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Fermentative hydrogen and methane cogeneration from cassava residues: Effect of pretreatment on structural characterization and fermentation performance

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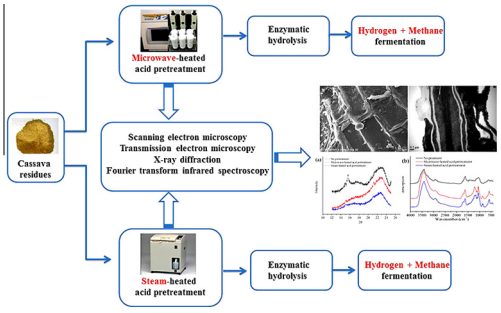
HIGHLIGHTS

- Cassava residue was pretreated by microwave (or steam)-heated acid (MHAP or SHAP).
- MHAP generated many regular micropores and SHAP generated many irregular fragments.
- SHAP generated wider cracks (~0.2 μm) in delaminated cell walls than MHAP (~0.1 μm).
- MHAP resulted in a higher crystallinity index (33.00) than SHAP (25.88).
- MHAP with enzymolysis led to a higher H_2 yield than SHAP, but CH_4 yield reversed.

GRAPHICAL ABSTRACT



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ABSTRACT

The physicochemical properties of cassava residues subjected to microwave (or steam)-heated acid pretreatment (MHAP or SHAP) were comparatively investigated to improve fermentative hydrogen and methane cogeneration. The hydrogen yield from cassava residues with MHAP and enzymolysis was higher (106.2 mL/g TVS) than that with SHAP and enzymolysis (102.1 mL/g TVS), whereas the subsequent methane yields showed opposite results (75.4 and 93.2 mL/g TVS). Total energy conversion efficiency increased to 24.7%. Scanning electron microscopy images revealed MHAP generated numerous regular micropores (~6 μm) and SHAP generated irregular fragments (~23 μm) in the destroyed lignocellulose matrix. Transmission electron microscopy images showed SHAP generated wider cracks (~0.2 μm) in delaminated cell walls than MHAP (~0.1 μm). X-ray diffraction patterns indicated MHAP caused a higher crystallinity index (33.00) than SHAP (25.88), due to the deconstruction of amorphous cellulose. Fourier transform infrared spectroscopy indicated MHAP caused a higher crystallinity coefficient (1.20) than SHAP (1.12).

1. Introduction

The search for sustainable and alternative energy is significant considering the increasing energy demands and diminishing fossil fuels. Hydrogen is a promising candidate because it is renewable, carbon neutral, and environment-friendly (Turner, 2004).

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Currently, more attention has been focused on bio-hydrogen production from lignocellulosic wastes (Cheng et al., 2011; Chu and Majumdar, 2012; Somerville et al., 2010). Cassava is widely grown throughout southern China, and is an important raw material for starch production in industry. The pulverized cassava was screened through a mesh sieve to produce starch (<125 μm). The large particles remained on the sieve were collected as cassava residues (>125 μm), which were mainly composed of lignocellulose biomass. According to the statistics from the Food Agricultural Organization of the United Nations, cassava production in China was approximately 4.56 million tons in 2012, which indicates that large amounts of cassava residues was also produced by cassava-based starch and ethanol industries. If not properly managed, these cassava residues can cause severe environmental pollution. However, cassava residue is a typical lignocellulosic material that could potentially provide a sustainable source for biofuel production owing to its abundance, low cost, and availability.

Cassava residues, which mainly consist of cellulose, hemicellulose, and lignin, do not biodegrade easily due to the three lignocellulosic components being cross-linked to each other, forming a cellulose–hemicellulose–lignin matrix. Cassava residues consist of both crystalline and amorphous cellulose structures, and the microfibril bundles of cellulose are bound by hydrogen bonding. Lignin consists of a complex array of polymers that are associated with each other, and provides structural support. Hemicellulose connects the cellulose and lignin, which provides more rigidity to the entire matrix. To improve the digestibility of lignocellulosic biomass and further enhance subsequent biofuel yields, various pretreatment technologies have been recently reviewed (Hendriks and Zeeman, 2009; Kallioinen et al., 2013; Monlau et al., 2013; Zheng et al., 2014), which can be classified into biological, physical, chemical, and physicochemical pretreatments. The degradation of cassava residues by complex microbial communities with high cellulose-degradation ability is an effective pretreatment method, which resulted in 96.6% increase in methane yield (Zhang et al., 2011). When subjected to mechanical activation pretreatment, the crystal structure of cassava residues is significantly destroyed, resulting in increased amorphization and decreased crystallinity (Liao et al., 2011). The hydrolysis of sugar beet residues significantly improved under dilute acid pretreatment with 150% increase in ethanol yield (Zheng et al., 2013). Among these pretreatments, dilute sulfuric acid pretreatment is one of the most studied and widely used methods (Chen et al., 2012; Cheng et al., 2014; Guragain et al., 2011; Zheng et al., 2013). However, to our knowledge, few studies discussed the use of microwave-heated acid pretreatment (MHAP) or steam-heated acid pretreatment (SHAP) on cassava residues to enhance its bio-hydrogen and biomethane production. Still, few attempts tried to reveal the physicochemical properties of cassava residues after MHAP and SHAP. Therefore, this study investigated the effects of MHAP and SHAP on the microstructure changes of cassava residues. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) were used to determine the physicochemical properties of cassava residues after MHAP and SHAP. A two-stage fermentation process, which consisted of dark hydrogen and methane fermentation, was conducted to increase the energy conversion efficiency.

