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Reduction in environmental impact of sulfuric acid hydrolysis of bamboo for production of fuel ethanol

Zhao-Yong Sun [a], Yue-Qin Tang [b], Shigeru Morimura [a], Kenji Kida [a,b,*]

[a] Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto City, Kumamoto 860-8555, Japan
[b] College of Architecture and Environment, Sichuan University, No. 24 South Section 1, First Ring Road, Chengdu, Sichuan 610065, China

HIGHLIGHTS

- Effluent from biological treatment of stillage could be reused to recover sugar from residue.
- Rinse water and recovered sulfuric acid could be reused in the saccharification process.
- Condensate without acetate could be reused as elution water in acid–sugar separation.
- 86.3% of the process water and 77.6% of the sulfuric acid could be recycled.
- Environment impact was reduced by reuse of stillage and sulfuric acid.

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ABSTRACT

Fuel ethanol can be produced from bamboo by concentrated sulfuric acid hydrolysis followed by continuous ethanol fermentation. To reduce the environmental impact of this process, treatment of the stillage, reuse of the sulfuric acid and reduction of the process water used were studied. The total organic carbon (TOC) concentration of stillage decreased from 29,688 to 269 mg/l by thermophilic methane fermentation followed by aerobic treatment. Washing the solid residue from acid hydrolysis with effluent from the biological treatment increased the sugar recovery from 69.3% to 79.3%. Sulfuric acid recovered during the acid–sugar separation process was condensed and reused for hydrolysis, resulting in a sugar recovery efficiency of 76.8%, compared to 80.1% when fresh sulfuric acid was used. After acetate removal, the condensate could be reused as elution water in the acid–sugar separation process. As much as 86.3% of the process water and 77.6% of the sulfuric acid could be recycled.

1. Introduction

Bamboo is a promising renewable feedstock for production of fuel ethanol because of its high growth rate and high content of holocellulose (up to 70% of the dry base) (Shimokawa et al., 2009; Yamashita et al., 2010; Sathitsuksanoh et al., 2010). Saka (2001) has reported that 3.3 million tons of bamboo could potentially be converted to ethanol every year in Japan; however, presently, most of the bamboo available is not being effectively utilized.

A process designed to utilize bamboo as a raw material for fuel ethanol production has been proposed previously (Sun et al., 2011). The process consists of hydrolysis with concentrated sulfuric acid, removal of color compounds, separation of acid and sugar, hydrolysis of oligosaccharides, and subsequent continuous ethanol fermentation. The sugar concentration (148.1 g/l) and the sugar recovery efficiency (81.6%) were higher than those reported previously (Clausen and Gaddy, 1993; Iranmahboob et al., 2002). A high fermentation yield of 92% based on glucose and a high ethanol productivity of 8.2 g/l/h were achieved in the continuous fermentation.

A major environmental concern with this process is the usage of large quantities of sulfuric acid. Although the sulfuric acid used during hydrolysis was recovered with anion exchange resins, its reusability was unknown. In addition, the stillage from the distillation process would require treatment to avoid negative environmental effects. At an industrial scale, recycling of recovered sulfuric acid as well as the treatment of stillage would have numerous benefits not only for the environment but also for the reduction of process water. There are two reports having previously been addressed on process water for production of ethanol from

* Corresponding author at: College of Architecture and Environment, Sichuan University, No. 24 South Section 1, First Ring Road, Chengdu, Sichuan 610065, China. Tel./fax: +86 28 8599 0936.
E-mail address: kida@gpo.kumamoto-u.ac.jp (K. Kida).

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wood biomass and swichgrass (Wei et al., 2009; Wu et al., 2009). About the sulfuric acid recovery, only Biosulfurol process was introduced with only the outline of the process but no detailed research data (Taherzadeh and Karimi, 2007).

In the present study, treatment of stillage, recovery of sugar lost during solid–liquid separation, recovery and reuse of the sulfuric acid and reduction of the process water were studied to reduce the environmental impact. The stillage from the ethanol distillation process was subjected to anaerobic then aerobic treatment. The effluent from these treatments was reused as washing water to recover the sugar lost during solid–liquid separation after saccharification, and the rinse water from the washing process was reused as process water during the hydrolysis with concentrated sulfuric acid. The recovered sulfuric acid was condensed and reused in the bamboo saccharification process. The condensate from the sulfuric acid concentration process was studied for its use as elution water in the acid–sugar separation process.

2. Methods

2.1. Materials

Bamboo was kindly provided by the National Agricultural Research Center for the Kyushu Okinawa Region (Kumamoto, Japan). It was crushed to 1–3.35 mm in size.

Thermophilic digestion sludge and activated sludge were provided by Kumamoto Hokubu Sewage Works (Kumamoto, Japan), and used as seed for thermophilic methane fermentation and aerobic treatment, respectively.

