Effect of Ultrasonic Pretreatment on Methane Production Potential from Corn Ethanol Coproducts

W. Wu-Haan, R. T. Burns, L. B. Moody, C. J. Hearn, D. Grewell

Abstract. *This article addresses the biochemical methane potential (BMP) production from anaerobic digestion of corn-ethanol coproducts including dried distiller grain with solubles (DDGS), distiller's wet grains (DWG), thin stillage, and condensed distiller's solubles (CDS) as well as evaluating the effects of ultrasonic pretreatment on methane 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 (10, 20, 30, 40, and 50 s) to each of the four coproducts prior to conducting benchtop BMP trials. Ultrasonic pretreatment reduced mean particle size of DDGS and DWG by 45% and 43%, respectively. Without ultrasound pretreatment, CDS had the highest methane production potential (407 mL g^{-1} VS added) compared to the other coproducts. Ultrasonic pretreatment of DWG co-products (DDGS and DWG) resulted in greater increases in methane production than on liquid coproducts (CDS and thin stillage). Methane yields were increased by 25% and 12% for the ultrasound pretreated DDGS and DWG, respectively, compared with untreated samples. An energy balance for the DWG, thin stillage, and CDS coproducts indicated that ultrasonic pretreatment required more energy than was generated by the process in terms of additional biogas production. However, an energy balance for ultrasonic pretreatment of DDGS provided 70% more energy than was required to operate the ultrasonic unit.*

Keywords. *Biochemical methane potential (BMP), Corn-ethanol coproducts, Dry distillers grains with solubles (DDGS), Methane, Ultrasonic.*

Ethanol is a renewable fuel that can be derived from a variety of biomass sources, including starch crops, sugar crops, and cellulosic materials. In January 2009, the U.S. had approximately 170 ethanol plants in service with a production capacity of more than 39 billion L (10.5 billion gal) per year (RFA, 2009). Since 2000, corn ethanol production capacity has nearly tripled with recent increases by as much as 15% to 20% per year (Cheesbrough et al., 2008). Yeast fermentation in the production of corn ethanol does not utilize all of the available organics and results in coproducts, including dry distiller's grains with solubles (DDGS), distiller's wet grains (DWG), condensed distiller's solubles (CDS), and thin stillage. For an ethanol dry milling process, typical by-product production is as follows: 233 kg DDGS m^{-3} corn (18 lbs DDGS per bushel), 182 kg DWG m^{-3} corn (14 lbs DWG per bushel), 122 kg CDS m^{-3} corn (9.5 lbs CDS per bushel), and 1,108 kg thin stillage m^{-3} (86 lbs thin stillage per bushel) (Dale and Tyner, 2006). However, it should be noted that at a given plant these by-product quantities are not available collectively because thin stillage is utilized to make CDS, DWG is the base of DDGS, and CDS is added to DWG to make DDGS.

Cheesbrough et al. (2008) estimated that even with modest continued growth the ethanol industry could be producing as much as 35 to 70 million metric tons of DDGS by 2020. By the end of 2008, the Renewable Fuels Association (RFA, 2008) reported that the U.S. was producing over 20 million metric tons of DDGS per year. The typical compositions of dry matter, crude protein, and fat content for the coproducts evaluated in this study are shown in table 1. Coproducts from the corn-ethanol industry have traditionally been used for livestock feed. However, as the ethanol coproducts supply continues to increase, market saturation of coproducts as a livestock feed source should be avoided to maintain economic viability (Cheesbrough et al., 2008). Anaerobically digesting coproducts for energy production may be an alternative use for coproducts, and it could provide a means for ethanol facilities to offset a fraction of their energy costs.

Anaerobic digestion is a natural process that has been utilized for decades to recover energy in the form of biogas from

Table 1. Typical composition for dry distiller's grains with solubles (DDGS), distiller's wet grains (DWG), condensed distiller's solubles (CDS), and thin stillage.

Parameter	DDGS[a]	DWG[b]	CDS[a]	Thin Stillage
Dry matter (%)	88 to 90	34	23 to 45	6.19[c]
Crude protein, dry matter basis (%)	25 to 32	33	20 to 30	--
Fat content, dry matter basis (%)	8 to 12	10	9 to 15	--

[a] DDGS and CDS composition obtained from Lardy (2007).
[b] DWG composition obtained from IRFA (2009).
[c] Obtained from Rosentrater et al. (2006).

