6-2008

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Abstract

This paper reviews the biochemical methane potential (BMP) production from anaerobic digestion of corn-ethanol by-products including dried distiller grain with solubles (DDGS), centrifuge solids, thin stillage, and corn-syrup as well as evaluating the effects of ultrasonic pretreatment on biogas production from these feedstocks. Ultrasonic pretreatment was applied with three amplitude settings of 33% (52.8 μm $_{pp}$), 66% (105.6 μm $_{pp}$), and 100% (160 μm $_{pp}$) as well as five time settings of 10, 20, 30, 40, and 50 seconds, respectively, to each of the four by-products before setting up a bench top BMP trial. Biogas production was measured and analyzed for methane content and accumulated methane production. Without ultrasound pretreatment, corn-syrup had the highest methane production potential (408 ml/g VS added) compare to the other by-products. Methane production was increased by 25 and 12% for the ultrasound pretreated DDGs samples and solids samples, respectively, compared with untreated samples. The ultrasonic pretreatment of ethanol co-products was shown to increase methane production from the anaerobic digestion of these products. The ultrasonic pre-treatment of solids co-products (DDGS and centrifuge solids) was far more effective than on liquid co-products (syrup and thin stillage). An energy balance showed that ultrasonic pretreatment of DDGS provided 70% more energy than was required to operate the ultrasonic unit. An energy balance for other co-products however, indicated that the ultrasonic pre-treatment required more energy than was generated by the process in terms of additional biogas production.

Keywords

Biochemical methane potential (BMP), methane, ultrasonic, dry distillers grains and solubles (DDGS), Corn-ethanol by-products

Disciplines

Agriculture | Bioresource and Agricultural Engineering

Comments

This is an ASABE Meeting Presentation, Paper No. 084099.

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An ASABE Meeting Presentation

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Written for presentation at the
2008 ASABE Annual International Meeting
Sponsored by ASABE
Rhode Island Convention Center
Providence, Rhode Island
June 29 – July 2, 2008

Abstract. *This paper reviews the biochemical methane potential (BMP) production from anaerobic digestion of corn-ethanol by-products including dried distiller grain with solubles (DDGS), centrifuge solids, thin stillage, and corn-syrup as well as evaluating the effects of ultrasonic pretreatment on biogas production from these feedstocks. Ultrasonic pretreatment was applied with three amplitude settings of 33% (52.8 μm_{pp}), 66% (105.6 μm_{pp}), and 100% (160 μm_{pp}) as well as five time settings of 10, 20, 30, 40, and 50 seconds, respectively, to each of the four by-products before setting up a bench top BMP trial. Biogas production was measured and analyzed for methane content and accumulated methane production. Without ultrasound pretreatment, corn-syrup had the highest methane production potential (408 ml/g VS added) compare to the other by-products. Methane production was increased by 25 and 12% for the ultrasound pretreated DDGs samples and solids samples, respectively, compared with untreated samples. The ultrasonic pretreatment of ethanol co-products was shown to increase methane production from the anaerobic digestion of these products.*

The ultrasonic pre-treatment of solids co-products (DDGS and centrifuge solids) was far more effective than on liquid co-products (syrup and thin stillage). An energy balance showed that ultrasonic pretreatment of DDGS provided 70% more energy than was required to operate the ultrasonic unit. An energy balance for other co-products however, indicated that the ultrasonic pre-treatment required more energy than was generated by the process in terms of additional biogas production.

Keywords. Biochemical methane potential (BMP), methane, ultrasonic, dry distillers grains and solubles (DDGS), Corn-ethanol by-products.

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Introduction

Ethanol is a renewable fuel source that can be derived from a variety of biomass sources including starch crops, sugar crops, and cellulosic materials. Currently, the US has approximately 134 ethanol plants in service with a production capacity of 27 million liters (7.2 million gallons) per year (Renewable Fuels Association 2007). Yeast fermentation in the production of corn ethanol does not utilize all of the available organics resulting in aqueous co-products including dry distiller's grains with solubles (DDGs), solids, syrups and thin stillage. Co-products from the corn-ethanol industry have traditionally been used for livestock feeding. However, these by-products can potentially be used for the production of biogas for energy through the anaerobic digestion process.

Anaerobic digestion is a natural process that has been utilized for decades to recover energy in the form of biogas from organic waste-streams. It has been estimated that anaerobic digestion can remove more than 50% of the chemical oxygen demand (COD) from ethanol stillage and convert it to biogas, which can be used to power the ethanol facility (Wilkie et al. 2000). Stover et al. (1984) demonstrated that significant amounts of methane could be recovered with a process of treating thin corn stillage using mesophilic anaerobic digesters. Stover estimated that a daily production of 3,681 m^3 (130,000 cubic feet) of methane could be achieved from 227,125 liters (60,000 gallons) of thin stillage per day. The next step in the development of this technology is to improve biosolids degradation and enhance methane production.

