2008

Evaluation of ultrasonic pretreatment on anaerobic digestion of biomass for methane production

Wei Wu-haan
Iowa State University

Evaluation of ultrasonic pretreatment on anaerobic digestion of biomass for methane production

by

Wei Wu-Haan

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Co-majors: Environmental Science; Biorenewable Resources and Technology

Program of Study Committee:
Robert T. Burns, Co-major Professor
Shihwu Sung
Raj D. Raman
David Grewell

Iowa State University

Ames, Iowa

2008

TABLE OF CONTENTS

ACKNOWLEDGMENTS v

ABSTRACT vi

CHAPTER 1. GENERAL INTRODUCTION 1

Thesis Organization 1
Introduction 1
Hypothesis 4
Objectives 4
Literature Cited 4

CHAPTER 2. LITERATURE REVIEW 7

2.1 Overview of Anaerobic Digestion 7
2.1.1 Historical development 7
2.1.2 Principles 9
2.1.3 Operational parameters 11
pH 11
Temperature 12
Carbon to nitrogen (C/N) ratio 13
2.1.4 Pretreatment method 14
Thermal pretreatment 15
Mechanical pretreatment 16
Chemical pretreatment 16
Ultrasonic pretreatment 17
Comparison of various pretreatment methods 17
2.1.5 Biochemical methane potential (BMP) assay 19
2.2 Anaerobic Digestion of Corn Ethanol Stillage 21
2.2.1 Background 21
2.2.2 Stillage production 22
Dry-grind corn process 22
Availability 22
Utilization 23
2.2.3 Stillage characterization 24
2.2.4 Anaerobic digestion of ethanol stillage 25
Anaerobic digestion of ethanol stillage under mesophilic conditions 25
Anaerobic digestion of ethanol stillage under thermophilic conditions 26

2.3 Anaerobic Digestion of Animal Manure 27
- 2.3.1 Background 27
- 2.3.2 Historical development 28
- 2.3.3 Anaerobic digestion of cattle waste 29
  - Characterization 29
  - Effect of manure liquid-solids separation on methane production 29
  - Review of application and effectiveness 30
- 2.3.4 Anaerobic digestion of swine slurry 30
  - Characterization 30
  - Effect of manure liquid-solids separation on methane production 30
  - Review of application and effectiveness 31

2.4 Co-digestion 32

2.5 Ultrasonic Pretreatment Applied to Anaerobic Digestion Process 34
- 2.5.1 Principles 34
  - Mechanism of ultrasonic 34
  - Ultrasonic system 35
- 2.5.2 Review of application and effectiveness 35
  - Evaluation of ultrasonic disintegration efficiency 36
  - Factors affect the ultrasonic disintegration efficiency 37
  - Ultrasonic pretreatment applied to digestion of wastewater sludge 38

Literature Cited 42

CHAPTER 3. EVALUATION OF ULTRASONIC PRETREATMENT ON METHANE PRODUCTION POTENTIAL FROM CORN ETHANOL BY-PRODUCTS 55

- Abstract 55
- Introduction 56
- Materials and Methods 58
- Results and Discussion 61
- Conclusions 76
- Literature Cited 77

CHAPTER 4. EVALUATION OF ULTRASONIC PRETREATMENT ON ANAEROBIC DIGESTION OF DIFFERENT ANIMAL MANURES 79

- Abstract 79
- Introduction 80
- Materials and Methods 81
- Results and Discussion 85
- Conclusions 98
- Literature Cited 101

CHAPTER 5. GENERAL CONCLUSIONS 104
General Discussion and Suggestions for Future Research 104
Literature Cited 111

ACKNOWLEDGMENTS

Special thanks should be given to my major professor, Dr. Robert Burns, not only for his invaluable guidance, and suggestions but also for his support and efforts while I was trying to find a route for my research. I also would like to thank Dr. David Grewell, Dr. Raj Raman and Dr. Shihwu Sung for their direction and guidance on my research. In addition, I wish to thank Mr. Cody Hearn for his help in processing samples. Thanks are also due to Ms. Lara Moody for her assistance.

Finally, words alone cannot express the thanks I owe to my husband and parents for their trust in me and encouraging me in what I choose, and who have always been exceptional and loving to me.

ABSTRACT

This thesis evaluated the effectiveness of ultrasonic pretreatment on biochemical methane potential (BMP) of corn-ethanol by-products (dried distiller grain with solubles (DDGs), centrifuge-solids, thin stillage, and corn-syrup) and four types of animal manure (swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent) and energy efficiency of ultrasonic pretreatment. Ultrasonic pretreatment was applied with various amplitude and treatment time settings. Biogas production was measured and analyzed for methane content and methane yield. Ultrasonic pretreatment of DDGs, centrifuge-solids, swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent increased methane production by 25, 12, 14, 55, 37 and 8%, respectively. An increase in ultrasonic amplitude and treatment time resulted in an overall increase in methane production, but with a reduction of energy efficiency. The greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with the shortest treatment time used.

Key words: Animal manure; Biochemcial methane potential assay (BMP); Corn-ethanol by-product; Methane yield; Ultrasonic

CHAPTER 1. GENERAL INTRODUCTION

THESIS ORGANIZATION

This thesis is organized as a general introduction to the research followed by a brief description of the hypothesis for developing this research and its objectives. Chapter 2 is a literature review followed by two manuscripts (chapters 3 and 4) for submission to *Biomass and Bioenergy*. Following the manuscripts is a general conclusion section.

INTRODUCTION

The current energy crisis and global climate change due to the combustion of fossil fuels have created considerable interest in bio-renewable energy resources. One way to reclaim energy from biomass is anaerobic digestion. Anaerobic digestion (AD) is a natural process that has been utilized for decades for the recovery of energy as biogas from organic waste. Anaerobic digestion of organic wastes could produce energy and reduce environmental impact, particularly greenhouse gas emissions. A wide range of biomass feedstocks have been considered as potential sources for methane production through anaerobic digestion including ethanol stillage and animal manure.

Currently, the US has approximately 134 ethanol plants in service with a production capacity of 34 billion liters (9 billion gallons) per year [1]. Yeast fermentation in the production of corn ethanol does not utilize all of the available organics resulting in 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 as livestock feed. However, these by-products can potentially be used for the production of energy as biogas through the anaerobic digestion process. Olguin et al. [2] reported that the COD of thin ethanol stillage effluents is usually more than 100,000 mg/L which suggests a great potential for energy recovery. It has been estimated that anaerobic digestion can remove more than 50% of the chemical oxygen demand (COD) from ethanol thin stillage and convert it to biogas, which could be used to power the ethanol facility [3]. However, the COD concentration of stillage can vary considerably, depending on feedstocks. Wilkie et al. [3] reported the typical COD and BOD of corn thin stillage were 56,000 and 37,000 mg/L, respectively. Stover et al. [4] demonstrated that significant amounts of methane could be recovered with a process of treating thin corn stillage using mesophilic anaerobic digesters. Stover et al. 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 logical step in the development of this technology is to improve biosolids degradation and enhance methane production.

In addition, considerable amounts of animal manure are available for methane production. Anaerobic digestion of animal manure produces renewable energy that can be used for heat and power and also reduces air emissions from livestock wastes which includes substantial odor reduction and reduction of greenhouse gas (GHG) emissions. Anaerobic digestion of manure also potentially reduces pathogens in manure.

Anaerobic digestion is a process in which microorganisms convert biodegradable material in the absence of oxygen into biogas which contains mainly methane (CH_4) and inorganic end-products such as carbon dioxide (CO_2). This process is the consequence of a series of metabolic interactions among various groups of microorganisms under anaerobic conditions [5]. Anaerobic digestion of organic material occurs in four stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. During the first stage of hydrolysis, fermentative bacteria convert the soluble complex organic matter and high molecular weight compounds such as lipids, polysaccharides, proteins, and nucleic acids into soluble molecules such as sugars, amino acids, and fatty acids. The hydrolysis stage is usually identified as the rate limiting step, when high solids materials are digested. Therefore, enhanced performance of the anaerobic process could be achieved by finding a pretreatment to accelerate hydrolysis. Compared with other pretreatment methods, ultrasonic treatment exhibits a great potential, since it is not hazardous to the environment and is economically competitive [6].

Ultrasonic pretreatment is known to disintegrate sludge flocs and disrupt microbial cell walls resulting in the release of soluble substance [7]. Tiehm et al. [8] found that applying ultrasonic (3.6 kW, 31 kHz, 64s) to sludge disintegration can release the organic substances into the sludge and the soluable chemcial oxygen demand (SCOD) in the supernatant increased from 630 to 2270 mg/L. Lafitte-Trouqué and Forster [9] indicated that gas production rates from anaerobic digestion of ultrasonic pretreated sludge were higher than those for untreated sludge. Grönroos, et al. [10] demonstrated that ultrasonic pretreatment enhanced methane production during the anaerobic digestion process and ultrasonic power as well as ultrasonic treatment time had the most significant effect on increasing methane production. Dewil et al. [11] concluded that particle size reduction caused by ultrasonic enhanced hydrolysis, the rate-limiting step of the anaerobic process, resulting in more degradable substrate and increased in methane production.

However, only ultrasonic pretreatment applied to anaerobic digestion of waste active sludge (WAS) has been reported and there is limited data on the effectiveness of ultrasonic pretreatment prior to anaerobic digestion of ethanol stillage and animal manure.

HYPOTHESIS

The hypothesis of this study is that ultrasonic pretreatment prior to anaerobic digestion of corn-ethanol by-products and animal manure would increase the digestibility of corn-ethanol by-products and animal manure resulting in increased methane production.

OBJECTIVES

This thesis investigated the biochemical methane potential (BMP) production from anaerobic digestion of corn-ethanol by-products including dried distillers 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.

In addition, the effectiveness of ultrasonic pretreatment on biochemical methane potential (BMP) and soluble chemical oxygen demand (SCOD) of four types of animal manure including swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent as well as energy efficiency of ultrasound pretreatment were also evaluated.

LITERATURE CITED

[1] Renewable Fuels Association (RFA). 2007. Industry Statistics. Available at: http://www.ethanolrfa.org/industry/statistics/#A. Accessed 25 April, 2007.

[2] Olguin EJ, Doelle HW, Mercado G. Resource recovery through recycling of sugar processing by-products and residuals. Resources, Conservation and Recycling 1995, 15: 85-94.

[3] Wilkie AC, Riedesel KJ, Owens JM. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass and Bioenergy 2000,19:63-102.

[4] Stover EL, Gomathinayagam G, Gonzalez G. Use of methane gas from anaerobic treatment of stillage for fuel alcohol production. In: Proceedings of the 39th Industrial Waste Conference, Purdue University, West Lafayette, Indiana. Boston Butterworth 1984, p. 57–63.

[5] Appels L, Baeyens J, Degreve J, Dewil R. Principal and potential of the anaerobic digestion of waste-activated sludge. Progress Energy Combust Science 2008, doi:10.1016/j.pecs.2008.06.002.

[6] Tiehm A, Nickel K, Neis U. The use of ultrasound to accelerate the anaerobic digestion of sewage sludge. Water Science Technology 1997, 36(11):121-128.

[7] Wang F, Wang Y, Ji M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. Journal Hazard Material 2005, 123:145-150.

[8] Tiehm A. Nickel K, Zellhorn M, Neis U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. J. Water Res 2001, 35(8):2003–2009.

[9] Lafitte-Trouqué S, Forster CF. The use of ultrasound and γ-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures. Bioresource Technology 2002, 84:113–118.

[10] Grönroos A, Kyllönen H, Korpijärvi K, Pirkonen P, Paavola T, Jokela J, Rintala J. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. Ultrasonic Sonochemistry 2005, 12(1):115-120.

[11] Dewil R, Baeyens J, Goutvrind R. Ultrasonic treatment of waste activated sludge. Environmental Progress 2006, 25: 121-128.

CHAPTER 2. LITERATURE REVIEW

2.1. Overview of Anaerobic Digestion

2.1.1 Historical development

Anaerobic digestion (AD) is a natural process that has been utilized for decades for the recovery of energy as biogas from organic waste. Volta is recognized as the first person to find that anaerobic processes result in the conversion of organic matter to methane. Volta showed that “combustible air” was derived from sediments in lakes, ponds, and streams in 1776 [1]. Later, Reiset reported that methane could be formed from decomposing manure in 1856 [1].

The first full-scale application of anaerobic treatment was a septic tank used for treating domestic wastewater, developed by Moigno [2] in 1881. He named this system “Mouras’ Automatic Scavenger’’ and described this air-tight chamber in the French journal *Cosmos*. In 1890, Scott Moncrieff constructed the first hybrid anaerobic system, consisting of a tank digester and an anaerobic filter. The tank contained a bed of stones above and an empty space below. The sludge volume was significantly decreased after seven years using this system; this result is also supported by other studies. Donald Cameron remodeled the “septic tank” in 1895 and because of new system’s success, the City of Exeter approved the treatment of the entire city’s wastewater by this means [1]. Karl Imhoff modified the septic tank to prevent wastewater from flowing through the “hydrolyzing” chamber which allows the sludge to stay in this chamber for a longer time and by the end of 1914, about 75 cities in the United States had received license to use the Imhoff tank, as described by Metcalf and Eddy [3]. By the end of the 1930s, sufficient understanding of the separated anaerobic sludge treatment process had developed to allow wide scale practical application.

Beginning in the 1920s, Arthur Bunswell started to apply the anaerobic process for industrial wastewater treatment. He and his colleagues conducted extensive research on the nature of the process and its potential application for treatment of industrial wastewaters and agricultural residues [4] and the single tank anaerobic digester was typically used in their studies which offered no provision of separating microbial biomass from the wastewater and resolted in long residence time in the reactor [1]. Later, Stander discovered that the importance of solids residence time for reducing reactor size and detention time and in the 1950s began separating the anaerobic bacteria from the effluent stream and keeping them in the reactor [5]. Taylor [6] developed the first large scale anaerobic filter to treat wheat starch wastewater in 1972 and Switzenbaum [7] applied biofilm concept and developed an expanded-bed reactor used for denitrification in 1980. In 1970s, Lettinga conceived the upflow anaerobic sludge blanket reactor (UASB) which is the one of most successful new reactor design in its broad application to a variety of industrial and municipal wastewaters [1].

Currently, the anaerobic digestion process has been well applied to energy recover as methane gas from wastewaters, solid wastes, agricultural residues, forest residues, and food processing residues. As reported by Frankin [8], anaerobic digestion technology has developed into a standard treatment for a wide variety of industries and is functional in over 65 countries and a total of approximately 2,154 anaerobic treatment plants for industrial applications in 2001. With the current energy crisis and global climate change due to combustion of fossil fuels, more research towards biomass energy is clearly needed.

Anaerobic digestion of organic wastes not only produces energy but also reduces environmental impact, particularly greenhouse gas emissions.

2.1.2 Principles

Anaerobic digestion (AD) is a process in which microorganisms break down biodegradable material in the absence of oxygen into biogas which contains mainly methane (CH_4) and inorganic end-products such as carbon dioxide (CO_2). It can be used to treat various organic wastes and recover bio-energy in the form of biogas. This process is the consequence of a series of metabolic interactions among various groups of microorganisms under anaerobic conditions (oxidation reduction potential < -200 mV) to proceed [9]. The anaerobic process includes anaerobic fermentation and anaerobic respiration. During anaerobic fermentation, since there is no external electron acceptor such as oxygen, the product generated during this process accepts the electors from the breakdown of organic matter. Therefore, organic matter serves as both the electron donor and acceptor. Some energy is released through the fermentation process, but the major portion of the energy is still contained in the fermentative product such as ethanol. Anaerobic respiration on the other hand requires an external electron acceptor which could be sulfate (SO_4^{2-}), nitrate (NO_3^-), or CO_2 in this case. More energy is released under aerobic conditions compared to anaerobic fermentation. The end products of anaerobic respiration include CH_4, CO_2, nitrogen (N_2), and hydrogen sulfide (H_2S).

Anaerobic digestion of organic material occurs in four stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis as shown in Figure 1. During the first stage of hydrolysis, fermentative bacteria convert the soluble complex organic matter and high molecular weight compounds such as lipids, polysaccharides, proteins, and nucleic acids into soluble molecules such as sugars, amino acids and fatty acids. The complex polymeric matter is hydrolyzed to a monomer by hydrolytic enzymes (lipases, proteases, cellulases, amylases, etc.) secreted by the microorganisms. Lipids, polysaccharides, protein, and nucleic acids are converted to fatty acids, monosaccharide, amino acids, purines and pyrimidines, respectively, during this stage. If high solids organic waste is degraded, the hydrolysis step may become the rate limiting step. Many mechanical and chemical pretreatment methods could be applied to overcome this limitation and enhance hydrolysis. A review of such options is detained in section 2.1.3.

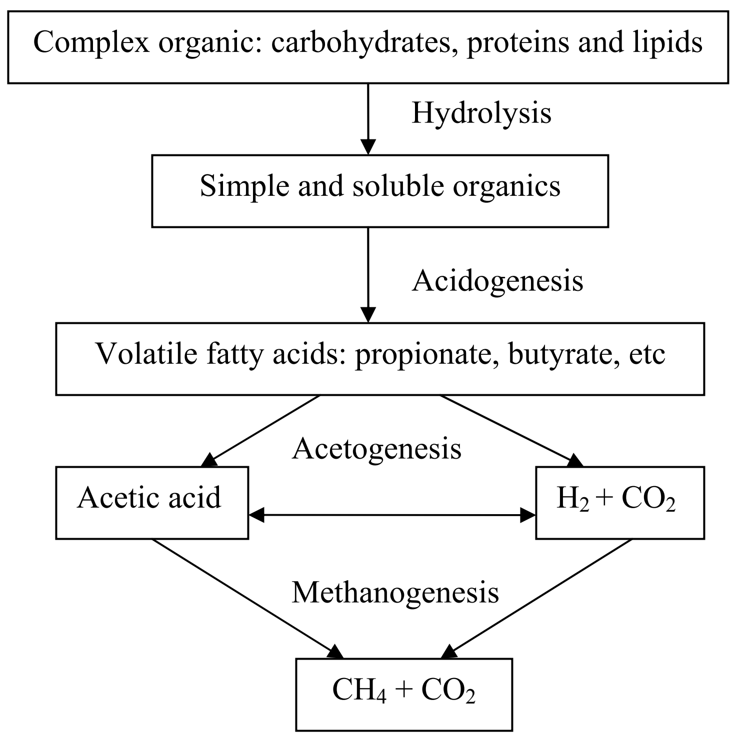


Figure 1. Subsequent steps in the anaerobic digestion process.

The components formed during hydrolysis are further split during the acidogenesis stage. In this stage, acidogenic bacteria convert the end products of the hydrolysis stage into volatile fatty acids (VFA), CO_2, H_2S, ammonia (NH_3), and other products. The principal acids produced during this step include acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), and ethanol (C_2H_5OH) [9].

The next stage in AD is acetogenesis, where end-products from acidogenesis stage are further digested by acetogens to form acetic acid, CO_2, and H_2.

The final stage in AD is methanogenesis, where CH_4 is produced by two groups of methanogenic bacteria. One group called acetate consumers degrades acetic acid to generate CO_2 and CH_4, while, the other group called H_2/CO_2 consumers uses hydrogen (H_2) as electron donor and CO_2 as acceptor to produce CH_4. Omstead et al. [10] suggested that limited H_2 concentration in digesters results in the acetic acid reactions and actetic acid is the primary producer of methane.

2.1.3 Operational parameters

Like any other microorganisms based process, the successful operation of anaerobic digestion process depends on maintaining environmental factors to optimize the microbial activity and increasing the anaerobic degradation efficiency of the system.

<u>2.1.3.1 pH</u>

Various groups of microorganisms are involved in the anaerobic digestion process and each group of microorganisms has a different optimum pH range. The fermentative microorganisms are less sensitive and can function over a wider pH range. However, the best pH range for acetogenic bacteria is 5.5-6.5 and for methanogens is 6.7-8.0 [11]. Therefore, the ideal pH range for anaerobic digestion is 6.8-7.2 [12]. A decrease in pH below 6 significantly reduces the activity of the methanogens more than that of the acidogens and causes a buildup of VFAs and H_2. At higher partial pressure of H_2, propionic acid degrading bacteria could be severely inhibited and excessive accumulation of higher molecular weight VFAs and the pH can drop further.

An anaerobic treatment system has its own buffering capacity against pH drop. Methanogenic bacteria produce alkalinity in the form of CO_2, NH_3, and bicarbonate (H_2CO_3). The system pH is controlled by the concentration of CO_2 in the gas phase and the H_2CO_3-alkalinity of the liquid phase [9]. If the CO_2 concentration in the gas phase remains constant, the addition of H_2CO_3-alkalinity of the liquid phase could raise the pH. One good example is that NH_3 released from the degradation of protein reacts with CO_2 to form ammonium bicarbonate (NH_4HCO_3) as alkalinity.

