-oil.[4,5,13−17] The present research focuses of this field are discovery of the relationship between the colloidal properties and basic fuel specifications through measuring and determining viscosity, volatiles, molecular weight distribution, water content, heating value, density, flash point, surface tension, thermal conductivity, etc. To date, the thermal deterioration process of bio-oil is unclear yet. A better understanding of the thermochemical characteristics of bio-oil is beneficial for adequate handling and eventual upgrading such a unique liquid fuel.

There are many analytical methods for bio-oil analysis, such as gas chromatography with flame ionization detector (GC/FID),[9] gas chromatography with mass spectrometry detector (GC/MS),[12,14,17] high-pressure liquid chromatography (HPLC),[18] gel permeation chromatography (GPC),[15,17,19] and nuclear magnetic resonance (NMR).[19] These methods require either expensive instruments or time-consuming sample pretreatment. This hinders their use for practical situations, for example, monitoring the changes of their behaviors in the thermal process.

Fourier transform infrared spectroscopy (FTIR) is a fast, cheap, reliable, accurate, and nondestructive analytical technique and allows the qualitative determination of the characteristic vibrational mode of each molecular group in samples.[11,18,19]

FTIR spectroscopic analysis methods are rapidly becoming a workhorse technique for providing data on bio-oil component analysis.[5,18−20] The libraries of FTIR bands are available for component analysis. The usefulness of this technique has also been demonstrated in similar fields, such as olive oil,[21] sunflower oil,[22] soy oil,[23] wine,[24] beer,[25] etc., to tackle thermal deterioration, authentication, and adulteration problems. During the bio-oil storage process, a series of deterioration reactions occurred, and many new functional groups would be formed. The FTIR method can provide such information on the functional groups rapidly and accurately. It is highly recommended for quickly monitoring the bio-oil quality in the storage and/or process control in refinery processing. FTIR analytical results can also give some useful information to elucidate the bio-oil thermal deterioration mechanism through monitoring the thermal process and its deterioration products.

Thus, the main objective of this study is to evaluate the quality of bio-oil in thermal treatment and/or long-term storage at ambient temperatures by the FTIR method and to investigate the deterioration mechanisms of bio-oil under thermal treatment and/or long-term storage at ambient temperatures (20−30 °C).

## ■ MATERIALS AND METHODS

**Bio-oil Sample Production.** Bio-oil was pyrolyzed from rice husk using a continuous autothermal fast pyrolysis set, which was described in detail elsewhere.[5,6] The naturally air-dried rice husk with a moisture content of 12 wt % was transported into the fluidized bed dryer with a screw feeding system. The residence time of pyrolysis vapors in the reactor was less than 2 s, and the pyrolysis temperature was 450 °C. The fresh bio-oil was filtered by centrifugation to remove large-sized solid particles and then stored at −20 °C for use.

**Bio-oil Characterization.** Bio-oils pyrolyzed from extractive-rich biomass materials were separated into two phases: the top phase rich in extractives and the bottom phase closely resembling the usual bio-oils derived from extractive-free feedstocks.[16] Because a thin top phase floating on the bottom phase in the oil tank was found, the bottom phase of the bio-oil was used for analysis and regarded as the rice husk bio-oil in this study. Both the rice husk with a moisture content of 12 wt % and the bio-oil were analyzed for their elemental compositions using an element analyzer (Vario EL-III, Elementar Inc., Germany). Other physicochemical properties were also determined according to a previous study.[5] The main physicochemical properties of the bio-oil are listed in Table 1.

**GC/MS Analysis.** GC/MS analysis of bio-oil was performed with a Thermo Trace GC/Ploars Q ion Trap mass spectrometer. The GC has a TR-35MS capillary column (30 m × 0.25 mm × 0.25 μm). Helium (99.99%) was used as the carrier gas with a constant flow rate of 1.0 mL/min. An autosampler was used, and split injection was performed at a split ratio of 50. The oven temperature was programmed from 50 °C for 5 min then 4 °C min$^{−1}$ to 280 °C and held for 15 min. MS was operated with the following conditions: transfer line, 220 °C; ion source, 220 °C; and electron energy, 70 eV.

