

Potential of Pyrolysis for the Recovery of Heavy Metals and Bioenergy from Contaminated *Broussonetia papyrifera* Biomass

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Heavy metal contaminated biomass is a severe environmental problem. Presently, the disposal of heavy metal contaminated biomass tends to seek the recovery of both heavy metals and bioenergy. In this study, pyrolysis technology was employed to pyrolyze contaminated biomass to elucidate the influence and fate of the heavy metals and the potential for recovering bioenergy. The results showed that heavy metals in biomass reduced the reaction energy in the main decomposition stage by approximately 10%, while 25% of the biomass decomposed to solid products. Moreover, 63.2% to 68.2% of the Cd and 69.0% to 77.9% of the Cu were retained in the solid, and the metals in the residues existed as metal elements that can be recovered by general smelting. The majority of the biomass (75%) generated volatile products and was only slightly influenced by heavy metals. Compared with the uncontaminated biomass, the component of bioenergy was reduced only slightly, which suggests strong potential for recovering bioenergy. The finding of this paper can be a theoretical foundation to support the responsible disposal, through pyrolysis, of biomass contaminated by heavy metals.

Keywords: Contaminated biomass; Pyrolysis; Copper; Cadmium; Bioenergy

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INTRODUCTION

Biomass has been an essential alternative to fossil fuels for manufacturing processes such as mining, smelting, and power generation. Biomass and its elaboration products (Idrees *et al.* 2016) are also being applied in phytoremediation and biomass adsorbents to solve the problem of heavy metal contamination in soil (Lombi *et al.* 2001) and water (Tran *et al.* 2017). Therefore, the disposal of heavy metal contaminated biomass to recover the bioenergy and recycle the trapped metals has attracted increasing attention.

The application of phytoremediation for heavy metal contaminated soil has been widely used (Ali *et al.* 2013). Hyperaccumulators, such as *Pteris vittata* (Salido *et al.* 2003), *Polygonum perfoliatum* L. (Xue *et al.* 2016), *Agrostis capillaris*, *Solanum nigrum*, and *Vicia faba* (Austruy *et al.* 2013), are widely used in phytoremediation engineering. The capacity for heavy metals in these plants is considered to be 8500 mg·kg⁻¹ of Pb (Reeves and Brooks 1983), 1000 mg·kg⁻¹ of Cd (Baker *et al.* 2000), 2400 mg·kg⁻¹ of Cu, and 7880 mg·kg⁻¹ of Ni (Robinson *et al.* 1997). However, most phytoremediation engineers prefer to use local species with excellent viability and higher biomass (Kord and Kord 2011) rather than hyperaccumulator plants (Ahemad 2014). Although the heavy metal content in the local plants is considerably lower than in hyperaccumulators, the metals will accumulate in the biomass and cause harm to humans and other organisms. In contrast,

biomass with abundant pore structure and functional groups can be regarded as a common water absorbent material for heavy metals (Mahmood *et al.* 2010). Biomass can adsorb $0.77 \text{ mmol}\cdot\text{L}^{-1}$ to $1.63 \text{ mmol}\cdot\text{L}^{-1}$ of heavy metals (da Silva Filho *et al.* 2006; Gurgel and Gil 2009), with the capacity differences being caused by the diversity of biomass and the metals' characteristics.

One essential item related to the application of biomass related technology for heavy metals pollution is the management of the heavy metals in contaminated biomass (Martín-Lara *et al.* 2018). Although heavy metal contaminated biomass treated through both phytoremediation and biosorbent must be disposed of, at present there is very little information available regarding how to do so. Generally, the disposal methods for waste biomass include leaching (Liu *et al.* 2012), compost (García-Gil *et al.* 2000), combustion (Demirbas 2005), and pyrolysis (Raveendran *et al.* 1996). Comparatively, for heavy metal contaminated biomass, leaching, composting, and combustion are not appropriate disposal methods because the metals will be discharged with leachate and smoke emission. Contrarily, most heavy metals can be controlled in the solid phase products (Fu *et al.* 2008).

