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Activated carbons for the hydrothermal upgrading of crude duckweed bio-oil

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ABSTRACT

This study examined a two-stage (noncatalytic pretreatment followed by catalytic upgrading) hydrothermal processing of crude bio-oil produced from the hydrothermal liquefaction of duckweed. The activities of six activated carbons (ACs)-pine wood AC, coconut shell AC, bamboo stem AC, apricot pit AC, peach pit AC, and coal AC-toward the deoxygenation and denitrogenation of the pretreated duckweed bio-oil were determined in supercritical water at 400 °C for 1 h with the addition of 6 MPa of H_2 and 10 wt% AC. All of the ACs exhibited activity similar to Ru/C toward the denitrogenation and deoxygenation of the pretreated duckweed bio-oil. Of the ACs tested, bamboo stem AC produced an upgraded bio-oil with the highest yield (76.3 wt%), the highest fraction (90.13%) of material boiling below 350 °C, and the highest energy density (44.1 MJ/kg). Decreased ash and acidic groups in the pre-treated AC disfavored the production of upgraded bio-oil but aided denitrogenation and desulfurization. The ACs are suspected to leach ions and weak acids into the reaction solution, which would catalyze denitrogenation and desulfurization. The gases mainly consisted of unreacted H_2, CO_2 and CH_4 together with small amounts of C_xH_y ($x \leq 5$, $y \leq 12$) hydrocarbon gases produced from the cracking of the upgraded bio-oil.

1. Introduction

Bio-oils, which are produced from the thermochemical conversion of biomass, have been recognized as a potential alternative renewable energy source to petroleum-based transportation fuels. Developing bio-oil from renewable biomass would provide environmental and social benefits. As a novel feedstock with high biomass yield and high protein and starch content, duckweed has recently gained increasing attention from researchers and governments for biofuel production [1]. Thermochemical conversion (e.g., pyrolysis and hydrothermal liquefaction (HTL)) is one the main avenues for converting duckweed into a tar-like material (crude bio-oil), which has a considerably higher energy density than that of duckweed biomass [2–6]. However, this type of crude bio-oil is typically too viscous to flow at room temperature, is chemically unstable, and contains quantities of N, O, and S that are significantly higher than the American Society for Testing and Materials (ASTM) requirement [7]. Thus, this type of crude bio-oil cannot be directly used as a transportation fuel. Further treatments regarding the reduction of viscosity and the removal of heteroatoms from the crude duckweed bio-oil to form hydrocarbons are necessary.

To date, there have been few reports on the heterogeneous catalytic upgrading of crude duckweed bio-oil. Only two recent articles from the authors' lab have been reported [8,9]. In these previous studies, the effects of different commercially available materials, such as Ru/C, Pd/C, Pt/C, Pt/γ-Al_2O_3, Pt/C-sulfide, Rh/γ-Al_2O_3, activated carbon (AC), MoS_2, Mo_2C, Co-Mo/γ-Al_2O_3, and zeolite, on the product fraction yields and the deoxygenation, denitrogenation, and desulfurization of crude duckweed bio-oil were examined in subcritical water. All of the materials, including AC, displayed catalytic activity for deoxygenation, denitrogenation and desulfurization of the crude duckweed bio-oil (relative to noncatalytic treatment). These results motivated the present investigation of whether AC alone could be an effective catalyst for the deoxygenation, denitrogenation, and desulfurization of crude duckweed bio-oil. Water above its boiling point is known as subcritical or supercritical (above the critical point, SCW) water, which typically exhibits many desirable properties, such as a low dielectric

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Table 1a
Proximate and ultimate analyses (wt%, as-received basis) of duckweed.

Proximate and ultimate analyses											
M	A	V	FC	L	P	CH	C	H	N	O	S
13.2	18.0	71.5	10.5	9.0	23.1	26.2	35.4	4.8	3.7	32.3	1.0

M: moisture; A: ash; V: volatiles; FC: fixed carbon; L: lipid; P: protein; CH: carbohydrate.

Table 1b
Inorganic composition (wt%, as-received basis) of duckweed.

Na	Mg	Al	Si	P	Cl	K	Mn	Fe	Ni	Cu	Zn	Br	Sr	Ca	Ti	Cr	Mo	Ru
0.45	0.61	0.28	1.89	1.17	3.91	6.12	0.16	0.71	0.01	0.01	0.02	0.02	0.08	8.24	0.04	0.01	0.03	0.03

constant, high diffusivity, and adjustable solvency, making it a potential medium for the processing of crude bio-oil [10].

