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Fermentation of sewage sludge using the MixAlco process

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Abstract

Under non-sterile anaerobic conditions, biomass is converted to intermediate acids products, such as acetic acid, which is in turn converted to methane by methanogens. In the MixAlco process iodoform is used as inhibitor so that the acids formed accumulate in the fermentor. To maintain the pH, ammonium bicarbonate is added, and it reacts with the acids to form carboxylate salts, such as ammonium acetate. After dewatering and drying, the carboxylate salts are thermally converted to ketones, which are further converted to other chemicals and mixed alcohols (biofuel) by hydrogenation. In this study, mixed sewage sludge was fermented under anaerobic conditions at 55^{o}C, and the total acids yield was 0.34g total acids/g VS digested.

Keywords: MixAlco, sewage sludge, mixed acids, fermentation.

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1. INTRODUCTION

Sludge is a by-product that results from the treatment of wastewater. Due to its high moisture content and pollutant loads, sludge is difficult to manage and dispose. Sewage sludge consists mainly of the excess biomass produced during biological treatment, and is usually in the form of a liquid or semi-solid liquid that contains around 0.25 – 12% solids by weight. It is composed largely of the substances responsible for the offensive character of untreated wastewater, such as putrescible organic matter, nutrients, pathogens, heavy metals and toxic organics. In 2005, about 60,000 tonnes of sewage sludge with 25% dry solids was produced in Mauritius, and according to Fichtner (2002) about 122,000 tonnes of sewage sludge will be produced in 2010. In the absence of adequate treatment facilities, the sewage sludge produced is largely sent for ultimate disposal at the landfill, thereby accruing the pressure on the limited landfill space. Hence, this study aims at assessing the potential of using sewage sludge as biomass for the production of mixed acids using the MixAlco process.

The MixAlco Process is a patented technology that converts any biodegradable material (e.g, sorted municipal solid waste, sewage sludge, industrial biosludge, manure, agricultural residues, energy crops) into a mixed alcohol fuels containing predominantly 2-propanol, but also higher alcohols up to 7-tridecanol *(Holtzapple et al., 1999)*. Figure 1 below gives a process flow diagram of the various operations involved.

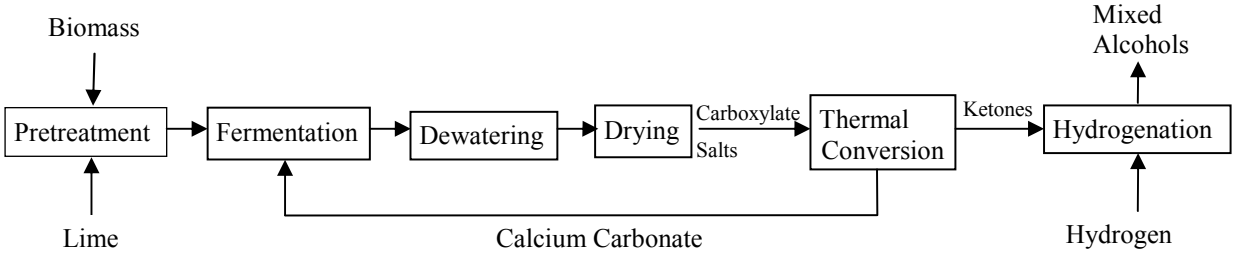

Figure 1. *Overview of the MixAlco Process*.

The traditional method of converting biomass to alcohol is by simultaneous saccharification and fermentation, which uses certain specific enzymes to hydrolyse lignocellulosic material to sugars and then to alcohol. The MixAlco process uses a mixed culture of acid-forming microorganisms to convert biomass to a mixture of carboxylic acids under anaerobic conditions. The biomass is first pretreated using lime to increase its digestibility and then fermented with addition of iodoform, which inhibits the production of methane. To control the pH in the fermentor, calcium carbonate or ammonium bicarbonate is added, which results in the formation and accumulation of carboxylate salts. Using thermal conversion, the carboxylate salts are converted to ketones and after hydrogenation, the ketones can

be converted to a mixture of alcohols. The mixed acids formed typically consist of ethanoic (61.5%), propanoic (13.5%), butanoic (9.5%), pentanoic (4.5%), hexanoic (6.8%) and heptanoic (4.6%) (M. Holtzapple et al, 1999).