2.1.3.2 Temperature

Temperature plays an important role not only on the growth rate and metabolism of microorganisms but also on the physicochemical properties of the components found in the digestion substrate. Two primary temperature ranges provide optimum digestion conditions for maximum methane production- the mesophilic (30-35°C) and thermophilic ranges (50-55°C); even though anaerobic digestion can take place at psychrophilic temperates below 20°C [14]. The structures of the active microbial communities at those two temperature optima are different [12]. A rapid temperature change from mesophilic to thermophilic may bring about a population shift if the groups are not compatible and cause a significant decrease in biogas yield [15].

Numerous studies have been done to compare the performance of mesophilic and thermophilic anaerobic reactors. Kim et al. [18] compared process stability and efficiency of mesophilic and thermophilic anaerobic digestion for four different reactor configurations and reported that thermophilic two-phase anaerobic digester showed better performance than mesophilic during both the start-up and the long-term periods. Yilmaz et al. [17] concluded that thermophilic digesters exhibited better performance compared to mesophilic digesters, particularly under high organic loadings and shorter retention times. Madenovska and Ahring [16] suggested that specific biogas production rates were higher under thermophilic conditions than under mesophilic conditions, attributed mainly to a higher maximum specific growth rate (2-3 times) of thermophilic microbes compared to their mesophilic counterparts. In addition, thermophilic digestion is now becoming of great interest, due to its potential in higher reduction of pathogens compared to mesophilic digestion.

Overall, the thermophilic digestion process has better methane production but the process does have the reputation of being more sensitive to environmental changes than mesophilic digestion [17] [18]. In addition, increase in methane yield or production rate from a thermophilic process has to be balanced against the increased energy requirement for maintaining the reactor at the higher temperature.

2.1.3.3 Carbon to nitrogen ratio (C/N ratio)

The relationship between the amount of carbon and nitrogen present in organic materials is represented by the C/N ratio. The best C/N ratios range for anaerobic digestion is 20-30. A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens resulting in lower gas production. While, a lower C/N ratio may cause ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria. Optimum C/N ratios of the digester materials can be achieved by co-digestion materials of high and low C/N ratios, such as energy crops or silage mixed with sewage or animal manure. A review of such option is detained in section 2.4.

2.1.4 Pretreatment methods

Anaerobic digestion has been demonstrated to be a valuable treatment. However, most wastes with high TS content, such as waste active sludge, animal manure, and agricultural residue, are only slowly degradable as a result of the particulate characteristics of the waste. Therefore, the applications of AD to these high-solid wastes are often limited by very long retention times and low overall degradation efficiency.

As described in section 2.1.2, anaerobic digestion consists of four stages (hydrolysis, acidogenesis, acetogenesis, and methanogenesis). The hydrolysis stage is usually identified as the rate limiting step when high solids organic waste is degraded [19]. During hydrolysis, cell walls are ruptured and extracellular polymeric substances are degraded resulting in the release of readily available organic material for acidogenic bacteria. This mechanism is particularly important in the digestion of sludge, since the major constituents of its organic fraction are cells, being a relatively low degradable substrate for microbial degradation [20].

In order to reduce the impact of the rate-limiting step, many pretreatment methods have been developed, especially for the treatment of waste active sludge (WAS). These methods include thermal, mechanical, chemical, biological, ultrasonic, and combinations of these. These pretreatments cause the lysis or disintegration of sludge cell permitting the release of intracellular matter that becomes more accessible to anaerobic microorganisms [21].

2.1.4.1 Thermal pretreatment

Thermal pretreatment was shown as early as 1970 to be an effective pretreatment method for anaerobic digestion [22]. This pretreatment method was designed to improve anaerobic digestibility and dewatering properties. Heat produced during thermal treatment disrupts the chemical bonds of the cell wall and cell membrane resulting in the release the intracellular components and enhance anaerobic digestibility.

Stuckey and McCarty [23] examined the effect of thermo-chemical pretreatment on the anaerobic biodegradability of WAS under mesophilic and thermophilic conditions and found that WAS biodegradability increased with increasing pretreatment temperature up to maximum at 175˚C , and this resulted in an increase in methane production of 27% compared to a control. Valo et al. [24] evaluated the effects of temperature and time of thermal pretreatment on anaerobic digestion of sludge and reported those increments in SCOD of around 25% and 60% after thermal treatment of secondary sludge at 130 and 170˚C, respectively and increments of 21% and 45% in biogas production. However, Climent et al. [25] found that only low temperature thermal treatment (70˚C) increased biogas production by 50% and found no effect for high temperature treatment.

Mladenovska et al. [26] investigated application of thermal treatment at 100-140°C for 20 and 40 minutes as pretreatment method prior to anaerobic digestion of a mixture of cattle and swine manure using BMP assay. They found the ultimate methane potential determined after 80 days of incubation revealed that in comparison to the control, an enhancement of specific methane yield was in the range of 9-24% and 10-17% for the 20 and 40 min treatment, respectively. A similar study, designed by Bonmati et al. [27], to determine whether low temperature thermal pretreatment (80°C) for 3 hr improves pig slurry anaerobic digestion using BMP assays reported a decrease of the methane yield.

2.1.4.2 Mechanical pretreatment

Mechanical treatment is physically disintegration resulting in a disruption of particle structure.

Nah et al. [28] investigated the effect of mechanical pretreatment of WAS by jetting and colliding to a collsion-plate at 30 bar and found enhanced volatile mass reduction as well as biogas production. Kopp et al. [29] evaluated mechanical cell disintegration using stirred ball mill, high-pressure homogennisation, and shear gap homogenisation on anaerobic digestion and found that the degradation is accelerated by 20% after 4 days and the digestion time could be reduced, especially when using immobilized microorganisms. Choi et al. [30] pre-treated WAS with mechanical jet and reported that VSS increased by 50%.

2.1.4.3 Chemical pretreatment

Chemicals have also been used as pretreatment methods to hydrolyze the cell wall and membrane resulting in higher solubility of the organic matter contained within the cells.

A pilot-scale study on the enhancement of anaerobic co-digestion of primary sludge and WAS using low-level alkaline (NaOH) was performed by Knezevic et al. [31] and they found that there was no significant improvement in VSS reduction. However, gas production was improved

Effects of alkaline (NaOH) treatments on the anaerobic digestion of WAS were also investigated by Tanaka et al. [32]. They compared pretreatment methods of NaOH addition, heating (thermal), and heating with NaOH addition and found that best results among three were thermo-chemcial pretreatment.

Liao et al. [33] studied chemical pretreatment for the solublilization of organic materials from fibers contained in dairy manure. Their study demonstrated that treating dairy manure with sulphuric acid was an efficient method for the release of monosugars from lignocellulosic material, but the anaerobic biodegradability of this waste was not further tested.

2.1.4.4 Ultrasonic pretreatment

The principle of ultrasonic treatment relies on the cavitation process to disintegrate cell walls. Researchers 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 [34] [35]. Tiehm et al. [36] demonstrated that the pretreatment of waste activated sludge by ultrasonic disintegration significantly improved microbial cell lysis and increased the volatile solids degradation as well as biogas production. More details on ultrasonic pretreatment are described in section 2.3.

2.1.4. 5. Comparison of various pretreatment methods

A study conducted by Kim et al. [19] evaluated the effects of various pretreatment methods (thermal, chemical, ultrasonic, and thermo-chemical) on the biogas production from WAS and pollutants reduction owing to solubilization enhancement, particle size reduction, increased soluble protein, and increased soluble COD. The thermal pretreatment was applied at 121°C for 30 min. For the chemical pretreatment, NaOH was added to 300 ml of WAS at final concentrations ranging from 0-21 g/L. Ultrasonic pretreatment was performed at 42 kHz for various times (from 10 to 120 min). They found that methane production was significantly increased by the four pretreatments and the thermo-chemical pretreatment producted greatest amount of biogas (an overall 34.3% greater methane yield and 67.8% more SCOD compared with the control).

The effect of three pretreatment methods (mechanical, chemical, and thermal) on methane production and anaerobic biodegradability of swine wastes was tested by Gonzalez-Fernandez et al. [37]. They concluded that the best pretreatment was thermal application prior to AD which increased methane production by 35%.

Ardic and Taner [38] investigated the effects of thermal, chemical and thermo-chemical pretreatment on biogas and methane yield of fresh chicken manure. The aqueous slurries of the chicken manure (10% TS) were treated with NaOH, H_2SO_4 (10, 15 and 20%) and without chemicals, at room temperature as well as at 100°C for one and two hours. They reported that thermo-chemical pretreatment of chicken manure for two hours was the most effective method.

Weemaes et al. [20] compared the effectiveness of different pretreatment methods on sludge disintegration. They concluded that mechanical disintegration often appears to require high capital cost and is also energy intensive. Thermal and thermo-chemical treatments on the other hand require high temperatures and sometimes high pressure. Therefore, expensive construction materials are required in order to prevent construction problems. Chemical treatments were shown not to be effective on sludge digestion at ambient temperatures.

2.1.5 Biochemical methane potential (BMP) assay

Anaerobic digestion is usually considered to be a capital intensive project. Thus, it is important to determine the potential methane yield from feedstock under anaerobic conditions using simple and rapid methods. A number of techniques are available to provide this information, however BMP test is the most popular method [39].

The BMP assay process was first established by Owen et al. [40] as a simple method to evaluate the anaerobic biodegradability of feedstock by monitoring cumulative methane production from a sample which is anaerobically incubated in a nutrient defined medium.

The BMP assay is conducted with serum bottles (250 ml), rubber septums, a gas syringe, compressed CO_2 and N_2 gas as well as anaerobic inoculum (optional). An aliquot of substrate is placed in a serum bottle with anaerobic inoculum at certain ratio based on experiment design. For samples that already contain anaerobic bacteria (such as wastewater sludge and animal manure), adding additional anaerobic inoculum is not necessarily required. After adding inoculum and substrate, additional deionized water is added to bring the volume to 160 ml and then gassed at a flow rate of approximately 0.5 L/min for 5 min with a mixture of 30% CO_2 and 70% N_2.

After purging with gas, bottles are sealed with rubber septums. Sealed serum bottles are then placed on a shaker (150-200 rpms) and incubated under a temperature controlled conditions (usually mesophilic or thermophilic) for 30 days. The incubation period is typically 30 days to eliminate variations due to different metabolism rates. However, some substrates may require a longer incubation period, especially if no anaerobic inoculum were added.

Gas-volume sampling and removal during incubation is performed with glass syringes equipped with 20-gauge needles. The sample syringe is initially flushed with the mixed gas (30% CO_2 and 70% N_2) and lubricated with deionzed water. Measure the biogas as needed by inserting the needle of syringe horizontally into the septum. Gas-volume determinations are made by allowing the syringe plunger to move and equilibrate between the bottle and atmospheric pressures. Readings could be verified by drawing the plunger past the equilibrium point and releasing; the plunger should return to the original equilibration volume. Biogas collected from the assay bottles are analyzed for methane content using gas chromatography or other type gas analyzer. In order to minimize the methane yield contributed from inoculum, a blank (only inoculum with deionized water) is required for a baseline check.

Proper sample size and space volume are important for the precision and accuracy of results, and are chosen with the following guide-lines: a) provide a measurable, but not excessive, amount of methane, usually 20-120 ml, b) ensure that nutrients will not be limiting, and c) eliminate possible substrate toxicity [41]. Typically for a readily-degradable and non-toxic organic, a 2-20 ml liquid sample containing 150 mg COD is generally used with a final total liquid volume in the assay bottle of 160 ml [40]. Total liquid volumes up to 200 ml could also be used, in order to decrease the void-volume and improve the accuracy of methane determinations when low gas production is expected.

BMPs have been used to evaluate the anaerobic digestibility of various feedstocks. Kirk and Bickert [42] utilized BMPs to evaluate biogas production potential from mechanically sand separated dairy manure and chemical phosphorus separated dairy manure. Demirer and Chen [43] utilized BMPs to evaluate the performance of leaching bed reactors applying in anaerobic digestion of undiluted dairy manure. Chynowetch et al. [44] determined the effect of the inoculum-to-feed ratio on the rate of conversion of biomass and waste feedstocks using BMPs assays and reported that an inoculum-to-feed ratio of 2:1 was shown to give maximum conversion rates.

2.2 Anaerobic Digestion of Ethanol Stillage

2.2.1. Background

Current attitudes toward the environment and a political movement that desires to reduce dependence on foreign oil have bolstered liquid biofuel production in the United States. Total annual U.S. corn ethanol production has increased considerably between 1997 and 2007 from 1.3 billion gallons to 7.2 billion gallons [45]. Currently, the U.S. has approximately 168 ethanol plants in service with a production capacity of more than 9 billion gallons per year [45]. In comparison, the U.S. consumed approximately 146 billion gallons of petroleum in 2007 (EIA). Much of the fuel ethanol production capacity in the United States is concentrated in Midwestern states. Iowa had 30 ethanol plants in operation by the end of 2007 and produces nearly 2.1 billion gallons of ethanol annually (Iowa State University Extension, 2008).

Corn is converted into ethanol primarily by two processes: wet milling and dry milling . In wet milling, the corn kernel is fractionated into primary components (germ, fiber, and starch) resulting in several process streams and co-products. In dry milling, the corn kernel is not fractionated and only one co-product is produced at end: distillers dried grains with solubles (DDGs). Compared to wet milling, dry-grind requires less equipment and less capital investment. Traditionally, most ethanol has been produced by wet milling. Recently, dry milling has increased rapidly due to relatively lower capital costs.

Some of the environmental-based criticism of corn-ethanol has mainly focused on the small positive net energy balance that is achieved [46]. According to the U.S. Department of Agriculture, ethanol yields 1.64 units of energy for each unit of energy it took to produce. Hill et al. [47] calculated through life-cycle assessment and reported that 26% (a 1.26 net energy balance ratio) more energy is gained from ethanol than is required fossil fuels energy for ethanol production. However, this net gain is mostly due to energy credit of ethanol co-products. They also reported a relatively large input of 0.6 units energy per unit ethanol-energy output for processing the corn grain into ethanol and co-products. One way to improve the net energy balance ratio is to recover the energy from ethanol co-products.

Anaerobic digestion can serve as an effective method for recover of energy from corn ethanol co-products (such as stillage) and convert it to biogas, which is a readily usable fuel for the ethanol facility. This treatment option is detailed in current section.

2.2.2. Stillage production

2.2.2.1 Dry milling process

The dry milling process is designed for fermentation of the entire corn kernel. First, the ground corn is mixed with water. After the slurry has been liquefied, yeast is added to the mash and allowed to ferment. Yeast fermentation to produce ethanol does not utilize all of the available organics, which results in an aqueous co-product referred to as whole stillage.

After fermentation, whole stillage is withdrawn from the bottom of the distillation unit and is centrifuged to produce wet grains (centrifuge solids) and thin stillage. Using an evaporator, thin stillage is concentrated to form syrup. This is added to the wet- grains process stream and dried to form DDGs. Therefore dry-grind processing results in several potential co-products including centrifuge solids, syrup, DDGs, and thin stillage. This whole process is shown in Figure 2.

2.2.2.2 Availability

Up to 10 to 13 gallons of stillage may be generated for every gallon of ethanol produced [48]. Currently, the US has approximately 168 ethanol plants in service with a production capacity of more than 9 billion gallons per year [45]. That means the estimated annually stillage production could be up to 90 to 117 billion gallons.

2.2.2.3 Utilization

Distillers' dried grain with solubles is traditionally disposed of by direct feeding to livestock. DDGs contains a mixture of crude fat, protein, and fiber. High fiber content limits the use of DDGs to animal diets [49]. However, since DDGs is rich in protein and fat, it is still widely used as an excellent source of supplemental bypass protein for cattle. Syrup and wet grains sometimes are also marketed as animal feed. Syrup is difficult to dry to a free-flowing powder [49]. Therefore, it usually handled in liquid form and added directly as a dietary ingredient. Its use is usually limited to local producers as result of high moisture content. Syrup contains relatively high concentrations of Na, K, and P which may raises concern on the long term physiologic effects on animals [49].

Historically, market prices of corn ethanol co-products are similar to corn and soybean meal. However, supply and demand play an important role on ethanol co-product prices and the economics of producing a certain type of ethanol co-product, such as DDGs. As the ethanol industry has rapidly expanded across the nation, the supply of various corn co-products has become more abundant and the price of co-product may drop in the future.

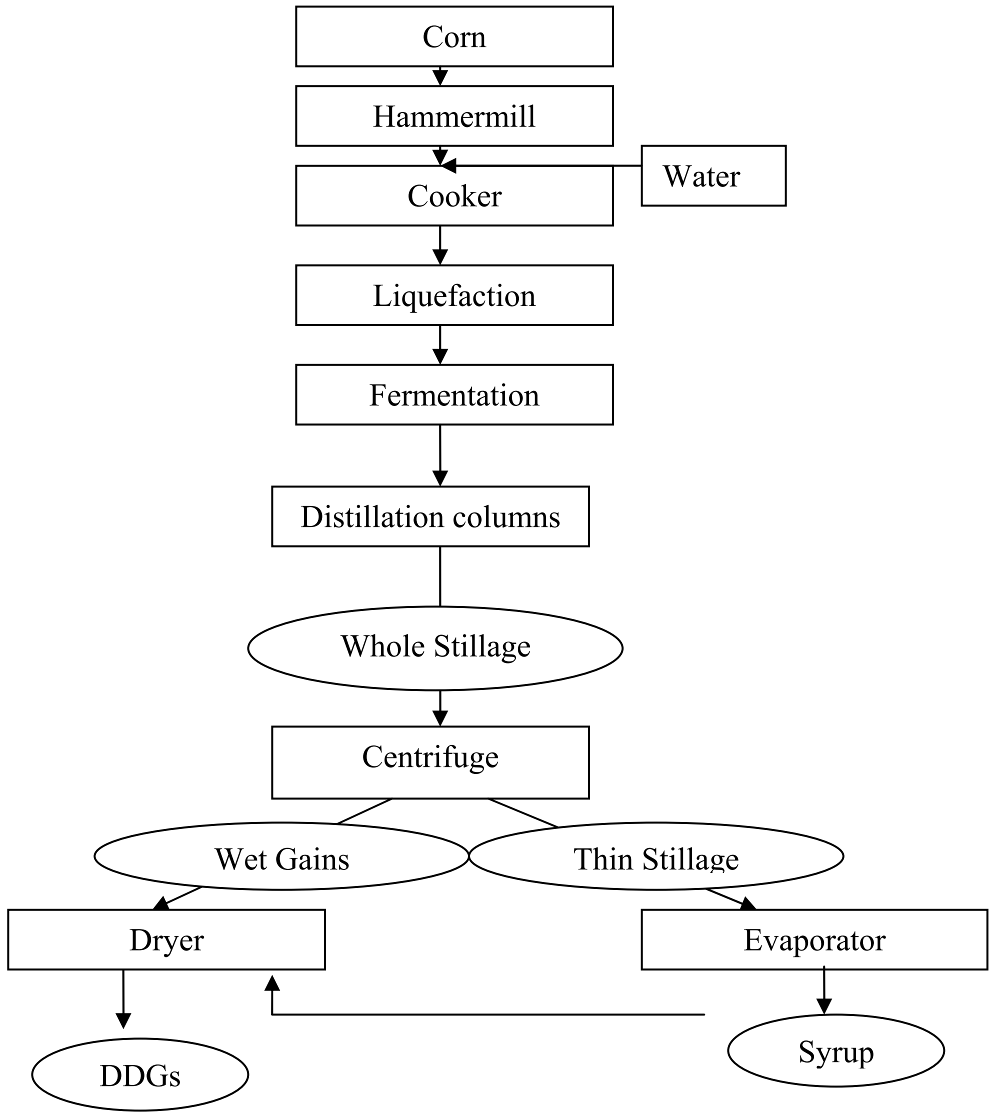


Figure 2. Dry-grind corn process

2.2.3 Stillage characterization

Olguin et al. [50] reported that the COD of stillage effluents are usually more than 100,000 mg/L which suggest a great potential for energy recovery. However, the COD concentration of stillage may vary considerably and depends on feedstock and operating conditions in the dry mill. Stillage usually contains sufficient nitrogen and phosphorus to support microbial growth. Dahab and Young [51] reported the COD and BOD of thin stillage were 59,000 and 43,000 mg/L, respectively. Thin stillage tested in their study contained 546 mg/L nitrogen, 228 mg/L phosphorus, and 299 mg/L sulfur. DDGs typically contain 95-98% dry matter (DM), 4.2% nitrogen, 0.71% phosphorus, and 0.33% sulfur [49]. Chemcial characteristic of syrup was reported to be 30-40% DM, 3.2% nitrogen, 0.54% phosphorus, and 0.5% sulfur [49].

2.2.4 Anaerobic digestion of ethanol stillage

2.2.4.1 Anaerobic digestion of ethanol stillage under mesophilic condition

Stover [52] and his colleagues were the earliest scientists to demonstrate 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 of methane could be achieved from 60,000 gallons of thin stillage per day.

Later, Ganapthoi [53] developed a study to test the anaerobic digestion of diluted liquid portion of liquid-solid separated thin stillage effluent under mesophilic conditions using a continuously stirred tank reactor (CSTR).