**Thermal Stability.** The bio-oil thermal stability during storage was tested under ambient and/or accelerated aging conditions at 80 °C. In the ambient aging tests, the FTIR spectra of the bio-oil samples after

### Table 1. Main Physicochemical Properties of the Bio-Oil Pyrolyzed from Rice Husk

| property | value | property | value |
|---|---|---|---|
| pH | 2.8 | extractives (wt %) | 1.3 |
| density (g/mL, 25 °C) | 1.115 | ash (wt %) | 0.25 |
| water content (wt %) | 30.0 | higher heating value (MJ/kg) | 16.5 |
| solids (wt %) | 0.5 | flash point (°C) | 68 |

### Table 2. Elemental Compositions of Bio-oil and Rice Husk (wt %)

| element | bio-oil | rice husk |
|---|---|---|
| carbon | 39.91 ± 0.07 | 38.68 ± 0.07 |
| hydrogen | 8.16 ± 0.09 | 5.42 ± 0.08 |
| oxygen | 51.28 ± 0.10 | 55.02 ± 0.12 |
| nitrogen | 0.62 ± 0.02 | 0.67 ± 0.04 |
| sulfur | 0.03 ± 0.01 | 0.21 ± 0.01 |
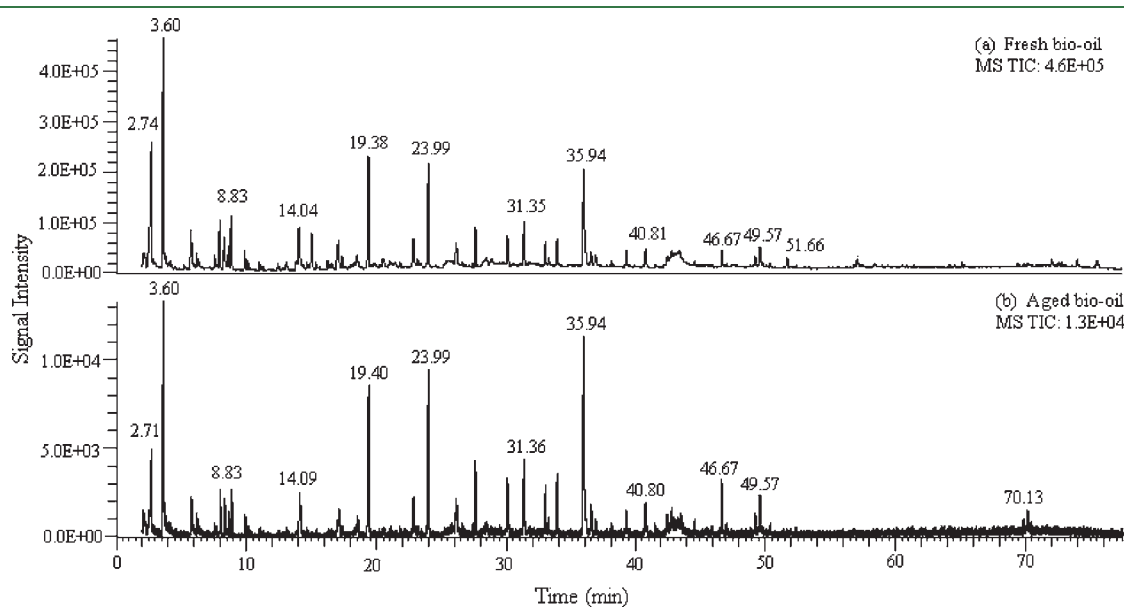


**Figure 1.** GC/MS chromatograms of the bio-oil samples pyrolyzed from rice husk: (a) Fresh bio-oil and (b) bio-oil aged at an elevated temperature of 80 °C for 72 h.