Fermentation of lignocellulosic materials has been the main focus of studies using the MixAlco technology. For example Chang et al. (1998) studied lime pretreatment of crop residues bagasse and wheat straw. The study found that a lime loading of 0.1g $Ca(OH)_2$/g dry biomass is recommended, and that a 3-d reducing sugar yield of the pretreated bagasse increased from 153 to 659 mg Eq glucose/g dry biomass and for a wheat straw, pretreatment resulted in an increase from 65 to 650 mg Eq glucose/g dry biomass.

Fermentation of sludge and municipal solid waste has been studied by C. Aiello-Mazzarri et al. (2005). For the experiments simulated municipal solid waste (pretreated and non-pretreated) and sewage sludge were combined in an 80:20 ratio. The highest carboxylic acid concentration was obtained for lime-treated MSW and sewage sludge with 26.0g carboxylic acids/L liquid, which surpassed the economic goal of 22g carboxylic acids/L liquid.

Advantages of the MixAlco are that it does not require sterile condition or expensive enzymes. Low cost fermentors can be employed, and the process can use a variety of feedstocks (e.g., municipal solid waste, sewage sludge, manure, agricultural residues, energy crops, etc.). The other advantage is that when compared to gasoline which has an energy content of 34.9MJ/L and ethanol with 23.4MJ/L, mixed alcohols has an energy value of 29MJ/L.

2. METHODOLOGY

2.1 Substrate and fermentation media

The mixed sewage sludge (primary and secondary) was obtained from Burton's Creek Treatment Plant (College Station, TX) treating mainly domestic wastewater. It contained 97.9% (SD = ±0.002) moisture. Due to its excessively high moisture content, the sludge was first centrifuged to a moisture content of 88.4% (SD = ± 0.04). Batch fermentation was carried at 50g dry solids/L liquid in two fermentors. Deoxygenated distilled water and marine innocula (12.5% by volume), from sediments at East Beach, Galveston TX, were also added to the fermentor bottles. No additional nutrients were added.

2.2 Inhibitor

Iodoform (CHI_3) solution containing 20g CHI_3/L ethanol was used as methanogen inhibitor in this experiment. Due to light sensitivity, the iodoform solution was kept in an amber coloured bottle, and the bottle was capped and kept refrigerated when not used.

2.3 Experiment and analysis

The fermentor, shown in Fig.1 has been assembled with a 1-L polypropylene copolymer centrifuge bottle (98 x 169 mm), Nalgene brand NNI 3120-1010. The centrifuge bottle was capped with an 11-inch rubber stopper consisting of a glass tube inserted in the center. The glass tube external end was covered with a rubber septum for gas sampling and venting. Two pieces of 0.25 inch stainless steel tubes, with welded ends were inserted through the rubber stopper. These tubes functioned as stirrers. The centrifuge bottle was placed in a Wheaton Modular Cell Production Roller Apparatus (Model III) consisting of rollers that rotate the fermentors horizontally at 1 rpm so as to ensure mixing of substrate. The whole set up was placed in an incubator maintained at 55^{o}C.

