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Improving bioavailability of fruit wastes using organic acid: An exploratory study of biomass pretreatment for fermentation

Shouvik Saha [a], Mayur B. Kurade [a], Marwa M. El-Dalatony [a], Pradip K. Chatterjee [b], Dae Sung Lee [c], Byong-Hun Jeon [a,*]

[a] Department of Earth Resources and Environmental Engineering, Hanyang University, Seoul 133-791, Republic of Korea
[b] Energy Research and Technology, CSIR Central Mechanical Engineering Research Institute, Durgapur 713-209, India
[c] Department of Energy and Mineral Resources Engineering, Dong-A University, 37 Nakdong-Daero, Busan 604-714, Republic of Korea

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ABSTRACT

Maximizing the bioavailability of fermentable biomass components is a key challenge in biomass pretreatment due to the loss of sugars during conventional pretreatment approaches. Pretreatment of fruit peels and wastes (FPWs) with dilute acetic acid assisted in maximizing sugar recovery. Optimized conditions (0.2 M acetic acid, 100 °C, 1 h) at 10% substrate loading resulted in enhanced sugar recovery from banana peels (99.9%), pineapple wastes (99.1%), grape pomace (98.8%), and orange peels (97.9%). These high sugar recoveries retained the high C/N ratios (41–47) suitable for effective bioenergy production through the fermentation of these pretreated biomasses. Scanning electron microscopy (SEM) indicated considerable disruption of biomass structural integrity during acetic acid treatment, enhancing the surface area available for better microbial attachment. Fourier transform infrared spectroscopy (FTIR) showed that the acetic acid pretreatment yielded only minor changes to the functional groups in the biomasses, strongly suggesting minimal loss of fermentable sugars. Thus, acetic acid pretreatment aids in enhancing the bioavailability of fermentable sugars from these FPWs biomass, enabling improvements in bioenergy production.

1. Introduction

The global crisis of conventional fossil fuels and growing energy demands have led to increased dependency upon the production of sustainable bioenergy. Greenhouse gas emissions from the burning of conventional fuels are an alarming environmental concern that is motivating a search for clean alternatives [1,2]. Bioenergy has gained a lot of attention as an eco-friendly means to overcome the tremendous demands for energy [3]. Production of bioenergy from biomass fermentation has already been initiated in the last decade [4]; however, the accessibility for fermentation of desired sugars in biomass is a major challenge due to the complex polymeric structures of the various biomasses.

Fruit wastes are considered to be valuable substrates for fermentative bioenergy production. Fruit processing industries generate gigantic amounts of solid waste every day. Fruit wastes consist mainly of carbohydrate polymers, which are a convenient nutritional source of the fermentative microbes used in bioenergy production. Orange processing industries produce approximately 15–25 million tons of solid waste (peel, rag, juice sacs, and seeds) per year from the 68 million tons of oranges produced globally [5]. Brazil, the United States of America, China, India and Mexico are the largest producers of oranges [6], are among the largest consumers of energy [7], and thus have the greatest need to develop sustainable bioenergy to replace fossil fuel use. Pineapple has a solid weight of almost 75% (pulp, peels, core and crown), which is discarded as solid waste after juice extraction [8]. Wineries generate a large quantity of grape pomace (seeds, skin and pulp) as solid waste (~13.4 million tons per year) [9], representing about 18–20% of the whole grape weight [10]. A recent study conducted in Portugal estimated that, during processing, each winery discards 13% and 3% of initial grape weight as pomace and stalks, respectively, from the processed grapes, along with a large amount of wastewater (1.65 m^3 per ton) each year [11]. Also, bananas are one of the largest biomass resources, as they represent almost 16% of world fruit production [6]. Banana peels (30–40% of fruit weight) are left over as waste and contain huge amounts of sugars in the forms of soluble and insoluble fibers [12]. Fermentation pro-

* Corresponding author.
E-mail address: bhjeon@hanyang.ac.kr (B.-H. Jeon).

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cesses using fruit wastes to produce biomethane and bioethanol have already been initiated [12–15]. Fruit wastes having abundant fermentable carbohydrate and low protein content, are suitable substrates for fermentative production of bioenergy, as their high carbon/nitrogen (C/N) ratios are favorable for achieving high bioenergy yields [16,17].

Several pretreatment strategies have been attempted to liberate the fermentable fractions of biomass [18]. The National Research Council of the USA has standardized specific criteria for an effective pretreatment strategy that includes the elimination of biomass particle size reduction before pretreatment, minimum loss of fermentable sugars in the liquid phase during pretreatment, limited production of fermentation inhibitors and minimum external energy utilization to reduce the overall processing costs [19]. Application of strong mineral acids for biomass pretreatment, such as sulfuric acid, has been well established in recent decades [18,20]. The lignin in lignocellulosic biomass requires comparatively strong pretreatment methods for the release of soluble fermentable sugars, but acidic environments lead to the loss of fermentable sugars in the form of furfural and 5-hydroxymethyl furfural [20]. This loss of fermentable sugars during pretreatment is undesirable and may reduce the commercial feasibility of bioenergy production [21].

