



# Vacuum co-pyrolysis of Chinese fir sawdust and waste printed circuit boards. Part II: Influence of heating conditions



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## ABSTRACT

Vacuum co-pyrolysis of Chinese fir sawdust (CFS) and waste printed circuit boards (WPCBs) at different heating conditions were examined in this paper. The composition of the pyrolysis oils was analyzed by gas chromatography–mass spectrometry (GC–MS). It was found that the content of most of the compounds with relatively long molecular chain had a higher value at relatively low temperature (400–600 °C) and short holding time (10 min), and decreased at relatively high temperature (800 °C) and long holding time (30–90 min); while the content of most of the compounds with relatively short molecular chain presented an adverse trend. The co-pyrolysis process was also analyzed by thermogravimetric (TG) analysis with evolved product analysis by Fourier transform infrared (FTIR) spectroscopy. The results showed that the volatiles were mainly generated between 300 and 500 °C, and after 500 °C, noncondensable gases (CO<sub>2</sub>, CO and CH<sub>4</sub>) were the main components in the pyrolysis process.

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## 1. Introduction

Nowadays, research and development of biomass resource and recovery of waste printed circuit boards (WPCBs) have become two international hotspot issues, due to more and more attentions to the environmental protection and the status quo of energy shortage all of the world. There are many methods for recycling of biomass and WPCBs at present. Thereinto, pyrolytic method [1–7] is one of the most promising methods for recovering materials from biomass and WPCBs. Through pyrolysis, the organic components of biomass and WPCBs can be transformed into high value-added liquid products. However, bottleneck still exists in the follow-up utilization of these liquid products. First of all, bio-oils have a series of disadvantages of high oxygen-containing, low calorific value, strong corrosion, ignition delay and storage instability, and so on, while WPCBs pyrolysis oils contain an amount of brominated compounds (flame retardant), which greatly limits the utilization of bio-oils and WPCBs pyrolysis oils as power fuels. To solve this problem, there are some researchers focused on how to modify the product oils, like upgrading of bio-oils [8], elimination of bromine from WPCBs pyrolysis oils [9,10], and so on. However, the results are not good enough and there is still a long way for the modified oils to replace gasoline and diesel oil as power fuels. Secondly, considering that these liquid products contain large amounts of phenolic

compounds, some researchers have carried out researches to use these liquid products to synthesize phenol-based resins [11–13]. However, the properties of low phenol substitution and less reactive than pure phenol of bio-oils, and the poor performance of the synthetical polymer materials from WPCBs pyrolysis oils made the prospect of this way is not very competitive. As for the separation and purification of valuable components in these liquid products, it is limited to the current equipments and technologies, leading to a poor efficiency. Thus, finding a more reasonable, feasible and preponderant way for utilizing these liquid products is a new and urgently to be solved topic in recycling of biomass and WPCBs.

In this series of researches, the obtained pyrolysis oils will be finally used to synthesize phenol-based resins. As the bio-oils contain some soft phenolic compounds (like guaiacol, 4-methylguaiacol, and so on), which can improve the mechanical properties of the synthesized resins [14,15], and the WPCBs pyrolysis oils contain a large number of high reactive phenolic compounds (like phenol, 4-isopropylphenol, bisphenol A, and so on), co-pyrolysis of biomass and WPCBs can combine the two advantages, that is, obtaining a satisfactory quality requirement of synthesized resin by adding no or less extra phenol. For this purpose, it is necessary to find an optimum condition to obtain pyrolysis oils with as high yield and phenol content as possible, and know the influence of each condition on the co-pyrolysis process as well, so as to provide guidance for the following researches. In this paper, the composition of the pyrolysis oils at different heating conditions (final pyrolysis temperature and holding time) were analyzed by gas chromatography–mass spectrometry (GC–MS) and

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the total phenol contents of the pyrolysis oils were also determined by a bromine method. In order to know the co-pyrolysis process better, the change laws of the evolved products as a function of temperature were also analyzed by thermogravimetric (TG) analysis with evolved product analysis by Fourier transform infrared (FTIR) spectroscopy.

## 2. Experimental

### 2.1. Materials and methods

The materials and methods used in this paper were just the same as our previous paper [16]. The Chinese fir sawdust (CFS) was collected from a large-scale wood processing plant in Changsha city, Hunan, China, and screened out 200–40 meshes components as raw materials after washing, drying, and crushing process. The WPCBs were the leftover boards without any metal components during the manufacture process of printed circuit boards, which were cut into fragments about 2 mm × 5 mm size. 5.00 g of each raw material was exactly weighed and put into the self-made pyrolysis reactor for co-pyrolysis under vacuum. This paper examined the influence of heating conditions (final pyrolysis temperature and holding time) on the product yields and composition of the pyrolysis oils, so as to reflect the vacuum co-pyrolysis process better. The other pyrolysis parameters were set at the same value when one parameter was changed. The initial system pressure was pumped to the minimum using vacuum pump and regulated to 10 kPa by the needle valve. The heating rate was set as 40 °C/min to heat to the experimental final pyrolysis temperature (300–800 °C), holding at the temperature for a certain time (10–90 min). The volatiles generated were condensed and collected at the condensation temperature of –40 °C. After the experiment, the solid and liquid pyrolysis yields were determined by weighing the weight of each obtained, while the gas yield was calculated by difference. Each experiment repeated at least twice and averaged.

