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Thermo-carbide slag pretreatment of turfgrass pruning: Physical-chemical structure changes, reducing sugar production, and enzymatic hydrolysis kinetics

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ABSTRACT

Alkaline pretreatment shows a good effect on delignification of lignocellulosic biomass, and carbide slag, an alkaline industrial waste, was first applied to pretreat turfgrass pruning. Three thermo-alkaline pretreatment methods were compared to evaluate their ability to destroy the biomass structure and to enhance the enzymatic hydrolysis efficiency of turfgrass pruning, namely thermo-NaOH pretreatment, thermo-lime pretreatment, and thermo-carbide slag pretreatment. Results showed that the maximum net reducing sugar yield of 269.55 mg/g $_{\text{raw biomass}}$ was achieved by thermo-carbide slag pretreatment. Compared with raw biomass, the lignin and hemicellulose content of turfgrass pruning after thermo-carbide slag pretreatment reduced by 35.57% and 62.40%, respectively. SEM and FTIR analyses showed that the surface structure and chemical groups of turfgrass pruning were obviously destroyed by thermo-carbide slag pretreatment. There was a high positive correlation between the enzymatic hydrolysis efficiency and cellulose content of substrate. However, a high negative correlation was observed between the enzymatic hydrolysis efficiency and lignin content of substrate. The enzymatic hydrolysis kinetics with different pretreatments were well described by the fractal-like kinetics model, and the rate constant of enzymatic hydrolysis of thermo-alkali pretreated turfgrass pruning was about three times of that of the unpretreated turfgrass pruning. Overall, carbide slag is an ideal pretreatment material for enzymatic hydrolysis of turfgrass pruning in terms of hydrolysis efficiency and waste reuse.

1. Introduction

Along with the rapid development of urbanization, urban greening is more and more practiced. The expanding urban greening, especially lawn area, results in the production of large amounts of turfgrass pruning [1]. Turfgrass pruning as municipal solid waste may cause an adverse impact on the environment, so converting the turfgrass pruning to biofuel will be an environment-friendly technology [2]. With several advantages, such as fast growth, large production and renewability, the turfgrass pruning is a new feedstock for biofuel production. However, due to the complex inherent structure of lignocellulosic biomass, enzymatic hydrolysis of lignocellulosic biomass without pretreatment is difficult to achieve a high biofuel yield [3–5].

Therefore, various pretreatments have been introduced to promote the reducing sugar production from lignocellulosic biomass, including microwave irradiation [6], high pressure homogenization [7], thermo-alkaline pretreatment [8], thermo-acid pretreatment [9], biological pretreatment [10], and combined pretreatments [11,12]. Among these pretreatment methods, thermo-alkaline pretreatment is the most promising because of its high efficiency [13]. Thermo-alkali pretreatment of pine wood resulted in the highest methane yield with 8% NaOH at 100 °C for 10 min [14]. The maximum biogas yield from rice straw reached 574.5 ml/g VS with a 10% $Ca(OH)_2$ pretreatment, 36.7% higher than that of the control [15]. Chen et al. reported that cumulative biogas yield from *Spartina alterniflora* increased by 68.17–153.29% after thermo-NaOH pretreatment [16]. Jin et al. compared thermo-NaOH and thermo-lime pretreatment of catalpa sawdust and found that thermo-lime pretreatment yielded more reducing sugar [17]. Although thermo-alkaline pretreatment is effective for lignocellulosic biomass, there are still some disadvantages, such as high alkali dosage and corresponding high cost of alkaline material [2].

Carbide slag, an industrial waste, is an alkaline mixture containing

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more than 60% CaO [18]. To explore its utilization, many researchers have applied carbide slag as transesterification catalyst, neutralizing agent for acidic wastewater treatment, adsorbent for capturing CO_2, and raw material for cement production [19,20]. In this study, carbide slag was employed to pretreat the turfgrass pruning. The results will expand the utilization approach of carbide slag, and save the cost of lignocellulosic biomass pretreatment for biofuel production.

The objective of this study was to evaluate the efficiency of thermo-carbide slag pretreatment of turfgrass pruning for biofuel production, and the results were compared with those using thermo-water, thermo-NaOH, and thermo-lime pretreatment. The chemical composition and surface structure of turfgrass pruning after pretreatment were analyzed. Furthermore, the relationship between enzymatic hydrolysis efficiency and the structure change of turfgrass pruning was investigated, and the enzymatic hydrolysis kinetics was also studied.

2. Materials and methods

2.1. Materials

In this study, turfgrass pruning (*Poa pratensis*) was collected from a local lawn in Beijing, China. After air-drying, the turfgrass pruning was milled by a laboratory mill (DF-25S, Dade, China), and screened to obtain a fraction of 20–60 mesh, then stored in plastic bags at room temperature. All chemicals were of analytical grade and purchased from Beijing Chemical Industry Group Co., China. The commercial enzyme was provided by Hunan Chemical Ltd. (China) and its filter paper activity was 200 FPU/g. Carbide slag was taken from a polyvinyl chloride production factory (China) and its components are listed in Table 1.