Anaerobic digestion of stillage from various fermentation feedstocks, such as barley, red wine, beet molasses, and cane molasses has also been studied with a diverse group of reactors. For example, Shin et al. [54] reported that anaerobic digestion of distillery (barley and sweet potato) wastewater in a two-phase upflow anaerobic sludge blanket (UASB) system resulting in a daily methane production of 0.28 L/g COD_{added} under mesophilic condition. The UASB reactor was also well applied for mesophilic anaerobic digestion of stillage from distilleries using sugar beet, sugar cane molasses, wine, or corn [55]. Garcia-Calderon et al. [56] found that using down-flow fluidization technology for anaerobic digestion of red wine stillage produced 0.3 L methane /g COD added under mesophilic conditions.

2.2.4.2 Anaerobic digestion of ethanol stillage under thermophilic conditions

Thin stillage contains relatively high fats, oils, and grease (FOG). When thin stillage is digested in a mesophilic digester, FOG could accumulate and cause foaming problem [57]. However, it is not a problem in thermophilic digesters resulting from sufficient solubilization and degradation of FOG at higher temperatures [58]. In addition, application of thermophilic digestion would only require cooling the stillage to less than 60°C, which occurs naturally during temporary stillage storage.

Agler et al. [59] studied the applicability of an integrated method of thermophilic anaerobic digestion of thin stillage from dry mill corn grain- to- ethanol plants by utilizing anaerobic sequencing batch reactors (ASBRs). They estimated the methane yield by total COD loading rates and removal rates. The estimated methane yield was 0.245 L/g COD_{added} (approximately equals to 0.35 L/g VS added) after reaching sustainable operating performance. They also suggested that methane generated from thermophilic anaerobic digestion of corn thin stillage could replace 51% of natural gas consumed at a conventional dry mill and improve the net energy balance ratio from 1.26 to 1.70.

Schaefer et al. [60] tested anaerobic digestion of corn ethanol thin stillage at thermophilic temperature (55°C) using two completely stirred tank reactors. A significant reduction of VS (89.8%) was observed at the 20-day hydraulic retention times (HRTs). Methane yield ranged from 0.6 to 0.7 L/g $VS_{added.}$during steady-state operation. Ultrasonic pretreatment was used for one digester, however, no significant improvement was observed. They estimated that ethanol plant natural gas consumption could be reduced by 43-59%.

Results from a full-scale plant using thermophilic anaerobic digestion of stillage from a beet molasses-to-ethanol process presented by Vlissidis and Zouboulis [61] showed that daily methane production from an UASB reactor was up to 0.43 L/g COD removed and the efficiency in converting organic solids to CH_4 was 70%. A similar study [62] demonstrated that a daily methane production of 0.12 L/g COD added from an alcohol distillery wastewater (cane molasses vinasse) using USAB reactors under thermophilic anaerobic condition. Biogas production of anaerobic digestion stillage from cane molasses-to-ethanol plant was also evaluated by Rintala [63] and a methane yield of 0.17 L/g COD added was reported using a 2-staged continuously stirred reactor (2-CSTR) under thermophilic condition. A laboratory experiment that tested anaerobic fluidized bed (AFB) technology as a means for the treatment of stillage from wine distillery plant at thermophilic conditions was presented by Perez et al. [64] and they indicated that AFB systems can achieve daily methane yield of 0.33 L/g COD removal with a daily COD loading rate of 32.3 g COD/L. They also reported a methane yield of 0.18 L/g COD added/day from thermophilic anaerobic treatment of stillage from wine distillery plant using an up-flow fixed film (UFF) reactor.

2.3 Anaerobic Digestion of Animal Waste

2.3.1 Background

Anaerobic digestion of animal manure: 1) produces renewable energy that can be used for heat and power; 2) reduces greenhouse gas and ammonia emissions from livestock waste; 3) substantially reduces odor; 4) potentially reduces pathogens in manure; 5) reduce surface and groundwater contamination, 6) digested manure is high quality fertilizer.

The limited application of manure AD systems in the U.S. is mainly attributed to high capital cost, operation and maintenance costs, lacking of management and technical expertise, and potential safety issues.

As of April 2008, EPA AgSTAR estimated that there were 114 farm-scale digesters operating at commercial livestock farms in the United States [65]. According to AgSTAR, the majority of those operational digesters (108 digesters) were used for generating electrical power for on-farm use. It is estimated that annually 182,000 MWh of electricity were generate by these systems and the combustion of biogas prevented the emissions of approximately 36,600 metric tons of methane annually [65].

2.3.2 Historical development

Reiset reported that methane could be formed from decomposing manure in 1856 [1]. Beginning in the 1930s, Arthur Bunswell and his colleagues conducted extensive research on the nature of the process and its potential application for treatment of industrial wastewaters and agricultural residues including animal waste [66]. During the 1970s, rising oil prices bolstered an interest in developing “commercial farm-scale” biogas systems in the United States [67]. However, in the 1980s, anaerobic digester interest declined resulting from low-cost fuels and digester problems. Many of these initial biogas systems failed possibly because: 1) operators lacked skill to operate the digester; 2) selected digester systems were not compatible with manure handing system; 3) operation and maintenance was too expensive; 4) no technical support was available; and 5) equipment was not appropriately installed [67].

Recently, the development of anaerobic digesters for livestock manure treatment has accelerated for various reasons including: increased technical reliability of anaerobic digesters, growing concerns of environmental quality, reduction of land applied manure, and available finance support offered by government.

2.3.3 Anaerobic digestion of cattle waste

2.3.3.1 Characterization

The physical and chemical characteristics of cattle manure vary considerably depending on many factors such as: diet, bedding material, and manure management method. Cattle manure slurry contains a large fraction of particulate matter (6-8% on a w/w basis) and most of the biologically degradable component of the slurry is contributed by the particulate matter [68]. Some feed additive includes antibiotics which may be harmful to anaerobic bacteria.

2.3.3.2 Effect of manure liquid-solids separation on methane production

A study conducted by Lo et al. [69] evaluated the effect of liquid-solids separation pretreatment on methane production from mesophilic digestion of dairy cattle manure and found that the methane production rate from screened waste (0.5 L CH_4/L/day) was approximately double on per gam VS basis that obtained from unscreened slurry at 6 days hydraulic retention time (HRT).

Later, Liao et al. [70] conducted a similar study and found similar results that screening out the coarse solids from manure before digestion increased total methane production on per gam VS basis.

2.3.3.3 Review of application and effectiveness

Lo et al. [72] compared the performance of digestion dairy manure using conventional digester and fixed film digester and reported that the conventional digester would not sustain a high gas production rate because of bacteria biomass washout and a maximum methane productivity was of 6.33 L CH_4/L/day was obtained from the fixed-film reactor with a loading rate of 672 g VS/L/day.

One-phase (fix-film reactor) and two-phase anaerobic digestion systems (completely mix reactor and fixed-film reactor) were also studied by Lo et al. [73] in 1985 using screened dairy manure as feed material and they demonstrated that reactor performance was greatly improved when acidogenic and methanogenic phases could be controlled and operated independently.

Recently, Demirer and Chen [74] designed a study on two-phase anaerobic digestion of unscreened dairy manure. The results indicated that the use of a two-phase reactor resulted in 50 and 67% higher biogas production at organic loading rate (OLR) of 5 and 6 g VS/L, respectively.

2.3.4 Anaerobic Digestion of Swine Slurry

2.3.4.1 Characterization

Hansen et al. [75] concluded that a free ammonia concentration of 1.1 g-N/L or more could cause inhibition of anaerobic digestion of swine manure process at pH 8.0, and higher free ammonia concentrations resulted in a decreased apparent specific growth rate.

2.3.4.2 Effect of manure liquid-solids separation on methane production

González-Fernández et al. [76] evaluated the effect of three pretreatment methods (mechanical, chemical, and thermal) on methane production and anaerobic biodegradability of swine wastes, including 1) separation of liquid and solid using a 0.25 mm pore size screen (mechanical pretreatment); 2) adding a flocculant agent, and strong acid and alkali (chemical pretreatment); 3) thermal application (170°C). They reported that methane production was enhanced by flocculation pretreatment (11%), alkali (13%), and thermal treatment (35%). However, no mechanical pretreatment improvement of methane yield was observed in this study.

2.3.4.3 Review of application and effectiveness

Numerous studies have been done on anaerobic digestion of swine lurry under psychrophilic, mesophilic, and thermophilic conditions using different types of digesters.

Masse et al. [77] investigated the feasibility of using psychrophilic anaerobic digestion in sequencing batch reactors to digest ground swine carcasses and swine manure slurry at 20 and 25°C and the methane production ranged from 0.27 to 0.33 L CH_4/ g COD_{added} with methane content ranged from 72% to 76%.

Hill and Bolte [78] conducted a study to determine the methane production characteristics of low concentration liquid swine waste using conventional anaerobic fermentation under mesophilic condition. They found that conversion to methane is practical for 5 and 3 day HRT but that considerable stress occurred at the 2 day HRT or less. Methane production was observed to be 0.36 L/g VS_{added} ranged for the 5 day HRT.

Creamer et al. [79] investigated the potential of biogas production from swine manure as the sole substrate under thermophilic conditions and showed that anaerobic microorganism can be readily acclimated when nitrogen concentrations is less 7.2 g/L under thermophilic conditions.

The effects of different digesting temperature, temperature shocks and feed loads, on the biogas yields and methane content were evaluated by Chae et al. [80]. They found ultimate methane yields of 327, 389, and 403 ml/g VS_{added} were obtained at 25, 30 and 35°C. The methane content increased at increasing digestion temperatures.

Lo et al. [81] evaluated two hybrid USAB reactors to treat screened swine wastewaters and reported that over 57% COD removal and 0.71 L CH_4/L/day were obtained.

A pilot study conducted by Feng et al. [82] showed that biogas production from the mixture of swine feces and urine was the highest (865-930 L/g VS_{added}) compared with swine feces alone at the OLR of 0.5-5.3 kg-VS/m^3/d and the HRT of 9 days.

Kotsopoulos et al. [83] tested the effect of natural zeolite on the thermophilic anaerobic digestion of swine slurry and suggested that adding natural zeolite (8-12 g/L) could increase methane production.

2.4 Co-digestion

Co-digestion is the simultaneous digestion of a homogenous mixture of two or more substrates. Traditionally, anaerobic digestion was a single substrate, single purpose treatment. Recently, it has been realized that AD as such became more stable when the variety of substrates applied at the same time is increased.

The most common situation is when a major amount of a main basic substrate (e.g. manure or sewage sludge) is mixed and digested together with minor amounts of a single, or a variety of additional substrates. In the co-digestion of plant material and manures, manures provide buffering capacity and a wide range of nutrients, while the addition of plant material with high carbon content balances the carbon to nitrogen (C/N) ratio of the feedstock, thereby decreasing the risk of ammonia inhibition and increasing biogas production [84].

Co-digestion can provide a better nutrient balance and therefore better digester performance and higher biogas yields. Desai et al. [84] reported the combination of whey and poultry manure had been found to be capable of maintaining the proper C/N ratio (20-30:1) in the reactor. According to Murto et al. [85], a highly buffered system was obtained by co-digestion of solid slaughterhouse waste, manure, and fruit and vegetable waste and the process worked well with gas yields of 0.8-1L/g VS_{added}.

Anaerobic co-digestion of grass silage, sugar beet tops, and oat straw with cow manure was evaluated by Lehtomaki et al. [86] in semi-continuously fed laboratory continuously stirred tank reactors (CSTRs). It showed that co-digestion compared with manure alone at a similar loading rate, volumetric methane production increased by 65, 58 and 16% in reactors fed with 30% VS of sugar beet tops, grass, and straw, respectively, along with manure. Gelegenis et al. [87] examined a series of laboratory experiments in continuously stirred tank reactors at mesophilic conditions, fed semi-continuously with various mixtures of diluted poultry manure and whey and found biogas production increased almost 40%. The possible use of potato tuber and its industrial by-products (potato stillage and potato peels) on farm-scale co-digestion with pig manure was examined by Kaparaju and Rintala [88]. The results showed that the potato tuber and its industrial by-products can be co-digested with pig manure at a loading rate of 2 kg VS m^{-3} day^{-1} in CSTR at 35°C.

2.5 Ultrasonic Pretreatment Applied in Anaerobic Digestion Process

The rate-limiting process of anaerobic digestion is usually the hydrolysis stage. Therefore, enhanced performance of the anaerobic process could be achieved by finding a pretreatment to accelerate hydrolysis. Compared with other pretreatment methods, ultrasonic pretreatment exhibits a great potential of not being hazardous to the environment and is potentially economically competitive (no data is provided yet) [89].

2.5.1 Principles

2.5.1.1 Mechanism of ultrasonic

The frequency of ultrasonic waves is between 20 kHz and 10 MHz [90]. When acoustic energy is supplied to a liquid, gas bubbles are formed and grow by absorbing gas and vapor that was previous dissolved in the liquid [91]. These bubbles can implode resulting in very extreme conditions of temperature (5000 K) and pressure (50 MPa) and cavity, this phenomenon is called cavitation. The localized temperature and pressure increases are sufficient to increase chemical reactivity, polymer degradation, and chemical free-radical production. Dewil et al. [90] concluded that cavitation could result in 1) the acceleration of chemical reactions resulting from a locally high temperature and pressure; 2) extreme shear forces in the liquid, thereby mechanically attacking components; 3) the formation of highly reactive radicals which can assist chemical reactions to take and 4) the additional destruction of specific compounds since cavitation bubbles are surrounded by a liquid hydrophobic boundary layer which permeates volatile and hydrophobic substances, subsequently reacting in the gas bubble.

Ultrasonic treatment is known to disintegrate sludge flocs and disrupt microbial cell walls resulting in the release of soluble substances [92]. Tiehm et al. [93] demonstrated that applying ultrasonic (3.6 kW, 31 kHz, 64s) for sludge disintegration can release the organic substances into the sludge and the SCOD in the supernatant increases from 630 to 2270 mg/L. Beneabdallah EI-Haji [94] reported that ultrasonic pretreatment decreased sludge particle size and increased the SCOD in the supernatant.

2.5.1.2 Ultrasonic system

There are four major components of an ultrasonic system including the power supply, converter (transducer), booster and horn (Figure 7). The electrical energy provided by the power supply is fed to the converter that transforms it to mechanical motion at ultrasonic frequencies. The mechanical motion is then transmitted through a booster to the horn. The booster is a mechanically amplifier to help increase the amplitude generated by the converter. The horn is an acoustic tool that transfers the vibratory energy directly to the media being treated.

2.5.2 Review of application and effectiveness

Numerous studies have been conducted to evaluate the performance of ultrasonic applications for wastewater sludge pretreatment. Recently published literature on ultrasonic applications in wastewater sludge pretreatment will be briefly reviewed in this section.

Figure 7. Major components of an ultrasonic system

2.5.2.1 Evaluation of ultrasonic disintegration efficiency

The purpose of ultrasonic pretreatment is to destroy the cell wall and release the intracellular materials [96]. In addition, ultrasonic pretreatment also disintegrates sludge flocs and break large organic particles into smaller-size particles. Different parameters have been applied to evaluate sludge disintegration efficiency including physical (such as particle size analysis) and chemical (such as SCOD analysis) analysis.

Particle size analysis is one of the techniques adopted to evaluate the effectiveness of ultrasonic disintegration. Bougrier et al. [97] investigated the effect of ultrasonic pretreatment on the particle size distribution at different specific energy inputs and found that particle size distribution was a peak centered on 30 µm and the volume occupied by small particles increased with the specific supplied energy. In addition, the volume was occupied by particles bigger than 100 resulting from a re-flocculation phenomenon. They concluded that the minimum energy required to break cell walls was about 1000 kJ/kg TS. Chu et al. [98] studied the effect of different ultrasonic densities and times on floc size at a frequency of 20 kHz and founded that only when the power level has exceeded 0.22 W/ml would the particle size apparently decrease. At 0.44 W/ml, the floc size reduced to less than 3 µm in 20 min. However, further ultrasonc would only mildly reduce the floc size further. Another study conducted by Tiehm et al. [99] showed that ultrasonic pretreatment applied at a frequency of 31 kHz for 29.5 and 96 s could decreased the sludge particle size from 165 µm to 135 µm and 85 µm, respectively.

The SCOD is another parameter that is used to evaluate the efficiency of sludge disintegration. It is much more quantitative measurement compared to particle size analysis. However, ultrasonic pretreatment also disintegrates extra-cellular matter and extracellular polymer substances [96]. Therefore SCOD is a gross parameter to quantify the solubilization of the sludge. Nearly all literature published on ultrasonic disintegration included SCOD measurement as a measure of sludge disintegration efficiency [96].

A number of studies evaluated SCOD release at different specific energy inputs [96]. Varitations are most likely attributed to energy transfer efficiencies of ultrasonic units, TS content of sludge, pH, and temperature.

2.5.2.2 Factors affect the ultrasonic disintegration efficiency

Many factors could affect the ultrasonic disintegration including the sludge characteristics (TS content, temperature, pH, and particle size) and the ultrasonic conditions (ultrasonic time, intensity, density, frequency, amplitude, and power input).

Grönroos et al. [100] reported that ultrasonically assisted disintegration clearly increased the amount of SCOD of sludge. In addition, ultrasonic power, TS of sludge, sludge temperature, and ultrasonic treatment time have the most significant effect on the disintegration. They also noticed that the energy efficiency with high ultrasonic power along with short treatment was higher than with low ultrasonic power with long treatment time.

Wang et al. [101] suggested that ultrasonic density, ultrasonic intensity, disintegrated sludge pH and sludge concentration all have impact on the sludge disintegration. The SCOD release was shown to increase when the sludge was ultrasonic at a higher pH. They also found that the SCOD release increased from 3,966 to 9, 9019 mg/L as the TS content increasing from 0.5 to 1% during 30 min of ultrasonic at ultrasonic density of 1.44 W/ml. In addition, better sludge disintegration was achieved at higher ultrasonic density for a short ultrasonic duration time than a lower ultrasonic density for a longer time. Based on the kinetics model with SCOD as dependent variable, the magnitude of the effect of each parameter on ultrasonic disintegration in the order: sludge pH > sludge concentration > ultrasonic intensity > ultrasonic density.

Operating frequency is also an important factor that controls the efficiency of ultrasonic systems. The cavitations effect generally decreases at high frequency range and increases at lower frequency range. Therefore, nearly all sludge disintegration tests are conducted at the lower frequency range of 20 kHz [96].

2.5.2.3 Ultrasonic pretreatment applied to anaerobic digestion of wastewater sludge

The effect of ultrasonic pretreatment on sludge degradability was investigated using ultrasonic at a frequency of 31 kHz and treatment time of 64 s by Tiehm et al. [99]. The temperature of the sludge increased from about 15°C to nearly 45°C. Ultrasonic treatment resulted in raw sludge disintegration, which was indicated by increase of SCOD in the sludge supernatant and size reduction of sludge solids. In the fermenters operated with identical residence times of 22 days, VS reduction was 45.8% for untreated sludge and 50.3% for ultrasonic pretreated sludge. The fermentation of ultrasonic pretreated sludge was stable even at the shortest residence time of 8 days with biogas production 2.2 times that of the untreated sludge. The authors suggested that due to ultrasonic disintegration a better degradability of raw sludge was achieved which permitted a substantial increase in throughput.

Later, Tiehm et al. developed another study [93] to investigate the pretreatment on waste activated sludge by ultrasonic disintegration to enhance the anaerobic sludge stabilization. The ultrasonic frequency varied from 41-3217 kHz. Sludge disintegration was most significant at low frequencies. The decreasing sludge disintegration efficiency at higher frequencies was due to smaller cavitation of bacterial cells. In addition, longer ultrasonic brought about the break-up of cell walls, the sludge solids were disintegrated and then dissolved organic compounds were released. The increase in digestion efficiency was proportional to the degree of sludge disintegration.

Yin et al. [103] conducted a study on anaerobic digestion behaviors of sewage sludge pretreated with ultrasonic at low frequency (20 kHz). They reported that treating the sludge with 600 W/m^2 for 1 min could reduce sludge volume. Ultrasonic pretreatment could also enhance digestion and reduce digestion time. To the same resolution ratio (49 %), the digestion time of sludge with ultrasonic pretreatment was 7 days less compared with the digestion time of sludge without ultrasonic. Their study again demonstrated that ultrasonic pretreatment could improve efficiency of anaerobic digestion of wastewater sludge.

Wang et al. [104] investigated the effect of ultrasonic pretreatment on anaerobic digestion WAS. They pretreated WAS with ultrasonic for 30 min with a frequency of 9 kHz. The authors found that the organic destruction efficiency enhanced by 11, 20, 38, and 46 % compared to a control on day 11 of anaerobic digestion, when the WAS was pretreated with ultrasonic for 10, 20, 30, and 40 min, respectively. The authors concluded that both the solubilization ratio of WAS and the corresponding methane generation depended on ultrasonic pretreatment time and the optimum pretreatment time for upgrading the anaerobic digestion of WAS should be 30 min.

Akin et al. [105] examined the effectiveness of ultrasonic pretreatment on WAS disintegration at different specific energy inputs, ultrasonic densities, and TS contents. The results showed that in order to achieve the same degree of particle size reduction, higher densities of 1.03 and 0.86 W/ml is required for higher TS contents of 4 and 6%, respectively. Ultrasonic density (W/ml) showed a significant effect on the efficacy of ultrasonic disintegration measured as SCOD release. The results indicated that the sludge disintegration efficiency declined significantly at higher TS content. Therefore, there is a limiting TS concentration that could be effectively disintegrated by ultrasonic, and this is governed by the capability of an ultrasonic unit in producing cavitation.