2. Methods

2.1. Feedstock and bacteria

Cassava residues were obtained from a cassava processing plant in Guangxi Province, China. The cassava residues were oven dried, powdered to a 0.02 mm mesh size, and stored for use in subsequent experiments. Mixed hydrogen-producing bacteria (HPB) and methane-producing bacteria (MPB) were obtained from a biogas plant in Zhejiang Province, China. Bacterial isolation and enrichment were described in previous studies (Cheng et al., 2010).

2.2. Pretreatment and fermentation methods

2.2.1. MHAP

Microwave-heating pretreatment was conducted in a microwave digestion system (Shanghai Yiyao WX-4000, China). Due to the capacity limit of the microwave digestion system, 5 g of cassava residues were divided into four polytetrafluoroethylene reactors. 1.25 g of dried cassava residues were separately added into the four reactors, and then dilute H_2SO_4 (1.0%, v/v) was added to bring the combined volume to 25 ml in each reactor. The four reactors were then sealed and heated by microwaves to 135 °C for 15 min.

2.2.2. SHAP

Steam-heating pretreatment was performed in an autoclave (Sanyo MLS-3780, Japan). 5.0 g of dried cassava residues were placed in a conical flask, and then dilute H_2SO_4 (1.0%, v/v) was added to bring the combined volume to 100 ml. The conical flasks were then placed in the autoclave and heated by steam at 135 °C for 15 min.

2.2.3. Enzymatic hydrolysis

The enzymatic hydrolysis was performed in 250 mL flasks. After MHAP or SHAP, the pH of cassava residues solution was adjusted to 4.5 using NaOH. *Trichoderma reesei* cellulase (Shanghai Boao Biotechnology Corp., China) was added to the solution at 5 wt.% of the original cassava residues. The flasks were then sealed and placed in a shaker at 120 r/min for 120 h at 45 °C.

2.2.4. Dark hydrogen fermentation

Fermentation experiments were conducted in 300 ml glass bottles. Approximately 100 ml of hydrolyzed solution (containing 5.0 g of cassava residues) and 125 ml of deionized water were added to each bottle and then mixed with 0.5 g of yeast extract. The initial pH was adjusted to 6.0 ± 0.1 using 6 M HCl and 6 M NaOH solution. The bottles were then inoculated with 25 ml HPB, sealed with rubber stoppers, purged with nitrogen gas for 10 min, and maintained at 35 ± 1.0 °C for dark hydrogen fermentation.

2.2.5. Dark methane fermentation

The residual solutions of dark hydrogen fermentation were autoclaved at 121 °C for 20 min to inactivate the HPB. The pH of autoclaved solution was adjusted to 8.0 ± 0.1 using 6 M HCl and 6 M NaOH solution. The bottles were subsequently inoculated with 15 ml MPB, sealed with rubber stoppers, purged with nitrogen gas for 10 min, and maintained at 35 ± 1.0 °C for dark methane fermentation.

2.3. Analytical methods

Electron micrographs of the cassava residues before and after MHAP/SHAP were obtained under a field emission SEM (Hitachi S3700, Japan) after the samples were sputtered with a thick layer of gold. The structural changes of cassava residues were also examined by TEM (Hitachi H-7650, Japan) at 120 keV electron-energy emission after staining the samples with $KMnO_4$ and $UO_2(CH_3COO)_2$. XRD analyses were conducted on an X-ray diffractometer (X'Pert PRO, Netherlands) to determine changes in the crystallinity of cellulose from cassava residues. Chemical changes were