Ultrasonic pretreatment assisted sludge degradation has been studied recently to improve hydrolysis of sludge, usually the rate limiting step of anaerobic digestion. When high power ultrasonics is applied through a medium such as water could cause the surrounding particles in the solution to break apart due to the intense hyro-mechanical forces in the solution (Khanal et al. 2007). Chyi and Dague (1994) concluded that during anaerobic degradation cellulose with a particle size of 20-μm resulted in a higher conversion efficiency than that with 50-μm particle size. Researchers also found that high energy intensity enhances the disintegration of particulate matter which is evidenced by a reduction in particle size and increasing the soluble matter fraction (Wang et al., 2005; Benabdallah El-Hadj et al., 2006). Tiehm et al. (2001) demonstrated that pretreatment of waste activated sludge by ultrasonic disintegration significantly improved microbial cell lysis increasing the volatile solids degradation as well as biogas production. However, limited information is available on possibilities to increase the amount of methane production of anaerobic digestion of corn ethanol co-products using ultrasound technologies.

Biochemical methane potential (BMP) analysis is an efficient and economical method for evaluating the rate and extent of a waste stream conversion to methane under anaerobic conditions. Traditionally, BMP analysis has been used to evaluate the biodegradability of municipal and industrial wastes (Owens, 1993). A modified method based on the procedure outlined by Owen et al. (1979) was used to evaluate the digestibility and biogas production from corn ethanol co-products.

This paper reviews the biochemical methane potential production from anaerobic digestion of corn-ethanol by-products including DDGS, solids, thin stillage, and corn-syrup as well as evaluating the effects of ultrasonic pretreatment on biogas production from these feedstocks.

Material and Methods

Sample Collection

Ethanol co-products analyzed in this study including DDGs, solids, syrup, and thin stillage were obtained from the Lincoln Way Energy ethanol production facility (Lincoln Way Energy, Nevada, IA). These co-products were created at various steps in the ethanol production process, detailed by this process diagram below (Figure 1).

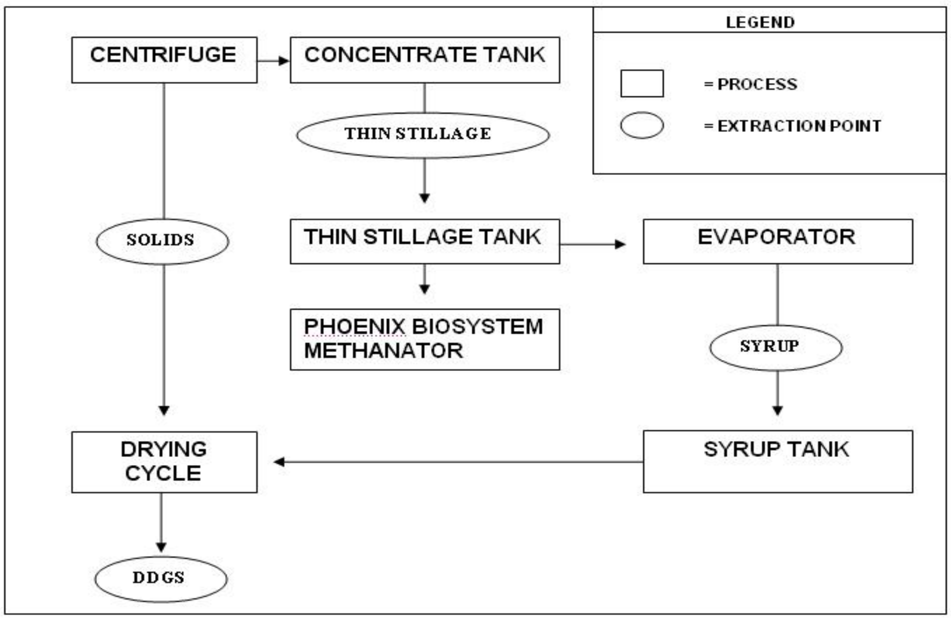

Figure 1. Diagram of co-products including DDGs, solids, syrup and thin stillage created after centrifuge step during corn to ethanol process.