A study regarding the effectiveness of ultrasonic pretreatment on WAS under thermophilic condition was developed by Forster et al. [106]. They reported that sludge pre-treated with ultrasonic at the frequency of 23 kHz for 4 min increased the biogas production by 15 % with a hydraulic retention time of 10 days.

Bien et al. [107] evaluated the performance of ultrasonic pretreatment on biogas yield from sewage sludge using an ultrasonic unit with a frequency of 20 kHz and the amplitude of 14 µm for 60 s. They found that sludge pretreatment by ultrasonic increased biogas production by 20-24% compared to the un-treated sludge.

The impacts of different ultrasonic times, ultrasonic densities and solids concentrations on ultrasonic pretreatment of primary and secondary sludge were examined by Mao et al. [108]. The experimental results indicated that higher ultrasonic density performed more effectively in terms of specific energy. The authors also found that there exists an optimal solids concentration for optimum ultrasonic. Within the optimal solids concentration range, efficient ultrasonic can be effected and sludge would be disintegrated efficiently.

Show et al. [109] conducted a study on the correlation of ultrasonic operation condition, sludge property, formation and behavior of cavitation bubbles in sludge disruption under low-frequency ultrasonic. The results demonstrated that ultrasonic density exhibited the most significant role in cavitation bubble formation. Particle disruption could be optimized for energy input by ultrasonic at higher ultrasonic density and shorter ultrasonic treatment time.

Several pilot-scale demonstration trials using V-shaped ultrasonic chambers with a donut horn was conducted by Hogan et al. [110] at various locations. Improved solids destruction, substantial increases in gas production, and better residual solids dewatering are the primary benefits observed with ultrasonic pretreatment. However, there were no control digesters in those studies.

A full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge was conducted in Singapore [111]. This study was tested in the field under tropical conditions with a full-scale ultrasonic facility and two 5,000 m^3 egg-shaped digesters (control and treatment). In comparison with the control, the five-month field study showed that ultrasonic pretreatment of the sludge increased the daily biogas production up to 45 %. There were no significant differences in biogas composition from the control and treatment. The authors reported that up to 30 % more sludge solids conversion could be achieved with ultrasonic pretreatment.

Literature Cited

[1] McCarty PL. The development of anaerobic treatment and its future. Water Sci. Technology 2001, 44:149-156.

[2] Moigno AF. Mouras' Automatic Scavenger. *Cosmos* 1881, 622.

[3] Metcalf L, Eddy HP. American Sewerage Practice, III. Disposal of Sewage (1ed). McGraw Hill Book Company, Inc., 1915, New York.

[4] Buswell AM. Fundamentals of anaerobic treatment of organic wastes. Sewage and Industrial Wastes 1957, 29:717-721.

[5] Stander GJ. Water pollution research-a key to wastewater management. Journal Water Pollution Control Federation 1966, 38: 774

[6] Taylor DW. Full-scale anaerobic filter treatment evaluation. In 3rd National Symopsium on Food Processing Wates, U.S. EPA 1972, pp. 151.

[7] Switzenbaum MS, Jewell WJ. Anaerobic-attached film expanded-bed reactor treatment. Journal Water Pollution Control Federation 1980, 50:1953.

[8] Frankin RJ. Full-scale experience with anaerobic treatment of industrial wastewater. Water Science & Technology; 2001, 44(8): 1-6.

[9] Appels L, Baeyens J, Degreve J, Dewil R. Principal and potential of the anaerobic digestion of waste-activated sludge. Progress Energy Combust Science 2008, doi:10.1016/j.pecs.2008.06.002.

[10] Omstead DR, Jeffries TW, Naughton R, Harry P. Membrane-controlled digestion: anaerobic production of methane and organic acids. Biotechnoloy and Bioengineering Symposium 1980, 10:247-258.

[11] Vaccari DA, Storm PF, Alleman JE. Envrionmental biology for engineerings and scientists. Wiley Interscience, 2006.

[12] Ward AJ, Hobbs PJ, Holliman PJ, Jones DL. Optimization of the anaerobic digestion of agricultural resources. Bioresource Techology 2008, 99:7928-7940.

[13] Yu HQ, Fang HHP. Acidogenesis of dairy wastewater at various pH levels. Water Science and Technology 2002, 45:201-206.

[14] Boullagui H, Ben Cheikh R, Marouani L, Hamdi M. Mesophilic biogas production from fruit and vegetable wastes: bioreactor performance. Biochemcial Engineering Journal 2003, 86:85-89.

[15] Ortega L, Barrington S, Guiot SR. Thermophilic adaptation of a mesophilic anaerobic sludge for food waste treatment. Journal of Environmental Management 2008, 88(3): 517-525.

[16] Ahn JH, Foster CF. Kinetic analyses of the operation of mesophilic and thermophilic anaerobic filters treating a simulated starch wastewater. Process Biochemistry 2000, 36(1-2): 19-23.

[17] Mladenovska Z, Ahring BK, Growth kinetics of thermophilic *Methanosarcina* spp. isolated from full-scale biogas plants treating animal manure. FEMS Microbiol. Ecol. 2000, (30):225–229.

[18] Yilmaz T, Yuceer A. Basibuyuk M. A comparison of the performance of mesophilic and thermophilic anaerobic filters treating papermill wastewater. Bioresource Technology 2008, 99(1): 156-163.

[19] Kim J, Park C, Kim T, Lee M, Kim S, Kim S, and Lee J. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. Journal of Bioscience and Bioengineering 2003, 95 (3): 271-275.

[20] Weemaes MPJ, Verstraete W. Evaluation of current wet sludge disintegration techniques. J Chem Technol Biotechnol 1998, 73:83-92.

[21] Climent M, Ferrer I, Baeza M, Artola A, Vazquez F, Font X. Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions. Chemical Engineering Journal 2007, 133(1-3): 335-342.

[22] Sawayama S, Inone, S, Tsukahara K, and Ogi, T. Thermochemical liquidization of anaerobically digested and dewatered sludge and anaerobic pretreatment. Bioresource Technology 1996, 55:141-144.

[23] Stuckey DC , McCarty PL. The effect of thermal pre-treatment on the anaerobic biodegradability and toxicity of waste activated sludge. Water Resource 1984, 18: 1343–1353.

[24] Valo A, Carrère H, Delgenès JP. Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion. J. Chem. Technol. 1998, 73:83-92.

[25] Climent M, Ferrer I, Baeza MD, Artola A, Vazquez F, Font X. Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions. Chem Eng J 2007, 133:335–342.

[26] Mladenovska Z, Hartmann H, Kvist T, Sales-Cruz M, Gani R, Ahring BK. Thermal pretreatment of the solid fraction of manure: impact on the biogas reactor performance and microbial community. Water Science and Technology 2006, 53:59-67.

[27] Bonmati A, Flotats X, Mateu L, Campos E. Study of thermal hydrolysis as a pretreatment to mesophilic anaerobic digestion of pig slurry. Water Science and Technology 2001, 44(4):109-116.

[28] Nah IW, Kang YW, Hwang KY, Song KW. Mechanical pre-treatment of waste activated sludge for anaerobic digestion process. Water Resource 2000, 34: 2362–2368.

[29] Kopp J, Muller J, Dichtl N, Schwedes J. Anaerobic digestion and dewatering characteristics of mechanically disintegrated excess sludge. Water Sci Technol 1997, 36:129–136.

[30] Choi HB, Hwang KY, Shin EB. Effects on anaerobic digestion of waste activated sludge pre-treatment. Water Sci Technol 1997, 35:207–211.

[31] Knezevic N, Mavinic DC, Anderson BC. Pilot scale evaluation of anaerobic codigestion of primary and pretreated waste activated sludge. Water Environ. Res. 1995, 67: 835–841.

[32] Tanaka S, Kobayashi T, Kamiyama K, Signey Bildan ML. Effects of thermochemical pre-treatment on the anaerobic digestion of waste activated sludge, Water Sci Technol 1997, 35: 209–215.

[33] Liao W, Liu Y, Liu C, Wen Z, Chen S. Acid hydrolysis of fibers from dairy manure. Bioresource Technology 2006, 97:1687–1695.

[34] Wang, F; Wang Y and Ji M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. J. Hazar. Mater. B. 2005, 123:145–150.

[35] Benabdallah EI-Hadj T, Dosta J, Marquez-Serrano R, Mata-Alvarez J. Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene removal. Water Research 2006, 41(1):87-94.

[36] Tiehm A.; K. Nickel, M. Zellhorn, and U. Neis. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. Water Research 2001, 35 (8): 2003-2009.

[37] Gonzalez-Fernandez C, Leon-Cofreces C, Garcia-Encina A. Different pretreatments for increasing the anaerobic biodegradability in swine manure. Bioresource Technology 2008, 99(18):8710-8714.

[38] Ardic I , Taner F. Effects of thermal, chemical and thermochemical pretreatments to increase biogas production yield of chicken manure. Fresenius Environmental Bulletin 2005, 14:373–380.

[39] Shanmugam P, Horan NJ. Simple and rapid methods to evaluate methane potential and biomass yield for a range of mixed solid wastes. Bioresource Technology 2008, 100 (1):471-474.

[40] Owens JM, Chynoweth DP. Biochemical methane potential of municipal solid waste (MSW) components. Water Science Technology 1993, 27:1-14.

[41] Owens WF, Stuckey DC, Healy JB, Young LY, Mc Carty PL, Biomass for monitoring biochemical methane potential and anaerobic toxicity. Water Research 1979, 13: 485-492.

[42] Kirk D, Bickert W. The use of biochemical methane potential tests to evaluate the digestibility of processed dairy manure. ASABE Paper No. 044066. St. Joseph, Mich. U.S.A. ASABE 2004.

[43] Demirer GN, Chen S. Anaerobic biogasification of undiluted dairy manure in leaching bed reactors. Waste Management 2008, 28(1): 112-119.

[44] Chynowetch DP, Dolenc DA, Ghosh S, Henry MP, Jerger D. Biochemical methane potential of biomass and waste feedstocks. Biomass and Bioenergy 1993, 5:95-111.

[45] Renewable Fuels Association (RFA). 2008. Industry Statistics. Available at: http://www.ethanolrfa.org/industry/locations/.

[46] Farrell AE, Plevin RJ, Turner BT, Jones AD, O'Hare M, Kammen DM. Ethanol can contribute to energy and environmental goals. Science 2006, 311:506–508.

[47] Hill J, Nelson E, Tilman, D, Polasky S, Tiffany D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proc. Natl. Acad. Sci. U. S. A. 2006, *103*:11206–11210.

[48] Yeoh BG. Two-Phase Anaerobic Treatment of Cane-Molasses Alcohol Stillage. Water Science and Technology 1997, 36: 441-448.

[49] Rausch KD, Belyea RL. The future of coproducts from corn processing. Appl. Biochem. Biotechnol. 2006, 128:47-86.

[50] Olguin EJ, Doelle HW, Mercado G. Resource recovery through recycling of sugar processing by-products and residuals. Resources, Conservation and Recycling 1995, 15: 85-94.

[51] Dahab MF, Young JC. Energy recovery from alcohol stillage using anaerobic filters. Biotechnol. Bioeng. Symp. 1981, 11:381–397.

[52] Stover EL, Gomathinayagam G, Gonzalez R. Use of methane gas from anaerobic treatment of stillage for fuel alcohol production. In: Proceedings of the 39th Industrial Waste Conference, Purdue University, West Lafayette, Indiana. Boston Butterworth; 1984, pp. 57–63.

[53] Ganapathi, G. Dissertation In Civil Engineering; Oklahoma State University, 1984.

[54] Shin HS, Bae BU, Lee JJ, Paik BC. Anaerobic digestion of distillery wastewater in a two-phase UASB system. Water Science Technology 1992, 25 (7): 361–371.

[55] DriessenWJ, Tielbaard MH and Vereijken TL. Experience on anaerobic treatment of distillery effluent with the UASB process. Water Science Technology 1994, 30(12):193–201.

[56] Garcia-Calderon DP, Moletta BR, Elmaleh S. Anaerobic digestion of wine distillery wastewater in down-flow fluidized bed. Water Resource 1998, 32 (12): 3593–3600.

[57] Jeganathan J, Nakhla G, Bassi A. Long-term performance of high-rate anaerobic reactors for the treatment of oily wastewater. Environ. Sci. Technol. 2006, *40*: 6466–6472.

[58] Reimann I, Klatt A, Markl H. Treatment of fat-containing wastewater from the food processing industry with a thermophilic microorganism. Chem. Ing. Tech. 2002, *74*: 508–512.

[59] Agler M, Garcia ML, Lee ES, Schlicher M, Angenent. Thermophilic anaerobic digestion to increase the net energy balance of corn grain ethanol. Environ. Sci. Technol. 2008, 42(17):6723-6729.

[60] Schaefer SH, Sung, S. Retooling the ethanol industry: Thermophilic anaerobic digestion of thin stillage for methane production and pollution prevention. Water Environment Research 2008, 80(2):101-108.

[61] Vlissidis AA, Zouboulis I. Thermophilic anaerobic digestion of alcohol distillery wastewaters. Bioresource Technology 1993, 43:131–140.

[62] Harada H, Uemura S, Chen A-C, Jayadevan J. Anaerobic treatment of a recalcitrant distillery wastewater by a thermophilic UASB reactor. Bioresource Technology 1996, 55: 215–221.

[63] Rintala, J, High-rate anaerobic treatment of industrial wastewaters. Water Science Technology 1991, 24(1):69–74.

[64] Perez, M., L.I. Romero and D. Sales, Comparative perfomance of high rate anaerobic thermophilic technologies treating industrial wastewater. Water Research 1998, 32 (3): 559–564.

[65] EPA AgSTAR. Guide to Anaerobic Digesters 2008. Available at: http://www.epa.gov/agstar/operational.html#addatabase. Accessed on: Oct. 24th, 2008.

[66] Buswell AM. Fundamentals of anaerobic treatment of organic wastes. Sewage and Industrial Wastes 1957, 29:717-721.

[67] EPA AgSTAR. The AgSTAR program-Managing Manure with Biogas Recovery Systems. Available at: http://www.epa.gov/agstar/pdf/handbook/full_pdf.pdf. Accessed on: Oct. 24th, 2008.

[68] Ong HK, Greenfield PF, Pullammanappallil PC. An operational strategy for improved biomethanation of cattle-manure slurry in an unmixed, single-stage digester. Bioresource Technology 2000, 73: 87–89.

[69] Lo KV, Bulley PH, Whitehead AJ. The effect of solids-separation pretreatment on biogas production from dairy manure. Agricultural Wastes 1983, 8(3):155-165.

[70] Liao PH, Lo KV, Chieng ST. Effect of liquid-solids separation on biogas production from dairy. Energy in Agriculture 1984, 3:61-69.

[71] Umaña O, Nikolaeva S, Sanchez E, Borja R, Raposo F. Treatment of screened dairy manure by upflow anaerobic fixed bed reactors packed with waste tyre rubber and a combination of waste tyre rubber and zeolite: Effect of the hydraulic retention time. Bioresource Technology 2008, 99(15): 7412-7417.

[72] Lo KV, Whitehead AJ, Liao PH, Bulley NR. Methane production from screened dairy manure using a fixed-film reactor. Agricultural Wastes 1984, 9(3):175-188.

[73] Lo KV, Liao PH. Two-phase anaerobic digestion of screened dairy manure. Biomass 1985, 8(2): 81-90.

[74] Demirer GN, Chen S. Two-phase anaerobic digestion of unscreened dairy manure. Process Biochemistry 2005, 40(11): 3542-3549.

[75] Hansen KH, Angelidaki I, Ahring BK. Anaerobic digestion of swine manure: inhibition by ammonia. Water Research 1998, 32(1): 5-12.

[76] Gonzalez-Fernandez C, Leon-Cofreces C, Garcia-Encina A. Different pretreatments for increasing the anaerobic biodegradability in swine manure. Bioresource Technology 2008, 99(18):8710-8714.

[77] Masse DI, Masse L, Hince JF, Pomar C. Psychrophilic anaerobic digestion biotechnology for swine mortality disposal. Bioresource Technology 2008, 99(15):7307-7311.

[79] Creamer KS, Williams CM, Chen Y, Cheng JJ. Implications of urine-to-feces ratio in the thermophilic anaerobic digestion of swine waste. Water Environment Research 2008, 80(3):267-275.

[80] Chae KJ, Jang A, Yim SK, Kim IS. The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure. Bioresource Technology 2008, 99(1):1-6.

[81] Lo KV, Liao PH, Gao YC. Anaerobic treatment of swine wastewater using hybride UASB reactors. Bioresource Techology 1994, 47(2): 165-171.

[82] Feng CP, Shimada S, Zhang ZY, and Maekawa T. A pilot plant two-phase anaerobic digestion system for bioenergy recovery from swine wastes and garbage. Waste Management 2008, 28-10:1827-1834.

[83] Kotspoulos TA, Karamanlis X, Dotas D. The impact of different natural zeolite concentrations on the methane production in thermophilic anaerobic digestion of pig waste. Biosystems Engineering 2008, 99(1):105-111.

[84] Desai M, Patel V, Madamwar D. Effect of temperature and retention time on biomethanation of cheese whey–poultry waste–cattle dung. Environ. Pollut. 1994, 83:311-315

[85] Murto M, Bjo rnsson L, Mattiasson B. Impact of food industrial waste on anaerobic co-digestion of sewage sludge and pig manure. J Environ Manage 2004, 70:101–7.

[86] Lehtom¨aki A, Huttunen S, Rintala JA. Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio. Resources, Conservation and Recycling 2007, 51: 591–609.

[87] Gelegenis J, Georgakakis D; Angelidaki I, Mavris V. Optimization of biogas production by co-digesting whey with diluted poultry manure. Renewable Energy 2007, 32:2147-2160.

[88] Kaparaju P, Rintala J. Anaerobic co-digestion of potato tuber and its industrial by-products with pig manure. Resources, Conservation and Recycling 2005, 43: 175-188.

[89] Tiehm A, Nickel K, Neis U. The use of ultrasound to accelerate the anaerobic digestion of sewage sludge. Water Science Technology 1997, 36(11):121-128.

[90] Dewil R, Baeyens J, Goutvrind R. The use of ultrasonic in the treatment of waste activated sludge. Chinese Journal Chemistry engineering 2006, 14(1):105-113.

[91] Laborde JL, Bouyer C, Caltagirone JP. Gerard A. Acoustic cavitation field prediction at low and high frequency ultrasounds. Ultrasonic 1998, 36:581-587.

[92] Wang F, Wang Y, Ji M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. Journal Hazard Material 2005, 123:145-150.

[93] Tiehm A. Nickel K, Zellhorn M, Neis U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. J. Water Res 2001, 35(8): 2003–2009.

[94] Benabdallah EI-Hadj T, Dosta J, Marquez-Serrano R, Mata-Alvarez J. Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene removal. Water Research 2006, 41(1):87-94.

[95] Liu YY, Yoshikoshi A, Wang BC, Sakanishi A. Influence of ultrasonic stimulation on the growth and proliferation of *Oryza sativa* Nipponbare callus cells. Colloids and Surfaces B: Biointerfaces 2003**,** 27: 287–293.

[96] Khanal SK, Grewell D, Sung S, van Leeuwen J. Ultrasound applications in wastewater sludge pretreatment: A review. Environmental Science and Technology 2007, 37(4):277-313.

[97] Bougrier C, Carrere H, Delgenes JP. Solubilization of waste-activated sludge by ultrasound treatment. Chemical Engineering Journal 2005, 106:163-169.

[98] Chu CP, Chang B, Liao GS, Jean DS, Lee DJ. Observations on changes in ultrasonically treated waste-activated sludge. Water Research 2001, 35(2):1038-1046.

[99] Tiehm A, Nickel K, Neis U. The use of ultrasound to accelerate the anaerobic digestion of sewage sludge. Water Sci. Technol. 1997, 36(11): 121-128.

[100] Grönroos A, Kyllönen H, Korpijärvi K, Pirkonen P, Paavola T, Jokela J, Rintala J. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. Ultrasonic Sonochemistry 2005, 12(1):115-120.

[101] Wang F, Wang Y, Ji M. Mechanisms and kinetic models for ultrasonic waste activated sludge disintegration. J. Hazard. Mater. 2005, B123: 145-150.

[102] Chu CP, Lee DJ, Chang B, You CS, Tay JH. “Weak” ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids. Water Research 2002, 36(1): 2681-2688.

[103] Yin X, Lu X, Han P, Wang Y. Ultrasonic treatment on activated sewage sludge from petro-plant of reduction. Ultrasonics 2006, 44(1): 397-399.

[104] Wang Q, Kuninobu M, Kakimoto K, Ogawa H, Kato Y. Upgrading of anaerobic digestion of waste activated sludge by ultrasonic pretreatment. Bioresource Technology 1999, 68(3): 309-313.

