Bioresource Technology 207 (2016) 52–58

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Enhancing ethanol production from thermophilic and mesophilic solid digestate using ozone combined with aqueous ammonia pretreatment

Dianlong Wang [a,b,d], Jiang Xi [c], Ping Ai [a,b,*], Liang Yu [d], Hong Zhai [a], Shuiping Yan [a,b], Yanlin Zhang [a,b]

[a] College of Engineering, Huazhong Agricultural University, Wuhan 430070, China
[b] Cooperative Innovation Center for Sustainable Pig Production, Wuhan 430070, China
[c] Biogas Institute of Ministry of Agriculture, Chengdu 610041, China
[d] Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164, USA

HIGHLIGHTS

- Recover residual organic carbon from solid digestate to produce ethanol.
- Pre-treat recalcitrant solid digestate using combined ozone with aqueous ammonia.
- Elucidate a combined and successive utilization of lignocelluloses.

ARTICLE INFO

Article history:
Received 5 December 2015
Received in revised form 29 January 2016
Accepted 30 January 2016
Available online 4 February 2016

Keywords:
Solid digestate
Anaerobic digestion
Methane
Ethanol fermentation
Pretreatment

ABSTRACT

Pretreatment with ozone combined with aqueous ammonia was used to recover residual organic carbon from recalcitrant solid digestate for ethanol production after anaerobic digestion (AD) of rice straw. Methane yield of AD at mesophilic and thermophilic conditions, and ethanol production of solid digestate were investigated. The results showed that the methane yield at thermophilic temperature was 72.2% higher than that at mesophilic temperature under the same conditions of 24 days and 17% solid concentration. And also the ethanol production efficiency of solid digestate after thermophilic process was 24.3% higher than that of solid digestate after mesophilic process. In this study, the optimal conditions for integrated methane and ethanol processes were determined as 55 °C, 17% solid concentration and 24 days. 58.6% of glucose conversion, 142.8 g/kg of methane yield and 65.2 g/kg of ethanol yield were achieved, and the highest net energy balance was calculated as 6416 kJ/kg.

1. Introduction

Anaerobic digestion (AD) technology has been widely applied for treating various wastes, such as crop straws, animal manure and municipal wastes, etc. (Liu et al., 2015). Methane or hydrogen can be obtained to meet the increasing need for energy (Jariyaboon et al., 2015; Razaviarani and Buchanan, 2015; Risberg et al., 2013). Although biogas is a promising renewable energy alternative, the sustainable development of AD mainly depends on the ability to deal with the excessive digestate (Dahlin et al., 2015). This is because an improper handling of digestate would lead to serious environmental problems.

Many large-scale biogas plants that use crop straws as feedstock have a low degradation rate compared with those that use animal manure. There is a high residual organic carbon in solid digestate after AD (Pokój et al., 2015). For example, Sambusiti et al. (2015) studied the recovery of methane from solid digestate in a mesophilic full-scale AD plant with mixed biomass. The solid digestate still contained 17.5% of cellulose, 20.3% of hemicellulose and 24.1% of lignin after AD. Wang et al. (2013) reported that the anaerobic digested corn stover still had 25.1% of cellulose, 1.1% hemicellulose and 21.7% of lignin after 20 days. These studies have demonstrated that the solid digestate can be further reused due to highly residual lignocelluloses.

Usually, anaerobic digestate can be used as fertilizer via composting to replace inorganic fertilizers and improve soil quality (Bustamante et al., 2012; Tambone et al., 2015). Although solid digestate has high fertilizing potential, its full year production needs large storage and heavy transportation due to the limitation

* Corresponding author at: Room B306, College of Engineering, Huazhong Agricultural University, No.1, Shizishan Street, Hongshan District, Wuhan 430070, PR China. Tel./fax: +86 27 87288723.
E-mail address: aiping@mail.hzau.edu.cn (P. Ai).

http://dx.doi.org/10.1016/j.biortech.2016.01.119
0960-8524/

of crop growth stage and soil type. Moreover, the increasing number of biogas plants has led to an oversupply of digestate. Therefore, one of the important challenges for AD development is how to handle large amounts of solid digestate.

In recent years, some researchers have proposed a new biorefinery way that would use solid digestate to produce ethanol. Teater et al. (2011) assessed the solid digestate for ethanol production and indicated that solid digestate is a suitable feedstock for biorefinery compared with switchgrass and corn stover. After an AD process, most hemicellulose was consumed, and crystal structure of lignocelluloses was broken. Yue et al. (2011) compared continuous stirring-tank reactor (CSTR) and plug flow reactor (PFR) to use solid digestate for ethanol production and indicated that CSTR was a preferred reactor type.

Since it is hard to reuse solid digestate in high conversion efficiency (Tambone et al., 2009), pretreatment is necessary to break down the recalcitrant structure in solid digestate. Ozone pretreatment has been proved to delignify with minimal effects on hemicellulose and cellulose. Different mechanisms including selective reaction with carbon–carbon double bonds and glycosidic bond cleavage have been proposed for lignin degradation by ozone pretreatment (Bule et al., 2013). Ozone pretreatment can result in condensation of lignin structures due to lignin–ozone interaction.

