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Co-pyrolysis characteristics of the sugarcane bagasse and *Enteromorpha prolifera*

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ABSTRACT

Enteromorpha prolifera, a green algae, has been spreading widely in China in recent years, resulting in a series of adverse impacts, such as the water eutrophication and the outbreak of green tides. Thus, it is necessary to develop an extensively available method to transfer marine biomass waste into high-value products. In this study, Co-pyrolysis of *sugarcane bagasse* and *E. prolifera* was carried out in a fixed-bed reactor. The positive effects between *sugarcane bagasse* and *E. prolifera* were evidenced, as the acidity and density of the bio-oils from co-pyrolysis decreased and calorific value increased with respect to that of the merely biomass pyrolysis. When the ratio of the two components was 50/50, the bio-oil got the highest yield of 56.12 wt% and the high heating value of the bio-oil was 26.4 MJ/kg, which were 11.48%, 2.47% higher than the theoretical values, respectively. The acidity and density of the co-pyrolysis bio-oil at 50/50 blends were 51.62 mgKOH/g and 1.1185 g/cm^3, which were 16.18%, 6.29% lower than the theoretical values, respectively. The analysis of bio-oil compositions showed that the bio-oil from co-pyrolysis of the blends could be a potential source of renewable fuel with lower content of acid, ketone, aldehyde, phenolic compounds and higher content of hydrocarbon, alcohol, ester compounds. In addition, the concentration of C_2–C_4 hydrocarbon gases produced through co-pyrolysis of the blends increased as the amount of *E. prolifera* increased in the blend. The co-pyrolysis chars had higher calorific values compared to that through pyrolysis of *E. prolifera* alone.

1. Introduction

With the development of world economy, energy consumption increases rapidly, and energy poverty is becoming more and more prominent. The exploration and development of safe and sustainable alternatives to fossil fuels are two of the most important global priorities today [1]. Bio-oil is a renewable and clean energy product, which is able to reduce dependence on fossil fuels, improve the security of supply, cut down greenhouse gas emissions, and create environmental benefits [2].

Biomass (such as agricultural crops and residues) that can be used as feedstock for the production of biofuels. The pyrolysis process of the biomass has received considerable attention. Many researchers [3–5] have investigated different pyrolysis conditions to determine the role of final temperature, sweeping gas flow rate and feed size on the product yields. They found that the highest liquid product yield was obtained at the final temperature of 500–550 °C, the sweeping gas rate of 0.1–2 L/min, and the particle size less than 2 mm. Papari et al. [6] used a lab-scale pyrolysis unit to investigate the pyrolysis of sawmill residues under different pyrolysis conditions. The results showed that the pyrolysis temperature in the range of 500–550 °C, the N_2 flow rate of 500 mL/min, and the average particle size of 0.3 mm were the optimum pyrolysis conditions. Others [7–9] investigated the catalytic pyrolysis of the biomass, the addition of the catalyst resulting in an improved yields and the properties of liquid organic products. Meanwhile, macro algae are gaining increasing interest as a feedstock for sustainable biofuels production. The chemical compositions of the seaweed mainly include fatty compounds, soluble polysaccharides, and proteins, which are easy to be pyrolyzed, different from the pyrolysis properties of terrestrial plants that are composed of cellulose, hemicellulose, and lignin. Ceylan and Goldfarb [10] used TG-FTIR to analyze the Ulva prolifera pyrolysis process, the apparent activation energy ranging from 130 to 152 kJ/mol, which was lower than other macroalgaes. Zhao et al. [11] researched the *Enteromorpha prolifera* in a free-fall reactor at different temperatures ranging from 100 to 750 °C, and the results showed that the average calorific value of the bio-oil was 25.33 MJ/kg and the oxygen content in the bio-oil was 30.27 wt%, which suggested that *E. prolifera* presented as a good bio-oil feedstock candidate.

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With research continued, more and more experts have already begun revealing the co-pyrolysis mechanism of biomass with different materials to improve the efficiency of pyrolysis reaction and the quality of the bio-oil. Li et al. [12] conducted the co-pyrolysis of rice straw and Shenfu bituminous coal in a fixed bed reactor under nitrogen atmosphere, and they found that the co-pyrolysis tar contained more phenolics, less oxygenate compounds than calculated values. Martínez et al. [13] conducted the co-pyrolysis of biomass with waste tyres, and the results showed that acidity, density and oxygen content in the co-pyrolysis bio-oil decreased, pH and calorific value increased with respect to that of the merely biomass pyrolysis liquid, leading to upgraded bio-oil. Brebu et al. [14] carried out the co-pyrolysis of pine cone with synthetic polymers, an increase in bio-oil yields and lower oxygenated compounds in the bio-oil were obtained compared to the pyrolysis of biomass alone. Samanya et al. [15] conducted co-pyrolysis of sewage sludge with wood, rapeseed and straw in a tubular furnace. They found that the maximum upper phase yield (33.2 wt%), the highest calorific value (34.8 MJ/kg) and the lowest acid number of the bio-oil were obtained with co-pyrolysis of 40% rapeseed. However, less works have been reported about co-pyrolysis of lignocellulose biomass with macroalgae. Wang et al. [16] researched the thermal behaviors of mixed rice husk and two types of seaweed by TG-FTIR, they found that the rice husk was mainly endothermic, the seaweed and the blended samples were exothermic, the synergistic effects existed in the co-pyrolysis of rice husk with seaweed. Nevertheless, the pyrolysis in a fixed bed reactor and the mechanism analysis of co-pyrolysis of lignocellulose biomass with seaweed has rarely been reported.