[105] Akin B, Khanal SK, Sung SW, Grewell D, van Leeuwen J. Ultrasound pre-treatment of waste actived sludge. Water Science & Technology: Water Supply 2006, 6(6): 35-42.

[106] Forster CF, Chacin E, Fernandez N. The use of ultrasound to enhance the thermophilic digestion of waste activated sludge. Environmental Technology 2000, 21(3): 357-362.

[107] Bien JB, Malina G, Bien J, Wolny L. Enhancing anaerobic fermentation of sewage sludge for increasing biogas generation. Journal of Environmental Science and Health 2004, 39 (4):939-949.

[108] Mao T, Hong SY, Show KY, Tay JH, Lee DJ. A comparison of ultrasound treatment on primary and secondary sludges. Water Science and Technology 2004, 50 (9): 91-94.

[109] Show KY, Mao TH, Lee DJ. Optimisation of sludge disruption by sonication. Water Research 2007, 41 (20): 4741-4747.

[110] Hogan F, Mormede S, Clark P, Crane M. Ultrasonic sludge treatment for enhanced anaerobic digestion. Water Science & Technology 2004, 50 (9): 25-32.

[111] Xie R, Xing Y, Ghani YA, Ooi KE, Ng SW. Full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge. Journal of Environmental Engineering and Science 2007, 6 (5): 533-541.

CHAPTER 3. EVALUATION OF ULTRASONIC PRETREATMENT ON METHANE PRODUCTION POTENTIAL FROM CORN ETHANOL BY-PRODUCTS

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), 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 prior to conducting bench top BMP trials. Biogas production was measured and analyzed for methane content and accumulated methane production. Ultrasonic pretreatment reduced mean particle size of DDGs and solids by 45 and 43%, respectively. Without ultrasonic pretreatment, corn-syrup had the highest methane production potential (407 ml/g VS added) compare to the other by-products. Methane yields were increased by 25 and 12% for the ultrasonic pretreated DDGs samples and solids samples, respectively, compared with untreated samples. The ultrasonic pretreatment of ethanol co-products was shown to increase methane yields from the anaerobic digestion of these products. The ultrasonic pretreatment of solids co-products (DDGs and solids) was 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 pretreatment required more energy than was generated by the process in terms of additional biogas production.

1. Introduction

Ethanol is a renewable fuel that can be derived from a variety of biomass sources including starch crops, sugar crops, and cellulosic materials. Currently, the US has approximately 168 ethanol plants in service with a production capacity of more than 34 billion liters (9 billion gallons) per year [1]. Yeast fermentation in the production of corn ethanol does not utilize all of the available organics resulting in 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 could be used to power ethanol facilities [2]. Stover et al. [3] 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 (130,000ft^3) of methane could be achieved from 227,125 liters (60,000 gallons) of thin stillage per day. Thus it is proposed the development of this technology 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 ultrasonic 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 [4]. Chyi and Dague [5] 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 ultrasonic enhances the disintegration of particulate matter which is evidenced by a reduction in particle size and increasing the soluble matter fraction [6] [7]. Tiehm et al. [8] 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 ultrasonic technologies.

Biochemical methane potential (BMP) analysis is an efficient method for evaluating the rate and yield 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 [9]. A modified method based on the procedure outlined by Owen et al. [10] 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.

2. Material and Methods

2.1 Sample Collection

Ethanol co-products analyzed in this study including DDGs, solids, syrup, and thin stillage which 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).

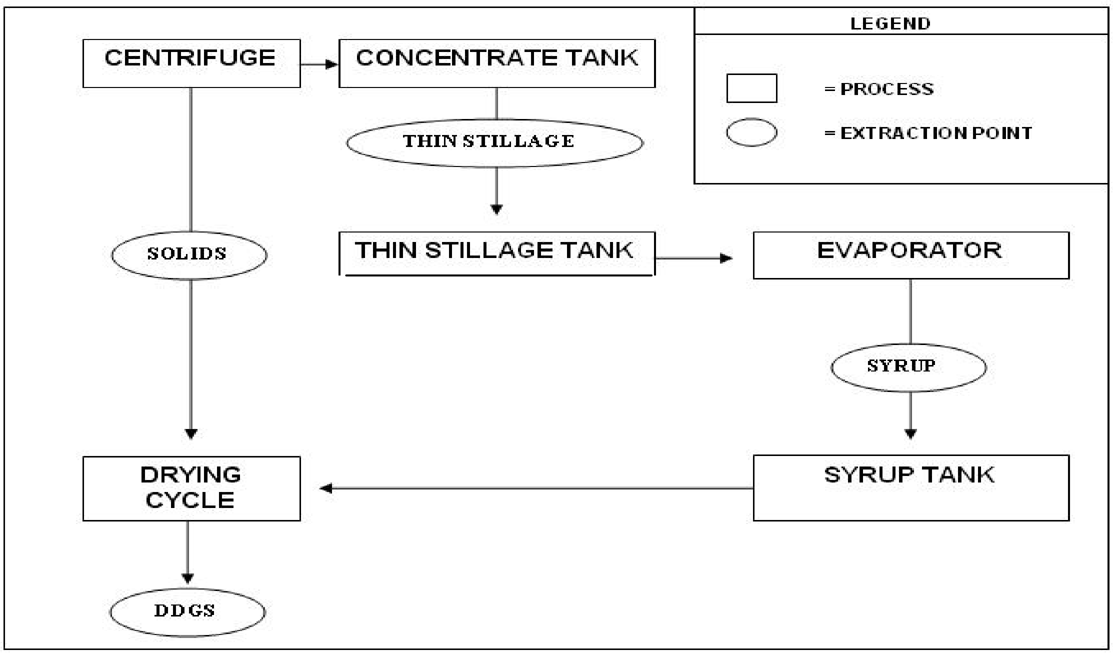


Figure 1. Diagram of co-products including DDGs, solids, syrup and thin stillage created after centrifuge step during corn to ethanol process.

2.2 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). The 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).

2.3 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 2.2 kW, 20 kHz Branson 2000 series equipped with a 0-20 μm_{pp} converter, a 1:1 gain booster and a 1:8 gain catenoildal horn (Branson Ultrasonic Corporation, Danbury, CT). Ultrasonic pretreatment was applied with three amplitude (AMP) 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 of 15 treatments (3x5 matrix) along with an untreated sample (control) that were tested for bio methane potential from anaerobic digestion of DDGS, solids, syrup, and thin stillage.

2.4 BMP Assays

In order to produce a measurable, but not excessive amount of methane, an aliquot of ethanol co-products was added to a 250 ml serum bottle with 100 ml anaerobic inoculum. The amount of co-product added varied by type and was sufficient to provide a sample to inoculums VS ratio of 1:1. Inoculum was obtained from a 60 liter mesophillic (35°C) continuous stirred-tank reactor (CSTR), fed daily of at a loading rate of 2 g VS/L/day. The average inoculum concentration was 3g/L VS. The head space 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 for 5 min. After the head space was removed using a glass syringe, sealed serum bottles were placed on a shaker (150-200 RPM) and incubated at 35°C for 30 days. Each BMP assay was performed in triplicate.

2.5 Biogas Production and Methane Content Measurement

Biogas production was monitored daily with a graduated syringe using a 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 the sample VS added to each bottle with a unit of ml/g VS added.

2.6 Particle Size Analysis

A Malvern Mastersizer 2000 Particle Distribution Analysis (PDA) system (Malvern Instruments, Westborough, Maryland) equipped with No. 20 and No. 35 sieves was utilized to compare particle size difference of DDGs, solids, syrup, and thin stillage samples pretreated with and without ultrasound. Particle size analysis was performed on a sub-set of the experimental treatments, which included four treatments (10s with 33% AMP, 50s with 33% AMP, 10s with 100%, and 50s with 100% AMP) along with control, to characterize particle size. Data were analyzed using the Malvern Mastersizer software.

2.7 Statistical Analyses

Methane production data were analyzed using the GLM procedure of SAS [11]. The model included the fixed effects of ultrasonic (untreated and ultrasonic pretreated), ultrasonic amplitude (33%, 66%, and 100%), ultrasonic time (10, 20, 30, 40, and 50s), and the interaction between ultrasonic amplitude and time. Significant differences among the means were assumed to correspond to a $P \leq 0.05$ value.

3. Results and Discussion

3.1 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 ultrasonic pretreated samples. Ultrasonic effect on the nutrient content of DDGs, solids, syrup, and thin stillage were not significant ($P > 0.05$). The VS of DDGs, solids, syrup and thin stillage were 95, 87, 37 and 3.0%, respectively, and the COD were 507, 400, 609 and 110 g/L, respectively.

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

Parameter	DDGs	Solids	Syrup	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)	507± 19	400± 11	609± 36	110± 4
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

3.2 Particle Size Analysis

Particle sizes of the majority of DDGs particles with or without ultrasonic pretreatment ranged from 110 to 1000μm (Figure 2). DDGs samples without ultrasonic pretreatment had the greatest percentage of particles (90%) at an approximate size of 700μm, and DDGs samples pretreated with ultrasonic for 50s at 100% AMP had least percentage of particles (50%) in this size range.

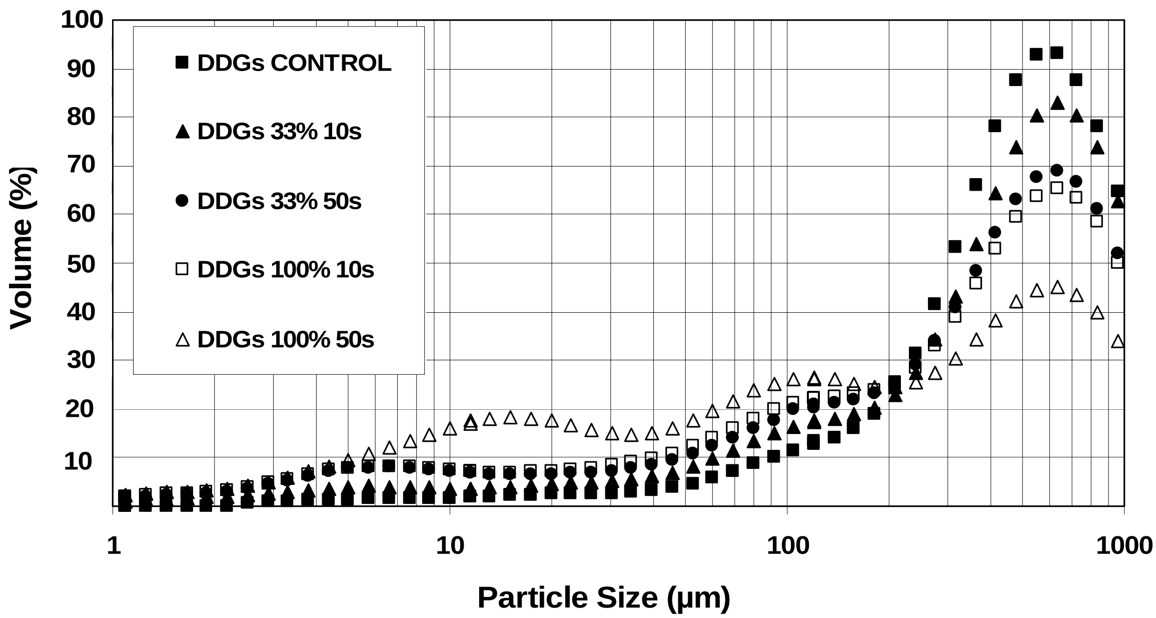


Figure 2. Particle size distribution of DDGs samples pre-treated without or with ultrasonic for 10 or 50s at varied amplitude (33 or 100%)

Similar results were seen with particle size distribution for the solids (Figure 3). The majority of solids samples were sized from 110 to 1000 μm. At approximately a size of 700μm, there was a lower percentage of particles in the solid samples pretreated with ultrasonic compared with the untreated samples. In general, an increase in ultrasonic time and amplitude resulted in a greater particle size reduction for DDGs and solids (Figure 4).

The ultrasonic pretreatment reduced the mean particle size of DDGs and solids by 45 and 43%, respectively. Our findings were similar to work conducted by others [7]. This study demonstrated that ultrasonic pretreatment can be utilized to decrease particle size of DDGs and centrifuge solids which potentially could result in higher bio-solids degradation.

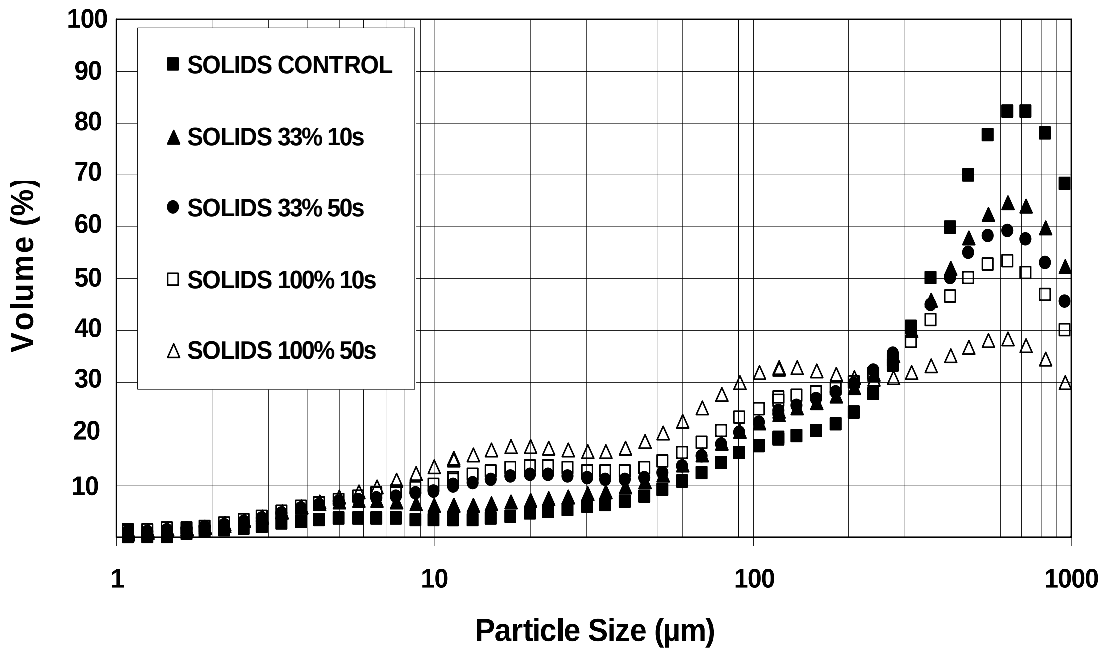


Figure 3. Particle size distribution of solids pre-treated without or with ultrasonic for 10 or 50s at varied amplitude (33 or 100%)

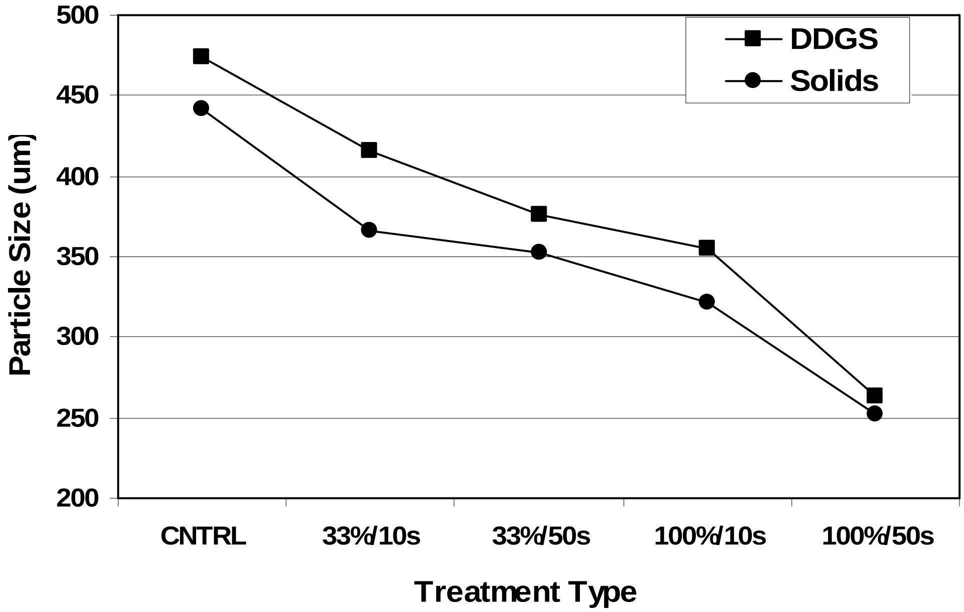


Figure 4. Mean particle size of DDGS and solids pre-treated without or with ultrasonic for 10 or 50s at varied amplitude (33 or 100%)

However, for the syrup and thin stillage, the majority of the particles with or without ultrasonic pretreatment ranged from 1 to 100μm (Figure 5 and 6) and particle size increase was observed for the syrup and thin stillage samples pretreated with ultrasound. Although the reason for this is not evident, differences between particle size reduction of DDG and solids as well as syrup and thin stillage are likely due to the initial smaller particle size of syrup and thin stillage compared to DDGs and solids. Doktycz and Suslick [12] suggested that high-intensity ultrasonic applied to solid-liquid slurries could drive particles together to induce melting upon collision. In current study, inter-particle collisions driven by ultrasonic are likely contributed to the observed particle size increase for the syrup and thin stillage samples.

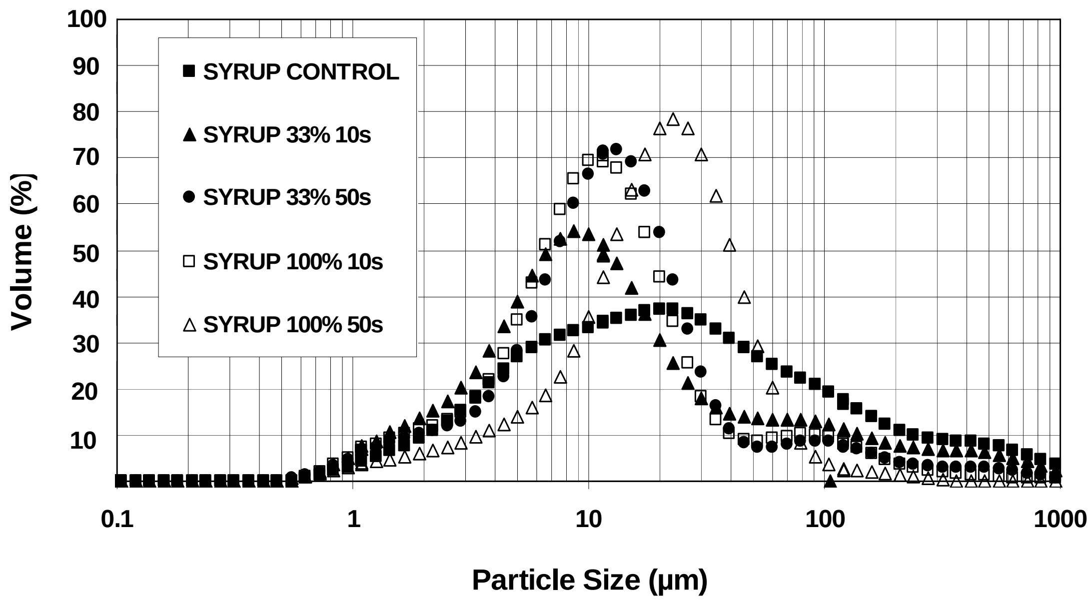


Figure 5. Particle size distribution of syrup pre-treated without or with ultrasonic for 10 or 50s at varied amplitude (33 or 100%)

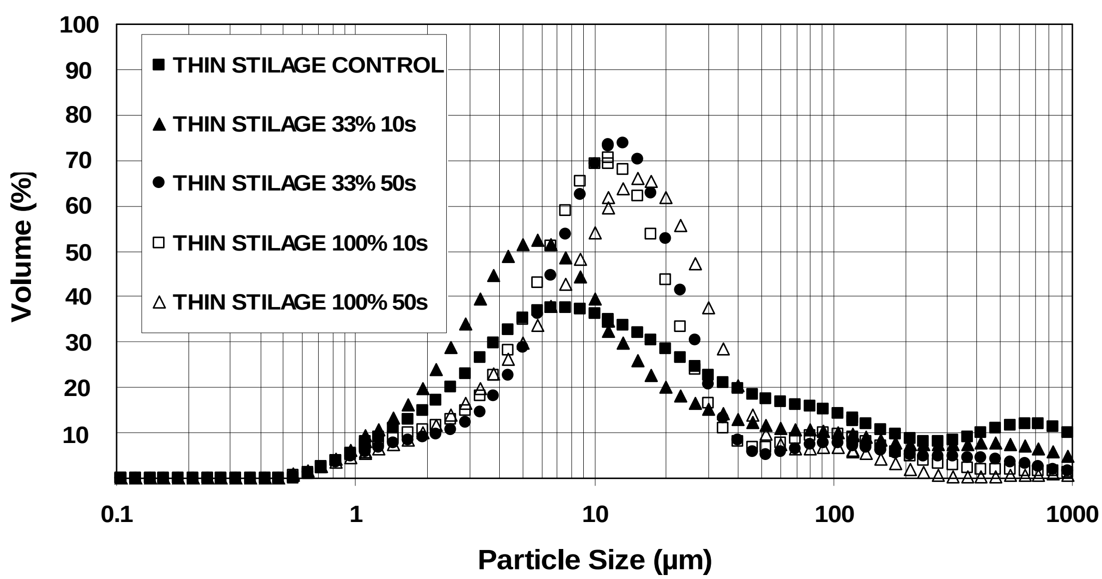


Figure 6. Particle size distribution of thin stillage pre-treated without or with ultrasonic for 10 or 50s at varied amplitude (33 or 100%)

3.3 Ultrasonic effect on cumulative methane production from DDGs, Solids, Syrup, and Thin Stillage

3.3.1 DDGs

The ultrasonic effects on methane yield from DDGs are presented in Table 2. In summary, ultrasonic pretreatment increased methane yield by 25%. Consistently, the cumulative methane production (yield) from samples pre-treated with ultrasonic (395 ml/g VS) were significantly higher than the non-treated samples (315 ml/g VS). It is also seen that cumulative methane production was generally proportional to amplitude. In more detail, it is seen that the samples pretreated with 33% ultrasonic amplitude (358 ml/g VS) were less than from samples at 66% (422 ml/g VS) and 100% (404 ml/g VS) ultrasonic amplitude. However, the cumulative methane yield from samples receiving 66% AMP were similar to the samples at 100% AMP, suggesting that 66% AMP corresponds to ultrasonic amplitude. In addition, it is seen that methane yields were proportional to treatment time (346, 379, 394, 396, and 459 ml/g VS, respectively). These results are consistent with the results that indicate a significant decrease in particle size for ultrasonically pretreated DDGs samples compared with untreated samples using particle distribution analysis. Reduced particle size is likely the largest contributor to enhanced methane production that was observed in the current study.