Pyrolysis is a heating method that uses the absence of oxygen to degrade biomass into biochar, tar, oil, and other products (Demirbas and Gönenç 2002), and this method has been reported to be a suitable technology for disposing of heavy metal contaminated biomass (Nzihou and Stanmore 2013). Koppolu *et al.* (2003) used acetate heavy metals to simulate heavy metals in an organic form, while Liu *et al.* (2012) adsorbed inorganic heavy metals from aqueous solutions; both found that heavy metals easily enter the solid phase of final products after rapid pyrolysis. However, rapid pyrolysis technology may not be realized in actual production, and the influence of heavy metals was not the focus. Therefore, the effects of heavy metals on pyrolysis and their fate should be studied to improve understanding of the influence of heavy metals pyrolysis.

Some studies (Lievens *et al.* 2008a,b) have indicated that Cd is easier to push into the volatile phase, while Cu has always been regarded as one of the most popular and valuable heavy metals. *Broussonetia papyrifera* is a resistant plant that has been applied for phytoremediation (Zhang *et al.* 2013), and the biomass has been regarded as a bio-sorbents for heavy metals removal in solution (Nagpal *et al.* 2011), the contaminated *Broussonetia papyrifera* biomass has been an environmental problem in some area.

Therefore, this paper selected Cd and Cu as its subject metals, and *Broussonetia papyrifera* biomass as subject biomass. The objectives of this study are i) to elucidate the pyrolysis characteristics of the metals-contaminated biomass (biomass mixed with sulfate and acetate Cd and Cu) using TGA analysis, ii) to study the influence of heavy metals on the pyrolysis of the biomass, and to investigate the possibility of recovering iii) heavy metals and iv) bioenergy *via* pyrolyzed products from metals-contaminated biomass. The overall process is represented in Fig. 1.

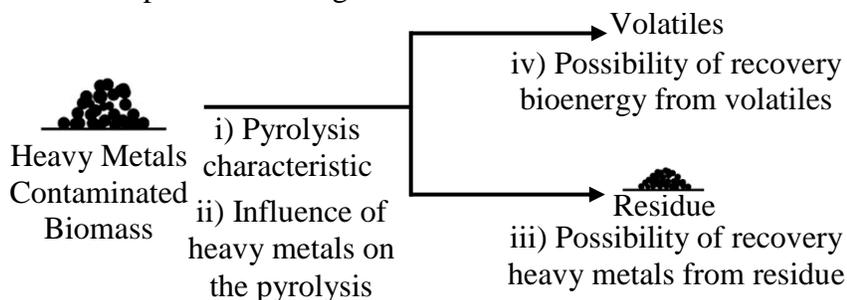


Fig. 1. Aim and structure of heavy metals contaminated biomass pyrolysis

EXPERIMENTAL

Materials

Tested biomass

The tested woody biomass of *Broussonetia papyrifera* was collected from a phytoremediation plot in China's Hunan province. The biomass was cut and ground into pieces with a particle size of less than 10 mm and then stored in the laboratory under dry conditions for the experiment. The basic chemical composition, proximate analysis, and lignin content of the biomass are summarized in Table 1.

Table 1. Basic Properties of Tested Biomass

| <i>Broussonetia papyrifera</i> Biomass | Content of Alkaline Earth Metals (mg·kg ⁻¹) | | | | Proximate Analysis (wt%) | | | | Heavy Metals Content (mg·kg ⁻¹) | |
|--|---|------|------|-----|--------------------------|------|-----------|--------------|---|----|
| | Na | K | Ca | Mg | Moisture | Ash | Volatiles | Fixed Carbon | Cd | Cu |
| | 63 | 6402 | 3205 | 514 | 4.08 | 7.33 | 71.64 | 15.50 | 1.6 | 6 |

Methods

A pyrolysis experiment (aimed to detect TG curve and FTIR spectra of the volatiles) was performed on a thermogravimetric analyzer (TGA; Netzsch STA499F3, Bavaria, German). Samples of 20 mg (biomass, reagents, and the mixtures) were placed in the burning room and pyrolyzed using a rising temperature from 25 °C (room temperature) to 950 °C at a heating rate of 10 °C·min⁻¹. A high purity nitrogen stream was continuously passed into the heath at a flow rate of 40 mL·min⁻¹ to control the air conditions. The volatiles gas during thermal decomposition was detected by the combined Fourier transform infrared spectroscopy (FTIR; Tensor27, Karlsruhe, German).