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organic waste streams. The ethanol coproducts listed above each contain considerable organic matter available for anaerobic digestion. Rosentrater et al. (2006) reported volatile solids concentrations for thin stillage and CDS to be 53.2 and 270.1 g L^{-1}, respectively; Rasmussen et al. (2007) reported the concentration of chemical oxygen demand (COD) in thin stillage to be 90 g L^{-1}; and Spiehs et al. (2002) reported results indicating that 94% of the dry matter content of DDGS was organic matter. 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 could be used to power ethanol facilities (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. They estimated that a daily production of 3,681 m^3 (130,000 ft^3) of methane could be achieved from 227,125 L (60,000 gal) of thin stillage per day. After performing biochemical methane potential (BMP) assays on several ethanol coproducts, Rosentrater et al. (2006) reported methane production rates of 66 and 187 mL CH_4 g^{-1} of thin stillage and CDS, respectively. While DDGS and DWG contain considerable organic matter, Rosentrater et al. (2006) reported limited methane generation with these materials in BMP assays.

Ultrasonic pretreatment assisted sludge degradation has been studied recently to improve hydrolysis of sludge, which is usually the rate-limiting step of anaerobic digestion. When high-power ultrasonication is applied through a medium such as water, the surrounding particles in the solution can be broken apart through intense hydro-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 ultrasonics enhance the disintegration of particulate matter, which is evidenced by a reduction in particle size and increase in the soluble matter fraction (Wang et al., 2005; Benabdallah EI-Hadj et al., 2007). 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 coproducts using ultrasound technologies.

Biochemical methane potentials were developed to determine the anaerobic degradability of a given material (Owens et al., 1979). Traditionally, BMP analysis has been used to evaluate the biodegradability of municipal and industrial wastes (Owens and Chynoweth, 1993). Biochemical methane potential assays can be used to (1) determine the concentration of organics in wastewater that can be anaerobically converted to CH_4, (2) evaluate the potential efficiency of the anaerobic process with a specific wastewater, (3) measure residual organic material amenable to further anaerobic treatment, and (4) test for non-biodegradables remaining after treatment (Speece, 1996).

This article addresses ultrasonication as a pretreatment for anaerobic digestion of corn ethanol coproducts including DDGS, DWG, thin stillage, and CDS. The objectives of this study were to (1) determine the influence of ultrasonic pretreatment on coproduct particle size distribution, and (2) determine the influence of ultrasonic pretreatment on biochemical methane production potential resulting from anaerobic digestion.

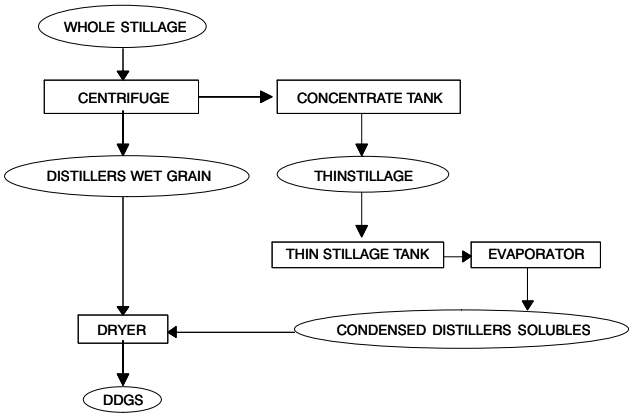

Figure 1. Diagram of coproducts including DDGS, distiller's wet grains (DWG), condensed distiller's solubles (CDS), and thin stillage created after centrifuge step during corn to ethanol process.

Material and Methods

Sample Collection

Ethanol coproducts analyzed in the study, including DDGS, DWG, CDS, and thin stillage, were obtained from the Lincoln Way Energy ethanol production facility (Lincoln Way Energy, Nevada, Iowa). These coproducts were created at various steps in the ethanol production process, as shown in figure 1.

Sample Characterization

All samples were analyzed in triplicate for total solids, volatile solids, pH, total Kjeldahl nitrogen, ammonia, COD, and total phosphorus. Total and volatile solids were analyzed using Standard Method 2540 G (APHA, 1998). The pH was determined with Corning pH combination gel-filled electrodes (Corning, Inc., Corning, N.Y.). Total Kjeldahl nitrogen and ammonia were analyzed using a Labconco digester (model 23012) and Rapidstill II (model 65200, Labconco Corp., Kansas City, Mo.) using the Kjeldahl method (AOAC, 2000). COD was measured using a colorimetric digestion method (method 8000, Hach Co., Loveland, Colo.). Total phosphorus was determined using a spectrophotometer (Genesys 6, Thermo Electron Corp., Waltham, Mass.) with the photometric method (AOAC, 2000).

