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ScienceDirect

Energy Procedia 160 (2019) 178–185

Energy Procedia

www.elsevier.com/locate/procedia

2nd International Conference on Energy and Power, ICEP2018, 13–15 December 2018,
Sydney, Australia

Slow pyrolysis of metal(loid)-rich biomass from phytoextraction: characterisation of biomass, biochar and bio-oil

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Abstract

Plants have successfully been used for phytoextraction of metal contaminated soils, however the use of these plants for energy production has been a subject of debates due to the potential conversion of the metals in the plants into airborne respirable particles. The aim of this study was to investigate the deportment of metal(loid)s during pyrolysis of a biomass cultivated in a highly contaminated soil in order to engineer best practice environmental approach for utilization of this biomass. A heavy metal(loid) contaminated mangrove (*Avicennia marina* var. *australasica*) biomass was used as a feedstock in this study. The biomass was subjected to slow pyrolysis under the heating rate of 60 °C/min and different pyrolysis temperatures. Inductively coupled plasma mass spectrometry, thermogravimetric analysis, Fourier-transform infrared spectroscopy, X-ray fluorescence spectroscopy and gas chromatography–mass spectrometry were introduced to characterise the biomass, biochar and bio-oil samples. Results showed that biochar yield decreased from 57.4 % to 35.3 % with the increase in pyrolysis temperature from 300 to 700 °C. Heavy metal(loid)s (chromium, manganese, iron, copper, zinc, arsenic and lead) were mainly bound in the biochar produced at 300 °C, while the recovery decreased substantially with the increase of pyrolysis temperature. Phenols, carboxylic acids and alcohols were the dominant compounds in all bio-oil samples. This study suggested further requirements of biochar quality and environmental risk assessment to provide a safe and value-added way of phytoextraction residual applications.

Selection and peer-review under responsibility of the scientific committee of the 2nd International Conference on Energy and Power, ICEP2018.

Keywords: pyrolysis; temperature; biochar; bio-oil; heavy metals

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10.1016/j.egypro.2019.02.134

1. Introduction

Contamination of land with metal(loid)s released from anthropogenic activities is a significant problem for many countries. Unlike organic contaminants, metal(loid) pollutants do not degrade by microbes or chemicals in soil, which poses an increasing threat to the environment and human health. To minimize the hazards, phytoextraction has been proved to be one of the most favored and cost-effective remedial strategies [2,3]. Phytoextraction is the technique that uses plants to uptake large amounts of one or several heavy metals from the soil, thus gradually reducing the amount of available metals in the soil to achieve decontamination of metal-polluted soils. These plants are named as phytoextractors or accumulators [3]. Apart from the low cost compared with conventional remediation techniques, flora improves the hydrological site conditions, increases soil organic matter and microbial activity, stabilizes soil to reduce erosion, and protects the soil from direct sunlight [4]. However, the disposal of metal(loid)-enriched biomass after harvesting is restricting the utilisation of phytoextraction on end-users [5].

Previous work presented some potential approaches towards disposal of contaminated biomass, such as direct disposal, compacting, combustion, gasification and pyrolysis [5]. Some disposal options may induce additional problems. For example, direct disposal returns the meal(loid)-rich biomass back to soil, and even increases the risk by releasing the immobilized contaminants during biomass decomposition; open combustion generates airborne respirable particles into the atmosphere and poses secondary pollution to the air and land [6]. Based on these concerns, pyrolysis under oxygen limited conditions is considered as one of the promising approaches for post-phytoextraction biomass disposition [7,8].