A lab-scale pyrolysis experiment (aimed to estimate the fate of the heavy metals) in a tube furnace was then designed (Han *et al.* 2017). A 15-g biomass sample was placed in a porcelain boat and heated for 2 h at a heating rate of 10 °C·min⁻¹ to a final temperature of 450 °C. The reactor was continuously purged with nitrogen at 0.5 L·min⁻¹ to sweep the related gases from the quartz tube.

To clearly show the effect of heavy metals on biomass pyrolysis characteristics, the tested biomass was mixed with 10% and 25% of sulfate and acetate Cd and Cu, respectively. The biomass and reagent were mixed using a blender mixer under dry conditions. The solid products of pyrolysis were digested by nitric-perchloric acid system, and the solution was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS intrepid II XSP, Shanghai City, IL, USA). X-ray diffraction (XRD, D/MAX2500, Beijing, China) was used to detect the crystalline phase of the solid products.

Data analysis

The heavy metal compounds (cadmium sulfate (CdSO₄), copper sulfate (CuSO₄), cadmium acetate (Cd(CH₃COO)₂), and copper acetate (Cu(CH₃COO)₂)) have different thermal stabilities in the temperature range of 100 °C to 1000 °C. The assessment of the reactions between the heavy metal compounds and biomass and the effect of the heavy metals on the pyrolysis was performed through the evaluation of the TG curve of the actual

mixture and the corresponding curve of a reference mechanical mixture (RMM). The RMM concept assumes that there is no interaction between the materials, and that they only bonded mechanically (Pilatau *et al.* 2017). Based on that assumption, an assessment was performed based on the following formulas,

$$m_{\text{metal}} + m_{\text{biomass}} = m_{\text{mixture}}; m_{\text{metals}} / m_0 = \alpha \quad (1)$$

$$TG_{\text{RMM}} = \alpha \times TG_{\text{metal}} + (1 - \alpha) \times TG_{\text{biomass}} \quad (2)$$

where m_{metal} and m_{biomass} are the initial sample masses (g) of heavy metals and biomass, α is the mass fraction of the heavy metals (10% and 25%), TG_{metals} and TG_{biomass} are the sample masses (g) of the heavy metals and biomass during the TG analysis, respectively, and TG_{RMM} is the sample mass (g) based on RMM assumption.

Biomass is a complex compound, although theoretically biomass can be considered as a single component substance; thus, the first-order reaction of thermal decomposition kinetics can be used to describe the pyrolysis process (Saddawi *et al.* 2010). Generally, a mathematical method was used for calculating the activation energy based on the TGA experiments. The equation below is a formula for the temperature dependence of reaction rates,

$$d\alpha / dt (\%) = kf(\alpha); \alpha = (m_0 - m) / (m_0 - m_\infty) \times 100 \quad (3)$$

where $f(\alpha)$ is the reaction model, α is the degree of decomposition, m_0 , m , and m_∞ are the initial mass (g), the mass at a certain time (g), and final residual mass (g) of the pyrolysis, respectively, t is the time (g), and k is the Arrhenius rate constant, which can be described as,

$$k = A \exp(-E/RT); T = t\beta \quad (4)$$

where A stands for the frequency factor, E is reaction energy ($\text{kJ} \cdot \text{mol}^{-1}$), R is gas constant 8.314, T is the absolute temperature ($^\circ\text{C}$), and β is the heating rate ($^\circ\text{C} \cdot \text{min}^{-1}$). The functional form $f(\alpha)$ depends on the reaction mechanism. Combining Eqs. 3 and 4, the function can be presented as:

$$d\alpha / dt = A \exp(-E/RT) f(\alpha) \quad (5)$$

For the TGA process, the heating rate can be regarded as:

$$\beta = Dt / dt, \text{ into Eq. 5:}$$

$$d\alpha / dt = (A\beta) \exp(-E/RT) f(\alpha) \quad (6)$$

The result can be expressed in differential form,

$$d\alpha / f(\alpha) = (A/\beta) \exp(-E/RT) dT \quad (7)$$

and after integration of Eq. 7:

$$\ln(-\ln(1 - \alpha)/T^2) = \ln(AR/\beta E) - E/RT \quad (8)$$

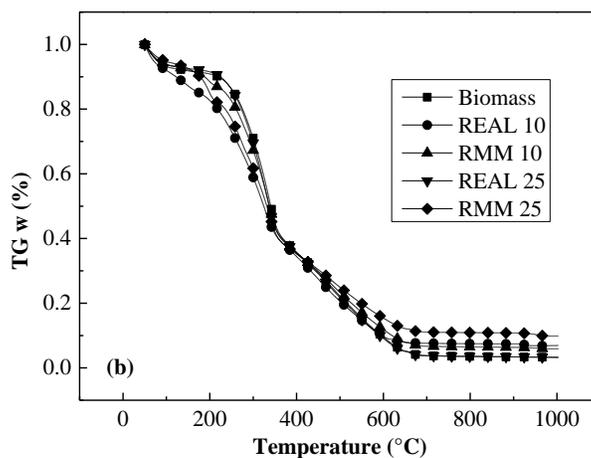
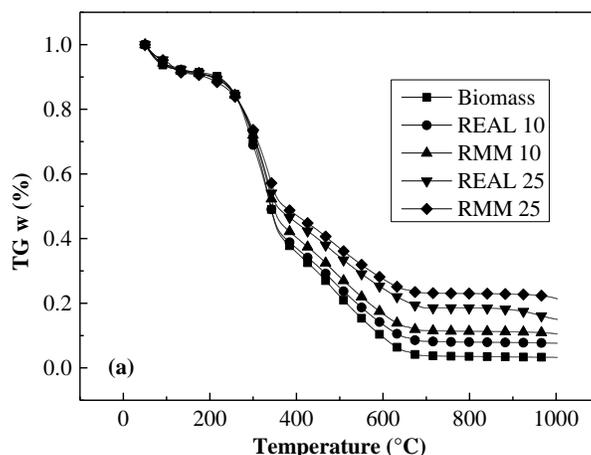
Plotting to $X = 1 / T$ with $y = \ln(-\ln(1 - \alpha) / T^2)$, if the coefficient of association is high, then the formula describes the pyrolysis process well. In the plot, the slope is $-E/R$ and the intercept is $\ln(AR/\beta E)$. Therefore, the activation energy E can be calculated to guarantee the correlation coefficient, while major reaction step (200 to 450 $^\circ\text{C}$) of the decomposition in TGA curve is applied.

RESULTS AND DISCUSSION

Effect of Cd and Cu on Pyrolysis of the Woody Biomass

Depending on the TG analysis (Fig. 2), the pyrolytic process of biomass can be divided into three steps. When the temperature was less than 200 °C, the surface water of biomass was eliminated considerably while the other components, such as lignin and cellulose, began to decompose (Antal and Varhegyi 1995). The weight loss of the biomass mainly occurred in the temperature range of 200 °C to 450 °C, with variations being caused by different biomass content. When the pyrolysis temperature rose higher than 450 °C, the decomposition process of biomass was almost complete and the residual was mainly composed of carbon and ash, which was slightly changed with the increase of temperature.

In comparison, with heavy metals mixed in, even though solid products may contain heavy metals, the overall three step decomposition process was not changed substantially. While the pyrolysis rate and final residue were slightly different from the original biomass, the results indicated that an increased amount of heavy metals mixed in resulted in an increased amount of residue produced. Comparing the mixtures of CdSO₄ (Fig. 2a) and CuSO₄ (Fig. 2b) with Cd(CH₃COO)₂ (Fig. 2c) and Cu(CH₃COO)₂ (Fig. 2d), respectively, the organic (acetic) or inorganic (sulfate) form of the metals showed no notable difference. However, comparing CdSO₄ (Fig. 2a) with CuSO₄ (Fig. 2b) and the mixture of Cd salts, which mixed Cd(CH₃COO)₂ with Cu(CH₃COO)₂, can increase the final residues of the TGA test, possibly because the proportion of the metal mass in Cd salts is higher than that in Cu.