In the present study, an effective pretreatment method based on the use of organic acid (acetic acid) was standardized to improve the bioavailability of fermentable sugars in pretreated fruit peels and wastes (FPWs) with the least loss. The low lignin content in FPWs [22] allows the selection of a comparatively weak organic acid (pKa of acetic acid: 4.75) as the pretreatment agent. To the best of our knowledge, this is the first report to study the effect of acetic acid on the bioavailability of FPWs. The alteration of the cellar integrity was determined using Scanning electron microscopy (SEM) after the pretreatment. The changes in the chemical composition of the FPWs were characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric (TG) analysis.

2. Materials and methods

2.1. Substrate collection and preparation

Orange peels, pineapple waste, grape pomace and banana peels were selected as the most widely available FPWs, and samples of these FPWs were collected from local juice vendors in Seoul, South Korea. Orange peels, banana peels and whole pineapple wastes were cut into 3–5 mm sized pieces, whereas the grape pomace was in uniform pieces (3–5 mm) as received. All samples were dried at 65 °C overnight [22] and stored in airtight plastic bags in a desiccator prior to use.

2.2. Optimization of pretreatment conditions

The FPWs were exposed to different concentrations (0.2, 0.4 and 0.7 M) of acetic acid (Sigma Aldrich, St. Louis, MO, USA) at 10% (w/v) substrate loading, under various conditions of temperature and treatment time to determine the optimal pretreatment conditions. The samples were incubated at 25, 50 and 100 °C for 24, 12 and 1 h, respectively. The samples were then subjected to suction filtration; the filtrates were stored at 4 °C for further analysis of the hydrolysates, and the solid residues were dried at 65 °C for 2 h and stored in airtight polyethylene bags. Sulfuric acid (0.2 M) was used as a conventional pretreatment agent [9,23,24] at 100 °C for 1 h to compare its hydrolysis efficiency with that of the organic acid.

2.3. Analytical methods

2.3.1. Physicochemical characterization of FPWs

Raw FPWs were characterized with respect to chemical composition, according to AOAC International [25]. To analyze total solids, all types of fruit waste were dried in an oven at 105 °C for 24 h after collection. To determine volatile solids and ash content, dried biomass samples were completely combusted at 550 °C for 16 h in a muffle furnace (Dong Yang Science Co. Ltd., Korea). The fixed carbon of each sample was calculated using the following equation [26]:

$$\text{Fixed Carbon } (\text{wt.}\%) = 100 - (\text{volatile solid}\% + \text{ash}\%) \quad (1)$$

The calorific value or heating value of each FPWs sample was calculated as a function of fixed carbon using the following equation [27]:

$$\text{Calorific value } (\text{MJ kg}^{-1}) = (0.196 \times \text{Fixed Carbon}) + 14.12 \quad (2)$$

The initial pH of each sample was recorded using a pH meter (Orion STAR A329, Thermo Fisher Scientific, USA). Approximately 5 g of overnight dried different FPWs were mixed with distilled water in a ratio of 1:5 and homogenized properly. The mixtures were allowed to equilibrate for 15–20 min and the pH was measured [23]. Total elemental compositions were analyzed using an elemental analyzer (FLASH EA1112, Thermo Electron Corporation, USA).

2.3.2. Combined Severity (CS) factor of pretreatment agents

The catalytic effects of the various pretreatment conditions were quantified based upon the treatment time t, the temperature T, and the room-temperature pH of the pretreatment agents [28]. The CS of acetic acid and sulfuric acid treatments were calculated using the pre-standardized conditions for individual treatment (acetic acid: 1 h, 100 °C and pH - 2.61, and sulfuric acid: 1 h, 100 °C and pH - 1.21) using the following equation:

$$\text{CS} = \log\left(t \times e^{\frac{T-100}{14.75}}\right) - \text{pH} \quad (3)$$

2.3.3. Total reducing sugar and carbohydrate analyses

The hydrolysates yielded by each pretreatment were evaluated for the content of reducing sugar released from the biomass using a modified dinitrosalicylic acid (DNS) colorimetric method [29]; 3,5-dinitrosalicylic acid is reduced to the strongly colored 3-amino-5-nitrosalicylic acid in the presence of pentose and hexose sugars. Each hydrolysate sample (0.3 mL) was mixed with 0.3 mL of DNS reagent and boiled for 15 min in a water bath to produce a dark orange red color; the reaction mixture was then cooled to room temperature, and its color intensity at 540 nm was measured using a spectrophotometer (DR3900 VIS, Hach, USA).

The total carbohydrate contents of FPWs were analyzed before and after pretreatments by means of a colorimetric phenol–sulfuric acid method [30], whereby concentrated sulfuric acid converts all polysaccharides and oligosaccharides into monosaccharides, pentoses into furfural, and hexoses into 5-hydroxymethyl furfural. These compounds then react with phenol to produce a yellow-golden color. Briefly, dried FPWs were weighed (25 mg) and mixed with 2 mL distilled water. One milliliter of 5% phenol stock and 5 mL of 98% concentrated sulfuric acid were added to each test tube containing an FPWs sample, the sample was agitated for 25 min to allow color development, and the absorbance was measured at 490 nm using a spectrophotometer (DR3900 VIS, HACH, USA). Glucose solution was used as an internal standard.