Pyrolysis of metal(loid)-rich biomass can effectively reduce the biomass bulk, generate bioenergy or bio-products, compensate the remediation costs and thus turn phytoextraction into a profitable economic business [9,10]. Monitoring of metal(loid) deportment in end products becomes particularly important which is not well documented. Pyrolysis temperature is believed to be the most significant parameter to influence the metal(loid)s distribution in end fractions. Lower pyrolysis temperature helps to accumulate and immobilize metal(loid)s in bio-char matrix and thus sequestrate heavy metal(loid)s, while higher temperatures contribute to their distribution in volatile fractions [9], [11-13]. For example, Stals et al. [11] found that the majority of zinc (Zn), cadmium (Cd) and lead (Pb) from biomass were recovered in chars produced under 623K and 723K, while higher pyrolysis temperature (823K) induced metal transfer into volatile products. Biomass properties and the pyrolysis set-up may also influence metal(loid) deportment and end-product quality. Al Chami et al. [12] compared the end products from flash and slow pyrolysis under the same heating temperature. Nickel (Ni) and Zn were found to be mainly recovered in biochar after slow pyrolysis while the metals retained in the char and the heating transfer medium in the case of flash pyrolysis; biochar and bio-oil yields were also found to be different. Therefore, characterizing the biomass and end products from pyrolysis of metal(loid) contaminated biomass is of great importance for phytoextraction residual utilization.

To date, there is limited scientific report on metal(loid)s behavior during pyrolysis of heavy metal(loid)s contaminated biomass grown on slag polluted soil. In this work, pneumatophores of mangrove (*Avicennia marina* var. *australasica*) biomass grown on a land area filled with black slag was used as a model feedstock for pyrolysis under different temperature to monitor the heavy metal(loid)s contribution in biochars and characterize the biomass, biochar and bio-oil samples in order to engineer best practice environmental approach for utilization of this biomass.

2. Experimental Methodology

2.1. Biomass preparation and characterisation

Pneumatophores of *A.marina* were collected from a contaminated land area filled with black slag from Pasminco zinc and lead smelter along the Creek Reserve Road (S 32°57.262’ E 151°36.911’) at Boolaroo, New South Wales, Australia. The root sample was washed three times by tap water and then twice by Milli-Q water to remove the soil and dust before air-drying for 3 days. The biomass was then dried in a vacuum oven for 4 h at 80 ℃ and 80 kPa and milled to less than 0.08 mm.

To determine the chromium (Cr), manganese (Mn), iron (Fe), copper (Cu), Zn, Arsenic (As) and Pb concentrations in biomass samples, the milled biomass sample was sent to Mark Wainwright Analytical Center in Sydney, Australia for inductively coupled plasma mass spectrometry (ICP-MS) analysis. The weight loss of biomass during heating was measured by Mettler Toledo thermogravimetric analysis (TGA) instrument (model TGA/DSC 1 STARe System). Approximately 25 mg of biomass was placed in a circular alumina crucible and loaded in the apparatus. For thermogravimetric analysis, biomass was heated from room temperature to 1000 °C at the heating rate of 60 °C/min, during which argon (Ar) was used as purging gas at a constant flow rate of 20 mL/min. Differential thermogravimetry (DTG, wt. %/min) were obtained by differentiating the TG (wt. %) data. Biomass sample was also subjected to proximate analysis using TGA. The system was set up to ramp at 10 °C/min from room temperature to 110 °C in nitrogen (N_2) at a constant flow rate of 50 mL/min, hold at 110 °C in N_2 for 5 min, then rising from 110 to 900 °C at the heating rate of 50 °C/min with N_2 as a carrier gas; the system was kept at 900 °C for 15 min in N_2 atmosphere before changed to air atmosphere (at a flow rate of 50 mL/min) and held for another 10 min. Moisture in biomass was considered to evaporate in N_2 between ambient temperature and 110 °C. Volatile matter was the mass lost under N_2 from 110 to 900 °C. Ash content was the residue after the combustion under air, while fixed carbon content was calculated by difference. Fourier transform infrared spectroscopy (FT-IR) spectra of the biomass was recorded by Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, Inc.). An attenuated total reflectance (ATR) accessory with a diamond crystal was used for sample analysis with a total scan of 32 and spectral resolution of 4 cm^{-1}.