Table 2. Cumulative methane production from DDGs, solids, syrup, and thin stillage pre-treat without or with ultrasonic at varied amplitude (33, 66, 100%) as well as time (10, 20, 30, 40, 50s)

Item	Cumulative Methane Production (ml/g VS added)			
	DDGs	Solids	Syrup	Thin stillage
Main effect				
Ultrasound				
Untreated	315 [a]	374 [a]	407	346 [a]
Ultrasonic pretreated	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-value)				
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-g] Means with a column lacking common superscripts differ ($P < 0.05$)

The average cumulative methane yield from anaerobic digestion of DDGs is presented in Figure 7. DDGs samples sonicated with 100% amplitude for a 50 second had the greatest methane production (489 ml/g VS added). This again showed that an increase in ultrasonic time and amplitude resulted in a higher methane production. For DDGs samples ultrasonic 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 receiving the 33% amplitude with times of 10s, 20s, 30s, 40s, and 50s were 322, 323, 347, 362, and 439 ml/g VS added, respectively. Samples receiving 66% amplitude showed a similar trend with only one exception. The 20 s sample (454 ml/g VS added) produced approximately the same amount of gas as the 50 s treatment (448 ml/g VS added).

Results from the 30 day BMP assays indicated methane production was 25% higher for the ultrasonic 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 detailed in section 3.4. Results are consistent with prior studies [13] [14]. Lafitte-Trouqué and Forster [13] indicated that gas production rates from anaerobic digestion of ultrasonic pretreated sludge were higher than those for untreated sludge. Grönroos, et al. [14] 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.

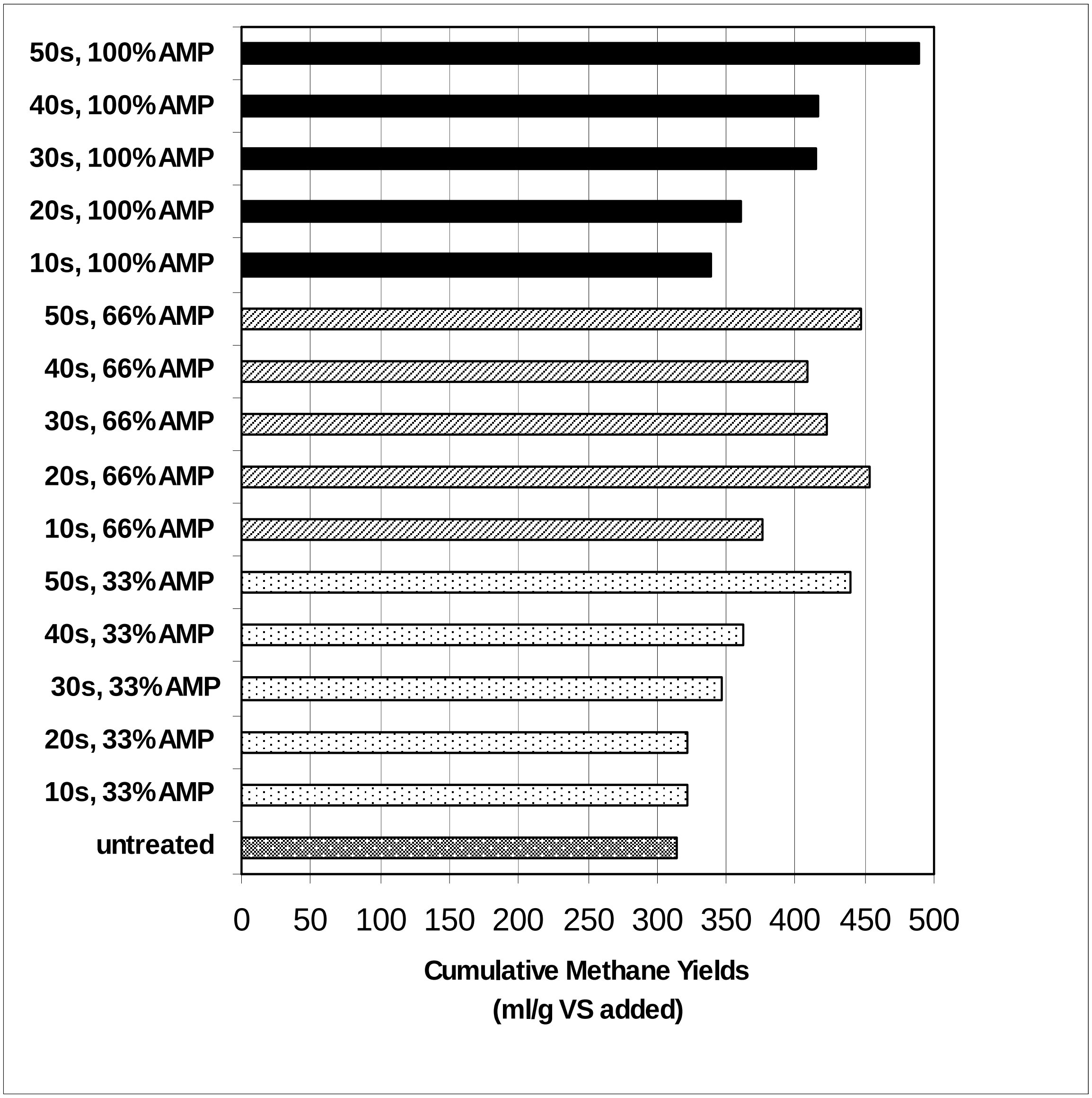


Figure 7. Ultrasonic effect on average of cumulative methane production from DDGs

3.3.2. Centrifuge Solids

Ultrasonic pretreatment had a significant effect on the cumulative methane production for the centrifuge solids (Table 2). Methane production was 12% higher for the ultrasonically pretreated samples compared to the untreated samples (control). 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. Methane yields were observed to increase with higher amplitude (412, 412, 433 ml/g VS, respectively) and longer treatment time (407, 418, 413, 426, 431, respectively). However, the effects of ultrasonic amplitude, time, or amplitude and time interaction effects were not significant.

As shown in Figure 8, 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 and particle size analysis.

3.3.3 Syrup

There was no significant ultrasonic effect on cumulative methane production from syrup (Table 2). Biogas production from the syrup trial was, for the most part, not consistent with results found for DDGs and solids (Figure 9). 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 ultrasonic pretreatment (408 ml/g VS added) produced a 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 is supported by the particle distribution analysis which suggested that no reduction of the syrup particle size occurred with ultrasonic pretreatment, since the syrup particle size is already much smaller as compared to the DDGs and solids samples without ultrasonic pretreatment.

3.3.4 Thin Stillage

The effect of ultrasonic pretreatment on the cumulative methane production from thin stillage was significant (Table 2). In more detail, thin stillage pre-treated with ultrasonic produced more methane (411 ml/g VS) as compared to the untreated samples (346 ml/g VS). However, similar to the results from the syrup, however the effects of ultrasonic time and amplitude were not directly correlated. For example, ethane production was not enhanced with increasing ultrasonic amplitude, but within the 100 and 33% amplitude ranges methane production was generally proportional to ultrasonic time. Cumulative methane yield from anaerobic digestion of thin stillage (Figure 10) 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 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 lower amplitudes were (33 and 66%) effective in enhancing methane production. In more detail, it is 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 ultrasonic time resulted in a higher methane production.

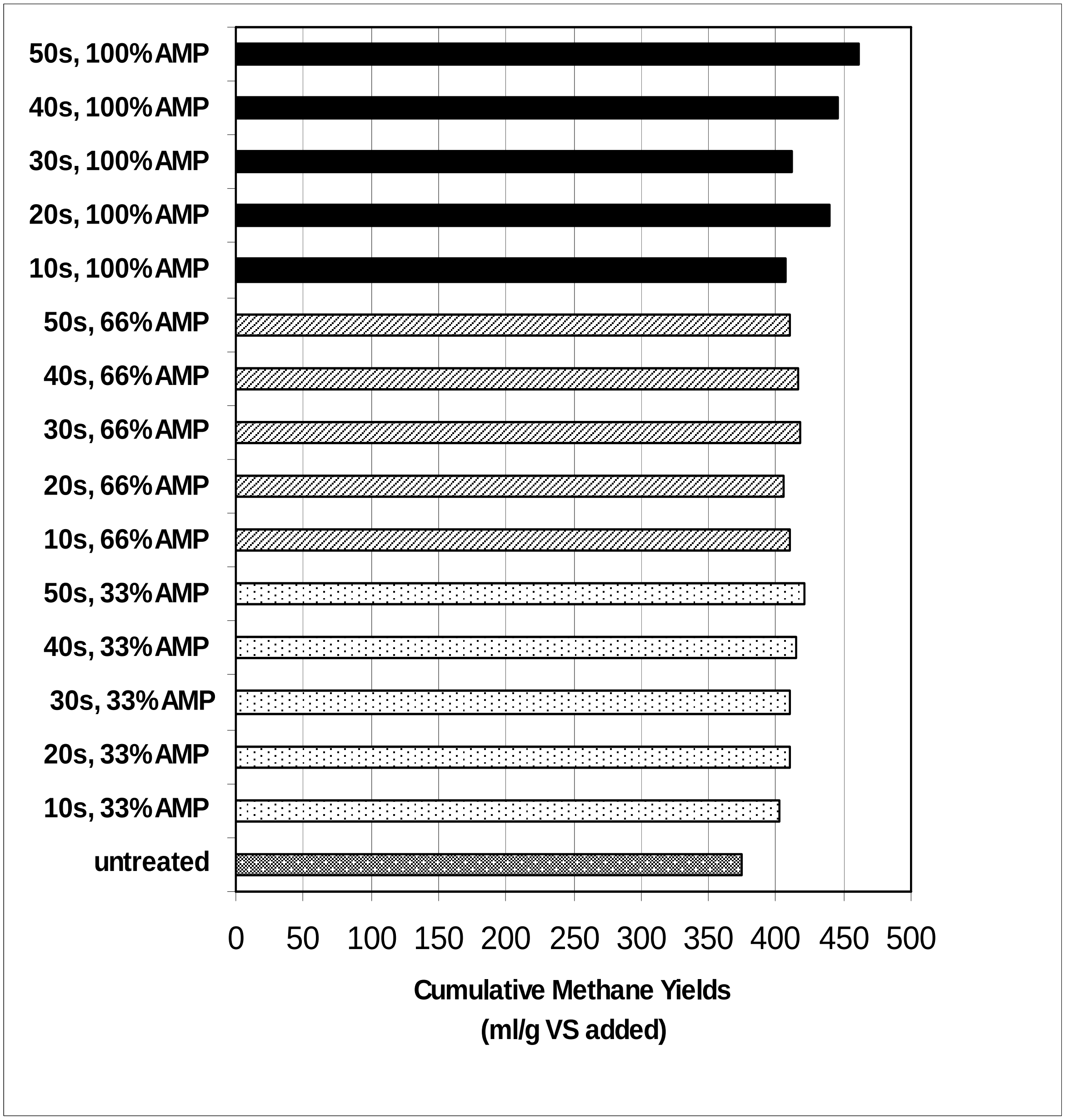


Figure 8. Ultrasonic effect on average of cumulative methane production from centrifuge solids

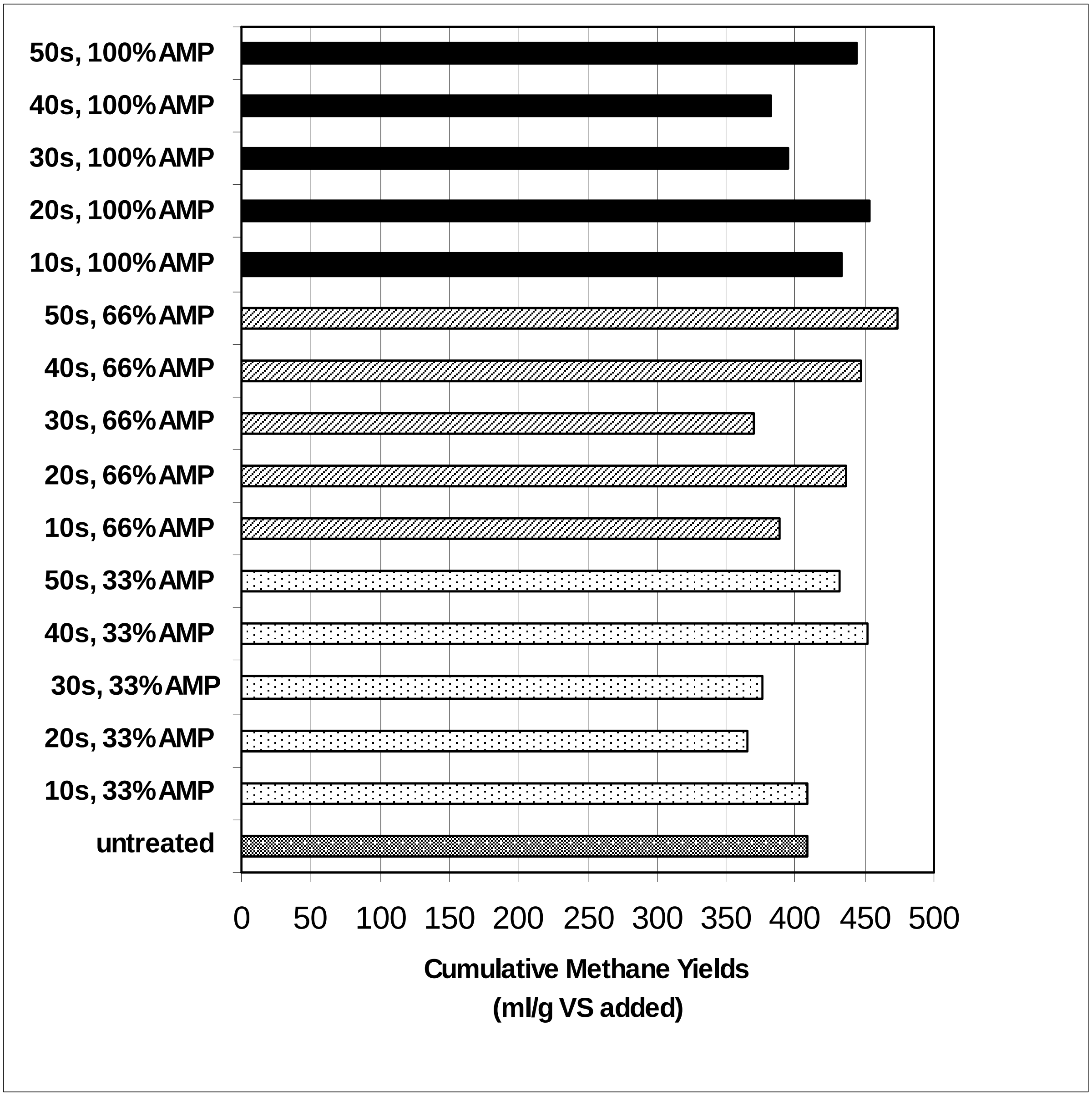


Figure 9. Ultrasonic effect on average of cumulative methane production of syrup

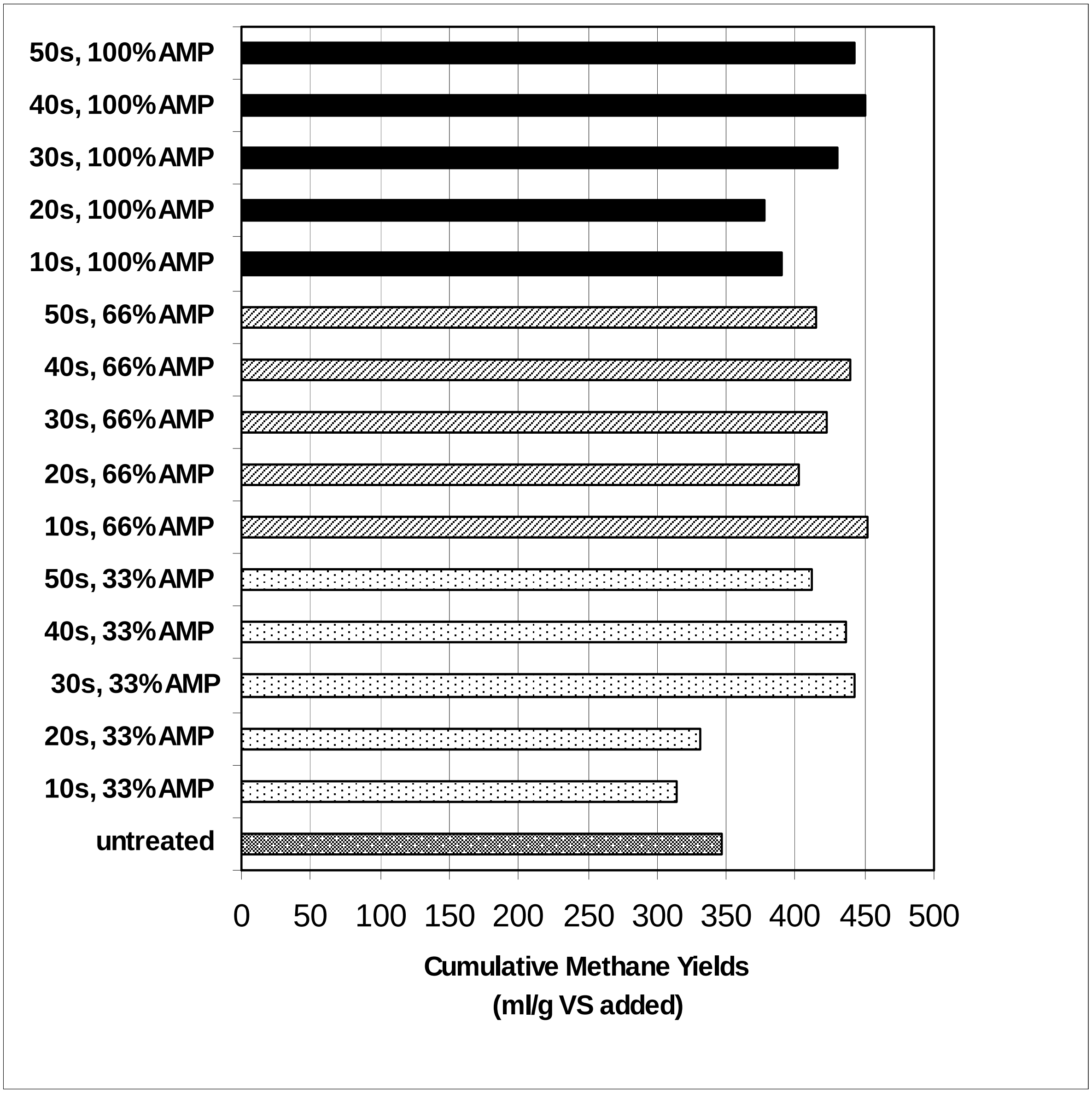


Figure 10. Ultrasonic effect on average cumulative methane production of thin stillage

3.4 Energy Balance Analysis

The optimization of energy consumption is essential for the use of ultrasonic 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 3).

Cumulative biogas production from ultrasonically pre-treated DDGs samples produced a higher amount of methane compared to the untreated samples (445 ml vs. 361ml). An additional 84 ml of methane was produced, corresponding to 3,209 J of chemical energy. For the DDGs, the energy input for the ultrasonic treatment was 1,883 J, yielding a net energy balance of 1,326 J. Following the same approach, it is seen that only 20 ml of additional methane was recovered using ultrasonic pretreatment for anaerobic digestion of solids samples. The energy recovered from additional methane production was less than the ultrasonic pretreatment energy input (764 J vs. 628 J).

