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Bio-oil production from hydrothermal liquefaction of *Pteris vittata* L.: Effects of operating temperatures and energy recovery

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ABSTRACT

Hyper-accumulator biomass, *Pteris vittata* L., was hydrothermally converted into bio-oils via hydrothermal liquefaction (HTL) in sub-supercritical water. The distributions and characterizations of various products as well as energy recovery under different temperatures (250–390 °C) were investigated. The highest bio-oil yield of 16.88% was obtained at 350 °C with the hydrothermal conversion of 61.79%, where the bio-oil was dominated by alcohols, esters, phenols, ketones and acidic compounds. The higher heating values of bio-oil were in the range of 19.93–35.45 MJ/kg with a H/C ratio of 1.26–1.46, illustrating its high energy density and potential for use as an ideal liquid fuel. The main gaseous products were CO_2, H_2, CO, and CH_4 with the H_2 yield peaking at 22.94%. The total energy recovery from bio-oils and solid residues fell within the range of 37.72–45.10%, highlighting the potential of HTL to convert hyper-accumulator biomass into valuable fuels with high conversion efficiency.

1. Introduction

Biomass has been perceived as an alternative and valuable resource for producing clean and sustainable fuels in terms of bio-oil, bio-gas and bio-char through appropriate thermo-chemical methods, illustrating a crucial role in meeting the increasing demands for clean and renewable energy with great social, economic, and environmental benefits (Cao et al., 2017a; Hu et al., 2018; Kumar et al., 2018). Similar to normal biomass in terms of chemical compositions, hyper-accumulator biomass, which was used to remove high levels of metallic pollutants from contaminated sites were also suitable candidates for bio-fuels. With the rapid development of this remediation technology, large quantities of high-energy biomass had been generated, for example, the yield of fresh biomass of *Pteris vittata* L. above ground could be up to nearly 36 tons per hectare (Chen et al., 2002), presenting an enormous potential in meeting the targets for exploitation of renewable energy sources. However, the accumulation of these hazardous materials would result in a secondary waste containing high levels of toxic heavy metals, therefore, needed to be disposed off in a safe manner. With these in mind, the crucial issue is whether and how this kind of waste can be converted from its natural form to fuel with a reduced environmental footprint, and which process is most suitable for this purpose.

Hydrothermal liquefaction (HTL), using water as medium at moderate temperatures (200–400 °C) and pressures (5–20 MPa), has been considered as the most appropriate technology for the direct conversion of wet biomass into liquid bio-fuel owing to the mild reaction conditions, lower energy costs without the drying process of feedstock and high bio-oil yields (Gollakota et al., 2018; Zhang et al., 2018; Zhu et al., 2017). When biomass was subjected to hydrothermal conditions, macromolecules in biomass would be hydrolyzed into simple compounds due to the special properties of water (i.e., its dielectric constant, density, viscosity and surface tension). Particularly, once beyond the critical point (374 °C, 22 MPa), the properties of water would present significant variations, such as further lower dielectric constant and higher diffusion coefficient, making water as an effective medium for most organic reactions due to complete miscibility and the absence of phase boundaries. After HTL treatment, the main product of liquid biocrude could be upgraded into bio-oils, transportation fuels or chemical products, while the solid bio-char could be used as a fuel or fertilizer and the gaseous products based on a mixture of hydrogen and methane could be used as a source for heat and electric generation (Cao et al., 2017a; Reißmann et al., 2018). In recent years, many studies have been carried out using various feedstock, such as woody biomass (Malins, 2017; Younas et al., 2017; Zhu et al., 2017), algae (Cheng et al., 2017; Parsa et al., 2018; Song et al., 2017), wastes (Couto et al., 2018; Hadhoum et al., 2016; Nazem & Tavakoli, 2017) and coal (Hartman & Hatcher, 2014; Shi et al., 2017; Wang et al., 2008) for the purpose of producing bio-fuels through HTL. However, at present, there are no

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reports that evaluate various products via HTL with the hyper-accumulator biomass produced from contaminated soils. The absence of comprehensive understanding of properties of various products produced from HTL treatment of this kind of biomass would bring a major challenge in the opportunity for its bio-energy recovery. Moreover, it was evident that operating temperature played a significant role on the yield and quality of bio-fuels during HTL, mainly due to the corresponding variations of water properties and series of related reactions under different temperatures, especially in the supercritical region (Chan et al., 2015; López Barreiro et al., 2013). However, there was no definite optimum operating temperatures due to the specific purpose of energy products, biomass types and other operating parameters (Cao et al., 2017b). Taking these into consideration, in the present study, we focused on evaluating the feasibility and effectiveness of this kind of biomass for bio-energy production via HTL. The influence of reaction temperatures on the yields and characteristics of bio-oil, gaseous and solid products were investigated. The products were further characterized using various technologies, such as elemental analysis (EA), gas chromatography-mass spectrometry (GC–MS), scanning electron microscopy (SEM) and gas chromatography (GC) for understanding the reaction pathway and mechanisms during HTL. Moreover, the carbon, hydrogen, and energy recovery from the HTL of *Pteris vittata* L. at different reaction temperatures were also evaluated. To the knowledge, this was the first study to identify the chemical characteristics of fuel-associated productions generated from *Pteris vittata* L. under both subcritical and supercritical conditions, which may present a potential for helping resolve waste management and converting renewable hyper-accumulator feedstock into sustainable bio-energy products.