2.2. Pyrolysis experiments

Biomass of mangrove pneumatophores previously prepared were used as feedstock in the pyrolysis experiments. Pyrolysis was carried out in a fixed bed horizontal tubular furnace described in detail by Strezov et al. [14]. 1 g of feedstock was packed into a quartz tube reactor and fixed by glass wool at both ends, then loaded into the furnace, and purged by ultra-pure helium (He) for 20 min to remove the residual air before each experiment. For pyrolysis experiments, feedstock was heated from room temperature to five final sample temperatures (300, 400, 500, 600 and 700 °C) separately at a heating rate of 60 °C/min, during which helium was also used as a purging gas at a constant flow of 50 mL/min. After each experiment, biochar and bio-oil samples were collected for subsequent analyses.

2.3. Biochar characterisation

After pyrolysis, biochar samples were weighed and calculated for biochar yields (wt. %). Olympus Delta Pro spectrometer with tantalum anode X-ray tube was used to analyse the metal(loid) concentrations in biochar samples. The heavy metal recovery (%) after each pyrolysis experiment (1 g of feedstock) was calculated by dividing the heavy metal concentration in biochar samples to the concentration in feedstock and multiplied by the corresponding biochar yields. TGA and FT-IR were also used for biochar and FT-IR spectra analysis, respectively, and the set-up method was the same as biomass analysis in 2.1.

2.4. Bio-oil characterisation

After pyrolysis, the bio-oils were collected from glass wool on the end of quartz reactor. The bio-oil samples were first dissolved with dichloromethane (DCM) solvent and subjected to gas chromatography – mass spectroscopy (GC-MS) analysis for qualitative analysis of organic compounds. The GC-MS analysis was performed on an Agilent 7890B gas chromatograph coupled with a 5977A mass spectrometer equipped with a HP-5MS capillary column (60 m × 0.25 µm). The system set-up and analysis were presented in detail by Weldekidan et al. [15]. The match factor in MassHunter software with the National Institute of Standards and Technology (NIST) database was set to over 80.

3. Results and discussion

3.1. Mass change of biomass during pyrolysis

Fig. 1 shows the thermogravimetric (TG, wt. %) and the differential thermogravimetric (DTG, wt. %/min) results of mangrove root biomass during pyrolysis from room temperature to 1000 °C at the heating rate of 60 °C/min. The DTG curve revealed a three-stage decomposition process of biomass during pyrolysis.

In the first stage, a small peak summiting at about 115 °C ranged from 35 to 190 °C in the DTG curve was observed, which indicated the evaporation of residual water and some light volatile compounds in biomass. The first stage of pyrolysis contributed to a sample loss of approximately 7 % of the initial biomass weight. The second stage of pyrolysis started at 190 °C and terminated at about 720 °C with an additional 55 % mass loss as volatiles. At this stage, a rapid decrease in the mass occurred between around 200 and 550 °C with two peaks overlapping each other. The DTG curve indicated that the maximum mass loss occurred at the temperature of 350 °C, while a lower loss occurred at 295 °C. This stage included the main complex reactions that accounted for the most significant mass loss, releasing a wide variety of organic and inorganic volatiles [16]. The temperature ranging from around 720 to 1000 °C can be defined as the last stage of pyrolysis, during which a very slow decomposition rate with a slight mass loss (around 3 %) was observed due to char consolidation, leaving a mass of 35 wt. % of the original biomass remaining at the final temperature.