Sample Characterization

All samples were analyzed for total solids, volatile solids, pH, total Kjeldahl nitrogen, ammonia, chemical oxygen demand (COD), and total phosphorus. Total and volatile solids were analyzed using Standard Method 2540 G (APHA et al., 1998). The pH was determined with a CORNING pH combination GEL Filled Electrodes (CORNING Incorporated, Corning, NY). Total Kjeldahl nitrogen and ammonia were analyzed using Labconco Digesters Model 23012 and Labconco Rapidstill II Model 65200 (Labconco Corporation, Kansas City, MO) using Kjeldahl method (AOAC, 2000). Chemical oxygen demand was measured using a Hach colorimetric digestion method (Method #8000, Hach Company, Loveland, CO). Total phosphorus was determined using a Thermo Spectrophotometer GENESYS^{TM}6 (Thermo Electron Corporation, Waltham, MA) with Photometric Method (AOAC, 2000).

Ultrasonic Pretreatment and Experimental Design

In order to assure uniform treatment, samples of DDGs, solid, and syrup's were mixed with water (sample: water = 3 g: 35 ml) before ultrasonic processing.

The ultrasonic system used in this study was a 2.2kW, 200kHz Branson 2000 series equipped with a 0-20 μm_{pp} converter, a 1:1 gain booster and a 1:8 gain catenoildal horn (Branson Ultrasonics Corporation, Danbury, CT).

Ultrasonic pretreatment was applied with three amplitude settings of 33% (52.8 μm_{pp}), 66% (105.6 μm_{pp}), and 100% (160 μm_{pp}) as well as five time settings of 10, 20, 30, 40, and 50 seconds, respectively, to each of those four co-products before setting up a bench top BMP trial. This resulted in a total 15 treatments (3x5 matrix) along with an untreated sample (control) were tested for bio methane potential from anaerobic digestion of DDGS, solids, syrup, and thin stillage.

BMP Assays

An aliquot of ethanol co-products (1.06g VS of DDGs; 0.45g VS of solids, 0.22g VS of syrup, and 0.28g VS of thin stillage, respectively) was added to a 250 ml serum bottle along with 100 ml anaerobic inoculum. Inoculum was obtained from a 60 liter mesophillic (35°C) CSTR reactor, fed daily of at a loading rate of 2 g VS/L/day. The inoculum concentration was 3g/L VS. The head space in the serum bottle was purged with gas mixture of 70% nitrogen and 30% carbon dioxide at a flow rate of approximately 0.5 L/min for 5 min. After the air in the head space was removed using a glass syringe, sealed serum bottles were placed on a shaker (150-200 rams) and incubated at 35°C for 30 days. Each assay was performed in triplicate.

Biogas Production and Methane Content Measurement

Biogas production was monitored daily with a graduated syringe by the volume displacement technique. The methane content of the biogas was determined using a gas chromatograph (Shimadzu Model GC-14A) equipped with a flame ionization detector. Injector, oven, and detector temperatures were 100°C, 60°C and 240°C, respectively. The nitrogen carrier gas flow was 25 ml/min. Methane volume was calculated using biogas production and methane content. Methane yields were calculated by dividing methane volume by the weight of sample VS added to each bottle with a unit of ml/g VS added.

Results and Discussion

Characteristics of DDGs, Solids, Syrup, and Thin Stillage

The nutrient analysis of DDGs, solids, syrup and thin stillage is presented in Table 1. The reported values are averages of untreated and sonicated samples. The VS of DDGs, solids, syrup and thin stillage were 7.1, 2.8, 6.5 and 3.0 %, respectively, and the SCOD were 38.0, 5.5, 45.7 and 109.4 g/L, respectively.

Table 1. Nutrient analysis of DDGs, solids, syrup and thin stillage

Parameter	DDGs	Solids	Syrup	Thin Stillage
TS (% ww)	7.4± 0.3	3.0± 0.1	7.2± 0.3	3.3± 0.1
VS (% ww)	7.1± 0.1	2.8± 0.2	6.5± 0.2	3.0± 0.1
SCOD (g/L)	38.0± 1.4	5.5± 0.1	45.7± 2.7	109.4± 4.0
TKN (mg/g TS)	32.3± 0.9	30.0± 0.5	32.1± 2.2	32.7± 0.9
NH4-N (mg/g TS)	4.4± 0.3	4.0± 0.1	4.2± 0.2	3.6± 0.4
P (mg/g TS)	5.2± 0.2	5.0± 0.1	5.0± 0.5	5.7± 0.4