**Table 3. Main Chemical Compositions of the Bio-Oil**

| sample no. | compd | retention time (min) | molecular weight |
|---|---|---|---|
| 1 | acetic acid | 2.71 | 60.05 |
| 2 | hydroxyacetic acid | 3.60 | 76.05 |
| 3 | ethyl acetate | 5.75 | 88.05 |
| 4 | methyl acetate | 6.17 | 74.08 |
| 5 | 2-ethenylfuran | 7.52 | 94.04 |
| 6 | methyl 3-butenoate | 7.94 | 100.05 |
| 7 | furfural | 8.29 | 96.02 |
| 8 | *cis*-1-cyclopentene-3,4-diol | 8.60 | 100.05 |
| 9 | methacrylic acid methyl ester | 8.83 | 100.05 |
| 10 | acetic anhydride | 9.85 | 102.03 |
| 11 | 2,3-pentanedione | 10.09 | 102.03 |
| 12 | 2-methyl-2-cyclopentenone | 10.98 | 96.02 |
| 13 | *trans*-cyclopent-1-nen-3,5-diol | 14.04 | 100.05 |
| 14 | valerolactone | 15.04 | 100.05 |
| 15 | 6-methyl-3,4-dihydro-2*H*-pyran-2-one | 17.12 | 112.05 |
| 16 | *m*-cresol | 17.35 | 108.05 |
| 17 | *p*-cresol | 18.54 | 108.05 |
| 18 | 4-methoxy-phenol | 19.38 | 124.05 |
| 19 | 4-ethyl-phenol | 22.84 | 122.07 |
| 20 | 2-methoxy-4-methyl-phenol | 23.99 | 138.06 |
| 21 | vinyloxy-benzene | 26.13 | 120.05 |
| 22 | 4-ethyl-2-methoxy-phenol | 27.62 | 152.08 |
| 23 | 2-methoxy-4-vinyl-phenol | 30.07 | 150.06 |
| 24 | eugenol | 31.35 | 164.08 |
| 25 | 3,4-dimethoxy-phenol | 33.00 | 154.06 |
| 26 | (3,4-dimethoxy-phenyl)-methoxy-methanol | 33.27 | 198.08 |
| 27 | 2-methoxy-5-propenyl-phenol | 33.89 | 164.08 |
| 28 | 2-methoxy-4-propenyl-phenol | 35.94 | 164.08 |
| 29 | 4-methoxy-3-methoxymethyl-phenol | 36.51 | 168.08 |
| 30 | 3-methyl-cyclohex-3-enecarbaldehyde | 36.84 | 124.09 |
| 31 | 2,6-dimethyl-benzene-1,4-diol | 38.13 | 138.07 |
| 32 | 1-(4-hydroxy-3-methoxy-phenyl)-ethanone | 39.33 | 166.06 |
| 33 | 1-(4-hydroxy-3-methoxy-phenyl)-propan-2-one | 40.80 | 180.08 |
| 34 | 4-allyl-2,6-dimethoxy-phenol | 42.46 | 194.09 |
| 35 | 4-(3-hydroxy-propenyl)-2-methoxy-phenol | 42.80 | 180.08 |
| 36 | 3-(3-hydroxy-4-methoxy-phenyl)-acrylic acid | 44.59 | 194.06 |
| 37 | 3-hydroxy-4,5-dimethoxy-benzaldehyde | 47.05 | 182.06 |
| 38 | 1-(4-hydroxy-3,5-dimethoxy-phenyl)-ethanone | 49.23 | 196.07 |
| 39 | 3-(4-hydroxy-2-methoxy-phenyl)-propenal | 49.57 | 178.06 |

different storage periods at ambient temperatures were measured. The bio-oil sample kept at −20 °C was used as a control. In the accelerated aging tests, 50 g of bio-oil samples was placed in 100 mL round-bottomed glass flasks equipped with reflux condenser and heated under magnetic stirring for 24, 48, 72, 96, and 120 h, respectively. The bio-oils

split into two phases in the accelerated aging process. The upper layer still kept liquid, and the bottom layer became waxy-like high molecular weight (MW) compounds. Weights of the flasks were measured before and after aging tests to ensure no loss of volatiles. Each test was conducted five times, and the upper layer samples of the aged bio-oil were collected for FTIR analysis.

**FTIR Measurements.** FTIR spectra were recorded on a VERTEX 70 FT-IR spectrometer (Bruker Inc., Germany) operated at a setting of 32 scans at a spectral resolution of 4 cm$^{-1}$. A small quantity (~2 $\mu$L) of the bio-oil samples was applied without dilution using the KRS-5 windows. Triplicate spectra were collected for each sample. All spectra were recorded from 4000 to 400 cm$^{-1}$ and processed with the OPUS software (Bruker Inc., Germany). A daily spectrum of the clean KRS-5 window was used as the background. All FTIR spectra were normalized after acquisition for comparison.

## ■ RESULTS AND DISCUSSION

**Elemental Compositions and GC/MS Results.** Bio-oil was produced by pyrolysis process, in which the rice husk with a moisture content of 12 wt % was fast heated in the absence of air, forming a gaseous product, and then condensed. The elemental compositions of the bio-oil with a moisture content of 30 wt % and the rice husk with a moisture content of 12 wt % are given in Table 2. The bio-oil had higher contents of carbon and hydrogen than the rice husk but lower contents of oxygen, nitrogen, and sulfur. As compared with the commonly used petroleum fuels, high oxygen and nitrogen contents indicate that a high level of polar functional groups (−OH, −NH$_2$, −COOH, etc.) was present in the bio-oil.

