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Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*)

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ABSTRACT

The chromium polluted water hyacinth was subjected to pyrolysis to understand its pyrolytic characteristic in a fixed bed. The results indicated that chromium has a positive effect on the bio-oil produced, accompanied by a decrease of gas yield and moderate formation of char. The maximum bio-oil yield obtained from Cr-WH pyrolysis reached the maximum of 63.1 wt.%. The acid number and high heating value of the Cr-WH pyrolytic bio-oil were 85.04 mgKOH/g and 26.72 MJ/kg, respectively. GC-MS analysis of the bio-oils showed that the amount of nitrogenous compounds, alcohols and phenols increased, while the number of esters reduced in the Cr-WH pyrolytic bio-oil which indicated that chromium promoted bond rupture of lignin and changed the degradation process of protein. Furthermore, after pyrolysis, Cr may transfer from the toxic state of ions into an amorphous state in the char, which reduce its harm to the environment.

1. Introduction

Increasing heavy metal pollution of contaminated surfaces and ground waters is causing an unknown long-term threat to wildlife and human health [1]. The removal of heavy metal ions from aqueous effluents has been taken into consideration in recent years for remediation of the environment [2]. Biosorption is a process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure [3]. But, following concern is the disposition of this heavy metal-absorbed biomass [4–6]. Traditional ways to deal with heavy metal-absorbed biomass were landfill and combustion. However, those may cause the second pollution such as high heavy metal concentration in soils, release of volatized compound in the atmosphere after combustion or accumulation into the human body through the food chain [7,8]. Therefore, there is a possibility to study biomass conversions such as pyrolysis which converts biomass into bio-oil, fuel gas, and charcoal powder adsorbent, and reduces the release of carbon dioxide and sulfur dioxide. Furthermore, pyrolysis can shift the heavy metal from a toxic state or free ions state into an inert condition under reducing atmosphere, which is regarded as eco-friendly method to dispose of heavy metal-absorbed biomass compared to combustion and landfill [9].

Recent articles have researched many kinds of heavy metals for pyrolysis of lignocellulosic biomass. Lievens et al. studied heavy metal contaminated biomass from birch and sunflower. Based on TG analysis at maximum decomposition of 623 K and 673 K, they found that cadmium compounds were more susceptible to volatilization than copper, lead and zinc compounds at high pyrolysis temperature [10]. Jiu B.B et al. found in another study that the maximum bio-oil yield of Pb-contaminated water hyacinth pyrolysis was approximately 56% higher than that of WH, and the HHV of the bio-oil was about 0.6% lower than that of the WH derived bio-oil. After pyrolysis, Pb was trapped in char as high as 92.6% which avoids forming the second pollution [11]. Liu W.J et al. specially studied effects of copper on fast pyrolysis of fir sawdust, the presence of Cu improved the yield and HHV of the bio-oil, and GC/MS results showed that the oxygen content in bio-oils decreased. Over 91% of Cu in the biomass was enriched in the char after pyrolysis [9]. Koppolu et al. analysed the pyrolysis of hyperaccumulators with heavy metals (Zn/Ni/Co/Cu/Cr) and found that the presence of heavy metal decreases the char yield and increases the tar yield compared to the blank run and the type of

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salt exert no effect on char and tar yield [12]. F. Cuypers et al. investigated pyrolysis of chromated copper arsenate treated wood waste at the elevated temperature and found that higher operating pressure improves heavy metal retention rate in char [13]. Samolada et al. tested commercial transition metal catalysts (Fe/Cr on model biomass, and observed an increase of the selective production of phenol and light phenolics and an enhancement of the water gas shift (WGS) reaction leading to a remarkable increase of hydrogen concentration in the gaseous products [14]. Thus, the biomass pyrolysis process possibly significantly alter via absorbed heavy metal.

Water hyacinth (WH) originates from the Amazon basin but extensively spread out due to lack of natural enemies in abroad area and rapid proliferation [15]. Due to rapid proliferation WH is a potential biomass source and an agent for wastewater treatment [16]. WH is a perennial aquatic plant in many tropical and subtropical countries. It can absorb heavy metals effectively while cause coverage of lakes and water pollution leads to a threat to benthonic organism [17,18]. Unlike widely studied terrestrial biomass pyrolysis, WH is a hydrophyte, its components and structure are different from terrestrial plants. Hydrophyte plants act as biological filters, enriching their cellular structure with metal through polluted water uptake. However, few paper reports on chromium(Cr) and WH under pyrolysis condition. Cr is non-essential micronutrient for most living bodies, its content increased with wastewaters via discharges from electroplating, dye and pigment manufacturing [19,20]. In this study, Cr-WH was subjected to pyrolyze in a fixed-bed reactor to investigate the effect of Cr on water hyacinth pyrolysis and to explore the mechanism of Cr pyrolysis process on the components of water hyacinth during pyrolysis process by analyzing the characteristics of liquid, gas and solid three-phase products. In order to trace migration and transformation of Cr, the form and content of Cr in the liquid and solid phase were also detected after pyrolysis. The results may provide a theoretical basis for recycling and harmless disposal of WH and other heavy metal-absorbed biomass.