2.2. Concentrated sulfuric acid bamboo saccharification

Concentrated sulfuric acid bamboo saccharification was carried out at an acid to substrate ratio of 1.4 (bamboo chips: 75 wt.% H_2SO_4 = 2.4 kg:4.4 kg). Saccharification consisted of treating bamboo chips with 75 wt.% sulfuric acid at 50 °C for 30 min (solubilization step) and 27 wt.% sulfuric acid at 80 °C for 60 min (hydrolysis step), as previously described (Sun et al., 2011). The resulting slurry of 12.1 kg was pressed at 20 MPa for 20 min to separate solids from the liquid. To determine the concentrations of glucose and xylose in the liquid, the liquid was diluted 10-fold with distilled water and treated for 30 min at 120 °C at a pH of 0.8 before HPLC analysis. Sugar recovery efficiency was calculated using the following equation:

$$\text{Sugar recovery efficiency}(\%) = \frac{\text{Total quantities of glucose and xylose in saccharified liquid}}{\text{Total quantities of glucose and xylose in bamboo chips}} \times 100.$$

2.3. Thermophilic methane fermentation of stillage using an upflow anaerobic filter (UAF) reactor

A 5-l aliquot of fermented broth from the continuous ethanol fermentation was decanted. The supernatant was distilled under vacuum by using a 10-l distillation vessel (Rotary Vacuum Evaporator N-11; Rikakikai Co., Tokyo). The 3 l of remaining liquid after distillation was diluted with tap water to a final volume of 5 l. The stillage was used for thermophilic methane fermentation.

Fig. 1A shows a schematic diagram of the UAF reactor for thermophilic methane fermentation. The reactor with a working volume of 0.8 l was made of glass and packed with a support material, which was a mixture of clay and high-density polyethylene, for microbial adhesion (Tokuda et al., 1998). The temperature was regulated by circulating water in the water jacket maintaining at 55 °C. A 0.8-l aliquot of thermophilic sludge was introduced into the reactor. The following day, the liquid in the reactor was circulated by roller pump P-2, and acclimatization was initiated by feeding synthetic wastewater (g/l: glucose, 35.0; corn steep liquor, 17.5; $(NH_4)_2CO_3$, 1.0; Na_2CO_3, 3.0; K_2HPO_4, 0.3; KH_2PO_4, 0.2; $FeCl_3 \cdot 6H_2O$, 0.1.) into the bottom of the reactor at a TOC loading rate of 2.0 g/l/d. After acclimatization, stillage was fed in the same manner, and the TOC loading rate was increased stepwise from 2.0 to 14.0 g/l/d. Evolved biogas was fed into a gas holder through vinyl tubing, and the amount of evolved biogas was measured. The operation period for each TOC loading rate was 1–2 weeks.

2.4. Aerobic treatment of anaerobically treated effluent in a submerged filter reactor

Fig. 1B shows a schematic diagram of the submerged filter reactor for aerobic treatment. The reactor was made of acrylic resin and a partition separated the 1.2-l settling zone from the 2.4-l aeration zone. Temperature was maintained at 30 °C by using a bimetal thermostat heater. Air was supplied at a rate of 1.0 l/min through a ball filter installed on the bottom of the reactor, which ensured that the liquid in the reactor was well mixed. About 2.4 l of activated sludge was initially placed in the reactor, and the sludge was acclimatized by feeding the 100-fold diluted wastewater of the synthetic wastewater used in the methane fermentation as described in Section 2.3. After acclimatization, the effluent from the thermophilic methane fermentation (pH adjusted to 4.7 with 1 M HCl), was fed into the reactor at a TOC loading rate of 0.5 g/l/d.

2.5. Washing of the solid residue and reuse the rinse water

The solid fraction from the solid–liquid separation process, as described in Section 2.2, was washed three times with 5.3 kg of effluent from the submerged filter reactor to recover the sugar remaining in the solid residue. For comparison, tap water was used to wash the solid residue in the same manner. Sugar concentrations in the liquid fractions and the rinse water from the washing process were determined. The rinse water was reused in the saccharification process as described in Section 2.2.

2.6. Condensation and reuse of sulfuric acid

The acid fraction obtained from the acid–sugar separation by using an improved simulated moving bed (ISMB) system (Labo-2LT; Nippon Rensui Co., Tokyo) (Sun et al., 2011) was condensed to approximately 70 wt.%. Condensed sulfuric acid (75 wt.%) was prepared by adding 97 wt.% fresh sulfuric acid and used in the saccharification process instead of the fresh sulfuric acid described in Section 2.2.

2.7. Recovery of acetic acid from the condensate

WA 30 anion exchange resin, purchased from Mitsubishi Chemical Co. (Tokyo, Japan), was used to recover acetic acid in the condensate from the sulfuric acid concentration process. The resin was mixed with 1 M HCl, and 50 ml was packed into a glass column ($10\varphi \times 200$ l). The column was washed with 5 l of tap water, followed by 1 l of a 1 M NaOH solution. Consequently, tap water was used to wash the resin until its pH was about 7.0.

The condensate (604 ml) was fed into the column at room temperature at a flow rate of 200 ml/h. A 0.75 M NaOH solution of 176 ml was fed into the column to elute the acetic acid absorbed on the resin. During this period, 20-ml samples were collected every 6 min to determine the concentration of acetate.