There are reports of the use of charcoals and ACs as catalysts for the deoxygenation of fatty acids [11] in SCW and for upgrading heavy oils without solvent or in supercritical toluene [12–14]. The results of these studies demonstrated that ACs are effective and suitable for upgrading heavy oil, especially heavy oils such as Maya that contain a large amount of heavy metals. ACs have an affinity for heavy hydrocarbon compounds, an adsorption selectivity for asphaltenes, and an excellent ability to restrict coke formation during the upgrading of heavy oils [12–14]. ACs are also used for the adsorptive removal of N and S from diesel oils [15–17]. However, to the best of the authors' knowledge, there have been no reports on the use of ACs to upgrade crude bio-oils in hydrothermal media, apart from the authors' single experiment [9]. If sufficiently active, these materials could be attractive as low-cost catalysts for this transformation. In this study, several different commercial ACs were used for the catalytic upgrading of crude bio-oil derived from the HTL of duckweed to fuel-range hydrocarbons in SCW with added H_2.

2. Experimental

2.1. Materials

Duckweed (*Lemna minor*) was collected from rice fields in Hebei Province in northern China and was grown in freshwater in summer for an average of four weeks. After four weeks of growth, the duckweed was harvested, washed with deionized water to remove impurities, and sun-dried. It was dried again in an oven at 110 °C for 12 h prior to use and then crushed in a multi-functional pulverizer to a #100-mesh particle size. The proximate and ultimate analyses of duckweed are listed in Tables 1a and 1b. The inorganic composition of the duckweed was measured by X-ray fluorescence (XRF) using a Bruker S8 TIGER XRF spectrometer, and the results are provided in Tables 1a and 1b.

Five biomass-derived ACs and one coal-derived AC were used in the present study. The ACs were commercially available from a local tap water purification company. The biomass-derived ACs were prepared from pine wood, coconut shells, apricot pits, bamboo stems, and peach pits.

High-pressure and corrosion-resistant batch reactors (164, 200, and 37 mL) were used to conduct the HTL, non-catalytic hydrotreatment (pretreatment), and catalytic upgrading experiments, respectively. The reactor was un-mixed. Prior to their use in the experiments, these reactors were loaded with water and seasoned at 400 °C for 4 h to remove any residual organic material from the reactors and expose the fresh metal walls to SCW. These reactors were heated using a molten-salt bath that consisted of potassium nitrate and sodium nitrate at a mass ratio of 5:4.

Freshly deionized water was used throughout the experiments. Dichloromethane was obtained from Aladdin, China, at a purity of 99.9% and was used as received.

2.2. Characterization of ACs

All of the ACs were dried in an oven at 110 °C for 12 h and crushed to #500 mesh prior to use. No further activation was performed because the authors sought to identify catalysts that would be active in their as-received form.

The ash content is determined by ignition of a known weight of the food at 600 °C until all carbon is removed. The residue is the ash, which represents the inorganic constituents of the biomass. The fixed carbon content was determined by subtracting the summation of the volatile matter and ash contents from the total sample mass.

The total BET surface area, pore volume, and pore size distribution of all of the ACs were measured by N_2 isothermal (77 K) adsorption (Micromeritics, ASAP 2020). The surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. The pore size distribution was obtained from the Horvath–Kawazoe differential pore volume plot, and the pore size was calculated by the Horvath–Kawazoe method (<2 nm) and the Barrett–Joyner–Halenda (BJH) method (>2 nm).

The surface structures of the ACs were observed by scanning electron microscopy (SEM). A thin layer of sample was mounted on a copper sample holder using double-sided carbon tape and was coated with gold (10 nm thickness) to make the samples conductive. SEM studies were carried out using a scanning electron microscope (JEOL JSM-6390LV) at an acceleration voltage of 15 kV.

The inorganic compositions of the ACs were determined by X-ray fluorescence (XRF) using a Bruker S8 TIGER XRF spectrometer. C, H, O, N, and S were detected using a Flash2000 (CHNS/O, Thermo Fisher Scientific, USA) elemental analyzer.

Fourier transform infrared spectroscopic analysis (FT-IR) was performed on a Vertex 70 FT-IR spectrometer (Bruker Optics Corporation) to determine the chemical functionality of the AC. A few milligrams of sample were mixed with approximately 200 mg of KBr powder. The pellet preparation involved grinding the sample with KBr using an agate mortar and pestle and using a hydraulic press and die to create a thin and transparent disk. FT-IR spectra (resolution: 4 cm^{-1}, scan: 254, range: 4000–400 cm^{-1}) were recorded at a controlled ambient temperature (25 °C). A background spectrum was also collected under identical conditions.

The XPS analysis was carried out on an ESCALAB 250Xi (Thermo Scientific, USA) spectrometer using monochromated Al KαX-rays with an energy of 1486.6 eV. The source operated at 12 kV and 20 mA. The measurements were performed under a vacuum at a pressure that was lower than 5×10^{-10} Pa. The survey scans were collected from 0 to 1400 eV. The high-resolution scans were performed over 280–295 eV (C 1s), 525–540 eV (O 1s), 392–408 eV (N