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Anaerobic treatment of lignocellulosic material to co-produce methane and digested fiber for ethanol biorefining

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HIGHLIGHTS

- Co-digestion of corn stover and swine manure benefited methane/ethanol production.
- The optimal stover-to-manure ratio was 40:60 for maximizing energy output.
- 18% increase on overall net energy output was obtained from the optimal mixing ratio.

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ABSTRACT

Five different ratios of corn stover to swine manure were investigated to evaluate the performance of anaerobic digestion and the quality of anaerobically digested fiber (AD fiber) as a feedstock for bioethanol production. The stover-to-manure ratio of 40:60 generated 364 L biogas and 797 g AD fiber per kg of dry raw feedstock daily. The AD fibers after digestion were pretreated and hydrolyzed to release sugars for ethanol fermentation. The stover-to-manure ratio of 40:60 was able to produce 152 g methane and 50 g ethanol per kg of dry raw feedstock. The net energy generated from the ratio 40:60 was 5.5 MJ kg^{-1} dry raw feed, which was an 18% increase on net energy output compared to the other ratios and proved to be most beneficial for a biorefinery.

1. Introduction

Fuels such as crude oil, natural gas, and coal have played an important part in the advancement of human society. With the intent to reduce foreign oil dependence, create new jobs, and limit pollution emissions, society is looking for new and effective ways to generate energy (Vispute and Huber, 2008). Anaerobic digestion (AD) as an effective method to convert organic material into biogas represents such a promising approach. European countries like Germany and Denmark have long utilized this conversion of waste to energy. The waste treatment capabilities and corresponding energy recovery makes it very attractive to provide a win–win solution for both waste management and bioenergy production (Chen et al., 2008; Vispute and Huber, 2008). Other benefits of anaerobic digestion include the reduction of odor, pathogens, organic matter, and the preservation of plants nutrients (Cantrell et al., 2008; Lansing et al., 2010; Zhu, 2000).

Recently, co-digestion of crop residues and animal manures has attracted much attention due to its capability of largely increasing biogas and methane yields (Wu et al., 2010). There have been recent studies on the co-digestion of swine manure with crop residues. Wu et al. studied the impact on co-digestion of swine manure with corn stocks, oat straw and wheat straw, and it showed a positive effect on biogas production (Wu et al., 2010). This was largely attributed to increasing the carbon to nitrogen ratio within the digesting reactors. Research was also performed with swine manure and cooking grease showing increased energy production as much as 124% (Lansing et al., 2010). Both studies were able to achieve methane concentrations at approximately 68%.

An area of study that has been overlooked is the utilization of the remaining residual solids after digestion for energy production. This is owing to the recalcitrant property and low nutrient value of the solid digestate (Tambone et al., 2009). Recent investigations, though, have concluded that anaerobically treated agricultural wastes, such as digested dairy manure, still contain important components of remaining carbohydrates and lignin that can be used as feedstock in a biorefinery concept (Chen et al., 2005; Yue et al., 2010).

The focus of this study was to apply co-digestion technology on corn stover and swine manure to investigate digestion performance

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as well as AD fiber quality for bioethanol production. Raw corn stover was mixed at five different ratios with swine manure as the feed. Biogas accumulation and content were factors to evaluate the digestion performance. AD fiber quality was examined by assessing the changes in fiber composition throughout the process and analyzing glucose production from enzymatic hydrolysis. Mass and energy balances were performed on the energy products to provide further insights for effective bioenergy generation.

2. Materials and methods

2.1. Feedstocks

The swine manure used for the experiments was taken from the Swine Teaching and Research Center at Michigan State University. Hogs were fed with a mixture of corn, soybean meal (SBM), and Start A300 Base manufactured from Provimi North America, Inc. Manure was collected in December of 2011, as well as February of 2012, and stored in a −20 °C freezer until use. Corn stover was harvested and collected in 2009 from a private farm in Muir, MI. Raw corn stover was then milled through a 2 mm screen using a Schutte Buffalo hammer mill (Model No. WA-6-H). The following feedstock characteristics were based on weight percentages (wt.%). The raw swine manure had 4.0 wt.% total solids (TS), and it contained 37.7 wt.% carbon, 3.8 wt.% nitrogen; 8.0 wt.% cellulose, 9.0 wt.% hemicellulose, and 23.8 wt.% lignin of its total solids. The corn stover had 92 wt.% TS. It contained 45.4 wt.% carbon, 0.4 wt.% nitrogen; 36.3 wt.% cellulose, 22.0 wt.% hemicellulose, and 18.6 wt.% lignin of its total solids.