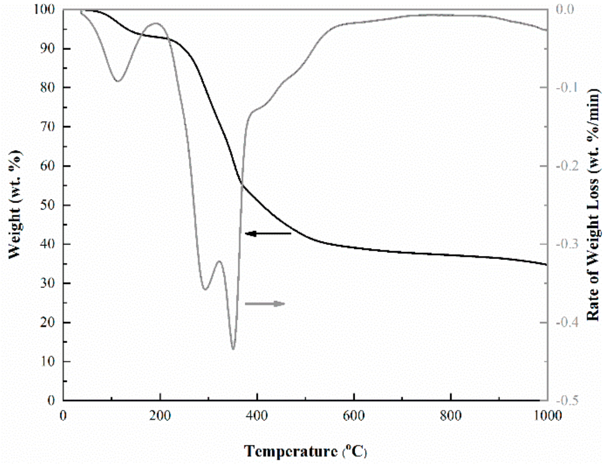

Fig. 1. Thermogravimetric analysis of biomass

3.2. Biochar characteristics

Pyrolysis of biomass under different temperatures has a significant influence on biochar characteristics. As shown in Table 1, the biochar weight, moisture and volatile matter content decreased along with the increase of pyrolysis temperature, while the ash and fixed carbon content in biochar samples has a reversed trend, which is in accordance with that observed on other biochars [11,16]. Higher pyrolysis temperature favors lower biochar weight and higher fixed carbon content, while energy input and heavy metal(loid) distribution should also be taken into consideration in the case of metal(loid)-rich biomass pyrolysis.

Table 1. Biochar yield and proximate analysis under different pyrolysis temperatures

Pyrolysis temperature (°C)	Proximate analysis of biochars (wt. %)				Biochar yield (wt. %)
	Moisture	Volatile matter	Ash	Fixed carbon	
Feedstock	6.41	57.95	15.141	20.50	/
300	4.73	24.23	30.27	40.77	57.4

400	4.62	19.30	32.02	44.06	40.3
500	4.44	14.31	34.64	46.61	38.2
600	3.34	10.94	38.51	47.21	36.2
700	3.08	6.87	39.65	50.40	35.3

The chemical bond structure in raw material and its subsequent biochar samples produced at different temperatures analyzed by FT-IR was shown in Fig. 2. Comparing the spectra of the chars to the raw biomass, nearly all bands were reduced or eliminated, indicating some of the detected functional groups were degraded during heating while some others were almost remained unchanged across the pyrolysis processes of the sample.

For the raw material, the presence of a broad band at between 3630 and 3024 cm^{-1} was mainly attributed to O-H vibration of hydrogen-bound hydroxyl functional groups, with a minor contribution of N-H groups [18]. The region between 2820 and 2980 cm^{-1} expressed the C-H stretching vibrations of lipids. The bands at 2919 and 2850 cm^{-1} was most likely related to the CH_2 and CH_3 groups in acyl chains of lipids [19]. This double peak was evident in the raw sample and biochar produced at 300 ℃, reduced with temperature and completely removed at 500 ℃, confirming the assignment of band vibrations to aliphatic compounds. This absorption peak reduced in the biochar sample produced at 300 ℃ and totally disappeared when the temperature was further increased. The minor peak observed in the raw sample's spectra at 1700-1610 cm^{-1} were principally C=O stretching vibrations with some N-H bending and C-H stretching vibrations of amide I bands. While amide II bands, at 1575-1480 cm^{-1} expressed the existence of N-H bending vibrations with some C-N stretching vibrations [20]. These two peaks both removed in the biochar samples. The most intensive peak in all the samples, observed at the wavelength of 1030 cm^{-1}, was associated with C-O and /or C-C group in carbonate.

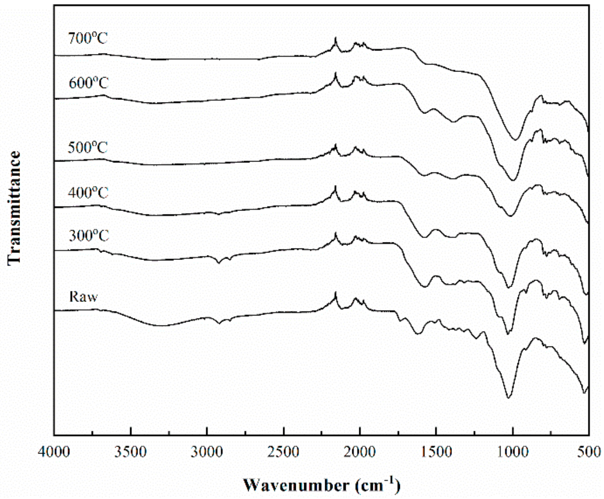

Fig. 2. FT-IR spectra of raw biomass and biochar produced under different pyrolysis temperatures

