Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass

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HIGHLIGHTS

- Surface structure of biomass had more visible changes after strong acid leaching.
- Some functional groups of biomass had slight changes after strong acid leaching.
- Volatile emission peak shifted to higher temperature after demineralization.
- Amount of releasing gas decreased after demineralization.
- AAEMs played a notable catalytic role during biomass pyrolysis process.

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ABSTRACT

To study the catalytic role of alkali and alkaline earth metallic species and eliminate their negative impact during biomass thermal utilization, different leaching methods have been applied in numerous experiments. Thus it is necessary to investigate the potential influence on biomass physicochemical structure using different agents. Rice straw was selected to study the demineralization impact on physicochemical structure and pyrolysis characteristics. It is shown that strong acid leaching exhibited higher removal efficiency of minerals, but it introduced more notable impact on physicochemical structure of biomass comparing to water and weak acid leaching. Different leaching methods give chance to study catalysis characteristics of intrinsic metals on biomass thermal reaction. Contrast to alkaline earth metals especially Ca hindering thermal decomposition, alkali metals promoted this reaction obviously. In addition, comparing to physicochemical structure changes created by leaching process, the influence of removal of minerals played the dominant role in biomass thermal behavior.

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1. Introduction

As a low-sulfur, low-nitrogen and carbon-neutral renewable energy, lignocellulosic biomass has great prospects of substituting for fossil fuels to reduce or eliminate energy crisis and environmental pressure around the world. Lignocellulosic biomass is generally composed of cellulose, hemicellulose, lignin, extractives and ash-forming minerals (Eom et al., 2011). One of the significant features of lignocellulosic biomass is the presence of considerable amounts of alkali and alkaline earth metallic species (AAEMs), such as sodium, potassium, calcium, magnesium and iron, etc. (Jiang et al., 2012; Keown et al., 2005). These metallic species are the main components of inorganics in biomass and their contents are generally less than 1% in lignocellulosic biomass. However, in some forestry residues and herbaceous biomass, the contents of AAEMs are up to 15% (Fahmi et al., 2007).

High AAEMs content in biomass feedstock would lead to serious problems such as ash slagging, fouling, agglomeration, deposition and heated side corrosion in the high temperature conversion system (Xiang and Li, 2012), resulting in bringing an extra threat to safe operation of system, increasing operation and maintenance costs of thermal system. Also, physicochemical characteristics of bio-oil can be changed easily during storage due to the presence of higher AAEMs content in the bio-oil products, and AAEMs catalyze the polymerization reactions and thereby increase the viscosity (Liu and Bi, 2011). On the other hand, the intrinsic AAEMs of biomass also play catalytic role during biomass thermal conversion process (Eom et al., 2012; Keown et al., 2005, 2008). It was likewise reported that some AAEMs acted as a poison to some catalysts during catalytic thermal processes (Liu and Bi, 2011). In addition, the

performance of activated carbon prepared from biomass, which is a significant catalyst support, could be also negatively affected by the presence of AAEMs (Schröder et al., 2007). Therefore, the modification of biomass feedstock to reduce AAEMs concentrations prior to utilization could be technically beneficial, and its economic potential typically requires site specific analysis.

Leaching biomass with water or acid has been demonstrated to be an effective way to remove AAEMs from biomass, and could improve biomass fuel properties for high temperature processes of biomass (Davidsson et al., 2002; Eom et al., 2011; Fahmi et al., 2008; Mourant et al., 2011). Therefore, different demineralization experiments using different agents such as water (Fahmi et al., 2008; Mourant et al., 2011), acetic acid (Davidsson et al., 2002; Liu and Bi, 2011), hydrochloric acid (Eom et al., 2011; Mayer et al., 2012), sulphuric acid (Fierro et al., 2007; Keown et al., 2008), hydrofluoric acid (Das et al., 2004; Eom et al., 2011), nitric acid (Mourant et al., 2011) et al. had been conducted. Leaching with water had minimal impact on structure of biomass, but it could hardly remove water-insoluble AAEMs (Mourant et al., 2011; Tan and Wang, 2009). Leaching with acids had higher removal efficiency of AAEMs, and could remove water-insoluble AAEMs (Mourant et al., 2011), but it had some potential in washing away some acid-soluble hydrocarbons (Lv et al., 2010), hemicellulose and cellulose constituents of biomass (Eom et al., 2011), which might create a negative impact to result in changes of the biomass physicochemical structure (Das et al., 2004; Liu and Bi, 2011). Thus it's necessary to evaluate the structure changes of biomass during different demineralization process.