2.2. Bioreactor systems

Five different ratios of corn stover to swine manure were used as feeds to feed the anaerobic reactors; 20:80, 40:60, 50:50, 60:40, and 80:20. The composition of each feed was calculated and presented in Table 1. All reactors contained a working volume of 0.50 L, with a headspace of approximately 0.25 L. The initial headspace was purged with nitrogen for exactly 30 s. Each reactor was based on 5% total solids (TS) and a hydraulic retention time (HRT) of 20 days. Duplicates were created for each ratio, which generated a total of 10 reactors. The reactors were shook on a New Brunswick Scientific, Innova 2000 platform shaker, set at 150 rpm. Rubber septa caps were used to contain produced biogas, where it can be penetrated to release and measure daily gas production. The biogas production was measured using a water displacement method. Feeding of reactors was performed every other day using a Plas Lab (Lansing, MI) Automatic Atmosphere Chamber. The chamber was purged with a medical grade specialty gas composed of 85% nitrogen, 10% hydrogen, and 5% carbon dioxide. A palladium catalyst heater was used to make the chamber completely anaerobic, suffice for feeding the anaerobic bacterial systems. Fresh feed was made every 20 days and stored in a refrigerator at 4 °C. The pH for all systems was controlled above a value of 6.70 by dosing a 5 wt.% sodium hydroxide (NaOH) solution.

Table 1
Raw feed characteristics of each reactor ratio[a].

Stover:Manure	20:80	40:60	50:50	60:40	80:20
Carbon (wt.%, TS)	39.3	40.8	41.6	42.3	43.9
Nitrogen (wt.%, TS)	3.2	2.5	2.1	1.8	1.1
C:N ratio	12.3	16.3	19.8	23.5	39.9
Cellulose (wt.%, TS)	13.7	19.3	22.1	25.0	30.6
Hemicellulose (wt.%, TS)	11.6	14.2	15.5	16.8	19.4
Lignin (wt.%, TS)	22.8	21.7	21.2	20.7	19.6

[a] Calculated based on reactor ratios and raw feedstock characteristics.

2.3. Dilute alkali pretreatment

During the semi-continuous culture of 60 days, the solid fiber was collected from each reactor using an Allegra X-12R centrifuge. Pretreatment conditions were adopted from a previous study (Teater et al., 2011). The pretreatment parameters were fixed at 5% TS, with 2% NaOH at 130 °C for 2 h. Treated samples were centrifuged and rinsed using de-ionized water. Wet solid samples were stored in a freezer at −20 °C. Solid residue and filtrate were taken for the analysis of mono-sugars, dry matter, and fiber content.

2.4. Enzymatic hydrolysis

Wet alkali-pretreated fiber samples containing 2 g total solids and sodium citrate buffer (50 mM, pH 4.8) were mixed to a total mass of 40 g into a 125 mL shake flask, which makes the solid concentration of 5 wt.%. All mixed samples were sterilized in autoclave prior to the addition of enzymes. No sugar was detected in the medium after autoclave. Cellulase (ACCELLERASE 1500, Genencor, Rochester, NY) at a loading of 26 FPU g^{-1} TS was used to perform a 72 h hydrolysis. The flasks were shaken at 150 rpm, and the reaction temperature was 50 °C. After 72 h, aliquots were heated to 100 °C for 5 min to inhibit enzyme activity. The liquid samples were filtered into HPLC vials with Millex-GS 0.22 μm membrane for analysis of glucose and other monomeric sugars such as xylose, arabinose, and galactose.

The glucose and xylose conversion of AD fiber and sugar concentrations after enzymatic hydrolysis were used as an indicator of fiber quality. The equation for the glucose conversion [%] is: glucose conversion [%] = ((total solids after pretreatment [g] × glucose concentration after enzymatic hydrolysis [g L^{-1}] × volume of enzymatic hydrolysate [L])/(cellulose content in AD fiber [%] × 1.11 × total solids of AD fiber before pretreatment [g] × 2 [g])) × 100. The equation for the xylose conversion [%] is: xylose conversion [%] = ((total solids after pretreatment [g] × xylose concentration after enzymatic hydrolysis [g L^{-1}] × volume of enzymatic hydrolysate [L])/(xylan content in AD fiber [%] × 1.14 × total solids of AD fiber before pretreatment [g] × 2[g])) × 100.

2.5. Analytical methods

Fiber composition was measured using the Laboratory Analytical Procedure (LAP) developed by the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008). Elemental microanalysis of carbon and nitrogen were analyzed by Atlantic Microlabs, located in Norcross, GA. Glucose and other mono-sugars were determined using a Shimazdu high-performance liquid chromatography (HPLC) system equipped with a Bio-rad Aminex HPX-87P analytical column, Micro Guard de-ashing column, and a refractive index detector. The mobile phase was degassed Millepore water with a flow rate of 0.6 mL min^{-1}. An oven temperature was set at 80 °C for the analytical column, while the de-ashing was placed outside of the oven at a room temperature of 22 °C. High purity standards including glucose (Catalog Number: 49158), xylose (Catalog Number: 95729), galactose (Catalog Number: 48259), arabinose (Catalog Number: 10840), and mannose (Catalog Number: 63582) were purchased via Sigma (St. Louis, MO).

Methane, carbon dioxide, and hydrogen sulfide content was measured using an SRI 8610C gas chromatography system. Helium was used as a carrier gas with pressure set at 21 psi. The system was equipped with a thermal conductivity detector and kept at a constant temperature of 150 °C. An injection volume of 3 mL was used with only 100 μL accepted from the instrument.