3.3. Heavy metal(loid) distribution in biochar samples

The total heavy metal(loid) concentrations of feedstock and biochar samples generated from different pyrolysis temperatures with a heating rate of 60 ℃/min are shown in Table 2. It can be seen that, compared to the feedstock, the metal(loid) concentrations in biochar were all enhanced.

Table 2. Heavy metal concentrations in feedstock and biochar samples from different pyrolysis temperature

Pyrolysis temperature (℃)	Total heavy metal concentrations (μg/g)						
	Cr	Mn	Fe	Cu	Zn	As	Pb
Feedstock	5.37	228.2	4796	51.50	306.3	28.70	118.0

300	8.64	385.4	8258	89.05	524.2	38.92	124.6
400	7.36	355.2	7548	84.50	489.7	41.60	126.1
500	9.28	389.1	8601	85.15	540.9	40.01	140.7
600	9.92	364.8	7987	108.55	530.0	48.32	133.4
700	6.40	384.0	8222	85.80	531.3	37.44	126.4

Volatilization of any other forms of transfer of heavy metal(loid)s during pyrolysis will affect the deportment of metal(loid)s in biomass. To understand better the fate of heavy metal(loid)s during the pyrolysis process, recovery rates were calculated based on the total amount of heavy metal(loid)s obtained in the biochar after pyrolysis (Table 3). The recovery results demonstrated that almost all Cr, Mn, Fe, Cu and Zn were retained in the char at pyrolysis temperature of 30 °C, while lower percentage of As and Pb were recovered. These results were in agreement with Bert et al. [21], who reported that almost all of the Cu, Zn and Pb were recovered in solid residue from metal-enriched poplars torrefaction (290 °C). Generally, the metal(loid)s recovery in biochar decreased with the increase of pyrolysis temperature, which means a weaker adhering of heavy metal(loid)s to solid fractions. Cr, As and Pb were strongly volatilized at 700 ℃ compared to other metals, with more than 50 % removed from the biochar samples.

Table 3. Heavy metal recovery in biochar samples after pyrolysis under different pyrolysis temperature

Pyrolysis temperature (℃)	Heavy metal recovery in biochar (%)						
	Cr	Mn	Fe	Cu	Zn	As	Pb
300	92.35	97.00	98.84	99.25	98.32	77.84	60.61
400	55.23	62.78	63.43	66.12	64.50	58.41	43.03
500	66.01	65.19	68.51	63.16	67.53	53.24	45.55
600	66.87	57.92	60.29	76.30	62.70	60.95	40.91
700	42.07	59.45	60.52	58.81	61.29	46.05	37.80