2.2. Pretreatment

For the pretreatments, 10.0 g dried turfgrass pruning was immersed in 200 ml distilled water, NaOH, lime and carbide slag solution of 1.75% (w/v) at 120 °C for 1 h in a sealed stainless-steel hydrothermal reaction kettle (Beijing Yanzheng Biotechnology co. LTD, China), respectively. The chemical dosage and heating temperature were chosen according to the literature and previous study [17,21,22], and the mixture pH was within a range from 12.43 to 13.19 with different alkaline pretreatments, which is the common pH used in alkaline pretreatments. After pretreatments, the mixture was cooled to room temperature, and the solid was separated from the liquor by filtration, and washed with tap water until a neutral pH. The solid fraction was dried at 65 °C and used as the feedstock for subsequent enzymatic hydrolysis. Raw turfgrass pruning was used as control without any pretreatment.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis was carried out for 72 h in 150 ml flasks with a solid loading of 2.5% (w/v) at a pH of 4.8, a temperature of 50 °C and a rotation speed of 150 r/min [2]. The samples were withdrawn at a certain time interval. The reaction mixture was filtered, and the liquid was used to analyze the reducing sugar yield. All enzymatic hydrolysis experiments were conducted in triplicates. Results were presented as mean value and standard deviations.

2.4. Analysis procedure

The chemical composition of turfgrass pruning samples were analyzed by a fiber analyzer (A2000i, Ankom, USA). The reducing sugar was measured using the 3,5-dinitrosalicyclic acid method (DNS). The surface morphology feature of turfgrass pruning samples was scanned by scanning electron microscopy (S-3400 N II, Hitachi, Japan), and all samples were sputter-coated with gold before scanning. Fourier transformation infrared spectra (FTIR) of the samples were detected by a Fourier transform infrared spectrometer (Vertex 7.0, Bruker, USA) in the range from 400 to 4000 cm^{-1}.

The water absorption capacity was calculated by Eq. (1):

$$\text{Water absorption capacity} = \frac{\text{Weight}_0 - \text{Weight}_1}{\text{Weight}_0} \times 100\% \tag{1}$$

where Weight_0 is the weight of substrate before drying, and Weight_1 is the weight of substrate after drying at 105 ± 3 °C for a minimum of 4 h.

The crystallinity index analysis of samples was carried out using an X-ray power instrument (Bruker, Germany), with Ni-filtered Cu Kα radiation (λ = 1.54 Å) at 40 kV and 40 mA. Scattered radiation was detected in the 2θ range from 5° to 35° at a scan rate of 0.2°/min. The crystallinity index (CrI) was calculated based on Eq. (2) [23]:

$$\text{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \tag{2}$$

where I_{002} represents the intensity of 002 lattice diffraction ($2\theta = 22.6°$) and I_{am} represents the intensity of amorphous section ($2\theta = 18°$).

The net reducing sugar yield based on 1 g raw material was calculated by Eq. (3):

$$\text{Net reducing sugar yield} = \text{Reducing sugar yield (mg/g)} \times \text{Solid recovery (\%)} \times 1\ \text{g (raw)} \tag{3}$$

where Reducing sugar yield (mg/g) is the reducing sugar yield based on 1 g pretreated biomass, Solid recovery is the percentage of remaining solid after pretreatment per unit of raw biomass, and 1 g (raw) is the weight of raw biomass.

The fractal-like kinetics model can be used to describe the enzymatic hydrolysis of biomass, and the reducing sugar concentration can be deduced as Eq. (4):

$$P = \frac{S_0}{0.9}\left[1 - \exp\left(-\frac{0.9 \times k}{1-h} t^{1-h}\right)\right] \tag{4}$$

where P is the concentration of reducing sugar, S_0 is the initial concentration of reducing sugar, h is the fractal dimension describing the substrate fractal, 0.9 is the conversion coefficient from cellulose to reducing sugar, k is the rate constant presenting the reaction rate between substrates and enzymes, and t is the enzymatic hydrolysis time.

3. Results and discussion

3.1. Solid recovery and composition of turfgrass pruning after pretreatments

Thermo-alkaline pretreatment solubilizes part of biomass, mainly lignin and hemicellulose. Thus the solid recovery of lignocellulosic biomass decreased after pretreatment. In this study, solid recovery

Table 1
Components of carbide slag.

Components	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3	P_2O_5	Na_2O	LOI
(%)	70.06	3.03	0.40	0.99	0.11	0.38	< 0.01	0.08	24.94

LOI: loss on ignition.