Ultrasonic Pretreatment and Experimental Design

To ensure uniform treatment, ten samples of DDGS, solids, and CDS were mixed with water (sample to water ratio = 3 g to 35 mL) before ultrasonic processing. The ultrasonic system used in this study was a 2.2 kW, 20 kHz Branson 2000 series equipped with a 0 to 20 μm_{pp} converter, a 1:1 gain booster and a 1:8 gain catenoidal horn (Branson Ultrasonic Corp., Danbury, Conn.). 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 (10, 20, 30, 40, and 50 s) to each of those four coproducts before setting up a benchtop BMP trial. This resulted in a total of 15 treatments (3 × 5 matrix) along with an untreated sample (control) that were tested for biomethane po-

tential from anaerobic digestion of DDGS, DWG, CDS, and thin stillage. All assays were performed in triplicate.

During the ultrasonic treatment, the voltage, current, and phase of the power supplied to the converter was monitored in order to measure dissipated power and energy. The calculated energy value and mass were then used to calculate the dissipated energy density (J g^{-1}).

Biochemical Methane Potential Assays

The BMP assays were performed based on a procedure described by Owens et al. (1979). The lab analyses used to characterize the coproducts were used to calculate the amount of coproduct (substrate) to add to the 250 mL assay bottle. The substrate volume in the assay was calculated to produce measurably sufficient, but not excessive, daily biogas production. The BMPs also contained inoculum and basal medium. The inoculum was an anaerobic conditioned bacteria cultivated in a 60 L mesophilic (35°C) continuous stirred-tank reactor fed daily at a loading rate of 2 g VS L^{-1} d^{-1}. The addition of anaerobic conditioned bacteria allowed the BMP to be completed in a shorter amount of time than if no bacteria were added. The average inoculum concentration was 3 g VS L^{-1}. The amount of coproduct added varied by type and was sufficient to provide a sample to inoculum VS ratio of 1:1. The basal medium was a supplement of inorganic nutrients and alkalinity. It was used in the inoculum reactor as well as the BMP assays to ensure optimal conditions. Content of the basal medium was based on material suggested by Speece (1996). The amount of inoculum and basal medium was calculated based on a ratio of substrate VS to inoculum VS. Each assay was replicated in triplicate. The headspace in the serum bottle was purged with a gas mixture of 70% nitrogen and 30% carbon dioxide at a flow rate of approximately 0.5 L min^{-1} for 5 min. The BMP assay bottles were sealed and placed on orbital shakers (150 to 200 rpm) in an incubator at 35°C for 30 days. The shakers were held at a constant setting throughout the study; because of variability between shakers, the settings yielded speeds between 150 and 200 rpm. Biogas volumes were monitored daily and analyzed for methane production.

To account for gas production by the inoculum, biogas and methane yields measured in blank samples were subtracted from the associated coproduct assay biogas and methane yields. The blanks contained inoculum and basal medium at rates identical to the coproduct assays.

Biogas Production and Methane Content Measurement

Biogas production was monitored daily via volume displacement using 50 mL wetted gas syringes with 1 mL gradations. The methane content of the biogas was determined weekly using a gas chromatograph (model GC-14A, Shimadzu Corp., Kyoto, Japan) 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^{-1}. Methane volume was calculated using biogas production and methane content at 35°C. Methane yields were calculated by dividing methane volume by the weight of the sample VS added to each bottle (mL g^{-1} VS added).

Particle Size Analysis

A particle distribution analysis (PDA) system (Mastersizer 2000, Malvern Instruments, Westborough, Md.) equipped with No. 20 and No. 35 sieves was utilized to compare particle size difference of DDGS, DWG, CDS, and thin stillage samples pretreated with and without ultrasound. Particle size analysis was performed on a subset of the experimental treatments, which included four treatments (10 s with 33% amplitude, 50 s with 33% amplitude, 10 s with 100%, and 50 s with 100% amplitude), along with the control, to characterize particle size. The average particle size determined in this study used the volume-weighted mean diameter, or De Brouckere mean diameter, which was provided by the equipment's software. Data were analyzed using the Malvern Mastersizer software.

Statistical Analyses

Methane production data were analyzed using the general linear model (GLM) procedure of SAS (version 9.1, SAS Institute, Inc., Cary, N.C.). The model included the fixed effects of ultrasound (untreated and treated), ultrasonic amplitude (33%, 66%, and 100%), ultrasonic time (10, 20, 30, 40, and 50 s), and the interaction between ultrasonic amplitude and time. Significant differences among the means were assumed to correspond to a p-value of $p \leq 0.05$. The nutrient analysis of samples was also analyzed using the GLM procedure of SAS. The model included the fixed effects of ultrasound (untreated and treated).

Results and Discussion

Characteristics of DDGS, DWG, CDS, and Thin Stillage

The nutrient analysis of DDGS, DWG, CDS, and thin stillage is presented in table 2. The reported values are averages of untreated and treated samples. The effects of ultrasound pretreatment on the nutrient content of DDGS, DWG, CDS, and thin stillage were not significant ($p > 0.05$). The VS of DDGS, DWG, CDS, and thin stillage were 95%, 87%, 37%, and 3.0%, respectively, and the COD were 507, 400, 609, and 110 g L^{-1}, respectively.