Table 3. Energy (E) balance analysis

		DDGs	Centrifuge Solids
Cumulative biogas production (ml)	Untreated	315	197
	Sonicated[1]	445	217
Increased biogas production[2] (ml)		84	20
Increased energy[3] (J)		3,209	764
Input energy[4] (J)		1,883	1,391
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 [14]). Energy content of methane used for computation was 38.2 MJ/m^3.

[4] Energy used for running ultrasonic unit

4. Conclusions

While ultrasonic pretreatment of ethanol co-products was shown to increase methane production from anaerobic digestion, this study indicates that ultrasonic pretreatment is far more effective on solids co-products (DDGS and centrifuge solids) than on liquid co-products (syrup and thin stillage). These results are also supported by the particle distribution analysis which suggested ultrasonic pretreatment can reduce mean particle size of DDGs and solids by 45 and 43%, respectively. An energy balance conducted for DDGs and centrifuge solids showed According to the DDGs and thin stillage results, an increase in amplitude resulted in an overall increase in methane production for ultrasonic pretreated samples. The DDGs results also showed that an increase in the length of exposure to ultrasonic treatment results in an increase in methane production. Without ultrasonic pretreatment, corn-syrup had the highest methane production potential. If DDGS were going to be used as a feed-stock for anaerobic digestion, the use of ultrasonic pretreatment shows merit for increasing methane production from the process.

Literature Cited

[1] Renewable Fuels Association (RFA). 2008. Industry Statistics. Available at: http://www.ethanolrfa.org/industry/locations/. Accessed on 9 September, 2008.

[2] Wilkie AC, Riedesel KJ, Owens JM. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass and Bioenergy 2000, 19:63-102.

[3] Stover EL, Gomathinayagam G, Gonzalez G. Use of methane gas from anaerobic treatment of stillage for fuel alcohol production. In: Proceedings of the 39th Industrial Waste Conference, Purdue University, West Lafayette, Indiana. Boston Butterworth 1984, p. 57–63.

[4] Khanal SK, Grewell D, Sung S, van Leeuwen J. Ultrasound applications in wastewater sludge pretreatment: A review. Environmental Science and Technology 2007, 37(4):277-313.

[5] Chyi YT, Dague RR. Effects of particulate size in anaerobic acidogenesis using cellulose as a sole carbon source. Water Environment Research 1994, 66(5):670-678.

[6] Wang F, Wang Y, Ji M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration, Journal of hazardous materials 2005, 123:145–150.

[7] Benabdallah EI-Hadj T, Dosta J, Marquez-Serrano R, Mata-Alvarez J. Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene removal. Water Research 2006, 41(1):87-94.

[8] Tiehm A, Nickel K, Zellhorn M, Neis U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. Water Research 2001; 35(8):2003-2009.

[9] Owens JM, Chynoweth DP. Biochemical methane potential of municipal solid waste (MSW) components. Water Science Technology 1993, 27:1-14.

[10] Owens WF, Stuckey DC, Healy JB, Young LY, Mc Carty PL, Biomass for monitoring biochemical methane potential and anaerobic toxicity. Water Research 1979, 13:485-492.

[11] SAS Institute. 1990. SAS User's Guide: Statistic. Version 6.3 ed. SAS Inst. Inc., Cary, NC.

[12] Doktycz SJ and Suslick KS. Interparticle collisions driven by ultrasound. Science 1990, 247 (4946): 1067-1069.

[13] Lafitte-Trouqué S, Forster CF. The use of ultrasound and γ-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures. Bioresource Technology 2002, 84:113–118.

[14] Grönroos A, Kyllönen H, Korpijärvi K, Pirkonen P, Paavola T, Jokela J, Rintala J. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. Ultrasonic Sonochemistry 2005, 12(1):115-120.

[15] Walsh JC, Ross C, Smith M, Harper S, Wilkins W. Handbook on biogas utilization. Prepared for U.S. Department of Energy, Southeastern Regional Biomass Energy Program. Prepared by Georgia Institute of Technology, Engineering Technology Branch. Atlanta, GA; 1988.

CHAPTER 4. EVALUATION OF ULTRASONIC PRETREATMENT ON ANAEROBIC DIGESTION OF DIFFERENT ANIMAL MANURES

ABSTRACT The effect of ultrasonic pretreatment on soluble chemical oxygen demand (SCOD) and biochemical methane potential (BMP) of four types of animal manure including swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent as well as energy efficiency of ultrasonic pretreatment were evaluated. Ultrasonic pretreatment was applied with two amplitudes, 80 and 160 μm_{pp} at two time settings, 15 and 30 s, to each of the four manure types. The sample SCOD was analyzed before and after ultrasonic pretreatment. In addition, BMP trials were run on each waste after ultrasonic pretreatment. As part of the BMP, biogas production was measured and analyzed for methane content and cumulative methane production. Ultrasonic pretreatment of swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent increased the average SCOD by 30, 18, 37, and 14%, respectively and the average methane yield by 14, 55, 37 and 8%, respectively. Increases in the ultrasonic amplitude and treatment time resulted in an overall increase in SCOD and methane production of ultrasonic pretreated manure, with the greatest methane production obtained with the highest power and longest treatment. The observed greatest methane production from beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent were 394, 230, 226, and 340 ml/g VS. In contrast, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with the shortest treatment time. From an energy efficiency standpoint, the most effective ultrasonic treatment appears to be low-power input with a short ultrasonic treatment time.

Keywords: Animal manure; Biochemical methane potential assay (BMP); Methane yield; soluble chemical oxygen demand (SCOD); Ultrasonic

1. Introduction

Anaerobic digestion is a natural process that has been utilized for decades to produce biogas from animal wastes for energy production. In addition, anaerobic digestion of manure will potentially reduce organic matter content and manure pathogens, provide substantial odor reduction, and reduce greenhouse gas emissions.

Ultrasonic pretreatment has been used to treat municipal wastewater activated sludge to improve hydrolysis of anaerobic digestion [1] [2]. The purpose of this treatment is to reduce the size of biosolid particles such that they more easily convert to biogas in the anaerobic digestion process. Chyi and Dague [3] concluded that the larger the particle size the longer the time required for hydrolysis, which is usually the rate-limiting step for anaerobic digestion. Nickel [4] and Tiehm [5] demonstrated that ultrasonic pretreatment can be utilized to disintegrate bacterial cells and increased the quantity of dissolved organic substrate as well as the degradation rate and the biodegradability of biosolids during the anaerobic digestion process. Other researchers also found that high energy intensity ultrasonic pretreatment enhances the disintegration of particulate matter which is evidenced by a reduction in particle size and increasing the SCOD in the supernatant [6] [7]. Numerous studies have been conducted to evaluate the performance of ultrasonic applications for wastewater sludge pretreatment [2]. However, the effectiveness of ultrasonic pretreatment applied to anaerobic digestion of animal manure has not been reported.

The objectives of the current study were to evaluate the effectiveness of ultrasonic pretreatment on biochemical methane potential (BMP) and soluble chemical oxygen demand (SCOD) of four types of animal manure and to evaluate the energy efficiency (increased energy by ultrasonic pretreatment vs. energy used for running the ultrasonic unit) of ultrasonic pretreatment of these manure compounds.

2. Material and Methods

2.1 Sample Collection

Four types of animal manure were analyzed in this study: swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent. Swine slurry was collected from a manure pit at a commercial farrow to finish farm (Crawford Swine Farm, Nevada, IA). Beef feedlot manure samples were collected from an open feedlot (Lytton, IA). Liquid dairy manure before and after a liquid-solid screw separation system were collected from the Iowa State University Dairy Farm (Ames, IA).

2.2 Sample Characterization

All manure samples were analyzed for total solids, volatile solids, pH, total Kjeldahl nitrogen, ammonia, chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD) and total phosphorus. Total and volatile solids were analyzed using Standard Method 2540 G [8]. 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 2001.11 [9]. The COD and SCOD were measured using a Hach colorimetric digestion method

(Method #8000, Hach Company, Loveland, CO). Supernatant for SCOD analyses before and after ultrasonic treatment was conducted after filtration through plastic microfiber syringe filters with pore size of 0.45 µm. Total phosphorus was determined using a Thermo Spectrophotometer GENESYS™6 (Thermo Electron Corporation, Waltham, MA) with Photometric Method 965.17 [9].

2.3 Ultrasonic Pretreatment and Experimental Design

In order to assure uniform treatment, all manure samples were mixed with water before ultrasonic processing. After mixing with water, all manure samples were adjusted to a volatile solids content of 3.9%; total solids content of diluted swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent were 4.5, 4.8, 4.6, and 5.3%, respectively. The ultrasonic system used in this study was a 2.2kW, 20kHz 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 two amplitude settings 80 and 160 μm_{pp} as well as two time settings of 15 and 30 seconds (s), respectively, to each of the four types of animal manure before setting up a bench top BMP trial. Ultrasonic amplitude and time settings utilized in the study were selected based on previous experiments [10]. The experiment had a total of four treatments (2x2 matrix) and a set of untreated controls that were tested for SCOD and bio-methane potential.

2.4 BMP Assays

A modified BMP method, based on the procedure outlined by Owen et al. [11], was used to evaluate anaerobic digestibility and biogas potential. An aliquot of animal manure

(0.17 g VS) was added to a 250 ml serum bottle along with 100 ml of anaerobic inoculum. Inoculum was obtained from a 60 liter mesophillic (35°C) continuous stirred-tank reactor (CSTR) with an inoculum concentration of 1.7 g/L VS. The ratio of manure sample to inoculum VS was 1:1. The head space 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 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 RPM) and incubated at 35°C for 30 days. In order to determine endogenous CH_4 production, blank samples that contained only 100 ml inoculum and de-ionized water were prepared as well.

Each assay was performed in triplicate. Biogas production was monitored daily at with a graduated syringe using a volume displacement technique. Biogas measurements were conducted under temperature-controlled conditions (35°C). The methane content of the biogas was determined using NDIR-CH_4 Gas-Analyzer (Sensors Europe GmbH, Germany). Methane volume was calculated using biogas production as well as methane content and was reported as methane yields at 35°C. Methane yields were calculated by dividing methane volume (ml) by the weight of the sample VS added to each bottle (g VS added) with a unit of ml/g VS added.

2.7 Calculation of Ultrasonic Efficiency

The optimization of energy consumption is essential for the use of ultrasound as a pretreatment method for the anaerobic digestion process to be economically feasible; therefore, a basic energy balance was prepared. The ultrasonic energy input (E_{in}, J/g VS) into each sample was calculated using the following equation:

$$E\,in = \frac{P \times t}{V \times VS} \tag{1}$$

Where P is the power (W); t is the ultrasonic treatment time (s); V is the volume of sample (ml), and VS is the volatile solids concentration of sample in g VS/ml.

In addition, the change in methane yields (ΔM, ml/g VS) due to ultrasonic pretreatment and the energy output (E_{out}, J/g VS) as increased methane yield due to ultrasonic pretreatment was calculated using the following equations:

$$\Delta M = Mt - Mc \tag{2}$$

$$E\,out = \Delta M \times E' \tag{3}$$

Where Mt is the methane yields from sample with ultrasonic pretreatment (ml/g VS); Mc is the methane yield from sample without ultrasonic pretreatment which is control (ml/g VS). E' is the energy content of methane (J/ml). Energy content of methane used for computation was 38.2 J/ml as reported by Walsh et al. 1998 [12].

The overall ultrasonic efficiency (Eff) was calculated using the following equation:

$$Eff = \frac{Eout - Ein}{Ein} \times 100\% \tag{4}$$

2.8 Statistical Analyses

Methane production data were analyzed using the GLM procedure of SAS [13]. The model included the fixed effects of ultrasonic pretreatment (untreated and ultrasonic pre-treated), ultrasonic amplitude (80 and 160 μm_{pp}) and ultrasonic time (15 and 30s). Significant differences among the means were assumed to correspond to a $P \leq 0.05$.

3. Results and Discussion

3.1 Manure Characteristic

The nutrient analysis of swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent is presented in Table 1. The reported values are an average of untreated and ultrasonic pre-treated samples. The VS concentrations of the swine slurry, beef feedlot manure, dairy manure slurry and solids separated dairy were 16.1, 24.6, 9.1 and 4.0%, respectively; the COD concentrations were 52.1, 44.9, 29.2, 70.3 g/L, respectively; and the ammonia concentrations were 14.1, 6.4, 9.7, and 25.2 mg/g TS.

Table 1. Nutrient analysis of pig slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent

Parameter	Pig slurry	Beef feedlot manure	Dairy manure slurry	Solids separated dairy manure effluent
TS (% ww)	18.4±0.1	29.8±1.1	10.5±0.3	5.3±0.1
VS (% ww)	16.1±0.1	24.6±0.8	9.1±0.3	4.0±0.1
pH	6.9±0.1	7.1±0.1	6.9±0.1	6.9±0.1
COD (g/L)	52.1±6.9	44.9±3.0	29.2±5.4	70.3±2.8
TKN (mg/g TS)	34.2±0.1	29.7±0.1	24.3±0.1	55.5±0.1
NH_4-N (mg/g TS)	14.1±0.1	6.4±0.1	9.7±0.1	25.2±0.1
P (mg/g TS)	14.0± 0.1	12.1±0.1	5.1±0.1	1.1±0.1

3.2 Energy Input for Ultrasonic Pretreatment

Energy input for ultrasonic pretreatment increased linearly as a function of ultrasonic amplitude and treatment time (Figure 1). In the current study, energy required of treated animal wastes at ultrasonic amplitude of 80μm for 15 and 30s were 625 J/g VS (531 J/g TS) and 1,243 J/g VS (1,057 J/g TS), respectively. Energy input for treating animal wastes at ultrasonic amplitude of 160 μm for 15 and 30s were 1,591J/g VS (1,353 J/g TS) and 3,053 J/g VS (2,596 J/g TS), respectively. The energy inputs reported in the literature on ultrasonic application of pretreated waste activated sludge ranged from 660 to 64,000 J/g TS in pilot-scale treatment systems[14] [15]. Limited data is available in the literature on energy inputs on the full scale treatment systems. The energy required for treating animal wastes were lower than the energy required for treating waste activated sludge. This is possibility due to differences in particle characteristic.

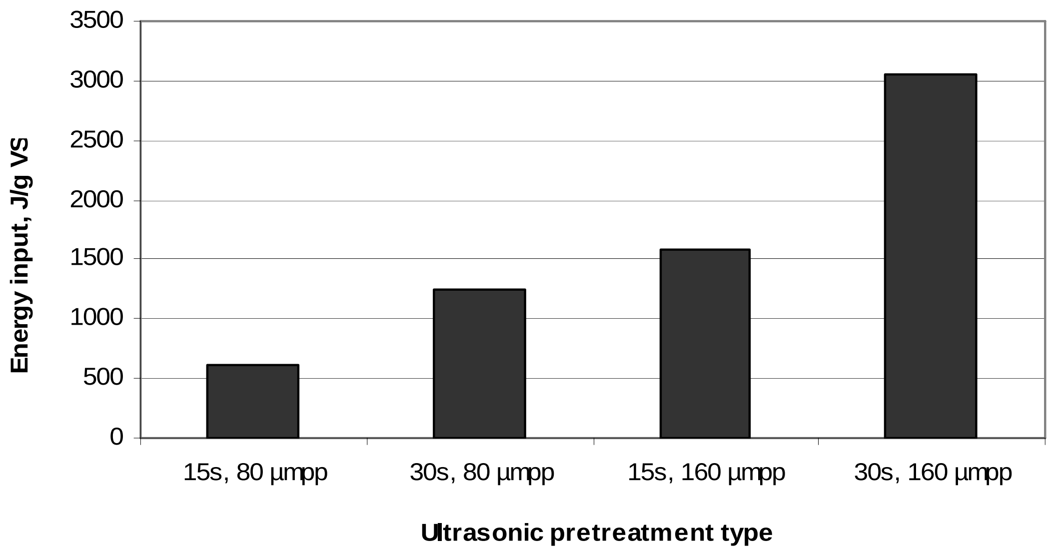


Figure 1. Energy input for various ultrasonic pretreatment type

3.3 Manure Soluble Chemical Oxygen Demand (SCOD)

The SCOD is an important parameter for quantifying the solubilization of the substrates and it is also commonly used for measuring ultrasonic disintegration efficiency. The effect of ultrasonic pretreatment on the SCOD concentration of swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent is shown in Table 2. Ultrasonic pretreatment had a significant effect ($P < 0.01$) on increasing SCOD of each pretreated animal manure sample.

Table 2. Soluble chemical oxygen demand (SCOD) of pig slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent pre-treat without or with ultrasonic pretreatment at varied amplitude (80 µm and 160 µm) as well as time (15s and 30s)

Item	SCOD (g/L)			
	Pig slurry	Beef feedlot manure	Dairy manure slurry	Solids separated dairy manure effluent
LSMEAN				
80 μm_{pp}, 15 s	8.2	8.6	7.7	23.5
80 μm_{pp}, 30 s	10.6	9.2	9.6	25.8
160 μm_{pp}, 15 s	10.6	9.8	11.8	25.2
160 μm_{pp}, 30 s	12.8	12.0	12.3	26.6
Ultrasound				
Untreated	8.2	8.4	7.6	22.1
Ultrasonic Pretreated	10.6	9.9	10.4	25.3
Amplitude (15 & 30 s)				
80 μm_{pp}	9.4	8.9	8.6	24.7
160 μm_{pp}	11.7	10.9	12.1	25.8
Time (80 & 60 μm_{pp})				
15 s	9.4	9.2	9.8	24.4
30 s	11.7	10.6	10.9	26.2
SEM	0.5	0.2	0.3	3.7
Probabilities (P-value)				
Ultrasound	< 0.01	< 0.01	< 0.01	< 0.01
Amplitude	< 0.01	< 0.01	< 0.01	0.01
Time	< 0.01	< 0.01	< 0.01	0.01

The average SCOD concentration of swine slurry pretreated with ultrasonic (10.6 g/L) was significantly greater than the untreated samples (8.2 g/L); which corresponds to a 30% increase. Both the ultrasonic amplitude and treatment time had an effect on swine slurry SCOD. Increasing ultrasonic amplitude and treatment time resulted in higher SCOD. Independent of time, the SCOD of samples pretreated with an ultrasonic amplitude of 80 μm_{pp} (9.4 g/L) was less than those samples pretreated with an amplitude of 160 μm_{pp}

(11.7 g/L). Independent of amplitude, the SCOD of samples pretreated with ultrasonic for 30s (11.7 g/L) was greater than samples pretreated with ultrasonics for 15 s (9.4 g/L).

Ultrasonic pretreatment had a significant effect on SCOD of beef feedlot manure ($P < 0.01$). The average SCOD of ultrasonically pretreated beef feedlot manure (9.9 g/L) was greater than the average SCOD of the untreated samples (8.4 g/L); an increase of 18 %. Ultrasonic amplitude and time effected SCOD of ultrasonically pretreated beef manure ($P < 0.01$). The SCOD concentration of beef feedlot manure was enhanced from 8.9 g/L to 10.9 g/L by increasing the ultrasonic amplitude from 80 μm_{pp} to 160 $\mu m_{pp.}$ In addition, SCOD of beef manure sample increased by 15% by extending the ultrasonic time from 15s to 30s. Overall, an increase in ultrasonic amplitude and the length of exposure to ultrasonic treatment results in an overall increase in SCOD.

The average SCOD concentration of dairy manure slurry treated ultrasonically was 37% higher as compared to the untreated samples. Ultrasonic pretreatment had a significant effect on SCOD of dairy manure slurry ($P < 0.01$). The average SCOD of the untreated and pretreated samples were 7.6 and 10.4 g/L, respectively. Ultrasonic amplitude and treatment time affected SCOD ($P < 0.01$). Independent of time, the SCOD of the dairy manure slurry pretreated with ultrasonic amplitudes at 80 and 160 μm_{pp} were 8.6 and 12.1 g/L, respectively. Independent of amplitude, the SCOD of dairy manure slurry samples pretreated with ultrasonic for 15 and 30s were 9.8 and 10.9 g/L, respectively. Again, an increase in ultrasonic amplitude and treatment time resulted in a higher SCOD.

Ultrasonic pretreatment increased average SCOD of the solids separated dairy manure effluent by 14 %. The SCOD concentration of the untreated samples (22.1 g/L) was less than the ultrasonically pretreated samples (25.3 g/L). In addition, SCOD of the solids separated dairy manure effluent was observed to increase as ultrasonic amplitude and treatment time increased ($P < 0.01$). Effluent treated with an ultrasonic amplitude of 160 μm_{pp} had a higher SCOD (24.7 g/L) than the samples treated with an ultrasonic amplitude of 80 μm_{pp} (25.8 g/L), and SCOD of samples pretreated with ultrasonic for 30 s had a higher SCOD (26.2 g/L) than samples treated for 15 s (24.4 g/L).