Ultrasound effect on cumulative methane production from DDGs

The corrected cumulative methane yield from anaerobic digestion DDGs (Figure 2) ranged from 315 to 489 ml/g VS added. Samples pre-treated with ultrasound (395 ml/g VS) were observed to produce greater methane compared with non-treated samples (315 ml/g VS). DDGs samples sonicated with 100% amplitude for a 50 second had the greatest methane production (489 ml/g VS added). This showed that an increase in sonication time and amplitude resulted in a higher methane production. For DDGs samples sonicated with 100% amplitude, those receiving 50 s treatment yielded the highest methane followed by the 40 s samples (417 ml/g VS added) and the 30 second samples (415 ml/g VS added). The 33% amplitude category showed a similar trend. Cumulative methane production from samples received from the 33% amplitude treated samples with times of 10s, 20s, 30s, 40s, and 50s were 322, 323, 347, 362, and 439 ml/g VSS added, respectively. Samples received 66% amplitude showed a similar trend with only one exception. The 20 second sample (454 ml/g VS added) produced approximately the same amount of gas as the 50 second treatment (448 ml/g VS added).

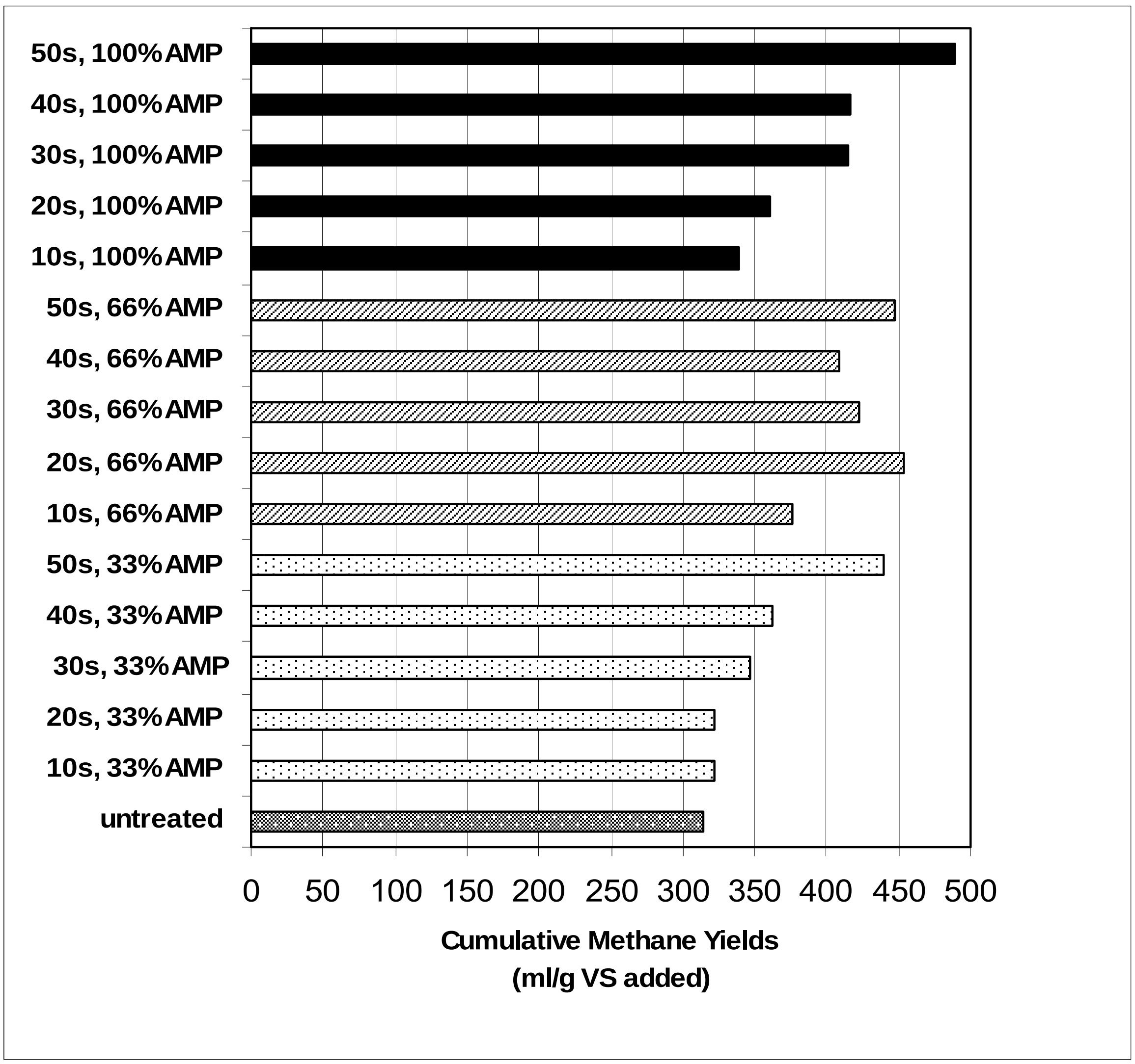

Figure 2. Ultrasound effect on cumulative methane production from DDGs

Results from the 30 day BMP assays indicated methane production was 25% higher for the ultrasound pretreated samples than for the untreated samples (control). Methane yields were found to increase with higher amplitude and longer treatment time. The greatest methane productions were obtained with the highest power and longest treatment. Results are consistent with prior studies (Lafitte-Trouqué and Forster 2002; Grönroos, et al. 2005). Lafitte-Trouqué and Forster (2002) indicated that gas production rates from anaerobic digestion of ultrasonic pretreated sludge were higher than those for untreated sludge. Grönroos, et al. (2005) concluded that ultrasonic pretreatment enhanced methane production during the anaerobic digestion process and ultrasonic power as well as ultrasonic treatment time have the most significant effect on increasing methane production. To demonstrate the effect of ultrasound treatment on the particles size, a further study was developed (Hearn, et al. 2008). It showed a significant decrease in particle size for ultrasonically pretreated DDGs samples compared with untreated samples using optical microscopy imaging as well as scanning electron microscopy imaging. Hearn et al. (2008) reported a maximum 44.51% decrease in particle size was measured using particle distribution analysis.

Ultrasound effect on cumulative methane production from solids