### 2.2. TG-FTIR analysis

Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA851<sup>e</sup>) with evolved product analysis by Fourier transform infrared (FTIR, Thermo Scientific Nicolet 6700) spectroscopy was also employed in the co-pyrolysis experiments. In this paper, the TG-FTIR analysis of the sample (blending ratio of 1:1) was carried out from 25 °C to 800 °C with a heating rate of 40 °C/min under nitrogen atmosphere, and the flow rate of the nitrogen was regulated to 120 mL/min. The volatile products passed through a 1 m length connecting pipe, which was preheated to 200 °C, and then went into the gas cell of the FTIR spectroscopy. The FTIR spectra were obtained every 10 s with a resolution of 4 cm<sup>-1</sup>, and a scan range of 4000–600 cm<sup>-1</sup>.

### 2.3. Characterization of the pyrolysis oils

The pyrolysis oils obtained were dissolved in 10.00 mL chromatographically pure methanol (got a homogeneous sample), and sent for gas chromatography–mass spectrometry (GC–MS) analysis. In our previous paper [16], a less reactive solvent, acetone, was used to dissolve the pyrolysis oils, which may get an original distribution of the pyrolysis oils, but some strong polar components, like acids (formic acid, acetic acid, vanillic acid, etc.), aldehydes (acetaldehyde, etc.) had a low separation resolution. In the presence of catalytically active material (HBr), methanol may act as methylating reagent, converting the strong polar components to weak polar components, and getting a high separation resolution of course. Moreover, as methanol has a relatively low molecular weight (lower than almost all of the components in the pyrolysis

oil), the detection can conduct without consideration of the oversaturation of the response value of the solvent if the scanning value of the mass to charge ratio ( $m/z$ ) were set higher than 30 amu in the mass spectrometry. This could get a more fully characterization of the volatile components, especially those with small retention time. The operation parameters of the GC–MS were just the same as the previous paper [16] except that the solvent cut time was 0.7 min.

Total phenol content of the pyrolysis oil was also determined by a classical bromine method (bromometry), which is expressed in a Chinese standard HJ 502-2009. This standard is mainly used to determine the volatile phenolic compounds in waste water. The principle of the bromine method is as follows: volatile phenolic compounds will react with excess bromine, which was produced by potassium bromate and potassium bromide under acidic condition, and generate tribromophenol. Then, excess potassium iodide will be added in the solution to react with the remaining bromide and generate iodine. However, the iodine can be determined by a known quantity of sodium thiosulfate solution. Finally, according to the consumption of the sodium thiosulfate solution, we can calculate the content of volatile phenolic compounds. In this paper, the method needs some modification, as the pyrolysis oils were slightly soluble in water. A certain concentration of sodium hydroxide solution was used to dissolve the pyrolysis oils firstly, which can improve the solubility to a certain degree. About 0.4400 g of each obtained of the above homogeneous sample was dissolved in 5 g/L NaOH solution, and set the volume to a 100 mL volumetric flask. As the phenol content of the sample solution is achieved to the detection limit of the standard, it is not necessary to carry out the procedure of distillation. The detected value was finally converted into weight fraction of the initial weight of the pyrolysis oil.

## 3. Results and discussion

### 3.1. Pyrolysis experiments

Single factor method was adopted to determine the influence of final pyrolysis temperature and holding time on the product yields and total phenol content of the pyrolysis oils.

### 3.2. Influence of final pyrolysis temperature

Temperature seems to be the most important variable that controls the pyrolysis reactions [17]. A different final pyrolysis temperature will lead to a different extent of decomposition of the raw materials, thus resulting in a different distribution of the solid, liquid and gas yields. Table 1 shows the product yields and total phenol content of the liquid oils at different final pyrolysis temperatures under the condition of system pressure of 10 kPa, heating rate of 40 °C/min, holding time of 30 min, and condensation temperature of –40 °C. It can be seen from Table 1 that within the temperature range of the experiment, the solid yield decreased gradually with increased final pyrolysis temperature, and the liquid yield had a peak value of 39.8 wt% at 500 °C, while the gas yield had a rising trend overall. At low temperature, the decomposition of the sample was not completed, leading to a relatively high solid yield and low liquid and gas yields. With the increase of the final pyrolysis temperature, the chemical bonds of the polymer macromolecule is easier to be broken, resulting in a more content of the volatile matter, thus obtaining more liquid product after condensation. However, if the temperature is too high, the extent of the cleavage reaction will be deepened, which may form more compounds with small molecule. It is the main reason for the significant increase of gas yield and decrease of liquid yield at high temperatures.

The change law of the total phenol content as a function of final pyrolysis temperature is similar to its liquid yield, which had a peak

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