In addition, biomass leaching is an effective method to investigate the role of intrinsic or added inorganic compounds in biomass thermal behavior. Extensive work about the effect of metal ions on biomass thermal behavior has been reported (Eom et al., 2011, 2012; Fahmi et al., 2008; Jakab et al., 2010; Jensen et al., 1998; Mayer et al., 2012; Mourant et al., 2011; Yang et al., 2006). Eom et al. (2012) points out magnesium and calcium chlorides content had opposite effects on maximum degradation rates of thermal degradation of poplar wood, but both two metals catalyzed its degradation evidenced by the decreasing in peak shapes in the DTG curves. Yang et al. (2006) found the addition of dolomite (main component of calcium and magnesium carbonates which are water-insoluble) behaved negligible influence on pyrolysis of cellulose and hemicellulose. Jakab et al. (2010) study the impact of Ca acetate on cotton fibers and pure cellulose pyrolysis, and found Ca^{2+} ions inhibited the decomposition of both cotton fibers and pure cellulose indicated by the higher decomposition temperatures at the maximum degradation rate. Jensen et al. (1998) investigated the effect of potassium chloride on the pyrolysis of wheat straw, and found the added salt did not behave in the same way as the inherent minerals in the straw. These results mean minerals presented in different forms show different even contrary behaviors, thus it's necessary to investigate catalytic role of different intrinsic metal ions in biomass pyrolysis.

Furthermore, numerous literatures have focused on the demineralization efficiency of leaching process using different agents (Fahmi et al., 2008; Mayer et al., 2012; Mourant et al., 2011), but only few systematical studies on the effects of demineralization on physicochemical structure of biomass using different agents (Liu and Bi, 2011; Tan and Wang, 2009) have been reported. Thus, it is also necessary to investigate potential changes of biomass physicochemical structure after demineralization process using different agents, and to study the influence of the physicochemical structure changes and AAEMs removal on the behavior of biomass pyrolysis. The present work aims at systematical study on the potential impact of different agents during demineralization process, as well as the effect of different demineralization efficiency on pyrolysis behavior of biomass.

A typical Chinese agricultural residue-rice straw which has a higher content of AAEMs was selected to be demineralized with the agents of deionized water, acetic acid, hydrochloric acid, sulphuric acid, nitric acid and orthophosphoric acid, respectively. Several analyses were conducted to observe the potential effect on physicochemical structure of samples. Moreover, pyrolysis behavior of different samples was studied by combined thermogravimetric Fourier transform infrared analysis (TG–FTIR). On the basis of above analyses results, the changes of biomass physicochemical structure, demineralization efficiency, as well as the effects of intrinsic metal ions on pyrolysis characteristics and on releasing of volatiles were discussed.

2. Methods

2.1. Material

A typical Chinese agricultural residue-rice straw (abbreviate for RS) which has a higher content of AAEMs was selected. The sample harvested at Wuhan area was pre-dried by sunlight, pulverized and sieved. The particle size fraction between 125 and 210 μm was used for experiments.

2.2. Demineralization process

Rice straw was leached with six different agents for removal of inorganics: deionized water, acetic acid, hydrochloric acid, sulphuric acid, nitric acid and orthophosphoric acid, and all acid agents which are analytically pure were diluted to 5 wt% solutions. The total volume of liquid used for the leaching process was 10 mL/g of sample, in which sample was immersed and stirred by magnetic stirrer for 2 h at room temperature (25 ± 3 °C). The biomass sample was then rinsed with deionized Milli-Q water until the pH value was neutral. After rinsing, all biomass samples were dried in an oven at 105 °C for 24 h, and then sealed in desiccator prior to be used for analyzing.

2.3. Method

2.3.1. Proximate and ultimate analysis

Proximate and ultimate analysis of raw and demineralized samples were carried out using TGA-2000 (Las Navas Instruments, Spain) and EL-2 analyzer (Vario Company, Germany), respectively. The results are listed in Table 1.

2.3.2. Inductively coupled plasma-mass spectroscopy (ICP-MS)

The AAEMs content of each biomass sample was quantified using a formerly established procedure (Jiang et al., 2012). Briefly, the biomass sample was digested by 2 ml H_2O_2 (30 wt%), 1 ml HF (38 wt%) and 10 ml HNO_3 (65 wt%) mixture reagent in a microwave digestion system (ETHOS-E, Italy Milestone Corporation), and then the digestion solution was determined by ICP-MS (ELAN DRC-e, PerkinElmer) to quantify the AAEMs content of samples. The measurement was conducted for three times with a relative standard deviation of 4–7% for each metal.

2.3.3. Scanning electron microscopy (SEM) analysis

The surface shape of the samples was studied from morphology by SEM (Quanta 200, Phillips) to investigate leaching efficiency and its potential change to physical structure.

2.3.4. Pore structure analysis

N_2 adsorption/desorption isotherms were measured at −196 °C using the Micromeritics ASAP 2020 gas adsorption analyzer. Just before the measurements, the samples were degassed in vacuum