Aqueous ammonia pretreatment was also extensively studied. It was found that the major effect of aqueous ammonia pretreatment is to remove lignin. Aqueous ammonia pretreatment can remove 60% of lignin from rice straw while achieving 70% of enzymatic digestibility (Ko et al., 2009). A fiber expansion theory was proposed that aqueous ammonia pretreatment resulted in the increased access for cellulosic enzyme due to the insertion of ammonia molecules (Gao et al., 2012). In addition, studies have shown that ammonia can selectively act with lignin bonds, as well as ester and ether bonds, especially C–O–C bonds, causing the selective removal of lignin in biomass. Above all, aqueous ammonia is inexpensive and recyclable in industrial applications. Jurado et al. (2013) used aqueous ammonia soaking to treat solid digestate of swine manure fiber, resulting in a 40–80% enhancement of methane yield from digested manure fibers. This research demonstrated that aqueous ammonia can be used to treat the recalcitrant solid digestate for the enhancement of methane productivity.

Yu et al. (2014) studied the combined pretreatment of ozone and aqueous ammonia soaking to improve enzymatic hydrolysis of grass, achieving 90% sugar recovery. Therefore, ozone combined with aqueous ammonia pretreatment may be a promising pretreatment method. However, to our best knowledge, the investigation on solid digestate using ozone and aqueous ammonia pretreatment to enhance ethanol production is limited. This investigation will be the theoretical basis for clarifying the combined and successive utilization path of organic carbon.

The aim of this study was to evaluate a two-stage conversion of waste biomass to methane and ethanol under both mesophilic (37 °C) and thermophilic (55 °C) conditions, and demonstrate overall improvement in energy yield upon pretreatment of the solid digestate with a combined ozone and aqueous ammonia soaking. The pretreatment and enzymatic hydrolysis of solid digestate after mesophilic and thermophilic AD were investigated. The ethanol production from the treated solid digestate was studied to clarify the residual organic carbon recovery. Furthermore, preliminary energetic balances were calculated for the integrated process of AD and ethanol fermentation to provide a useful insight in terms of the partitioning of energy into the methane versus ethanol product streams. Finally, the changes of crystallinity were measured in the entire process to reveal recovery mechanism of organic carbon in solid digestate.

2. Methods

2.1. Materials

Rice straw was collected from fields in a suburb of Wuhan, China. After collection, the straw was air dried, ground using a hammer mill and passed through a 2 mm aperture standard screen. The ground straw was then sealed in plastic bags and stored at room temperature for further use. The total solid (TS) and volatile solid (VS) of rice straw were 87.62% and 78.34%, respectively. The rice straw was composed of 38.29% cellulose, 27.23% hemicellulose, 2.42% lignin and 3.93% ash. The inoculum was taken from a mesophilic anaerobic digester operated for two years. The TS and VS of inoculum were 12.95% and 6.62%, respectively. Prior to use for thermophilic AD, the inoculum was gradually acclimated to thermophilic conditions in water bath through increasing 1.0 °C per day from 37 °C to 55 °C (Broughton et al., 1998).

2.2. Experimental methods

2.2.1. Anaerobic digestion

AD experiments were conducted at mesophilic (37 °C) and thermophilic (55 °C) conditions. The solid concentrations of 7% and 17% and the hydraulic retention time of 17 days and 24 days were considered. The batch experiments of rice straw were implemented using 0.5 L AD reactor. During each run, 25 g rice straw (28.53 g fresh rice straw) was added and inoculated with 10 g sludge (77.16 g fresh sludge). To avoid acidification, 2 g $NaHCO_3$ was added into the reactors. Then deionized water was added to make the final total solids concentrations of 7% and 17%. All reactors were capped with rubber stoppers and put into a water bath. Before the fermentation test, the reactors were flushed with nitrogen to remove oxygen from the headspace and maintain an anaerobic environment. To minimize errors, each run was conducted in duplicate. The biogas volume was measured by drainage method, and the biogas was collected by a 1 mL plastic syringe for the gas composition analysis.

2.2.2. Ozone combined with aqueous ammonia pretreatment

Ozone was produced by an Ozone Generator (XKH-YA10G, Wuhan, Hubei, China) with ozone concentration (16.67 mg/L) at a flow rate of 10 L/min. The solid digestate (10 g) was adjusted to a moisture content of 40% w/w and put into an enclosed stainless steel reactor. The reactor was operated in a semi-continuous mode. The ozone pretreatment was implemented for 45 min. The ozone dose was 0.75 g O_3/g-TS. The treated samples were dried at 50 °C and stored for further analysis and use. After ozone pretreatment, the solid digestate (7.5 g) was subsequently treated using 26–28% (w/w) ammonium hydroxide solution under the solid to liquid ratio of 1:10 at 50 °C for 6 h. After completion of soaking, the solid digestate was separated from the liquid by a vacuum filtration with 0.1 mm mesh, and the filter cake was washed with 1 L distilled water to neutralize pH. Then the treated samples were dried at 50 °C.

2.2.3. Enzymatic hydrolysis process

3 g dry solid fiber and 47 mL acetic acid-sodium acetate buffer (0.2 M, pH = 4.8) were mixed into a 100 mL shake flask, which made the dry matter concentration 6.0%. All flasks were added with 0.5 g mixed-cellulases containing β-glucanase $\geqslant 6 \times 104$ U, cellulase $\geqslant 600$ U and xylanase $\geqslant 10 \times 104$ U (Imperial Jade Biotechnology Co., Ltd). During the enzymatic hydrolysis, the flasks were shaken at 150 rpm at 50 °C for 48 h. The amounts of hydrolyzed sugars were determined by high performance liquid chromatography (HPLC).