In this study, full-scan GC/MS was applied to obtain peaks and spectra for individual compounds. The crude bio-oil was dissolved by methanol and then analyzed by GC/MS. A typical GC/MS chromatogram of the fresh bio-oil pyrolyzed from rice husk is displayed in Figure 1a, and the main organic components are listed in Table 3. However, bio-oil is a very complex organic mixture in terms of number of chemically distinct constituents. As listed in Table 3, the detected components were mainly low-MW oxygenated organic compounds in a range of $m/z$ = 60.05 to $m/z$ = 198.08, including organic acids, alcohols, aldehydes, esters, ketones, sugars, phenols, and furans. Abundant polar functional groups present in the bio-oil were further validated by the GC/MS analytical results. However, GC/MS is unable to detect some high MW or high boiling point products, which are retained in the injection system or the capillary column. After long-term storage at ambient temperatures or elevated temperatures aging process, the GC/MS total ion currents (TIC) of the aged bio-oil samples decreased significantly. Figure 1b shows a GC/MS chromatogram of the aged bio-oil at an elevated temperature of 80 °C for 72 h. The variation of the TIC intensity indicates that the volatile molecules decreased substantially caused by polymerization in the aging process at elevated temperatures or long-term storage at ambient temperatures.

**Thermal Stability.** A typical FTIR spectrum of fresh bio-oil sample is shown in Figure 2a. The functional groups identified from FTIR spectrum of the bio-oil are listed in Table 4. Accelerated aging upon heating of bio-oil at elevated temperatures enhances secondary reactions that require a high activation energy. To evaluate the thermal susceptibility of the bio-oil, FTIR analysis was performed in the thermal treatment process (80 °C).

Figure 2 shows the normalized FTIR spectra of bio-oil samples sampled at different aging times. A quick survey of Figure 2 reveals

9245

dx.doi.org/10.1021/jf202198u |*J. Agric. Food Chem.* 2011, 59, 9243–9249
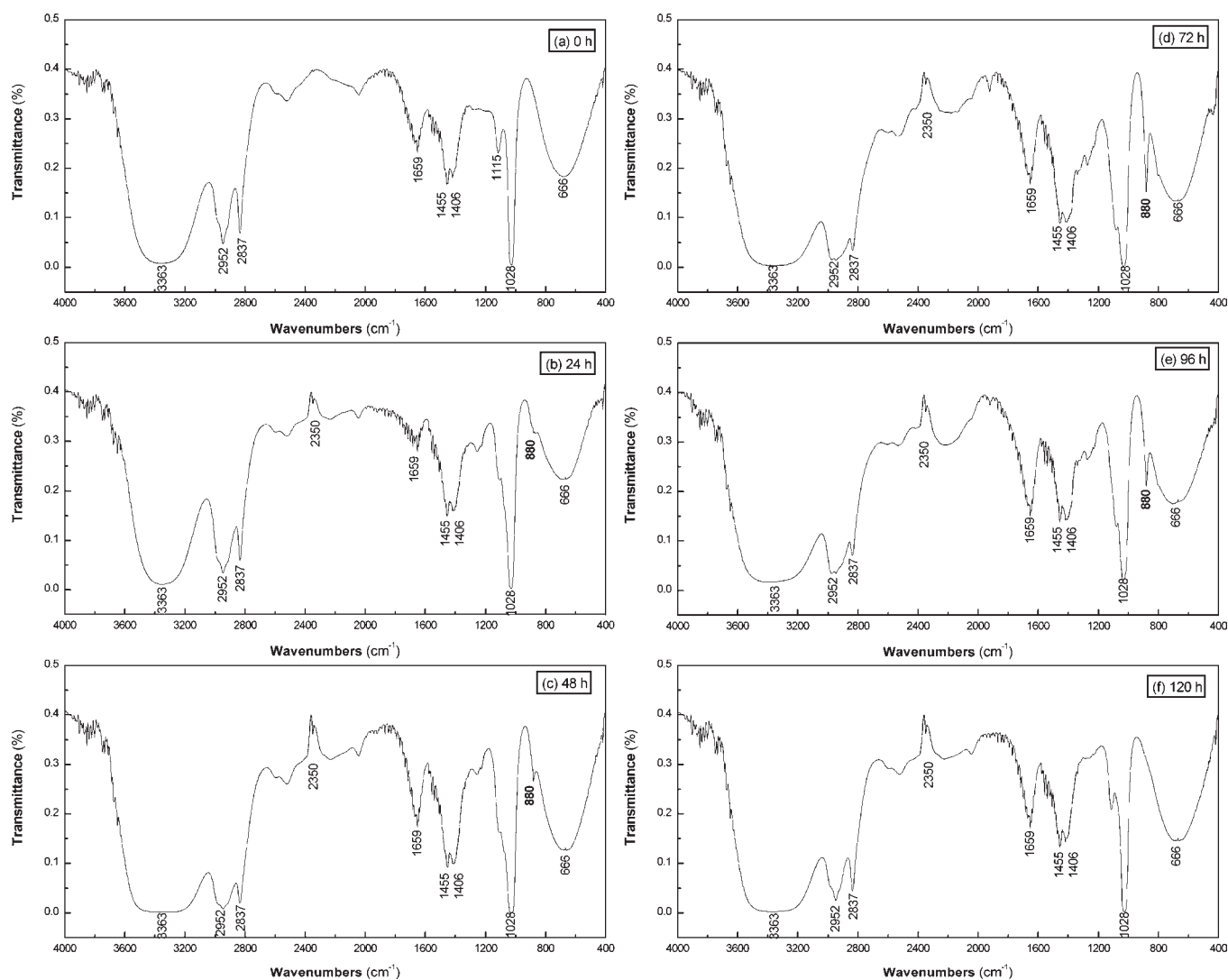
**Figure 2.** FTIR spectra of bio-oil samples at an elevated temperature of 80 °C with different aging times: (a) 0 (fresh bio-oil), (b) 24, (c) 48, (d) 72, (e) 96, and (f) 120 h.