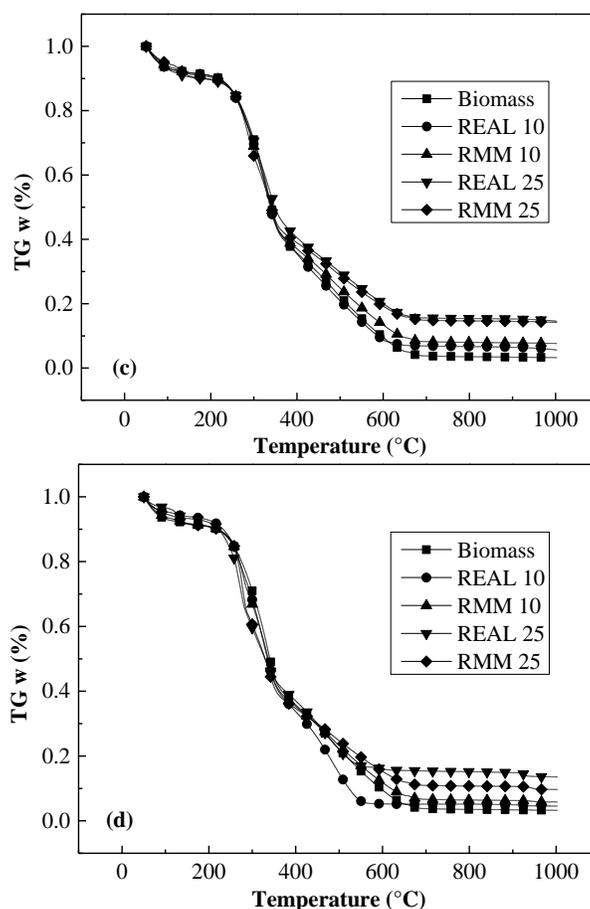


Fig. 2. TG curve for the original biomass and the mixture: (a) CdSO_4 ; (b) CuSO_4 ; (c) $\text{Cd}(\text{CH}_3\text{COO})_2$; and (d) $\text{Cu}(\text{CH}_3\text{COO})_2$

The calculation of TGA_{RMM} indicated that most of the RMM values were larger than that of the actual mixtures experiment, which meant that the interaction of the biomass with the heavy metals reduced the final solid products of the mixture. Other research has also reported the reduction of the solid phase products of the biomass due to the influence of heavy metals (Han *et al.* 2017), which may be caused by an exothermic inter-redox reaction of the biomass and the metal compounds.

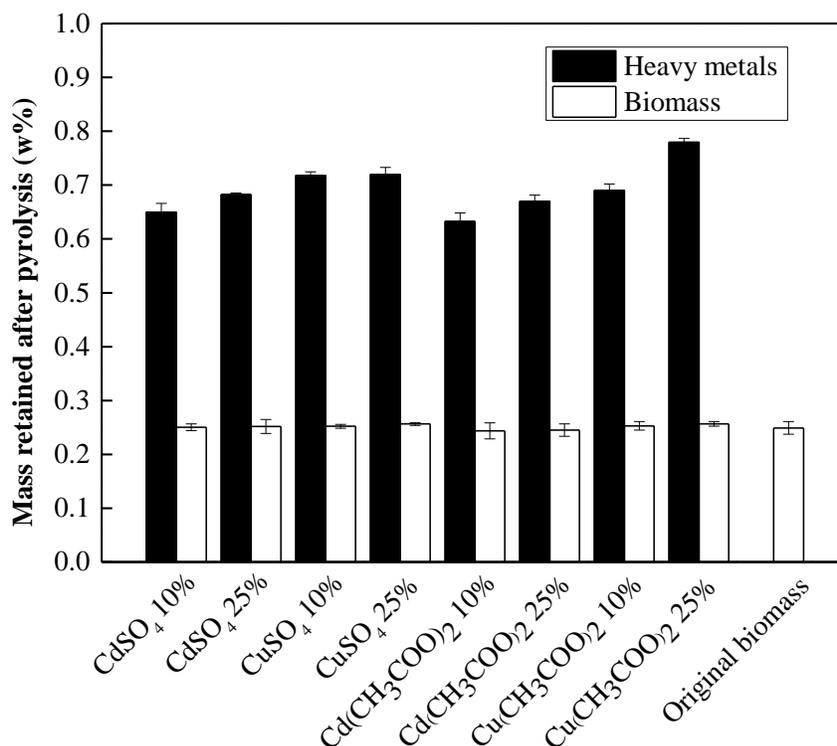
The auxo-action of heavy metals on pyrolysis may also be influential due to the activation energy. According to Eq. 8 and data from TGA_{RMM} and TGA_{REAL} , the activation energy of the main decomposition range can be calculated (Table 2). All of the correlation coefficients were greater than 80%, which meant that the equation hypothesis did agree with the TGA process. Most E_{RMM} were less than E_{REAL} , which meant the required thermal decomposition energy of RMM was less than that of REAL. Therefore, the mix of heavy metals promoted the thermal decomposition process of biomass by reducing the solid residuals and activation energy. In the authors' other research (Han *et al.* 2018), it was found that the metal compounds were reduced to metal elements, which may be the main reason for the promotion of the decomposition.