Particle Size Analysis

Particle sizes of the majority of DDGS particles with or without ultrasound pretreatment ranged from 110 to 1000 μm (fig. 2). The DDGS samples without ultrasound pretreatment had the highest percentage (85%) of particles larger than 200 μm; in comparison, DDGS samples pretreated with ultrasound for 50 s at 100% amplitude had only 45% of the particles in the size range greater than 200 μm. Similar results were seen with the particle size distributions for DWG (fig. 3). The majority of DWG samples were sized from 110 to 1000 μm. At approximately 700 μm, there was a lower per–

Table 2. Nutrient analysis of DDGS, DWG, CDS, and thin stillage (mean ±standard deviation).

Parameter	DDGS	DWG	CDS	Thin Stillage
TS (% ww)	97 ±4	96 ±4	40 ±1	3.3 ±0.1
VS (% ww)	95 ±1	87 ±3	37 ±3	3.0 ±0.1
COD (g L^{-1})	507 ±19	400 ±11	609 ±36	110 ±4
TKN (mg g^{-1} TS)	32.3 ±0.9	30.0 ±0.5	32.1 ±2.2	32.7 ±0.9
NH^{+}_{4}-N (mg g^{-1} TS)	4.4 ±0.3	4.0 ±0.1	4.2 ±0.2	3.6 ±0.4
P (mg g^{-1} TS)	5.2 ±0.2	5.0 ±0.1	5.0 ±0.5	5.7 ±0.4
pH	4.3 ±0.1	4.6 ±0.1	4.5 ±0.1	4.1 ±0.1

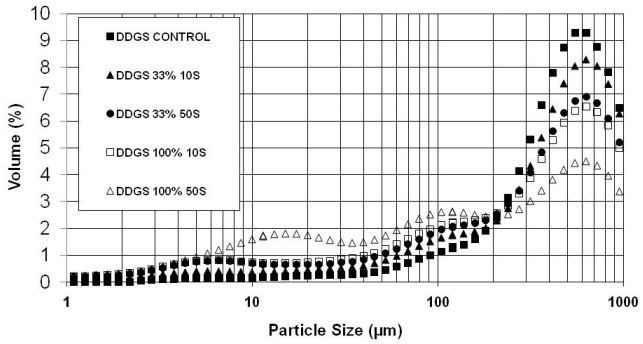

Figure 2. Particle size distribution of DDGS samples without (control) or with ultrasound pretreatment for 10 or 50 s at varied amplitude (33% or 100%).

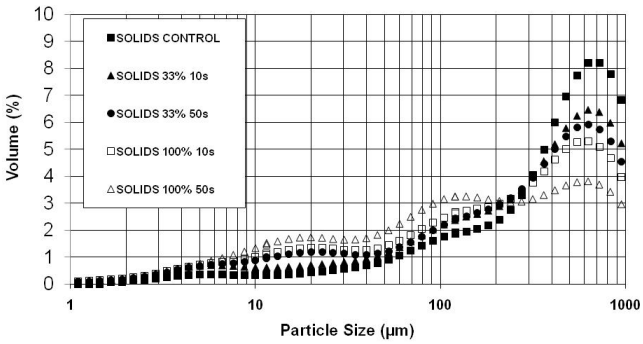

Figure 3. Particle size distribution of DWG without (control) or with ultrasound pretreatment for 10 or 50 s at varied amplitude (33% or 100%).

centage of particles in the solid samples pretreated with ultrasound compared with the untreated samples. In general, an increase in sonication time and amplitude resulted in a greater particle size reduction for DDGS and DWG (fig. 4). The ultrasonic pretreatment reduced the mean particle size of DDGS and DWG by 45% and 43%, respectively. These findings were similar to other ultrasonic pretreatment studies. In a series of ultrasonic pretreatment tests, Benabdallah El-Hadj et al. (2007) showed a 60% to 70% decrease in the particle size of sonicated raw sewage sludge. Statistical analysis of the mean particle sizes within each sonication time and amplitude treatment indicated that there were significant differences between the control and each subsequent treatment level. This study demonstrated that ultrasonic pretreatment

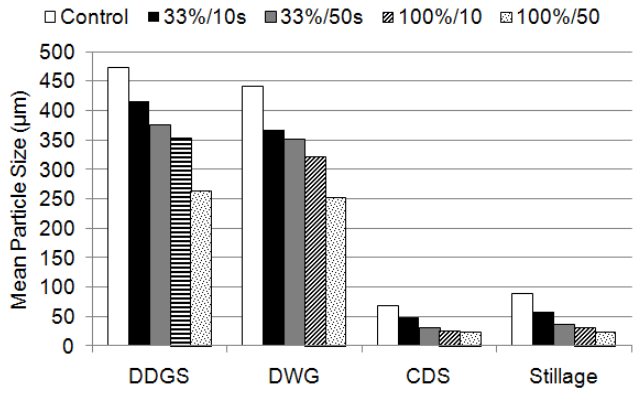

Figure 4. Mean particle size of DDGS, DWG, CDS, and thin stillage without (control) or with ultrasound pretreatment for 10 or 50 s at varied amplitude (33% or 100%).