that there was a difference in the condition of the bio-oil at the different aging times that correlate with the deterioration of the bio-oil. As shown in the normalized FTIR spectra, the absorbance intensity of the peak of 880 cm$^{-1}$ increased significantly in the initial 72 h and then decreased in the subsequent 48 h. In addition, decarboxylation of organic acids produced carbon dioxide in the accelerated aging process. Carbon dioxide was present at a high concentration, and it absorbs strongly at 2350 cm$^{-1}$ in the FTIR spectra of the aged bio-oil samples. The absorbance band at 880 cm$^{-1}$ was assigned to out-of-plane deformation vibration of C—H of terminal olefins, whereas the absorbance band at 2350 cm$^{-1}$ was attributed to asymmetric stretching vibration of C=O of carbon dioxide. The bio-oil was separated into an upper layer rich in polar compounds and a bottom layer mainly composed of polymerized waxylike materials in the thermal process. The phase separation and the variation of FTIR spectra indicate that a series of reactions occurred in the thermal treatment.

**Storage Stability of the Bio-oil at Ambient Temperature (20—30 °C).** To further explore the bio-oil stability, the FTIR spectra of the bio-oil samples after different storage periods at ambient temperatures were measured, as shown in Figure 3. The FTIR spectrum of the bio-oil sample kept at −20 °C showed no obvious change as compared to the fresh bio-oil. The FTIR results indicate no significant change in the first year at ambient temperatures. However, after storage for 2 years, there was a new peak at 880 cm$^{-1}$, indicating the formation of new terminal olefins in the aging process at ambient temperatures. The variation of persistent increase at the peak of 880 cm$^{-1}$ held on in the third year of storage.

The experimental results above clearly demonstrate that the FTIR method is an ideal fast monitoring method for monitoring the thermal deterioration process in the aging process at elevated temperatures and/or long-term storage at ambient temperatures. Key intermediates of the thermal deterioration process were identified qualitatively using the FTIR spectroscopy. The FTIR band shift at 880 cm$^{-1}$ was used as a signature in monitoring the bio-oil quality, which was assigned to the C—H out-of-plane deformation vibration of terminal olefins.

The chemical composition of bio-oils is very complex, and many components become polymerized and condensed with time, and such a process is accelerated by increasing temperature, oxygen exposure, and light exposure.[12,13] These reactions result