Table 2. Kinetic Parameters for the Heavy Metal Contaminated Biomass

| Heavy Metals Compounds | RMM | | REAL | |
|--|-------------------------|----------------------------|-------------------------|----------------------------|
| | Correlation Coefficient | Activation Energy (kJ·mol) | Correlation Coefficient | Activation Energy (kJ·mol) |
| Original biomass | - | - | 0.9314 | 69.33 |
| 10% CdSO ₄ | 0.9212 | 62.59 | 0.8632 | 60.02 |
| 25% CdSO ₄ | 0.9075 | 69.46 | 0.9230 | 64.41 |
| 10% CuSO ₄ | 0.8601 | 64.42 | 0.8463 | 58.24 |
| 25% CuSO ₄ | 0.8564 | 69.41 | 0.8477 | 65.28 |
| 10% Cd(CH ₃ COO) ₂ | 0.8584 | 60.38 | 0.8398 | 65.42 |
| 25% Cu(CH ₃ COO) ₂ | 0.8636 | 62.66 | 0.8724 | 66.11 |
| 10% Cd(CH ₃ COO) ₂ | 0.8308 | 61.82 | 0.8138 | 62.89 |
| 25% Cu(CH ₃ COO) ₂ | 0.8394 | 63.74 | 0.8376 | 66.76 |

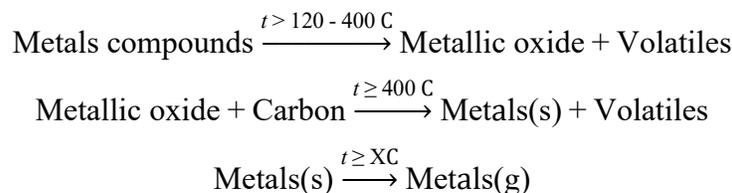
Fate of Heavy Metals During the Pyrolysis of Biomass

During pyrolysis, the biomass decomposed into solid (biochar and ash) and volatile (biogas and bio-oil) phase products. The TGA curve indicated that the yield of the volatile and solid phase products was not influenced significantly. In order to recover the heavy metals, the fate of the metals in the process must be elucidated. The concentrations of heavy metals in the final residue of the tube furnace experiment were detected and the results are shown in Fig. 3.

**Fig. 3.** Residue and heavy metal contents of the final solid products after pyrolysis

The influence of heavy metals on the solid phase products was not obvious. Approximately 25% of the biomass was revealed to be the residue, while the concentrations of the heavy metals retained were different. The results showed that 63.2% to 68.2% of Cd and 69.0% to 77.9% of Cu were retained, which indicated that most of the heavy metals,

especially Cu, were reserved in the solid products. Lievens *et al.* (2008a,b) found that Cd compounds were mainly lost in the temperature range of 400 °C to 500 °C. Depending on the results of this experiment and the research of Kistler *et al.* (1987), the interaction of metal compounds and the biomass can be described as,