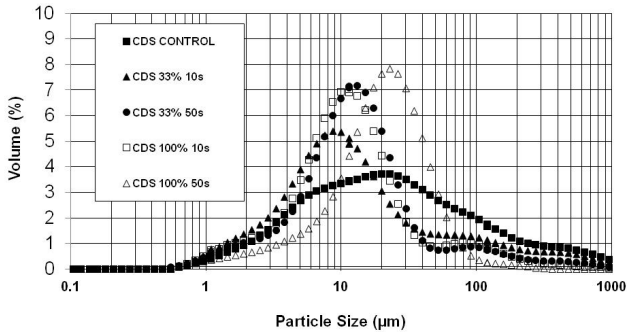

Figure 5. Particle size distribution of CDS without (control) or with ultrasound pretreatment for 10 or 50 s at varied amplitude (33% or 100%).

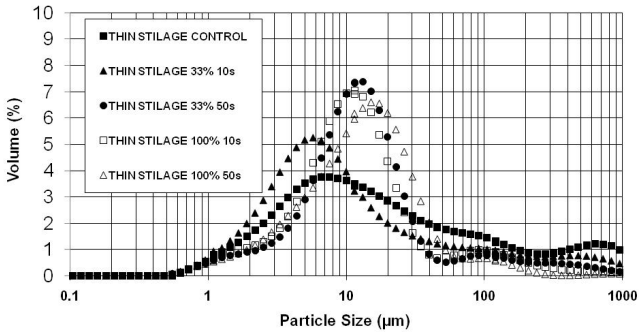

Figure 6. Particle size distribution of thin stillage without (control) or with ultrasound pretreatment for 10 or 50 s at varied amplitude (33% or 100%).

can be utilized to decrease particle size of DDGS and centrifuge DWG, which potentially could result in higher bio-DWG degradation.

For the CDS and thin stillage, the majority of the particles with or without ultrasound pretreatment ranged from 1 to 100 µm (figs. 5 and 6). Unlike the DDGS and solid samples, a particle size increase was observed for the CDS and thin stillage samples pretreated with ultrasound. Although the reason is not evident, differences between particle size reduction of DDGS and DWG versus CDS and thin stillage are likely due to the initial smaller particle size of CDS and thin stillage compared to DDGS and DWG. Doktycz and Suslick (1990) suggested that high-intensity ultrasound applied to solid-liquid slurries could drive particles together to induce melting upon collision. In this study, interparticle collisions driven by ultrasound likely contributed to the observed particle size increase for the CDS and thin stillage samples.

Ultrasound Effect on Coproduct Cumulative Methane Production

Dried Distiller's Grains with Solubles

The ultrasound effects on methane yield from DDGS are presented in table 3. Ultrasonic pretreatment increased methane yield by 25%. Consistently, the cumulative methane production (yield) for samples pretreated with ultrasound (395 mL g^{-1} VS) was significantly higher than for untreated samples (315 mL g^{-1} VS). The average COD conversion efficiency increased from 43% to 61% for the treated samples; however, the COD conversion efficiency should be considered an estimate due to possible COD measurement inaccuracies in solid and semi-solid samples. It can also be seen that

cumulative methane production was generally proportional to amplitude. Specifically, the samples pretreated with 33% ultrasonic amplitude (358 mL g^{-1} VS) had lower methane yield than samples pretreated with 66% (422 mL g^{-1} VS) and 100% (404 mL g^{-1} VS) ultrasonic amplitude. However, the cumulative methane yield from samples receiving 66% amplitude was similar to that from samples receiving 100% amplitude, suggesting that there is an amplitude setting between 33% and 100% at which amplitude saturation occurs. In addition, methane yields were proportional to treatment time (346, 379, 394, 396, and 459 mL g^{-1} VS, respectively). The results shown here, reporting methane yields proportional to treatment time, are consistent with the results from the previous section showing reduction in particle size proportional to treatment time. Reduced particle size is likely the largest contributor to enhanced methane production that was observed in the current study. Ultrasonic pretreatment to enhance anaerobic digestion of waste activated sludge has been studied extensively. Benabdallah El-Hadj et al. (2007) reported that for waste activated sludge, where hydrolysis is the rate-limiting step in the anaerobic digestion process, ultrasonic pretreatment reduced particle size in the waste and increased the soluble matter fraction. Both of these characteristics positively impact the anaerobic digestion process (Lehne et al., 2001).