9246

dx.doi.org/10.1021/jf202198u |*J. Agric. Food Chem.* 2011, 59, 9243–9249

**Table 4. Evaluation of the FTIR Spectrum of the Bio-Oil**

| absorbance frequency (cm$^{-1}$) | assignment |
| --- | --- |
| 3363 (broad absorbance) | O—H stretching vibration of the hydroxyl groups |
| | N—H stretching vibration of the amino groups |
| | broad absorbance: hydrogen bond effect in the present of water, alcohols, organic acids, etc. |
| 2957, 2837 | symmetric and asymmetric stretching vibration of the aliphatic CH$_2$ group |
| | symmetric and asymmetric stretching vibration shoulder of the aliphatic CH$_3$ group |
| 1659 | C=C stretching vibration of carbon—carbon double bonds |
| | C=O stretching vibration of carbonyl groups |
| 1455 | bending vibrations of the CH$_2$ and CH$_3$ aliphatic groups |
| 1406 | rocking vibrations of C—H bonds of olefins |
| 1028 | stretching vibration of the C—O ester groups |
| 880 | out-of-plane deformation vibration of C—H of terminal olefins |
| 666 (broad absorbance) | overlapping of the CH$_2$ rocking vibration and the out-of-plane vibration of *cis*-disubstituted olefins |
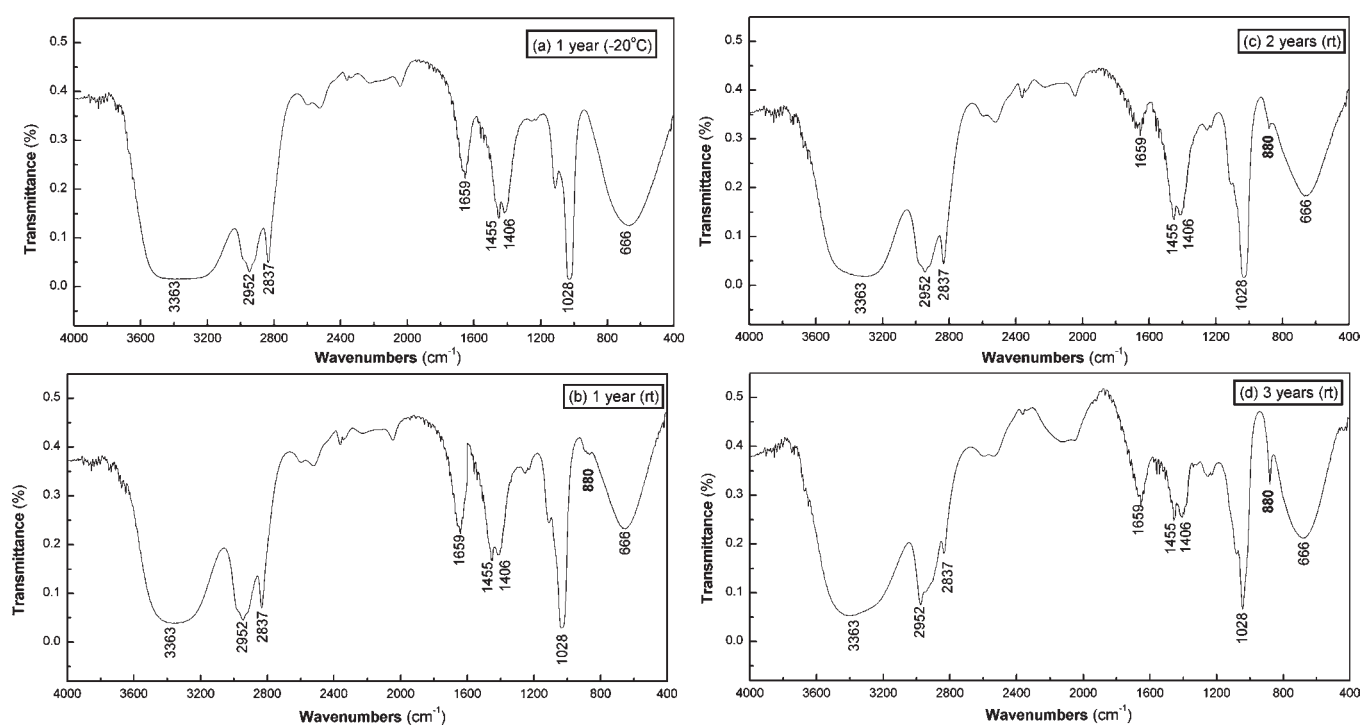


**Figure 3.** FTIR spectra of bio-oil samples at ambient temperatures of 20—30 °C with different storage times: (a) 1 year kept at −20 °C as control, (b) 1 year kept at ambient temperature, (c) 2 years kept at ambient temperature, and (d) 3 years kept at ambient temperature.

in an increasing viscosity and phase separation in the bio-oil.[13] The polycondensation reactions involve these polar functional groups, whose role is essential to the formation of new substances.[27−29] These functional groups (−OH, −NH$_2$, −COOH, etc.) are present in bio-oil at a high concentration.[12,13,17] The polycondensation reactions are accompanied by a release of low MW compounds such as water, alcohols, etc. When molecules contain more than two functional groups, higher MW compounds can be formed. Polymerization reactions usually pass through the formation of instable intermediates, such as olefins, which can spontaneously polymerize. Polymerization of olefin derivatives present in the bio-oil may occur when temperature, pH, and aging time are favorable. Oligomerization reactions may also occur between two functional acid and glycol groups to yield a polyether, which is a macromolecule with only carboxylic hydroxide groups at the end of the chain.[28]