where the volatiles can be CO, CO₂ (Koppolu *et al.* 2003), NO₂ (Liu *et al.* 2012), SO₂, and other biogases, which are highly reliant on the metal compounds. The temperature of char formation for the biomass was 400 °C and the carbon had strong reducibility; therefore, the metals and more volatiles would be produced in this stage. With increased temperature, the metals will reach the gas phase at X °C depending on the volatility of the metals. For example, at 765 °C, most Cd will turn to gas (Kistler *et al.* 1987). The X-ray diffraction patterns demonstrated that in the final stage, the Cd and Cu existed in the residue as metal element (Fig. 4). In the XRD patterns, besides the marked peaks for Cd and Cu, the broad peak situated at approximately 23° represents the amorphous carbon phase bands (Bourke *et al.* 2007), which means the residue still contained carbon with reducibility.

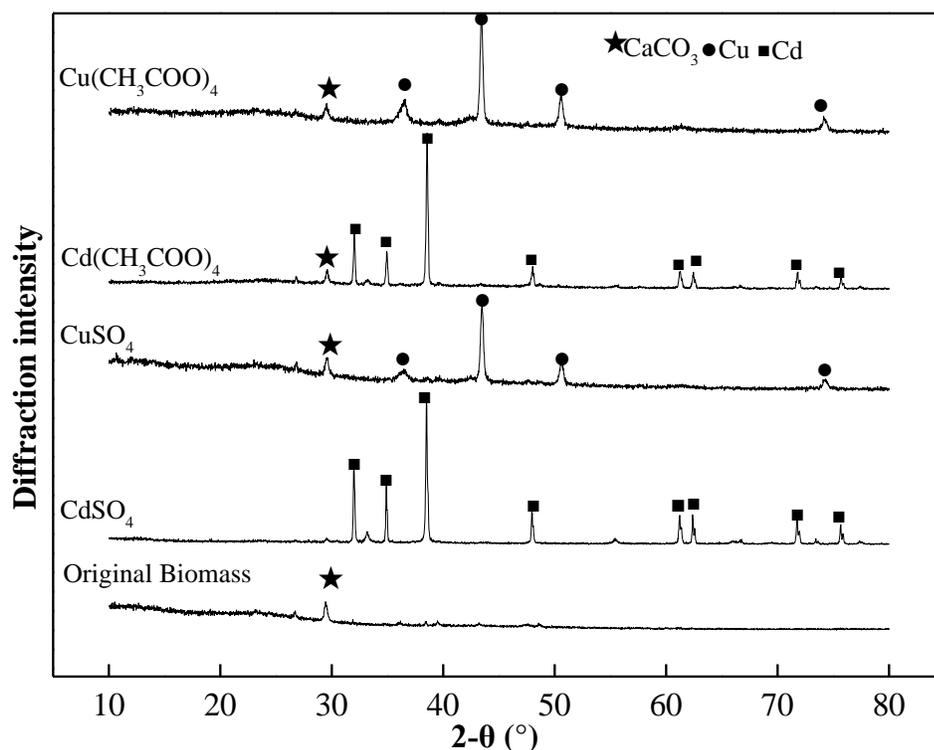


Fig. 4. XRD patterns of 450 °C pyrolysis products

The fate of the heavy metals suggested the possibility of recovering the metals from the biomass. Some research has indicated that at a higher temperature the heavy metals will be highly concentrated (Koppolu *et al.* 2003). While considering the energy consumption and volatility of the metals, 450 °C can be regarded as an appropriate temperature for

recovery. Solid products generated by the pyrolysis of heavy metal contaminated biomass are a valuable material for metal smelting (Boominathan *et al.* 2004). Besides, biomass has been reported as a source of carbon for metals production (Norgate *et al.* 2012). However, because the metal compounds are decomposed to a simple form, and the residues have reducibility, it means that most of the heavy metals can be recovered.