Ultrasonic amplitude and ultrasonic treatment time had a significant effect on the cumulative methane production for the centrifuge solids (Figure 3). Methane production was 12% higher for the ultrasonically pretreated samples compared to the untreated samples (control). The greatest methane production (462 ml/g VS added) was obtained with the highest amplitude (100%) and longest treatment time used (50s) which agrees with the results found in DDGs trial. Centrifuge solids without ultrasonic treatment produced the least amount of methane gas (374 ml/g VS added). Average cumulative methane production from samples that received ultrasonic pretreatment was 419 ml/g VS added.

Ultrasound effect on cumulative methane production from syrup

Biogas production from the syrup trial was, for the most part, not consistent with results found for DDGs and solids (Figure 4). The greatest methane production (474 ml/g VS added) was observed with the 66% amplitude and longest treatment time used (50s). In reference to the samples treated with 33% amplitude, samples without ultrasound pretreatment (408 ml/g VS added) produced similar amount of methane as the 10 s sample (408 ml/g VS added) and more than both the 20 s samples (365 ml/g VS added) and 30 s samples (376 ml/g VS added). The 100% amplitude category also showed the control ahead of two treated samples and like the 33% category, while the 50 s sample did not produce the highest amount of methane gas. No significant improvement in methane production was observed in this trial, most likely because the ultrasonic treatment provided limited particle size reduction. This hypothesis if supported by a particle distribution analysis (Hearn, et al. 2008) which suggested that no reduction of the syrup particle size ultrasound pretreatment, since the syrup particle size is already much smaller comparing with DDGs and solids samples without ultrasound pretreatment.

Ultrasound effect on cumulative methane production from thin stillage

Corrected cumulative methane yield from anaerobic digestion of DDGs (Figure 5) ranged from 315 to 452 ml/g VS added. In reference to the samples treated with 33% amplitude, the control (346 ml/g VS added) group produced more methane compared to the 10 and 20 second samples but the 40 and 50 s samples produced the most methane. The 66% category showed the control producing the least gas; however, the 10 s sample was the top producer. The 100% category was consistent with the trend that an increase in sonicated time and amplitude resulted in a higher methane production. Based on these results, it is generally seen that effect of ultrasonic pretreatment on the cumulative methane production from thin stillage was not significant. Again, it is believed that particle size reduction did not result from the ultrasonic treatment and thus, there was no significant benefit observed.