Table 4. GC-MS results of bio-oil from different pyrolysis temperature

Retention time (s)	Compound name	Formula	Area percentage under different pyrolysis temperatures (%)				
			300 ℃	400 ℃	500 ℃	600 ℃	700 ℃
616.9	2-methylpropan-1-ol	$C_6H_{12}O_3$	4.54	4.24	3.95	4.55	3.94
1241.0	furfuryl alcohol	$C_5H_6O_2$	1.84	1.26	1.29	1.41	1.20
1603.1	phenol	C_6H_6O	1.17	1.35	1.84	1.87	1.74
1625.0	3-pyridinol	C_5H_5NO	0.80	0.58	0.75	0.50	0.71
1666.6	3-methylphenol	C_7H_8O	0.91	0.44	0.89	1.28	1.30
2013.0	4-methylphenol	C_7H_8O	/	0.60	0.78	0.77	0.75
2202.7	guaiacol	$C_7H_8O_2$	0.81	1.77	1.64	2.11	1.79
2043.4	3-ethylphenol	$C_8H_{10}O$	/	/	0.44	0.42	0.38
2409.3	catechol	$C_6H_6O_2$	4.97	2.17	2.96	3.06	2.68
2698.8	3-methylcatechol	$C_7H_8O_2$	/	1.03	1.03	0.90	0.66
2712.4	vanillin	$C_8H_8O_3$	/	0.58	0.62	0.48	/
2731.5	syringol	$C_8H_{10}O_3$	3.26	/	4.02	3.43	3.25
2758.6	hydroquinone	$C_6H_6O_2$	1.48	0.48	0.58	0.72	0.66
3173.9	triethylene glycol	$C_6H_{14}O_4$	2.55	1.27	1.09	1.54	1.41
3364.6	eugenol	$C_{10}H_{12}O_2$	0.88	0.84	0.84	1.01	0.87
4895.1	palmitic acid	$C_{16}H_{32}O_2$	2.08	1.61	1.57	1.80	1.68
5338.5	9,12-octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$	1.09	1.30	1.08	1.14	1.04

5361.5	11-octadecenoic acid, (E)-	$C_{18}H_{34}O_2$	1.81	1.68	1.65	2.50	1.64
5428.0	stearic acid	$C_{18}H_{36}O_2$	0.67	0.48	0.45	0.49	0.45
6388.9	behenic acid	$C_{22}H_{44}O_2$	/	0.60	0.46	0.50	0.52
7883.6	germanicol	$C_{30}H_{50}O$	3.24	1.15	1.35	1.26	1.38

3.4. Organic composition of bio-oils

As one of the main products from biomass pyrolysis, bio-oil samples were also collected and subjected to GC-MS analysis for organic compounds identification. The major peaks were organised and presented according to the retention times with corresponding formulas identified in Table 4. As seen from the table, phenols, carboxylic acids and alcohols were the dominant compounds in all bio-oil samples while identified with varying concentrations. 2-Methylpropan-1-ol was the most abundant alcohol, while catechol was the most abundant phenol within all bio-oil samples generated from different pyrolysis temperatures. The prominent compounds at 300 ℃ were 2-methylpropan-1-ol (4.54 %), catechol (4.97 %), syringol (3.26 %) and germanicol (3.24). For the bio-oil produced at 500, 600 and 700 ℃, 2-methylpropan-1-ol, catechol and syringol were the three most abundant compounds. Noticeably, a variety of carboxylic acids were abundant within all the bio-oil samples, including syringol, palmitic acid, 9,12-octadecadienoic acid (Z, Z)-, 11-octadecenoic acid, (E)-, stearic acid and behenic acid, which restricted its potential for direct use as liquid fuel, due to its corrosive and unstable properties.

4. Conclusion

Pyrolysis of metal(loid)-enriched plant biomass poses a promising strategy to post-phytoextraction application. Deriving bio-products from phytoextraction will not only help to achieve the alternative energy demand up to a certain extent but can also provide an avenue for fostering a bio-based economy for sustainable development. The deportment of heavy metal(loid)s should be well monitored to prevent secondary pollution to the environment. In this study, properties of biomass, biochar and bio-oil samples produced at different pyrolysis temperatures were investigated on heavy metal(loid)s contaminated mangrove roots.

With the increase of pyrolysis temperature, the yield, moisture and volatile matter content of biochars were decreased, while the fixed carbon content, ash content and heavy metal(loid) concentrations in biochar samples were enhanced. The heavy metal(loid)s mainly retained in biochars at low pyrolysis temperature, but volatilised significantly with the heating temperature. This study suggested further requirements of investigation of the biochar quality and environmental risk assessment to provide a safe and value-added way of phytoextraction residual applications.

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