The average cumulative methane yield from anaerobic digestion of DDGS is presented in figure 7. The DDGS samples pretreated with 100% amplitude for 50 s had the greatest methane production (489 mL g^{-1} VS added). This again showed that an increase in sonication time and amplitude resulted in a higher methane production. For DDGS samples pretreated with 100% amplitude, those receiving 50 s treatment yielded the highest methane, followed by the 40 s samples (417 mL g^{-1} VS added) and the 30 s samples (415 mL g^{-1} VS added). The 33% amplitude category showed a similar trend. Cumulative methane production from samples receiving 33% amplitude with times of 10, 20, 30, 40, and 50 s were 322, 323, 347, 362, and 439 mL g^{-1} VS added, respectively. Samples receiving 66% amplitude showed a similar trend, with only one exception. The 20 s sample (454 mL g^{-1} VS added) produced approximately the same amount of methane as the 50 s treatment (448 mL g^{-1} VS added).

Results from the 30-day BMP assays indicated that 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. For all treatment conditions (amplitude and time), longer treatments were not considered because of a loss of efficiency, as previously described. Results are consistent with previous studies to determine the effect of ultrasonic pretreatment on anaerobic digestion of sewage sludge (Grönroos et al., 2005; Wang et al., 1999). Grönroos et al. (2005) hypothesized that ultrasonic pretreatment would increase the amount of soluble COD and thus increase methane yield. They 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. Sewage sludge ultrasonically pretreated for 2.5 and 10 min at 27 kHz and 200 W L^{-1} increased methane production to 8 to 17 times greater than that of the untreated samples, and methane yield was greater for the 10 min treatment than the 2.5 min treatment. Using a 9 kHz, 200 W ultrasonic disintegrator, Wang et al. (1999) achieved a 64% increase in methane production via anaerobically digested sewage sludge with a pretreatment time of 30 min, but increasing the pretreatment time to more than 30 min did not lead to continued increases in methane generation.

Table 3. Statistical analysis results: cumulative methane production from DDGS, DWG, CDS, and thin stillage without or with ultrasound pretreatment at varied amplitudes (33%, 66%, and 100%) and times (10, 20, 30, 40, and 50 s).

	Cumulative Methane Production (mL g^{-1} VS added)[a]			
Item	DDGS	DWG	CDS	Thin Stillage
Average biogas methane content	49%	52%	49%	51%
Main effect				
Ultrasound				
Untreated	315 a	374 a	407	346 a
Treated	394 b	419 b	418	411 b
Amplitude (%)				
33	358 c	412	407	387 c
66	422 d	412	423	427 d
100	404 d	433	423	418 d
Time (s)				
10	346 e	407	410	386 e
20	379 e,f	418	419	370 e
30	394 f	413	381 a	432 f
40	396 f	426	428	442 f
50	459 g	431	451 b	424 f
SEM	63	32	40	51
Probabilities (p-values)				
Ultrasound	<0.01	<0.01	0.51	<0.01
Amplitude	0.02	0.18	0.38	0.02
Time	<0.01	0.61	<0.01	<0.01
Amplitude × time	0.67	0.91	0.03	0.03

[a] Means within a column followed by different letters are different for a given coproduct ($p < 0.05$).

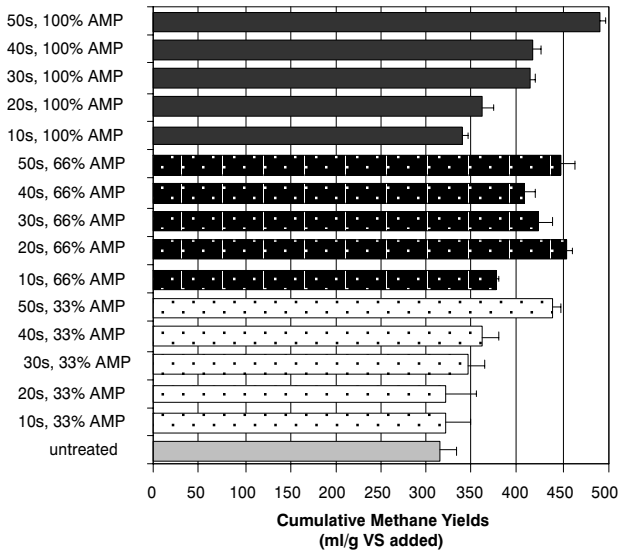

Figure 7. Ultrasound effect on average of cumulative methane production from DDGS.