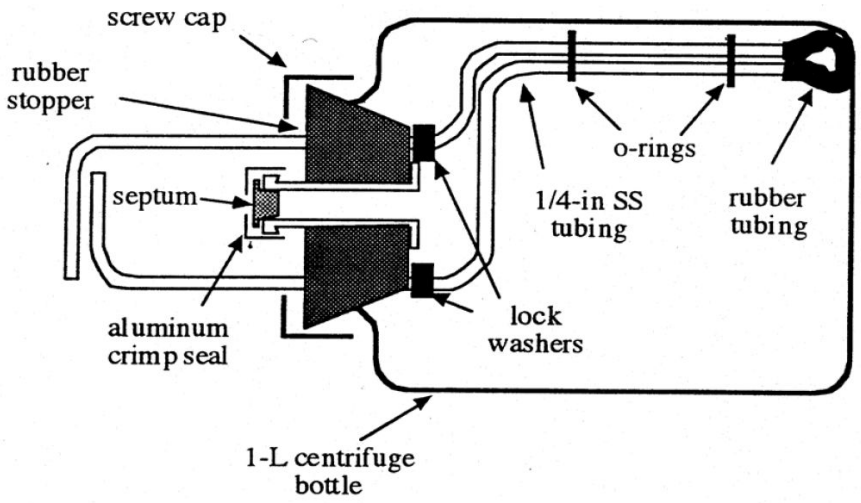

Figure 2. *Centrifuge bottle bioreactor (Ross, 1998).*

Total nitrogen and extractives was determined by the Soil and Forage Testing Lab (College Station, TX), whereas, the analysis for sugars was conducted by an HPLC using HPX-87C and -87P columns and RI detector, following the NREL standard procedure no.13.

To monitor the process, the fermentor was vented using a syringe connected to an air tight tube on alternate days. The tube was connected to a water column filled with a 30% weight by volume $CaCl_2$ solution. The length of water displaced times the cross-sectional area of the glass column gives the net volume of gas produced. Once every four days, the gas from the fermentors were sampled using a syringe and analysed for its composition in terms of N_2, CO_2 and CH_4 using a Gas Chromatograph (Agilent 6890 series) with thermal conductivity detector (TCD). In cases when methane was detected, the amount of inhibitor added was doubled.

A liquid sample of approximately 3ml was collected from the digester on every alternate day and immediately frozen for further analysis. Before analysis, the frozen samples were thawed and mixed by a vortex to ensure homogeneous acid concentration. The acids concentrations were measured using an gas

chromatograph (Agilent 6890 series) equipped with a flame ionization detector (FID) and a 7683 series injector. A 30-m fused silica capillary column (J&W Scientific, Model # 123-3232 CX, Agilent Technologies, CA) was used. The liquid samples were mixed with 1.162g/L of internal standard solution (4-methyl-n-valeric acid) and acidified with 3-M phosphoric acid. For calibration, a standard carboxylic acids mix (Matreya Inc., catalog #1075) was first injected prior to injection of samples.

Moisture content of substrates and final fermentation solid residue was found by drying in an oven at 105^{o}C until constant weight, and the dried solids were then ashed in a muffle furnace at 550^{o}C to determine volatile solids and ash.

3. RESULTS

Mixed sludge has a very high moisture content of 97.92 ± 0.02% and ash content of 35.4 ± 0.07%. It has a glucose content of 5.27% and a total nitrogen content of 4.40% by dry mass. This makes sludge a good substrate for fermentation.

The concentrations of total mixed acids in the fermentors are shown in Figure 2. Since the fermentation was carried in two fermentors, two graphs are shown. A gradual increase in concentration of acids with time, and as can be observed, stabilization in acid production occurred after 24 days of fermentation. The total fermentation time was 28 days.

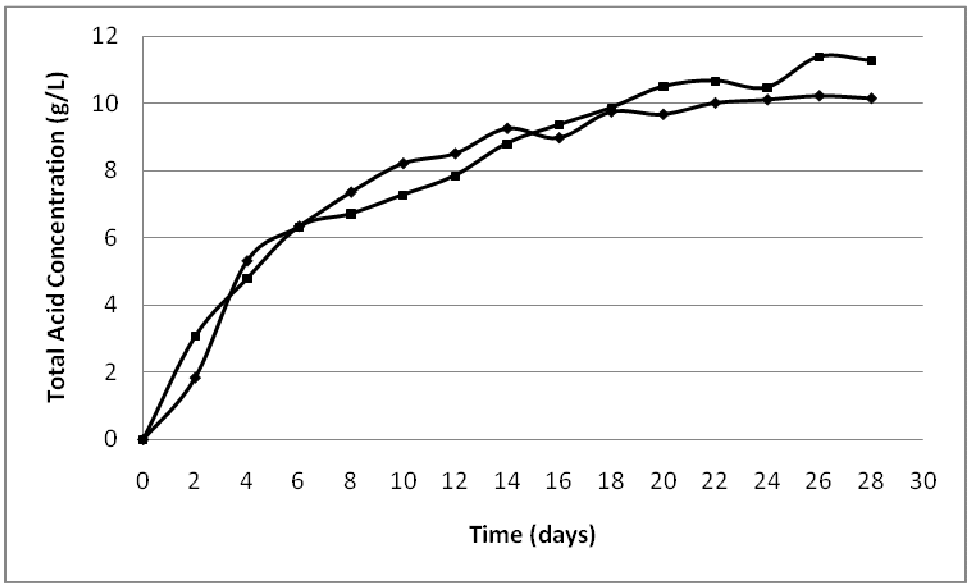

Figure 3. *Total carboxylic acids production.*

The following definitions were used to characterize the fermentation:

$$\text{Volatile Solids} = \text{Dry weight} - \text{Ash weight}$$

$$\text{Conversion} = \frac{\text{VS digested}}{\text{VS fed}}$$

$$\text{Yields } (y) = \frac{\text{Total carboxylic acids}}{\text{VS fed}}$$

$$\text{Total acid productivity } (p) = \frac{\text{Total carboxylic acids produced}}{\text{Total liquid volume in all fermentors.time}}$$

$$\text{Total acid selectivity } (s) = \frac{\text{Total carboxylic acids produced}}{\text{VS digested}}$$

Using the above definitions, the ferementation results were calculated and presented in Table 1. The yield is 0.34 g total acids/g VS fed, which implies that 34% of volatile solids of sludge fed to fermentor are converted into mixed acids. The conversion is 0.43, which means that 43% of volatile solids fed have been digested over the 28 days. The acid selectivity refers to the amount of acids produced from the fraction of volatile solids that is digested. In this experiment a very high selectivity of 0.79 was obtained.

Parameter	**Value**
Average acid concentration (g/L)	10.72 ± 0.55
Yield (g total acids/g VS fed)	0.34 ± 0.08
Conversion (g VS digested/g VS fed)	0.43 ± 0.08
Total Acids selectivity (g total acids/g VS digested)	0.79 ± 0.08
Total Acid productivity (g total acids/(L liquid·day))	0.34 ± 0.02

Table 1: *Process parameters*

Note: All errors are ± 1 standard deviation.

Figure 3 gives the percentage composition of the mixed acids produced. It shows that the major fraction was ethanoic acid with 69%, followed by butanoic acid and pentanoic acid with 12%, and finally propanoic acid with 7%.

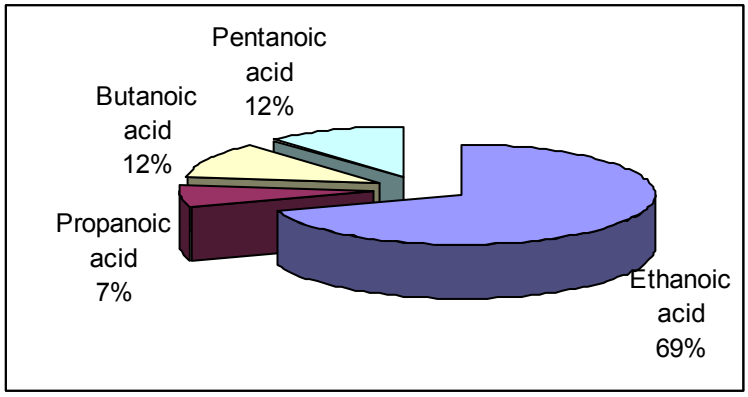

Figure 4. Composition of mixed acids produced.

4. CONCLUSION

From the characterisation tests performed, it was found that sewage sludge has a very high moisture content of 97.9% and volatile solids content of 64.6%. It has a glucose content of 5.27% and a total nitrogen content of 4.40% by dry mass. This makes sludge a good substrate for fermentation. Starting with a solids concentration of 50g/L, and using iodoform as inhibitor, the total carboxylic acids obtained was 10.72g/L, corresponding to a yield of 0.34 ± 0.19 g acids/g volatile solids fed. The conversion was 0.43, which means that 43% of volatile solids fed have been digested over the 28 days. Analysis of the composition of the acids formed showed that the major component was ethanoic acid (~69%), followed by an equal amount of butanoic and pentanoic acid (~12%), and lastly propanoic acid (~7%).

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