2. Materials and methods

2.1. Materials

The hyper-accumulator biomass *Pteris vittata* L. employed in this study as the feedstock for HTL was obtained from a test field in Henan province, China. The dried biomass was then reduced to a particle size of < 150 μm using a pulverizer. The physicochemical analyses of *Pteris vittata* L. including proximate and ultimate analysis and their test methods were shown in Table 1. It should be noted that the ash content in the biomass used was relatively high (18.73 wt%), consisting of a certain content of inorganic matter (including heavy metals such as Cd, Cr, Cu, and Ni). During HTL, the ash could not be converted into bio-oil; however, the heavy metals in the ash may play an important role (such as a catalytic effect) in the conversion reactions of biomass into bio-oil, and the synergy effect of the heavy metals in these reactions still need to be better elucidated. Acetone and dichloromethane (DCM) as extraction solvents were the analytical reagents (> 99.5%) and used as-received. Pure nitrogen (99.99%) and high-purity helium (99.999%) were adopted to purge the system for oxygen replacement and GC–MS analysis. In addition, deionized water, prepared using an ultra-pure water system, was used throughout the experiments.

2.2. Experimental procedure

The HTL experiments were performed in a double-wall batch reactor with an internal volume of 500 mL, as illustrated in the previous study (Li et al., 2018). The reactor was heated by a 2.0 kW electric heater to the expected temperature with an average heating rate of 5 °C·min^{-1}. Nitrogen was used at a constant rate of 500 mL min^{-1} for 5 min to remove residual air, and kept at 0.2 MPa for oxygen-free conditions in the reactor. A magnetic stirrer (set at 160 RPM) was fixed vertically inside the reactor for mixing the biomass and deionized water continuously during the tests. After maintaining the predetermined temperature for a sustained period (residence time), the reactor was cooled to the ambient temperature in 40 min by both a cooling coil inside the reactor and an electronic fan. Reaction temperatures were investigated in the range of 250–390 °C (corresponding to the pressures of 4–25 MPa) with a fixed residence time (15 min) and solid–liquid ratio (10 g: 100 mL). After cooling the reactor to the ambient temperature, various products were collected together and separated by series of filtration and extraction as illustrated in Fig. 1. The gases were vented through the exhausting lines and collected in aluminum-foil gas bags. The volumetric flow rate of the gases was recorded by an automatic mass flow controller. The remaining reaction mixtures were collected carefully from the reactor, following which the reactor and stirring rods were washed with acetone (350 mL) three times. The collected mixtures and rinsed solution were separated into solid- and liquid-phase products using a vacuum filter for 15 min. The solid phase was subsequently extracted with acetone (250 mL) using a double-layer membrane filtration funnel until the filtrate became colorless. The extracted filtrate was concentrated by a rotating evaporator at a speed of 40 RPM with a distillation temperature of 35 °C and a reduced pressure of 2 mbar. After removing the acetone solvent, the rest of acetone-soluble fraction was designated as the heavy oil. The products insoluble in the acetone solvent were dried in a drying oven at 105 °C for 16 h and designated as the solid residue. The liquid mixture was extracted with 200 mL of DCM into DCM-soluble and DCM-insoluble products in a separatory funnel. The DCM solution was then evaporated under 25 °C and 2 mbar to obtain the light oil. The DCM-insoluble fraction was designated as the aqueous product.

Table 1
Physicochemical characteristics of feedstock.

Proximate analysis (wt%)[a]				Ultimate analysis (wt%)[b]					Atomic Ratio		
Moisture	Volatile matter	Fixed carbon	Ash	C	H	O[c]	N	S	H/C	O/C	HHV[d]
6.35	60.69	20.58	18.73	51.49	6.50	38.06	3.54	0.41	1.51	0.55	19.93
Inorganics (wt%)[e]											
K	Si	Ca	Cl	Fe	P	Al	Mg	Ti	Na	Mn	
18.85	15.36	11.99	3.21	2.84	2.44	2.23	1.95	0.33	0.26	0.22	
Heavy metals in the biomass (mg/g)[f]											
Cd		Cr	Cu		Ni	Pb		Zn		As	
0.0053		0.128	0.0239		0.17645	0.09015		0.22505		8.547	

[a] Based on dry biomass.
[b] Based on dry ash-free basis.
[c] Calculated by subtraction method (O% = 100% − C% − H% − N% − S%).
[d] HHV: Higher heating value, MJ/kg.
[e] Tested by X Ray Fluorescence (XRF).
[f] Determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).