Distiller's Wet Grains

Ultrasonic pretreatment had a significant effect on the cumulative methane production for DWG (table 2). Methane production was 12% higher for the ultrasonically pretreated samples compared to the untreated samples (control). Distiller's wet grains without ultrasonic treatment produced the least amount of methane gas (374 mL g^{-1} VS added). Average cumulative methane production from samples that received ultrasonic pretreatment was 419 mL g^{-1} VS added. Methane yields were observed to increase with higher amplitude (412, 412, and 433 mL g^{-1} VS, respectively) and longer treatment time (407, 418, 413, 426, and 431 mL g^{-1} VS added, respectively). The average COD conversion efficiency increased from 44% to 54% for the treated samples. However, the effects of ultrasonic amplitude, time, or amplitude × time interaction effects were not significant.

As shown in figure 8, the greatest methane production (462 mL g^{-1} VS added) was obtained with the highest amplitude (100%) and longest treatment time (50 s). This result is similar to the results obtained with ultrasonically pretreated DDGS, where the greatest methane yield occurred at the highest amplitude and the longest treatment time. Additionally, particle analysis of the pretreated DWG showed that the average particle size was smallest at the highest amplitude and the longest treatment time.

Condensed Distiller's Solubles

There was no significant ultrasound effect on cumulative methane production from CDS (table 3). Biogas production from the CDS trial was, for the most part, not consistent with results found for DDGS and DWG (fig. 9). The greatest methane production (474 mL g^{-1} VS added) was observed with the 66% amplitude and longest treatment time (50 s). The average COD conversion efficiency increased from 52% to 60% for the treated samples. In reference to the samples treated with 33% amplitude, samples without ultrasound pretreatment produced a similar amount of methane as the 10 s samples (408 mL g^{-1} VS added) and more than the 20 s samples (365 mL g^{-1} VS added) and 30 s samples (376 mL g^{-1} VS added). The 100% amplitude category also showed the control ahead of two treated samples, similar to the 33% category, and 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.

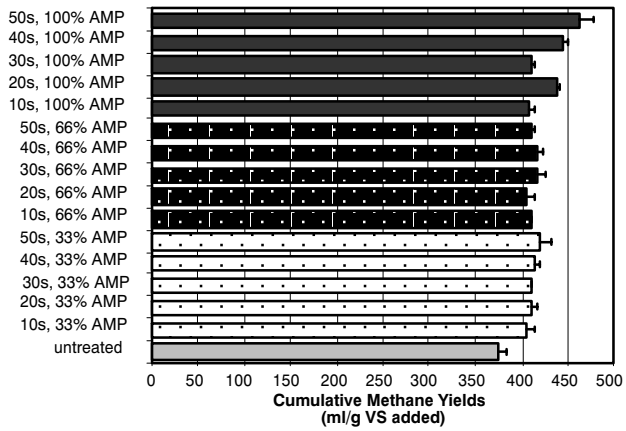

Figure 8. Ultrasound effect on average of cumulative methane production from DWG.

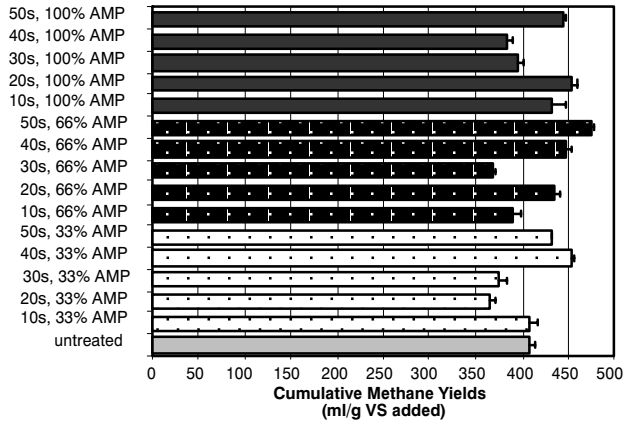

Figure 9. Ultrasound effect on average of cumulative methane production of CDS.

This reasoning is supported by the particle distribution analysis, which suggested that no reduction of the CDS particle size occurred with ultrasound pretreatment, since the CDS particle size is already much smaller as compared to the DDGS and DWG samples without ultrasound pretreatment.