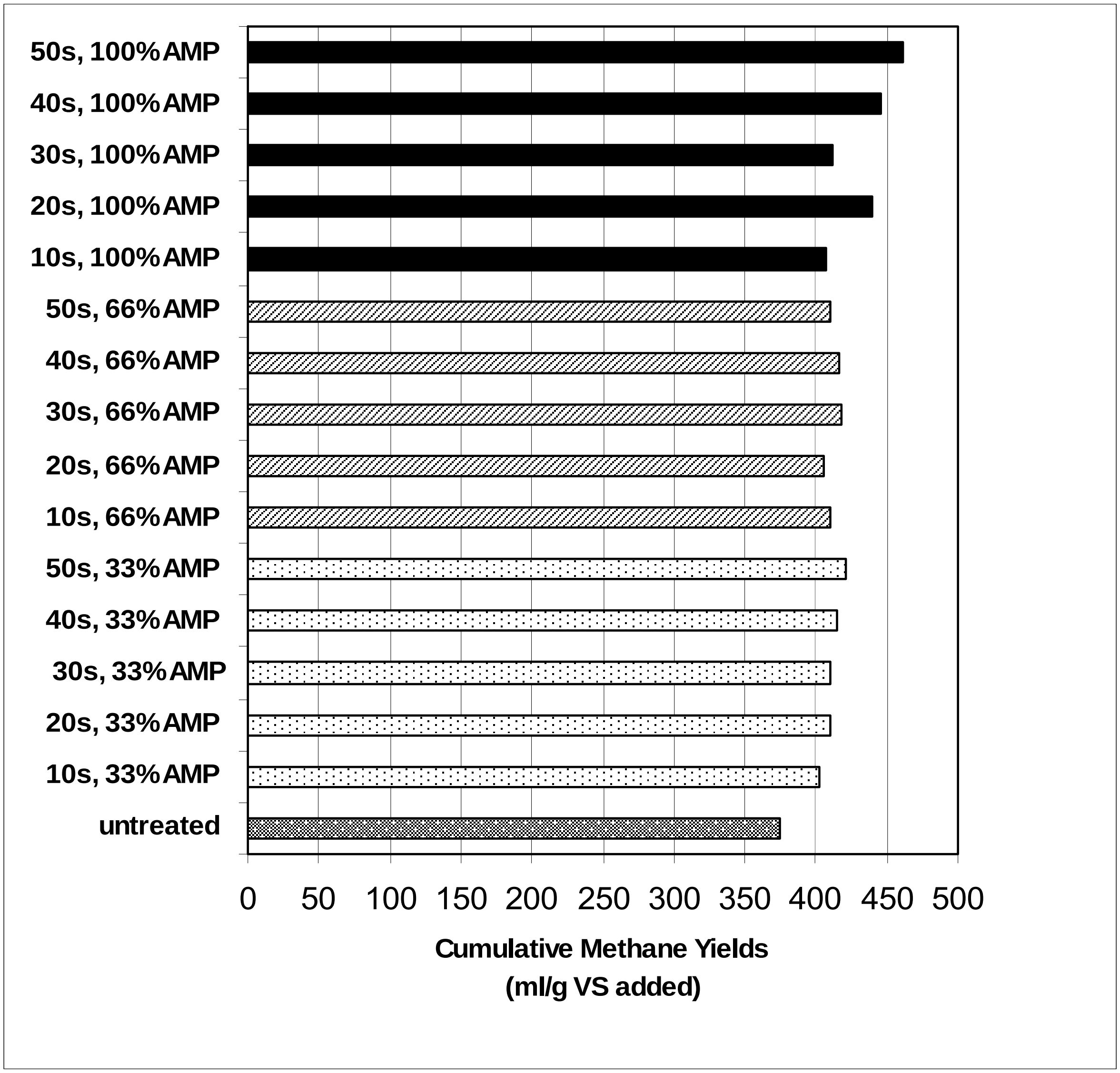

Figure 3. Ultrasound effect on cumulative methane production from centrifuge solids