2. Materials and methods

2.1. Materials and samples

The WH was harvested from a lake near Tongan district in Xiamen, China. Prior to use, WH was washed with deionized water in order to obviate soluble ions effect on pyrolysis and cleans sites for adsorption of chromium ion, then air dried again and desiccated in heating oven at 105 °C until constant weight, then grinded with a muller and sieved (<0.16 mm). No metallic container was used during this experiment in order to avoid metallic contamination. Component analysis of WH determined by the method of Van Soest is shown in Table 1 [21].

Samples of WH were pretreated with $K_2Cr_2O_7$ as chromium source to form Cr-WH samples. Different concentration of Cr in water at 298 K were poured on WH in conical flask and shaken in oscillator at 120 rpm for 24 h. Then, the mixture was detached by vacuum filtration. The obtained mixture was dried at 105 °C in an oven and pulverized again to collect the particle with a size under 0.16 mm. The concentration of heavy metals within WH in polluted lakes range from dozens of times to thousands of times compare to the original waters [22,23]. In this study, five contents (0.5 wt.%, 1.0 wt.%, 1.5 wt.%, 2.0 wt.% and 2.5 wt.%) below 3 wt.% of Cr concentration were discussed [9].

Table 1
Results of WH component and ultimate and proximate analysis.

Relative composition.% (dry and ash basis)		Proximate analysis.% (dry basis)		Element.% (dry basis)	
Extractives	44.07	Moisture	6.28	C	39.62
Hemicelluloses	30.24	Fixed carbon	15.36	N	3.66
Cellulose	23.37	Volatiles	70.26	H	5.39
Lignin	6. 37	Ash	8.11	O	51.33
Acid-insoluble ash	2.32				

2.2. Method of experiment

The pyrolysis experiments were explored in a fixed-bed with four main parts (sweep gas, pyrolysis, condense, collect) as depicts in Fig. 1.

1. Nitrogen tank 2. Reducing Valve 3. Rotor flow meter 4. Quartz tube 5. Quartz boat 6. Graham condenser 7. Horizontal tube furnace 8. Wet type gas flow meter 9. Ice-water bath 10. Liquid collector 11. Filter 12. Air trap.

Weigh 15 g samples in a quartz horizontal tube reactor and then install the furnace with a settled heating rate of 30°C/min. High purity N_2 served as the sweep gas (300 mL/min) to create an inertia atmosphere. The temperature of pyrolysis starts from ambient temperature to the preset parameters (300 °C, 400 °C, 500 °C, 600 °C) and maintained for 10 min when reaching the final temperature. Prior to the experiment, a condenser was connected next to the outlet of the reactor. A series of U-tubes were installed in an ice-water bath for bio-oil condensing. The char collected in the horizontal tube was weighed as the solid product at the end of the experiment. The pyrolysis gas was collected in a bag through the whole process and then quantified by gas chromatography coupled to Thermal Conductivity Detector (GC-9160 from Xiamen Jinkejie fitted with TDX-01 packed column (1 m × 0.3 mm), carrier gas speed is 3.0 mL/min). The main gaseous products were CO_2, CO, H_2, and CH_4, by calculating the respective volume and then converting it into mass. The yield of bio-oil was calculated by subtraction of char yield and gas yield. The remnant of Cr in the char was calculated based on the following Eq. (1).

$$Cr_{trapping}(\%) = \frac{[Cr]_{char} \times m_{char}}{[Cr]_{Cr-WH} \times m_{Cr-WH}} \quad (1)$$

$[Cr]_{char}$ and $[Cr]_{Cr-WH}$ represent Cr content (wt.%) in char and in Cr-WH respectively. m_{char} and m_{Cr-WH} are the mass of char and Cr-WH.

2.3. Analytical methods

The released gaseous product was analysed by gas chromatography (GC-9160) with TCD. The condition of packed column required high purity argon as a carrier gas, the temperature of TCD and oven were 100 °C and 60 °C, respectively. The composition of bio-oil was analysed using gas chromatography coupled with mass spectrometry (GC-MS, QP2010 from Shimadzu fitted with an Agilent DB-WAX column, the length is 30 m, the carrier speed 3.0 mL/min), ethanol (C_6H_6O −2.0 ml) was used to dissolve the bio-oils before injection. HHVs of bio-oils were calculated by an automatic bomb calorimeter (ZDWH-2A). The acid value was quantum by titration method.

The distribution of Cr in the pyrolytic products was determined by Flame Atomic Absorption Spectroscopy (FAAS, TAS-990). Before measurement, the samples were digested with a microwave digestion system (Multiwave 3000) as follows: 200 mg of the sample was carefully weighed in a PTFE vessel and 5.00 ml of HNO_3 was added. After digestion, samples were diluted with purified water to 50.0 ml.