In view of the discussion above, a mechanistic pathway is proposed for the bio-oil thermal deterioration based on the variation of FTIR spectra in the thermal deterioration process. Figures 2 and 3 explain, to a fair extent, the formation of terminal olefin derivatives in deterioration process. In the initial 72 h, new C=C double bond of terminal olefins are formed through E1 elimination reaction of the hydroxyl compounds, such as alcohols (Scheme 1), as confirmed by the appearance of an absorption peak at 880 cm$^{-1}$ in the FTIR spectra. This step is a reversible equilibrium reaction. Methanol addition has been confirmed to be a simple and effective way to improve the stability and other fuel properties of bio-oils.[3−5,13,15,26] This can be partially explained as methanol addition is propitious to reactants from the view of chemical reaction equilibrium. In the subsequent 48 h, the disappearance of the absorption peak at 880 cm$^{-1}$ might be explained by the fact that when the conditions required for the

**Scheme 1. Thermal Deterioration Scheme for Bio-oil**
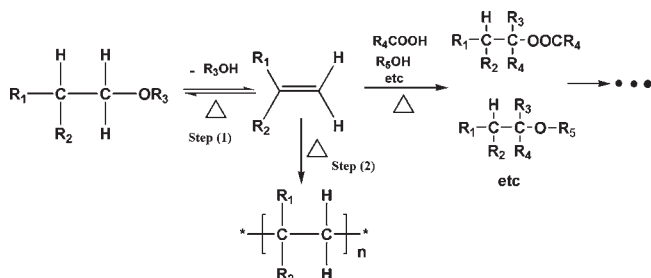


polymerization of terminal olefin derivatives are present, high MW compounds are formed as the thermal deterioration product of the bio-oil. The conditions required for polymerization of alkenes derivatives involve temperature, pH, and aging time. These high MW products generated by polymerization reactions particularly influence the physicochemical properties of the bio-oil. The formation of high MW products has also validated by the variations of viscosity, water content, and MW distribution in thermal treatment and/or long-term storage at ambient temperatures.[5,15] The decrease in the GC/MS TICs (Figure 1) and the phenomenon of phase separation also could indicate that the polymerization reaction occurred in the bio-oil during storage.

In summary, specific FTIR spectral regions are proven to be very useful for monitoring bio-oil deterioration process as well as for elucidating its thermal deterioration mechanism. Spectral changes appearing in the 880 cm$^{-1}$ region, after heating at elevated temperatures and/or long-term storage at ambient temperatures, aid the deterioration process monitoring. This methodology could be useful to evaluate the deterioration state of bio-oil in a simple and fast way. As compared with GC/MS, one of the most commonly used analytical methods, the FTIR instrument is cheaper and easier to obtain in bio-oil refinery. It can be used as a fast screening method in bio-oil analysis. The information from FTIR data may be useful to provide proper conditional maintenance for bio-oil production, storage, and utilization.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*Fax: +86-551-3601592. E-mail: gpsheng@ustc.edu.cn.

## ■ REFERENCES

(1) Lynd, L. R.; Cushman, J. H.; Nichols, R. J.; Wyman, C. E. Fuel Ethanol from Cellulosic Biomass. *Science* **1991**, *251* (4999), 1318–1323.

(2) Bridgwater, A. V.; Peacocke, G. V. C. Fast pyrolysis processes for biomass. *Renewable Sustainable Energy Rev.* **2000**, *4* (1), 1–73.

(3) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106* (9), 4044–4098.

(4) Czernik, S.; Bridgwater, A. V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004**, *18* (2), 590–598.

(5) Lu, Q.; Yang, X. L.; Zhu, X. F. Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk. *J. Anal. Appl. Pyrol.* **2008**, *82* (2), 191–198.

(6) Zheng, J. L. Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. *J. Anal. Appl. Pyrol.* **2007**, *80* (1), 30–35.

(7) Liu, R.; Deng, C.; Wang, J. Fast Pyrolysis of Corn Straw for Bio-oil Production in a Bench-scale Fluidized Bed Reactor. *Energy Sources, Part A* **2010**, *32* (1), 10–19.

(8) Demirbas, A. Bio-fuels from agricultural residues. *Energy Sources, Part A* **2008**, *30* (2), 101–109.

(9) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipila, K. Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. *Energy Fuels* **2010**, *24*, 1380–1388.