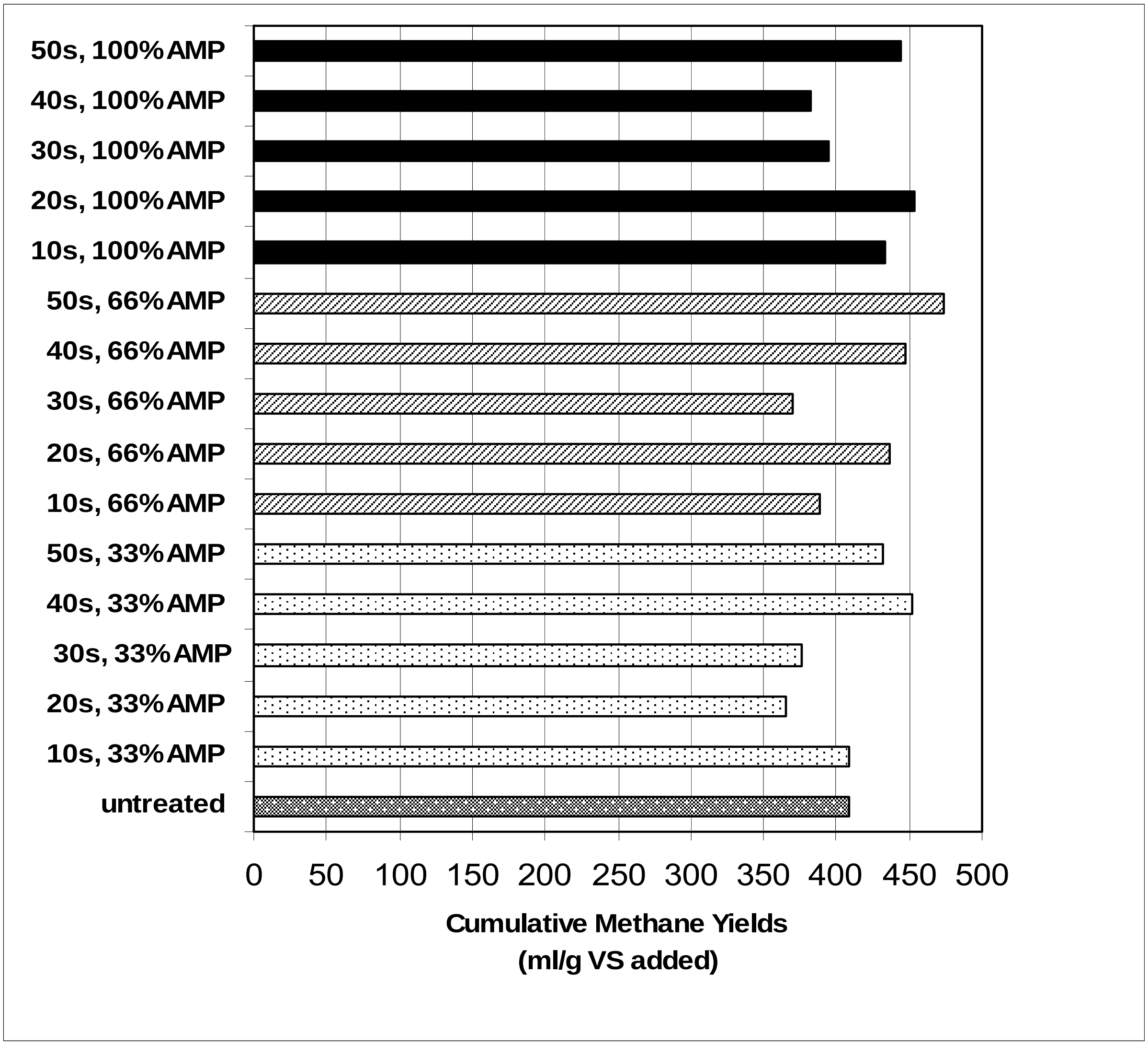

Figure 4. Ultrasound effect on cumulative methane production of syrup

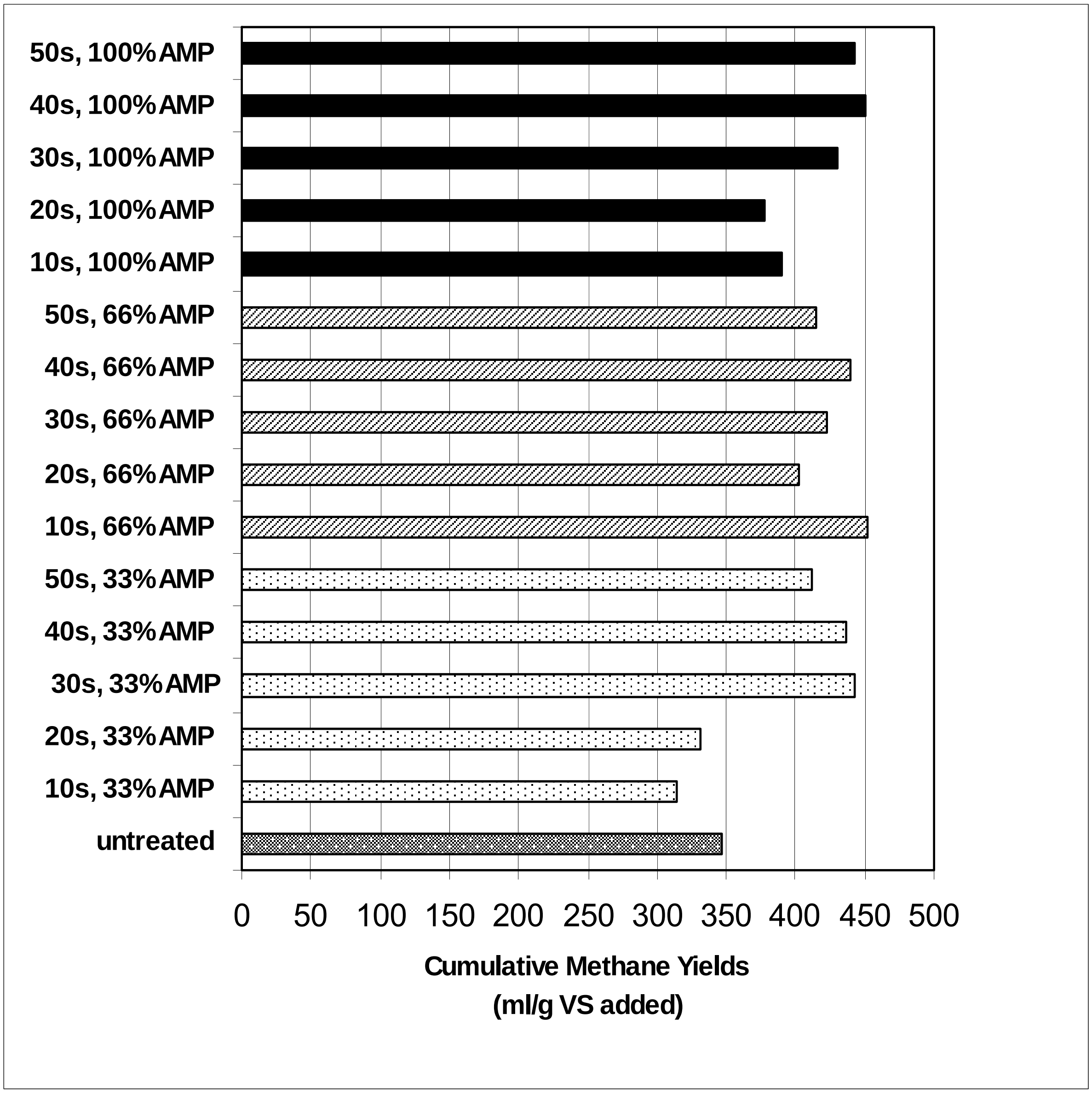

Figure 5. Ultrasound effect on cumulative methane production of thin stillage

Energy Balance Analysis

The optimization of energy consumption is essential for the use of ultrasonic pretreated before anaerobic digestion process to be economically feasible therefore, therefore, in reference to this critical aspect a basic energy balance was prepared (Table 2). Cumulative biogas production from DDGs samples ultrasonically pre-treated produced a higher amount of methane compared to the untreated samples (445 ml vs. 361ml). An additional 84 ml of methane was produced which corresponds to 3,209 J of chemical energy. In this case the ultrasound pretreatment the electrical input energy into the conveter was 1883 J. Thus a net energy balance of 1326 J was recovered. Following as similar approach, it is seen that only 20 ml additional methane was recovered using sonicated pretreatment from anaerobic digestion of solids samples. The additional energy recovered from this additional methane production was less than the energy input (764 J vs. 628 J).

Table 2. Energy (E) balance analysis

		DDGs	Centrifuge Solids
Cumulative biogas production (ml)	Untreated	361	197
	Sonicated[1]	445	217
Increased biogas production[2] (ml)		84	20
Increased energy[3] (J)		3209	764
Input energy[4] (J)		1883	1391
Net energy recovery (J)		1,326	-628

[1]Average of methane production from ultrasound pretreated samples

[2] Increased methane production = methane production from sonicated samples - methane production from untreated samples

