Biomass and Bioenergy 105 (2017) 73–82

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Converting wastewater sludge and lime-treated sugarcane bagasse to mixed carboxylic acids – a potential pathway to ethanol biofuel production

Hema Rughoonundun*, Mark T. Holtzapple

Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA

ARTICLE INFO

Article history:
Received 19 May 2016
Received in revised form
11 June 2017
Accepted 15 June 2017

Keywords:
Wastwater sludge
Mixed-acid fermentation
Carboxylic acids
Ethanol
Biofuel

ABSTRACT

Sludge is the solids recovered from wastewater treatment. Its high content of organic matter makes it a potential biomass resource for renewable energy production. In this study, batch and continuous countercurrent fermentations were performed with a 60:40 mixture (dry weight basis) of lime-treated bagasse:sludge. This combination provides an optimal C/N ratio and therefore enhances yield. Two trains of continuous fermentations were performed using different volatile solids loading rates (VSLR) and liquid retention times (LRT). The highest total carboxylic acids concentration obtained was 60.8 g L^{-1} with a total acid yield of 420 g kg^{-1} of VS added and an acid productivity of 2.31 g L^{-1} d^{-1}. In studies on co-fermentation of lignocellulosic biomass, this acid concentration is the highest reported in MixAlco™ (a patented process that converts biomass to a mixture of alcohols). This study shows that wastewater sludge is a valuable resource for liquid transportation fuels, and provides an attractive replacement for fossil fuels.

1. Introduction

Sludge is the solids recovered from wastewater treatment. Sludge is the most voluminous constituents removed from wastewater and therefore requires proper handling, treatment and disposal [1]. Sludge is usually a slurry that contains 0.25–12% solids by weight, depending on operations and processes used [2]. *Primary sludge* is the solids fraction that settles from wastewater in the primary sedimentation tank, and consists of organic solids, grit, and inorganic fines. *Secondary sludge* is the excess microbial biomass produced from aerobic bioconversion of soluble organic matter. This research uses *mixed sludge*, a combination of primary and secondary sludge, as obtained from a municipal wastewater treatment plant. According to Rulkens [3], sludge comprises up to 60% nontoxic organic carbon compounds. Other components are nitrogen- and phosphorous-containing components; toxic inorganic and organic pollutants, such as heavy metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins, pesticides, pathogens, and other microbiological pollutants; inorganic compounds; and water, which can vary from less than 3% to more than 95%.

The high water content of sludge makes it very difficult and expensive to handle, treat, and dispose. In a wastewater treatment plant, sludge management represents up to 35% of the capital cost, and 55% of annual operation and maintenance cost [4]. As more and more sewage treatment plants are built and environmental regulations for disposal of wastewater become more stringent, the generation of sludge is expected to increase world-wide. In Europe, *per-capita* production of dry sludge resulting from primary, secondary, and tertiary treatment averages 90 g d^{-1} [1]. Annually, Western Europe produces about 7 million tonnes of solids [5], whereas the United States produces around 6.5 million tonnes of sludge solids [6], each reported on a dry basis.

In developed countries, landfilling of sludge has been the most widely used disposal method. It is now recognized as being unsustainable because of environmentally harmful effects from methane and leachate production, loss of recyclable materials, and consumption of valuable land. Compared to landfilling, recycling and reuse of wastes is preferred for sustainable development.

Land application of sludge – an inexpensive reuse option – has been a very popular route for sludge disposal because it contains organic matter, nitrogen, and phosphorous. However, because of

* Corresponding author.
E-mail addresses: hrkhedun@gmail.com (H. Rughoonundun), m-holtzapple@tamu.edu (M.T. Holtzapple).

http://dx.doi.org/10.1016/j.biombioe.2017.06.007
0961-9534/

rigorous regulatory standards, land application faces both technical and social obstacles [7]. The technical issue is that sludge is produced throughout the year, whereas it can be applied only once or twice during the year. Public acceptance of sludge remains poor because it potentially contains heavy metals and pathogens (e.g., *E. coli* and *Salmonella*). Resources that can be recovered from sludge include phosphorous, building materials, volatile acids, and energy. Khan [8] found that the H/C (atomic ratio) of sewage sludge is 1.65, which is considerably higher than that of bituminous coal (H/C ratio of 0.89), and comparable to tar sand bitumen (H/C ratio of 1.5). In fact, the organic portion of sludge makes it a potential source of renewable energy that can be used directly as combustible fuel or converted to other fuel sources such as biogas, as established by several studies [3,6,8,9].

Unfortunately, the large quantity of water associated with sludge makes it a low-density energy source. Lee and Tay [9] report that based on its organic component, sludge has a heating value of approximately 25 MJ kg^{-1} (dry basis). When the inert fraction in sludge is included, this value reduces to 16–20 MJ kg^{-1} for raw sludge, or 10–14 MJ kg^{-1} for digested sludge. These values are reported on a dry basis, and are determined from the heat of combustion and are the upper limits of energy recoverable from sludge.