(10) Adjaye, J. D.; Sharma, R. K.; Bakhshi, N. N. Characterization and Stability Analysis of Wood-Derived Bio-Oil. *Fuel Process. Technol.* **1992**, *31* (3), 241–256.

(11) Czernik, S.; Johnson, D. K.; Black, S. Stability of Wood Fast Pyrolysis Oil. *Biomass Bioenergy* **1994**, *7* (1–6), 187–192.

(12) Ba, T. Y.; Chaala, A.; Garcia-Perez, M.; Roy, C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy Fuels* **2004**, *18* (1), 188–201.

(13) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Rodrigue, D.; Roy, C. Multiphase structure of bio-oils. *Energy Fuels* **2006**, *20* (1), 364–375.

(14) Oasmaa, A.; Kuoppala, E. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energy Fuels* **2003**, *17* (4), 1075–1084.

(15) Chaala, A.; Ba, T.; Garcia-Perez, M.; Roy, C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark: Aging and thermal stability. *Energy Fuels* **2004**, *18* (5), 1535–1542.

(16) Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y. Fast pyrolysis of forestry residue. 1. Effect of extractives on phase separation of pyrolysis liquids. *Energy Fuels* **2003**, *17* (1), 1–12.

(17) Oasmaa, A.; Kuoppala, E.; Solantausta, Y. Fast pyrolysis of forestry residue. 2. Physicochemical composition of product liquid. *Energy Fuels* **2003**, *17* (2), 433–443.

(18) Xu, J. M.; Jiang, J. C.; Lv, W.; Dai, W. D.; Sun, Y. J. Rice husk bio-oil upgrading by means of phase separation and the production of esters from the water phase, and novolac resins from the insoluble phase. *Biomass Bioenergy* **2010**, *34* (7), 1059–1063.

(19) Jiang, X. X.; Ellis, N. Upgrading Bio-oil through Emulsification with Biodiesel: Thermal Stability. *Energy Fuels* **2010**, *24*, 2699–2706.

(20) Hilten, R. N.; Das, K. C. Comparison of three accelerated aging procedures to assess bio-oil stability. *Fuel* **2010**, *89* (10), 2741–2749.

(21) Tena, N.; Aparicio, R.; Garcia-Gonzalez, D. L. Thermal Deterioration of Virgin Olive Oil Monitored by ATR-FTIR Analysis of Trans Content. *J. Agric. Food Chem.* **2009**, *57* (21), 9997–10003.

(22) Guillen, M. D.; Goicoechea, E. Detection of primary and secondary oxidation products by Fourier transform infrared spectroscopy (FTIR) and H-1 nuclear magnetic resonance (NMR) in sunflower oil during storage. *J. Agric. Food Chem.* **2007**, *55* (26), 10729–10736.

(23) Kadamne, J. V.; Jain, V. P.; Saleh, M.; Proctor, A. Measurement of Conjugated Linoleic Acid (CLA) in CLA-Rich Soy Oil by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR). *J. Agric. Food Chem.* **2009**, *57* (22), 10483–10488.

(24) Cavagna, M.; Dell'Anna, R.; Monti, F.; Rossi, F.; Torriani, S. Use of ATR-FTIR Microspectroscopy to Monitor Autolysis of Saccharomyces cerevisiae Cells in a Base Wine. *J. Agric. Food Chem.* **2010**, *58* (1), 39–45.

(25) Duarte, I. F.; Barros, A.; Almeida, C.; Spraul, M.; Gil, A. M. Multivariate analysis of NMR and FTIR data as a potential tool for the quality control of beer. *J. Agric. Food Chem.* **2004**, *52* (5), 1031–1038.

(26) Boucher, M. E.; Chaala, A.; Pakdel, H.; Roy, C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenergy* **2000**, *19* (5), 351–361.

(27) Adhvaryu, A.; Perez, J. M.; Singh, I. D.; Tyagi, O. S. Spectroscopic studies of oxidative degradation of base oils. *Energy Fuels* **1998**, *12* (6), 1369–1374.

(28) Levermore, D. M.; Josowicz, M.; Rees, W. S.; Janata, J. Headspace analysis of engine oil by gas chromatography/mass spectrometry. *Anal. Chem.* **2001**, *73* (6), 1361–1365.

(29) Vlachos, N.; Skopelitis, Y.; Psaroudaki, M.; Konstantinidou, V.; Chatzilazarou, A.; Tegou, E. Applications of Fourier transform-infrared spectroscopy to edible oils. *Anal. Chim. Acta* **2006**, *573*, 459–465.