The objective of present study is to investigate the impact of co-pyrolysis of lignocellulose biomass and seaweed at different mixed ratios on the products yields, characteristics of pyrolysis products and interaction mechanisms. *E. prolifera* (EP) and Sugarcane bagasse (BA) were chosen as the raw material, for the reason that EP is one specie of green algae which is widely distributed in the oceans, and BA is one kind of common lignocellulose material with low ash content. GC–MS was used to analyze the compositions of the bio-oils, which makes possible to better relate the liquid products compositions with the organic chemical compositions in the mixture samples.

2. Experimental

2.1. Materials and their characterization

The EP used as the raw material for this study was obtained from the Dadeng island, Xiamen, Fujian. The BA was collected from the surrounding of Huaqiao University. The EP was washed with water 3 times to remove the impurities, then it was sundried for 5 days and milled to 90 mesh. The BA was pulverized in a disintegrator until it passed through a 90 mesh sieve, then dried by heating at 105 °C for 24 h. The samples were stored in a desiccator. The BA/EP used were: 100/0, 70/30, 60/40, 50/50, 40/60, 30/70, 0/100. The proximate analysis of both materials were determined according to GB/T 28731-2012. The main constituents of the BA (hemicellulose, cellulose, lignin etc.) were determined by Van Soest [17]. The contents of crude protein, crude fat and carbohydrate in the EP were determined by Kjeldahl, Soxhlet extract and phenol-sulfuric acid method [18,19]. The crude fiber was determined by alkali-acid dissolve experiments [20]. Table 1 shows the feedstock characteristics.

Table 1
Properties of BA and EP.

Proximate analysis on dry basis (wt%)	EP	BA
Moisture	6.53	8.79
Volatiles	56.72	85.05
Fixed carbon*	17.03	0.71
Ash	19.72	5.45
Main constituents on dry basis (wt%)		
Extractives	ND[a]	24.33
Cellulose	ND[a]	38.01
Hemicellulose	ND[a]	33.27
Lignin	ND[a]	4.01
Crude protein	13.11	ND[a]
Crude fat	1.06	ND[a]
Carbohydrates	44.95	ND[a]
Crude fiber	14.63	ND[a]
HHV (MJ/kg)	13.23	17.05

[a] ND means not detected.

* Calculated value.

2.2. Pyrolysis procedure

The pyrolysis process was carried out in a laboratory scale reactor. The schematic diagram of experimental apparatus is shown in Fig. 1 where the spatial distribution of the equipment can be seen. A mass of 16 g mixture samples was used for production of bio-oil. The reactor used was a cylindrical shaped quartz boat 29 cm in length with an internal diameter of 3 cm. In order to maintain an inert environment during the experiments, the reaction occurred under a high grade pure nitrogen atmosphere with a flow rate of 250 mL/min. The reactor with samples were introduced into the furnace at the initial temperature 30 °C which was heated at a rate of 20 °C/min until 550 °C and kept isothermal for 10 min. All the pyrolysis experiments were carried out in duplicate.

The samples were dried, devolatilized, and finally decomposed to generate char, liquid, and non-condensable gas products. The volatiles evolved from the samples passed through two consecutive condensers placed in an ice bath. The non-condensable gas was collected in oxygen bags and analyzed by gas chromatograph (GC-9160) which equipped with a TDX-01 packed column (1 m × 0.3 mm) and a thermal conductivity detectors (TCD). Argon was used as the carrier gas and the temperature of TCD and oven were 133 °C and 60 °C, respectively. The mass of non-condensable gas was calculated according to its total volume, average relative molecular mass and the molar volume of the gas, which is 24.45 L/mol at room temperature. The total volume of non-condensable gas was determined by Wet gas flow meter and its average relative molecular mass was obtained through GC analysis. The char was recovered after pyrolysis and directly weighed as solid fraction, and then the mass of liquid fraction was evaluated by subtracting the weight of gas and solid. The gas, char and oil yield were determined by using Eqs. (1)–(3):

$$\text{Gas yield wt\%} = \frac{\text{mass of gas}}{\text{mass of feedstock biomass}} \times 100 \tag{1}$$

$$\text{Char yield wt\%} = \frac{\text{mass of char}}{\text{mass of feedstock biomass}} \times 100 \tag{2}$$

$$\text{Oil yield wt\%} = \frac{\text{16-mass of gas-mass of char}}{\text{mass of feedstock biomass}} \times 100 \tag{3}$$

After each experiment, the condenser and connection tubes were washed with acetone and the extraction liquid was identified by GC/MS-QP2010plus. The GC was fitted with a 30 m $*$ 0.25 mm capillary column coated with a 0.25 mm thick film of polyethylene glycol (Rtx-Wax). The carrier gas flow (He) was 1.5 mL/min and the split ratio was 10:1. The initial oven temperature of 40 °C was kept isothermal for 4 min and then heated to 140 °C at 5 °C/min and maintaining this temperature for 5 min, followed by continuously heating it to 225 °C at 15 °C/min and maintaining this temperature for 3 min. The temperatures of MS source and injector were 250 °C.