Thin Stillage

Ultrasonic pretreatment had a positive impact on the cumulative methane production from thin stillage (table 2). Generally, the pretreated thin stillage samples produced more methane (411 mL g^{-1} VS) than the untreated samples (346 mL g^{-1} VS). However, similar to the results for CDS, the effects of sonication time and amplitude were not directly correlated. For example, methane production was not enhanced with increasing sonication amplitude, but within the 100% and 33% amplitude ranges, methane production was generally proportional to sonication time. Cumulative methane yield from anaerobic digestion of thin stillage (fig. 10) ranged from 315 to 452 mL g^{-1} VS added. The average COD conversion efficiency increased from 44% to 57% for the treated samples. In reference to the samples treated with 33% amplitude, the untreated control produced more methane (346 mL g^{-1} VS added) than the 10 and 20 s 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. It is believed that the

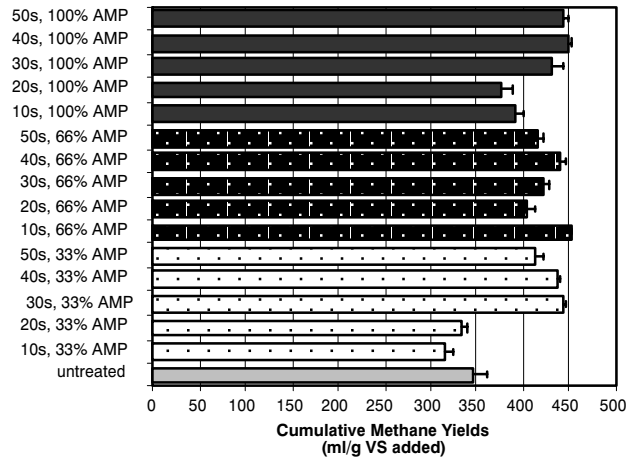

Figure 10. Ultrasound effect on average cumulative methane production of thin stillage.

Table 4. Energy balance analysis.

		DDGS	DWG
Cumulative methane production (mL)	Untreated	315	197
	Sonicated[a]	445	217
Increased methane production[b]	mL	84	20
Increased energy[c]	J	3,209	764
	J g^{-1} VS	3,027	1,697
Input energy[d]	J	1,883	1,391
	J g^{-1} VS	1,776	3,091
Net energy recovery	J	1,326	-628
	J g^{-1} VS	1,250	-1395

[a] Average of methane production from ultrasound pretreated samples.
[b] Increased methane production = methane production from pretreated samples - methane production from untreated samples.
[c] Energy recovered from additional methane production. Energy content of methane used for computation was 38.2 MJ m^{-3}.
[d] Energy used for running ultrasonic unit.

lower amplitudes (33% and 66%) were effective in enhancing methane production. It is also believed that these amplitudes did not produce sufficient particle size reduction, as previously noted. The 100% category was consistent with the trend that an increase in sonication time resulted in a higher methane production.

Energy Balance Analysis

Optimization of energy consumption is essential for the use of ultrasonication as a pretreatment to anaerobic digestion for the process to be economically feasible; therefore, in reference to this critical aspect, a basic energy balance was prepared (table 4). Cumulative biogas production from ultrasonically pretreated DDGS samples produced a higher amount of methane compared to the untreated samples (445 vs. 361 mL). An additional 84 mL of methane was produced, corresponding to 3,209 J of chemical energy. For DDGS, the energy input for the ultrasound treatment was 1,883 J, yielding a net energy balance of 1,326 J. Following the same approach, only 20 mL of additional methane was recovered using pretreatment to anaerobic digestion of DWG samples. The energy recovered from additional methane production from pretreated DWG was less than the ultrasonic energy input (764 J vs. 628 J). While the basic energy balance shows a net energy gain for DDGS, the actual energy balance in a real-world application would depend on how the biogas was utilized and the conversion efficiency of the process selected.

Conclusion

While ultrasonic pretreatment of ethanol coproducts was shown to increase methane production from anaerobic digestion, this study indicates that ultrasonic pretreatment had a greater influence on methane production for solid coproducts (DDGS and DWG) than for liquid coproducts (CDS and thin stillage). These results are also supported by the particle distribution analysis, which suggested that ultrasonic pretreatment can reduce the mean particle size of DDGS and DWG by 45% and 43%, respectively. A basic energy balance conducted for DDGS and DWG showed that ultrasonic pretreatment of DDGS provided 70% more energy than was required to operate the ultrasonic pretreatment process, while the increase in energy output from the ultrasonic pretreatment of DWG produced only 55% of the energy required to operate the process. According to the DDGS and thin stillage results, an increase in amplitude resulted in an overall increase in methane production for ultrasound pretreated samples. The DDGS results also showed that an increase in the length of exposure to ultrasonic pretreatment results in an increase in methane production. Without ultrasound pretreatment, CDS had the highest methane production potential. If DDGS were going to be used as a feedstock for anaerobic digestion, then the use of ultrasonic pretreatment shows merit for increasing methane production from the process.

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