Potential of Recovering Bio-energy from the Contaminated Biomass

Comparatively, the rates of volatilization of the biomass contaminated by heavy metals were similar with that of the original biomass, which meant that the stability of the biomass had not changed. The principal organic components of the volatile phase products during the decomposition were detected by the TG-FTIR (Fig. 5). The results suggested that the main decomposition phase occurred from 100 °C to 450 °C and that CO₂ (2359 cm⁻¹ to 2388 cm⁻¹), H₂O (3300 cm⁻¹ to 3654 cm⁻¹), and volatile components, such as aldehydes (1540 cm⁻¹ to 1620 cm⁻¹), esters, and formic acid (-C-O- detected at 1160 cm⁻¹ to 1430 cm⁻¹), were generated (Batool *et al.* 2017). With the acetate and sulfate metals mixed in, the majority of the volatiles were not obviously changed, while with the sulfate mixed in, the SO₂ (1300 cm⁻¹ to 1450 cm⁻¹) (Cheng *et al.* 2013) was discharged with the rising temperature. The relative intensity of SO₂ reached a maximum at approximately 450 °C, and then decreased. For the organic acid heavy metals, the composition was similar to the biomass, and thus there was no notable difference in volatile compositions. In contrast, for the inorganic heavy metals, the corresponding gas (SO₂) was produced. However, the generation rate of volatiles and the main component did not change remarkably with the metal salts mixed in; that rate was much higher than the practical situation of phytoremediation and biosorption. Additionally, the results showed that it was possible to recover the bioenergy.

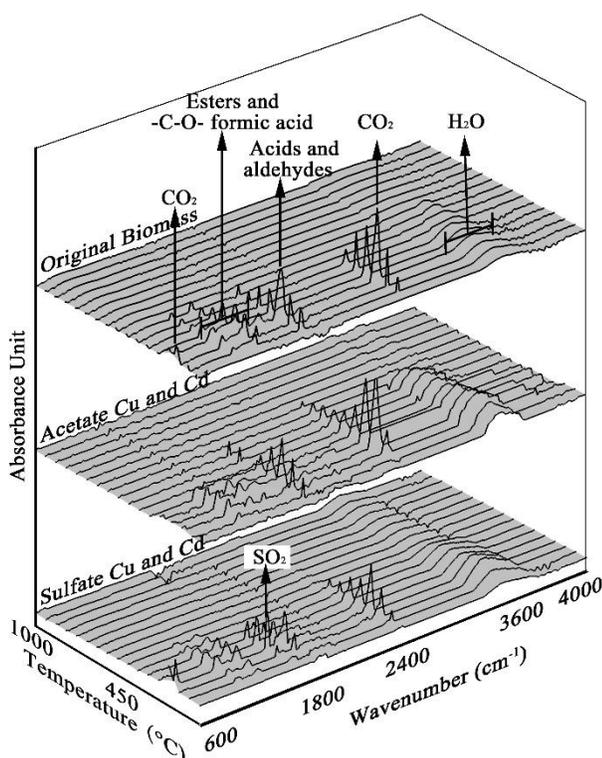


Fig. 5. TG-FTIR spectra for the pyrolysis of the biomass at 10 °C·min⁻¹

Concurrently, the utilization of the heavy metal contaminated biomass was also affected by the heating rate and the alkaline additives, which had a noticeable influence on the fate of the metals and should be solved in the near future. However, there was little heavy metal distributed in the volatile products, and this problem must be solved if pyrolysis is to be applied in the recovery of resources in the contaminated biomass.

CONCLUSIONS

1. This study demonstrated that heavy metals and the bioenergy in a contaminated biomass can be recovered by pyrolysis.
2. Heavy metal compounds promoted the thermal decomposition of the biomass by reducing the final residue and the activation energy compared with the calculated reference mechanical mixture (RMM) value.
3. There was a yield of approximately 25% of biomass after pyrolysis at 450 °C, while most of the heavy metals were retained in the solid phase products. The heavy metal compounds were reduced into metal elements while the carbon remained in the residue.
4. With heavy metals mixed in, the quality and the content of the volatile was not changed remarkably, which suggested strong potential for recovering the bioenergy.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of P. R. China (Grant No. 21577176) and the Research and Development Project of Hunan Province (2016SK2026).

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Article submitted: December 8, 2017; Peer review completed: January 28, 2018; Revised version received: February 5, 2018; Accepted: February 25, 2018; Published: February 28, 2018.

DOI: 10.15376/biores.13.2.2932-2944