[3] Energy recovered from additional methane production. Natural gas has a heating value of approximately 31,800 to 35,300 British thermal units (Btu) per cubic meter (900–1,000 Btu/ft3) (Walsh et al. 1998). Energy content of methane used for computation was 38.2 MJ/m^3.

[4] Energy used for running ultrasonic unit

Conclusions

While the ultrasonic pretreatment of ethanol co-products was shown to increase methane production from the anaerobic digestion of these products, this study indicates that ultrasonic pre-treatment is far more effective on solids co-products (DDGS and centrifuge solids) than on liquid co-products (syrup and thin stillage). An energy balance conducted for DDGS and centrifuge solids showed that ultrasonic pretreatment of DDGS provided 70% more energy than was required to operate the ultrasonic pre-treatment process. The increase in energy output from the ultrasonic pre-treatment of centrifuge solids produced only 55% of the energy required to operate the process however. According to the DDGs and thin stillage results, an increase in amplitude results in an overall increase in methane production for ultrasound pretreated samples. The DDGs results also show that an increase in the length of exposure to ultrasonic treatment results in an increase in methane production. Corn-syrup has the highest methane production potential, of co-products tested, without ultrasound pretreatment. If DDGS were going to be used as a feed-stock for anaerobic digestion, the use of ultrasonic pre-treatment shows merit for increasing methane production form the process.

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