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Dilute sulfuric acid fractionation of Korean food waste for ethanol and lactic acid production by yeast

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ABSTRACT

Fermentation of food waste biomass can be used to produce biochemicals such as lactic acid and ethanol in a cost-effective manner. Korean food waste (KFW) dewatered by a screw press contains 23.1% glucan on a dry basis and is a potential raw material for the production of ethanol and lactic acid through fermentation. This study was conducted to optimize the dilute acid fractionation conditions for KFW fermentation with respect to the H_2SO_4 concentration (0–0.8% w/v), temperature (130–190 °C), and residence time (1–128 min) using response surface methodology. Dilute sulfuric acid fractionation was carried out using a 30-mL stainless steel reactor under conditions, and then the dilute acid fractionation was scaled-up in 1-L and 7-L stainless steel reactors under the optimal conditions. The hydrolysate was concentrated, liquid-liquid extracted and neutralized for lactic acid and ethanol production. The highest concentration of glucose obtained from the KFW was 26.4 g/L using fractionation with 0.37% w/v H_2SO_4 at 156 °C for 123.6 min. Using recombinant *Saccharomyces cerevisiae* containing a codon-optimized lactate dehydrogenase, the yield of lactic acid and ethanol was 77% of the theoretical yield for 17.4 g/L of fermentable sugar at pH 5.5. Additionally, the yield of ethanol produced by *Issatchenkia orientalis* was 89% of the theoretical yield for 25 g/L of fermentable sugar at pH 3.

1. Introduction

Due to the use of non-renewable resources, the planet has been overloaded with pollutants, and global environmental pollution has increased. The main concern in terms of global climate change is the greenhouse effect caused by excess carbon dioxide in the atmosphere, which related directly to fossil fuel combustion by coal-fired power plants or automobiles (Han and Shin, 2004). In light of these global environmental considerations, bioethanol generation from renewable organic waste sources represents an important area of bioenergy production (Benemann, 1996). Moreover, one of the greatest challenges of the 21st century is to meet the food demand of the growing population while reducing the adverse effects of the food production system on the environment (Grizzetti et al., 2013). Consequently, large amounts of food waste (FW) is generated. The management of FW is a challenging task because of its high moisture content and propensity to decays under ambient conditions. The treatment and disposal of FW represent a major cost to communities served by landfill plants (Ventour, 2008). Since FW has high energy content, reducing FW by generating energy seems ideal. The fermentation of renewable resources, such as crop residues and FW, also has the potential to enhance the economic feasibility of waste treatment (Han and Shin, 2004; Kim and Dale, 2004).

A typical chemical fractionation of biomass involves the use of a dilute acid, usually sulfuric acid, and heating at temperatures of 150–200 °C. (Larsson et al., 1999) This acid-catalyzed fractionation causes the hydrolysis of glucan, resulting in a high recovery of glucose monomers in the liquid fraction (Sassner et al., 2008). Acetic acid is generated from the hydrolysis of the acetyl groups in the biomass; its generation mainly depends on the temperature and residence time of the dilute-acid fractionation until the acetyl groups are hydrolyzed (Aguilar et al., 2002). Acetic acid is one of the most widely used carboxylic acids. It is used in many reactions, for example, the synthesis of acetate esters or pharmaceutical products. Acetic acid biosynthesis is used to produces significant quantities of aqueous solutions from which acetic acid can be economically recovered (Park et al., 1991; Macias et al., 1997; Tesfaye et al., 2002). The toxicity of acetic acid is strongly pH-dependent

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because the non-dissociated form of the acid is liposoluble and, thus, able to diffuse through cell membranes. The uptake of acetic acid inhibits the activity of certain enzymes (Pampulha and Loureiro-Dias, 1990), and intracellular acetate ions are also toxic to yeast cells (Zhang et al., 2011). A solution to the problem of acetic acid toxicity and inhibition of fermentation processes is to remove these inhibitors from biomass prior to fermentation. Liquid–liquid extraction (LLE) is an excellent method to extracts organic acids from aqueous solutions. This process is widely employed in the chemical industry owing to its simplicity, low costs, and ease of scale up, and the purification of biomolecules using LLE has been successfully carried out on a large scale. The advantages of using this system are its lower viscosity, lower cost of chemicals, and shorter phase separation time. (Simon and Otto, 2005; Mazzola et al., 2008).

Plant- and crop-based plastics, including poly-D-lactic acid (PLA), are being developed as renewable alternatives to conventional petroleum-based plastics (Ohara et al., 2001). Engineered *Saccharomyces cerevisiae* with an introduced heterologous D-lactate dehydrogenase gene (D-LDH) is used for lactic acid production and is stable at low pH; therefore, high density cultivation is possible (Porro et al., 1995; Adachi et al., 1998; Dequin and Barre, 1994). Moreover, the MF-121 strain of *Issatchenkia orientalis* has been isolated from a river (pH 3) flowing in a hot spring area in Japan, and can facilitates ethanol fermentation in a medium containing 5% sodium sulfate at pH 2 (Hisamatsu et al., 2006). Thus, it is a multiple stress-tolerant yeast, as it is ethanol tolerant, salt tolerant, acid tolerant, and thermo tolerant. Because sulfuric acid is used for the fractionation and produces undesirable by-products, such as furfural and acetic acids, multiple stress tolerance is an important factor for ethanol fermentation (Kitagawa et al., 2010).