Several studies have described energy production from sludge. For example, Rulkens [3] compared chemical/thermal processes and biological processes. In principle, it is possible to produce biologically a gaseous or liquid fuel, or to produce electricity directly from sewage sludge; however, Rulkens [3] concludes that methane production is the most promising route because of process simplicity. Unfortunately, methane is a low-value product (~5 $ GJ^{-1}), making it difficult to be profitable. In contrast, the mixed-acid fermentation produces a mixture of carboxylate salts that can be converted to chemicals and fuels through the carboxylate platform. An example of the carboxylate platform is the MixAlco™ process, which produces liquid hydrocarbons or alcohols that command a much higher value than methane (~25 $ GJ^{-1}) [10,11].

The objective of this study is to investigate the potential for producing liquid fuels from sludge using mixed-acid fermentation. Batch and continuous countercurrent fermentations were performed using 60% lime-treated bagasse and 40% (dry weight) sewage sludge. Continuous fermentation was conducted at various volatile solids loading rates (VSLR) and liquid retention times (LRT). Yield and other performance parameters are evaluated, and the energy recovery potential from mixed alcohols is estimated based on the theoretical ethanol yield using the carboxylate platform (MixAlco route).

2. Materials and methods

2.1. Substrates

Mixed sewage sludge (primary and secondary sludge) was obtained from Burton's Creek Treatment Plant (Bryan, TX, USA). The secondary sludge consisted of activated sludge prior to being sent to the anaerobic digester. The sludge was collected in buckets and carried to the laboratory where it was immediately centrifuged for 25 min at 3038 × g to remove excess liquid and air-dried at room temperature. It had the following mass fractions: 930 g kg^{-1} dry solids (SD ± 5.80) and volatile solids (VS) 660 g kg^{-1} of dry solids (SD ± 55.0). In this study, raw untreated sludge was used because it was earlier established that oxidative lime treatment of sludge led to a decrease in carboxylic acid yield [12].

Bagasse was obtained from Rio Grande Valley Sugar Growers, Inc. (Santa Rosa, TX, USA). It was carried in plastic bags to the laboratory and immediately stored at 4 °C until use. Based on the sieve test, bagasse particles were estimated (by weight) to be 36% fine material (less than 2 mm), 51% between 2 mm and 4.75 mm, and 13% longer than 4.75 mm. Long-term oxidative lime pretreatment, which is recommended for high-lignin content biomass [13], was used. The raw bagasse, as received, was mixed with excess lime ($Ca(OH)_2$) at a rate of 300 g kg^{-1} of dry biomass and distilled water and pretreated at 50 °C for 8 weeks in the presence of air. The pretreated bagasse was then allowed to dry in the air until constant weight. The solids mass fraction of the bagasse was 95 ± 0.06%, and the VS mass fraction of the dry baggasse was 84 ± 0.31%.

2.1.1. Fermentation media

The liquid media consisted of deoxygenated water with 0.275 g L^{-1} cysteine hydrochloride and 0.275 g L^{-1} sodium sulphide, which ensured oxygen-free water. The inoculum, comprising 12.5% by liquid volume, consisted of a mixture of marine inoculum obtained from sediments of coastal swamps collected at Galveston (TX, USA) and fermentation liquor from previous mixed sludge/bagasse fermentation. No additional nutrients were added.

2.1.2. Methane inhibitor

Iodoform (CHI_3) crystals were dissolved in ethanol 20 g L^{-1} and the solution was added to the fermentor on alternate days to inhibit conversion of carboxylic acids to methane. The rotation of bottles in the Wheaton roller apparatus ensured that iodoform was uniformly mixed. Being light sensitive, the iodoform solution was kept in an amber-colored glass bottle, covered with aluminum foil, and was refrigerated when not used.

2.1.3. pH control

Every two days, the fermentor bottles were opened under nitrogen purge and samples of the fermentation broth were taken for compositional analysis. While the bottles were open, the pH was adjusted by adding ammonium bicarbonate buffer (NH_4HCO_3) in small doses, and the buffer was mixed with the substrates using a spatula, until a pH close to 7 was obtained. The change in pH was instantaneous because ammonium bicarbonate is readily soluble.

2.1.4. Fermentor

The fermentor was made with a 1-L polypropylene centrifuge bottle (98 × 169 mm), Nalgene brand NNI 3120-1010. The centrifuge bottle was capped with a rubber stopper with a glass tube inserted in the center. The glass tube was plugged with a rubber septum through which a syringe needle could be inserted for gas sampling and venting. The stirrer consisted of two pieces of 6.35-mm-diameter stainless steel tubes, with welded ends, inserted through the rubber stopper. The fermentors were placed in a Wheaton Modular Cell Production Roller Apparatus (Model III) contained in an incubator, and were rotated horizontally at 0.017 Hz.

2.1.5. Batch fermentation

Batch fermentation of 60% pretreated bagasse and 40% sludge (by dry weight) was performed in triplicate at a dry solids concentration of 50 g L^{-1}. Deoxygenated distilled water and inoculum (12.5% by volume) were also added to the fermentor bottles. No additional nutrients were added. Fermentation was performed at 55 °C for 36 days.

2.1.6. Countercurrent fermentation

Two fermentation trains (I and II) with different feed loading rates were performed. The substrate consisted of 60% lime-treated bagasse and 40% dried sewage sludge by dry weight. As previously determined, this mixture produced the highest total carboxylic acid concentration [14].