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Effect of different pretreatments on the thermal degradation of seaweed biomass

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Abstract

This study aims to investigate the pyrolysis characteristics of seaweed biomass (*Enteromorpha*) after water-washed and acid-washed (7%, 10% of hydrochloric acid, 7% of sulfuric acid, 7% of phosphoric acid) pretreatments. These pretreatments of seaweed were signifi after water-washed and acid-washed (7%, 10, Ca, Na and Mg metals. Among these pretreatments the removal capacity of H_2SO_4 was the most obvious. The pyrolysis behaviors of materials after pretreatments have been studied using thermogravimetry-mass spectroscopy. During the pretreatments, O–H, C–O/C–H, S=O and C=O functional groups in *Enteromorpha* were cleaved. Phosphoric acid and hydrochloric acid made the intensities of the absorption peaks of O–H and S=O decrease the most obvious, respectively. Therefore, there was almost no NO_2 and SO_2 emission in the process of pyrolysis of *Enteromorpha* washed by hydrochloric acid and phosphoric acid. The volatile components of *Enteromorpha* were easy to evolve after the pretreatment. Sulfuric acid exhibited the best efficiency in the process of pyrolysis, and it manifested smaller influence on other volatile organics simultaneously. However, the maximum weight loss rate and the corresponding temperature reduced after pretreatments, and the maximum weight loss rate reduced more distinctly after 7% hydrochloric acid treatment. These results suggest that selective acid pretreatment would facilitate the thermal conversion of seaweed biomass.

Keywords: Seaweed biomass; Pretreatment; Pyrolysis

1. Introduction

With the continuous depletion of fossil fuels and the increasingly serious environmental pollution caused by burning of fossil fuels, new renewable alternative energy sources have aroused more and more attention all over the world. Biomass energy has attracted people's attention due to its low cost, renewable nature, carbon neutrality, and easy to obtain. Seaweed is a promising biomass resource because of their rapid growth, less competition with foods and easy cultivation in the sea [1,2].

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There are a variety of thermochemical conversion and utilization of biomass energy, such as pyrolysis, gasification, liquefaction, etc. Pyrolysis is a thermochemical decomposition of organic material in the absence of oxygen. In the process, biomass molecules could be decomposed to produce coke, condensed liquid and gaseous product, which is a kind of important utilization of biomass energy [3]. The main ingredients of seaweed are proteins, lipids, carbohydrates (including polysaccharide constituent of mannan, xylan, etc, and soluble polysaccharide sulfate) and inorganic ash [4]. Many researchers have studied the significant effect of inorganic metal ions in biomass ash on the thermal decomposition [5,6]. All of their studies indicated that metal ions (such as K, Na, Mg, etc.) would affect the characteristics and pyrolysis productions. Generally, metal ions will be attached on the surface of carbon rather than be evaporated in the process of pyrolysis. Thus metal ions can promote the process of pyrolysis and the formation of carbon [7]. It is common to study the effect of metal ions on pyrolysis by adding some metal ions or using the pretreatment to clear ions [8,9].

However, the effects of demineralization on the pyrolysis behaviors and products of algae biomass have rarely been studied [10]. The influence of pretreatment on biomass pyrolysis characteristics mainly focused on the terrestrial biomass [11–14]. The effects of pretreatment on algae mainly concentrated upon the hydrolysis, hydrothermal technology and the procession of bioethanol production [15–18]. Meanwhile, different pretreatments have different effects on the biomass pyrolysis. Mourant et al. [19] made the fast pyrolysis of mallee wood sample washed with water and a dilute acid solution in a fluidized-bed reactor at 500 °C. Their results indicated that the pretreatment due to its removal of AAEM species would influence the bio-oil composition and properties. Eom et al. [20] adopted the Py-GC/MS technique to investigate the effects of demineralization processes on pyrolysis behavior of poplar wood powders treated with distilled water, tap water, HCl and HF, respectively. The total amount of low molecular weight compounds, such as acetic acid, acetol, and 3-hydroxypropanal, was significantly low in the demineralized biomass. Fahmi et al. [21] drew a conclusion that washing of biomass can improve bio-oil quality and stability through comparing the pyrolysis products of washed feedstocks and raw material. Jiang et al. [22] found that the influence of removal of minerals played the dominant role in biomass thermal behavior. Tan and Wang [23] studied the influence of acid-washing pretreatment on biomass pyrolysis in a radiation reactor. The experiment indicated that the yield of tar would increase and the yield of the gas and char would decrease by acid treatment. Kumagai et al. [24] proved that the H_2SO_4 treatment could cleave the bond of C–O in the procession of cedar wood pyrolysis, which would result in increasing the yield of bio-oil but decreasing the char. In order to explore a better pretreatment method on the effect of the algae pyrolysis, several different pretreatments were utilized to remove the metals in seaweed biomass.

In this work, *Enteromorpha* (EN) was used as raw material to study the influence of pretreatment on large marine algae biomass pyrolysis characteristics after cleaned by deionized water and different concentrations of hydrochloric acid, sulfuric acid and phosphoric acid solution (raw sample, deionized water treatment, 7% hydrochloric acid treatment, 10% hydrochloric acid treatment, 7% sulfuric acid treatment and 7% phosphoric acid treatment were respectively represented by sample A, B, C, D, E and F). Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), infrared solid tablet (FTIR) were applied to analyze EN original sample, function groups. The structure of EN before and after pretreatment were also be analyzed. Thermogravimetric-mass spectrometry was used to analyze EN and gas products and function groups in the process of EN pyrolysis before and after pretreatment.

2. Experimental

2.1. Preparation of sample materials

Raw material EN derives from the South China Sea, Guangdong. It was washed by deionized water and different acids (7% hydrochloric acid, 10% hydrochloric acid, 7% sulfuric acid, 7% phosphoric acid). Seaweed and washing solution were mixed with a proportion of 1:100 and were washed for 12 h, then were centrifugal filtered. Afterward, the washed seaweed were dried for 4 h, the pickling algae was washed to be neutral and then was dried for 4 h. The proximate and ultimate analysis of EN and the concentration of metal ion are shown in Table 1.

The metal ion contents of each sample were determined by ICP. The result is listed in Table 2. It indicated that K, Ca, Na and Mg were removed after pretreatment. While the content of Al and Fe presented a different extent increased. Furthermore, H_2SO_4 was more effective on the removal of metal ions. There was a big difference between 7% and 10% HCl to remove metal ions, which revealed that the concentration of hydrochloric acid existed great influence. The comparison of the effects of the same concentration of different dilute acid to wash away metal ions: 7% H_2SO_4 > 7% H_3PO_4 > 7% HCl.

2.2. Experimental equipment and method

Hitachi scanning electron microscopy (SEM, TM3000) was applied to identify the morphology on the surface. The experiment condition was in