In this study, Korean food waste (KFW) was chosen for use in ethanol and lactic acid production. Response surface methodology (RSM) was used to optimize the conditions of the dilute acid fractionation of the KFW using sulfuric acid (H_2SO_4), with the specific aiming of obtaining the highest extraction of glucose (Kim et al., 2014). The dilute acid fractionation was scaled-up in both 1-L and 7-L reactors under the optimal conditions. Then, the hydrolysate was concentrated to achieve a high concentration of glucose, and LLE was performed using Tri-*n*-alkylphosphine oxide (TAPO) as the extraction solvent to remove organic acids. Following LLE, the extracted liquid was neutralized and fermented using recombinant *S. cerevisiase* and *I. orientalis*. The lactic acid and ethanol yields of the fermentation and the sugar consumption were assessed. A schematic diagram of the dilute sulfuric acid fractionation of KFW for lactic acid and ethanol fermentation is shown in Fig. 1.

2. Materials and methods

2.1. Korean food waste (KFW)

The Korean food waste (KFW) used in this study was collected from a KFW treatment plant (Fig. 2). The KFW was dewatered using a screw press and dried using a steam boiler at 150 °C. The dried KFW was ground, and foreign material was separated by a trommel magnet separator. The fermentable sugar content of the KFW was approximately 28.3% based on dry weight. Glucan and protein were the most abundant components of the KFW with contents of 23.1% and 21.5%, respectively. The KFW also contained 2.3% XMG (xylan, mannan, and galactan), 16.6% ash, and 36.5% other components (Table 1).

2.2. Dilute sulfuric acid fractionation

Dilute sulfuric acid fractionation was performed using 30 mL, 1-L, and 7-L stainless steel reactors. Schematics of the reactors are shown in Fig. 3. The temperature of the vessel contents was monitored using a thermocouple inserted into the reactor (Um and van Walsum, 2009). For the small-scale reaction, the 30-mL fractionation reactor was loaded with 4 g of air-dried KFW and 16 mL of sulfuric acid solution, to give a final ratio of 4 mL sulfuric acid solution per gram KFW on a dry basis. The dilute sulfuric acid fractionation was conducted under conditions ranging from 130 to 190 °C, 0% to 0.8% H_2SO_4, and 1 to 128 min residence time. The reactor was heated to the set temperature in an oil bath (Samwoo-ENG, Seoul, Korea). The heating time of the 30-mL reactor was approximately 10 min for the temperature range of 130–190 °C. Once the target temperature was reached inside the reactor, measurement of the residence time was started. After reaction was finished, the reactor was quenched in an ice bath for 10 min, and the liquid was separated by centrifugation using a small-scale centrifuge (FLETA-5, Hanil science industrial, Incheon, Korea) at 4500 rpm for 5 min, and then filtered (Um and van Walsum, 2009; Kim et al., 2014). The dilute sulfuric acid fractionation was scaled up in the rocking digesters with total volumes of 1-L (General Purpose Vessel 4600, Parr Instrument Company, Moline, IL, USA) and 7-L (KHT Engineering Co. Ltd., Gunpo, Gyeonggi, Korea). The 1-L and 7-L fractionation reactor were loaded with 0.1 kg and 0.8 kg of air-dried KFW and 0.4 L and 3.2 L of dilute sulfuric acid solution, respectively. The dilute sulfuric acid fractionation was conducted under optimized conditions. The heating time for the 1-L and 7-L reactors were approximately 35 and 45 min, respectively, at the optimal temperature. After the fractionation, the liquid was separated using a large-scale centrifuge (Supra, Hanil science industrial, Incheon, Korea) at 5000 rpm.

2.3. Acid hydrolysis

The acid hydrolysis was performed using National Renewable Energy Laboratory standard method No. 002 with conditions of 121 °C, 4% H_2SO_4, and 60 min residence time (NREL, 2004) to hydrolyze oligomeric sugars into monomeric sugars in an autoclave (SC ENG, Pocheon, Gyeonggi, Korea). The resulting concentrations of the hydrolyzed fermentable sugars were determined using high performance liquid chromatography (HPLC).

2.4. Response surface methodology experimental design

RSM was utilized to optimize the conditions of H_2SO_4 fractionation by evaluation with a three-level factorial model design. Three independent variables, concentration of sulfuric acid, temperature, and residence time, were selected. The 17 sets of treatment combinations were analyzed according to the Box-Behnken Design using Design-Expert statistical software (version 7.0.0, STATEASE Inc, Minneapolis, MN, USA). The validity of the model was expressed as a regression coefficient (R^2), and the significance of the regression coefficients was evaluated by analysis of variance (ANOVA). A quadratic model was generated from the data according to Eq. (1):

$$Y = a_0 + a_1A + a_2B + A_3C + a_{11}AB + a_{32}AC + a_{33}BC + a_{12}A^2 + a_{13}B^2 + a_{23}C^2, \quad (1)$$

where Y is the predicted response, A, B, and C are independent variables in code values, a_0 is a constant, and a_1 and a_2 are linear effects. The concentration of sulfuric acid (A), temperature (B), and residence time (C) for the fractionation were optimized using a central composite design experimental design to enhance the concentration of glucose. The design of this experiment, including the dependent variables or responses is shown in Table 2.

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