Ultrasonic pretreatment increased the average SCOD of swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent by 30, 18, 37, and 14%, respectively. In addition, an increase in ultrasonic amplitude and time resulted in a greater SCOD. The largest SCOD increase was obtained with the highest amplitude and longest treatment time used, which agrees with the studies conducted by others. Grönroos et al. [15] suggested that ultrasonic power as well as ultrasonic treatment time have significant effect on increasing the amount of SCOD available. Tiehm et al. [16] applied ultrasonic pretreatment to raw sludge and demonstrated ultrasonic pretreatment increased SCOD in the sludge supernatant and reduced the particle size of sludge solids. In the current study, increased SCOD is likely due to a reduction in particle size, offering an extended surface area, and increasing the soluble matter fraction [10].

The change of SCOD (ΔSCOD) of animal manures was used to quantify the ultrasonic disintegration efficiency. The ΔSCOD was determined as the difference in the SCOD before and after the ultrasonic treatment. Figure 2 illustrates the ΔSCOD in terms of the ultrasonic energy applied to animal manures. As evidence in Figure 2, an increase in energy input results in an overall increase in the SCOD release. This result is in an agreement with Khanal et al. [17], who studied the release of SCOD concentration of thickened waste activated sludge (3% TS) at different ultrasonic energy inputs and found that the SCOD release clearly increases with increasing energy input. In addition, there is a minimal energy required before the disintegration starts. For swine manure, beef feedlot manure, and dairy manure slurry, this minimum lies at about 600 J/g VS (and lower values of ultrasonic energy input have little effect on the SCOD release.

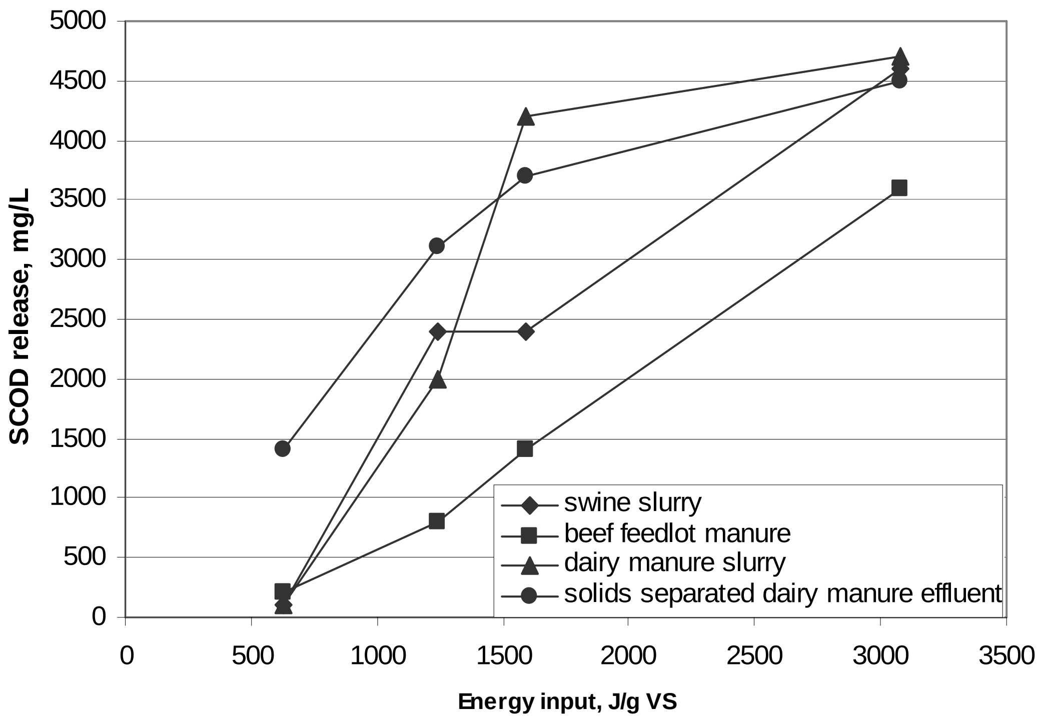


Figure 2. SCOD release (ΔSCOD) due to ultrasonic pretreatment as function of ultrasonic energy input

3.4 Ultrasonic effect on manure methane yield

The ultrasonic effects on cumulative methane yield from swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent are detailed in

Table 3. Reported methane yields were normalized across treatments and are reported as mL CH_4 per g of substrate VS. The methane yield resulting from endogenous methane production by the inoculum was determined with blank samples and has been subtracted from the reported yield.

Average methane yield from ultrasonically pretreated swine slurry (367 ml/g VS) was 14 % greater than the yield from untreated swine slurry (321 ml/g VS). However, no effect of ultrasonic amplitude and treatment time on cumulative methane yield was observed. Methane production from swine slurry treated with an ultrasonic amplitude at 80 μm_{pp} (358 ml/g VS) was similar to the samples treated with an amplitude of 160 μm_{pp} (375 ml/g VS) and methane yield from swine slurry samples receiving ultrasonic treatment for 15 and 30s were 354 and 380 ml/g VS, respectively.

Average methane yield from ultrasonically pretreated beef feedlot manure (186 ml/g VS) was significantly higher than the untreated samples (120 ml/g VS); ultrasonic pretreatment increased methane yield from beef feedlot manure by 55%. Both ultrasonic amplitude and treatment time effected methane production. Independent of time, methane yield from ultrasonically pretreated samples at 80 μm_{pp} amplitude (163 ml/g VS) was less than those samples at 160 μm_{pp} amplitude (209 ml/g VS). It was also seen that methane yield from samples ultrasonically pretreated for 30s (203 ml/g VS) was greater than samples ultrasonically pretreated for 15s (170 ml/g VS). The results suggest that an increase in ultrasonic amplitude and treatment time resulted in a higher methane yield and the greatest methane yield was obtained with the highest ultrasonic amplitude and longest ultrasonic treatment time.

Table 3. BMP methane yields from pig slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent pre-treat without or with ultrasonic pretreatment at varied amplitude (80 µm and 160 µm) as well as time (15s and 30s). Methane yields are normalized across treatments and are reported as mL CH_4 per g of substrate VS.

	Methane yields (ml/g VS)			
Item	Pig slurry	Beef feedlot manure	Dairy manure slurry	Solids separated dairy manure effluent
LSMEAN				
80 μm_{pp}, 15 s	352	151	174	279
80 μm_{pp}, 30 s	365	175	185	302
160 μm_{pp}, 15 s	356	189	190	317
160 μm_{pp}, 30 s	394	230	226	340
Mean effect				
Ultrasonic				
Control	321	120	142	255
Ultrasonic Pretreated	367	186	194	310
Amplitude (15 & 30 s)				
80 μm_{pp}	358	163	179	290
160 μm_{pp}	375	209	208	329
Time (80 & 60 μm_{pp})				
15 s	354	170	182	298
30 s	380	203	206	321
SEM	23	9	10	6
Probabilities (P-value)				
Ultrasonic	0.01	< 0.01	< 0.01	< 0.01
Amplitude	0.24	< 0.01	< 0.01	< 0.01
Time	0.10	< 0.01	< 0.01	< 0.01

Ultrasonic pretreatment increased the average methane yield of dairy manure slurry by 37%. Methane yield from untreated dairy manure (142 ml/g VS) was less than the ultrasonic pretreated samples (194 ml/g VS). In addition, methane production of dairy manure slurry was observed to increase with increasing ultrasonic amplitude and treatment time ($P < 0.01$). Dairy manure samples pretreated with 160 μm_{pp} ultrasonic amplitude had higher methane production (208 ml/g VS) than samples treated with 80 μm_{pp} ultrasonic amplitude (179 ml/g VS), and samples ultrasonically pretreated for 30s produced greater methane (206 ml/g VS) samples pretreated for 15s (182 ml/g VS).

Ultrasonic pretreatment had a significant effect on average methane yield from solid separated dairy manure effluent ($P < 0.01$). Ultrasonically treated solid separated dairy manure effluent (310 ml/g VS) produced more methane than the untreated samples (255 ml/g VS), an average increase of 22%. Ultrasonic amplitude and treatment time had significant effect on methane yield ($P < 0.01$). Methane production from solids separated dairy manure effluent was enhanced from 290 to 329 ml/g VS as amplitude was increased from 80 μm_{pp} to 160 $\mu m_{pp.}$ In addition, methane yield increased by 8% ultrasonic treatment was extended from 15s to 30s.

In summary, average methane yield from ultrasonic pretreated swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent was shown to increase by 14, 55, 37 and 8%, respectively. These results are consistent with results found in the SCOD trial indicating a significant increase in SCOD for ultrasonically pretreated manure. Lafitte-Trouqué and Forster [18] demonstrated that gas production rates from anaerobic digestion of ultrasonic pretreated sludge were higher than those for untreated sludge. Wang et al. [19] reported methane yields from waste activated sludge with ultrasonic pretreatment produced 64% more methane compared with untreated sludge. Dewil et al. [20] concluded that particle size reduction caused by ultrasonic pretreatment enhanced biological hydrolysis, the rate-limiting step of anaerobic process, resulting in more degradable substrate and increasing methane production. The large enhancement of methane yield that was seen in the current study is likely due to particle size reduction caused by the ultrasonic resulting in an enhanced biodegradability.

In addition, the current study also showed that an increase in ultrasonic amplitude and treatment time resulted in a higher methane production and the greatest methane productions were obtained with the highest power and longest treatment time. These findings are in agreement with the results found in SCOD analysis. However, the optimization of energy consumption is essential in ultrasonic assisted anaerobic digestion process.

Methane yield increase (ΔM) due to ultrasonic pretreatment as function of ultrasonic energy input (E_{in}) is shown in Figure 3. An increase in ultrasonic energy input resulted in a larger methane yield and the largest improvements in methane production were obtained with the highest ultrasonic energy input used. Larger improvement in methane production for beef and dairy manure slurry compared to solids separated dairy manure effluent and swine slurry were observed in this trial, likely because ultrasonic treatment provided limited particle size reduction since the particle size of solids separated dairy manure effluent and swine slurry were already small. It also suggested that ultrasonic pretreatment is more effective for animal wastes which contain a large fraction of particulate matter.

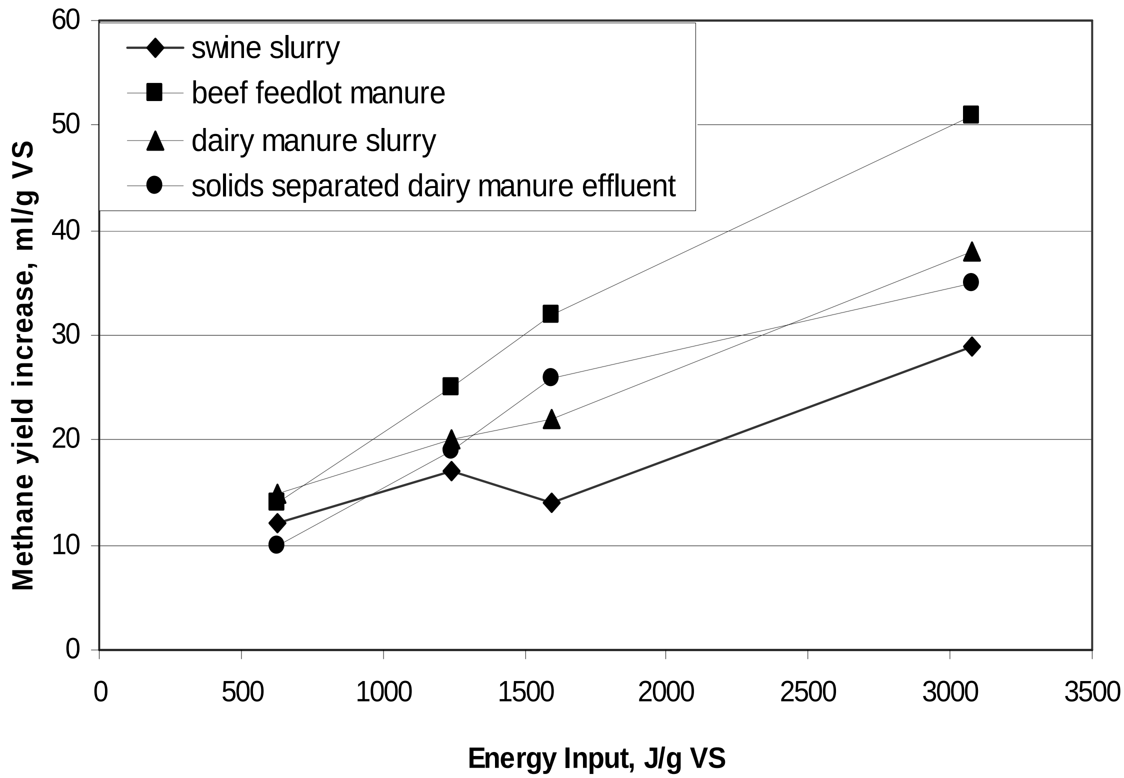
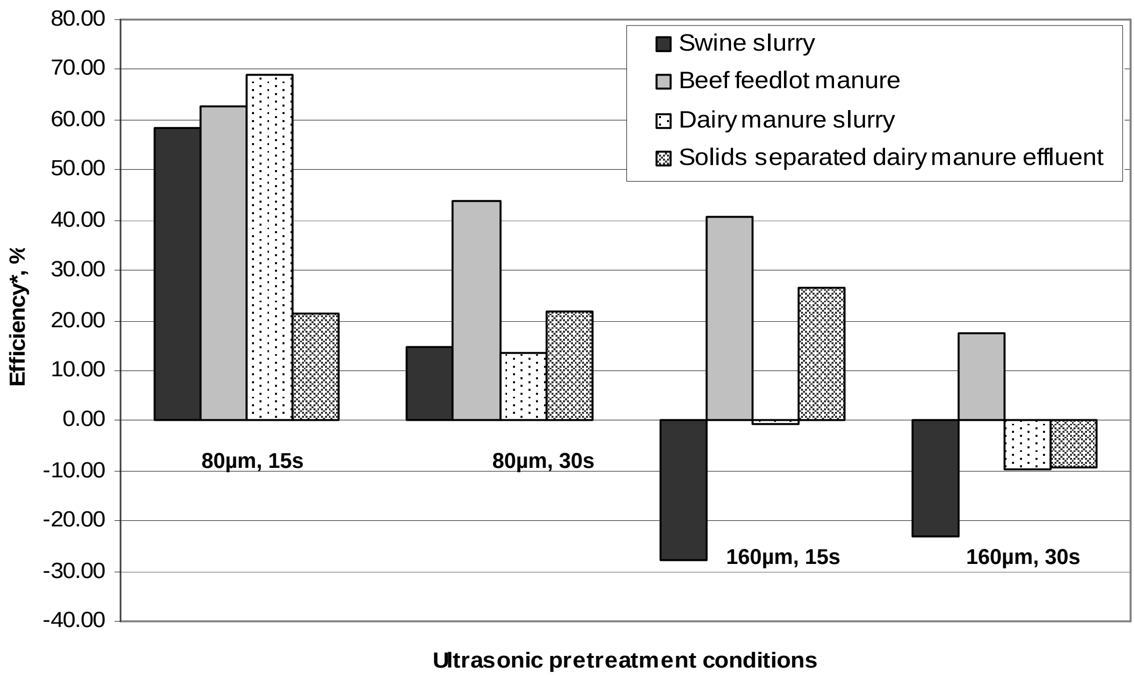


Figure 3. Methane yield increase due to ultrasonic pretreatment as function of ultrasonic energy input

3.5 Energy Balance Analysis

In order to evaluate the effectiveness of ultrasonic system in terms of net energy release, the energy balance calculation was conducted using Equation (1)-(4).

The energy efficiency of ultrasonic pretreatment at various ultrasonic amplitudes and treatment times is detailed in Figure 4. The overall efficiency of ultrasonic system ranged from -28 to 69%, depending on the treatment conditions. The negative efficiency indicates that the energy equivalent of increased methane yields was less than the energy input for ultrasonic pretreatment.



* The overall ultrasonic efficiency was calculated using: $Eff = \frac{Eout - Ein}{Ein} \times 100\%$

Figure 4. Energy efficiency of ultrasonic pretreatment at various ultrasonic pretreatment conditions

When ultrasonic pretreatment was applied with 80 μm_{pp} ultrasonic amplitude for 15s, ultrasonic pretreatment of swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent provided more energy (58, 63, 69, and 21%, respectively) than was required to operate the ultrasonic pretreatment process. For manure samples treated with 80 μm_{pp} amplitude for 30s, swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent produced greater energy (15, 44, 14, and 22%, respectively) than the energy required to operate the ultrasonic pretreatment process. Within the 160 μm_{pp} amplitude and treatment time of 15s, ultrasonic pretreatment of beef feedlot manure and solids separated dairy manure effluent provided 42 and 26%

greater energy than was required for operating the ultrasonic pretreatment process while swine slurry and dairy manure slurry provided less energy (-28% and -1%, respectively) than was required for operating the ultrasonic pretreatment process. When ultrasonic pretreatment was applied with 160 μm_{pp} amplitude for 30s, ultrasonic pretreatment of beef feedlot manure provided more energy (17%) than was required to operate the ultrasonic pretreatment process. However, the energy recovered from additional methane production from swine slurry, dairy manure slurry, and solids separated dairy manure effluent were less than (-23%, -10%, and -9%, respectively) the energy input when ultrasonic pretreatment was applied at 160 μm_{pp} amplitude for 30s. Overall, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude (80 μm_{pp}) combined with shortest treatment time used (15s). An increase in ultrasonic amplitude and treatment time resulted in a reduction of energy efficiency. Thus, from energy efficiency standpoint, the most effective ultrasonic appears to be low-power input with a short ultrasonic time.

3.6 Kinetics of anaerobic digestion of ultrasonic pretreated animal manures

A nonlinear regression model was used to predict the rate of anaerobic reactions under different ultrasonic pretreatment conditions. The nonlinear regression model was written as

$$Y= K_{max} (1-e\wedge^{-KT})$$

Where K_{max} is estimated maximum methane yield (ml/g VS added) based on model prediction; K is kinetic rate of anaerobic digestion; T is anaerobic digestion time (days). K_{max} and K were obtained by using non-linear regression to minimize the sum of squared errors (SSE) between raw data and predicted value.

As shown in Table 4, the estimated maximum methane yields from anaerobic digestion of swine slurry at energy inputs of 0, 625, 1243, 1592, and 3078 J/g VS added were 411, 427, 417, 396, and 491 ml/g VS added, respectively. The estimated kinetic rates of anaerobic digestion of swine slurry with ultrasonic pretreatment at different energy inputs were similar. The estimated maximum methane yield from anaerobic digestion of beef feedlot manure at energy inputs of 0, 625, 1243, 1592, and 3078 J/g VS added were 411, 427, 417, 396, and 491 ml/g VS added, respectively. For anaerobic digestion of ultrasonic pretreated beef feedlot manure, the highest kinetic rate was obtained at the greatest energy input (3078 J/g VS). For anaerobic digestion of ultrasonic pretreated dairy manure slurry, the estimated maximum methane yield at energy inputs of 0, 625, 1243, 1592, and 3078 J/g VS were 161, 188, 193,188, and 245 ml/g VS added, respectively. For anaerobic digestion of ultrasonically pretreated solids separated dairy manure effluent, the estimated maximum methane yield at energy inputs of 0, 625, 1243, 1592, and 3078 J/g VS were 355, 346, 419, 431, and 445 J/g VS. Overall, the ultrasonic energy input did not affect the estimated maximum methane yield (Km) and the kinetic rate (K) of anaerobic digestion of animal manures.

4. Conclusions

Average methane yield from ultrasonically pretreated swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent was shown to increase by 14, 55, 37 and 8%, respectively; average soluble chemical oxygen demand (SCOD) of ultrasonic pre-treated manure samples increased by 30, 18, 37, and 14%, respectively. Results from this study showed that an increase in ultrasonic amplitude and the length of exposure to ultrasonic treatment resulted in an overall increase in SCOD and methane production. The greatest methane yields were obtained with the highest ultrasonic amplitude and longest ultrasonic treatment time utilized. However, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with shortest treatment time. An increase in ultrasonic amplitude and treatment time resulted in a reduction in energy efficiency. With ultrasonic pretreatment, larger improvement in methane production for beef and dairy manure slurry were observed.

Table 4. Kinetic of anaerobic digestion of animal manure pretreated with ultrasonic

Ultrasonic Energy Input (J/g VS)	Swine Slurry			Beef feedlot manure			Dairy manure slurry			Solids separated dairy manure effluent		
	Kmax (ml/g VS)	K	SSE	Kmax (ml/g VS)	K	SSE	Kmax (ml/g VS)	K	SSE	Kmax (ml/g VS)	K	SSE
0	411	0.20	140	171	0.18	13	161	0.3	106	355	0.23	89
625	427	0.22	78	194	0.18	35	188	0.29	109	346	0.27	93
1243	417	0.25	84	238	0.15	18	193	0.31	101	419	0.22	231
1592	396	0.26	100	257	0.16	51	188	0.34	82	431	0.22	310
3078	491	0.23	76	218	0.35	129	245	0.27	148	445	0.23	460

Literature Cited

[1] Chu CP, Lee DJ, Chang B, You CS, Tay JH. "Weak" ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids. Water Research 2002, 36(1): 2681-2688.

[2] Khanal SK, Grewell D, Sung S, van Leeuwen J. Ultrasound applications in wastewater sludge pretreatment: A review. Environmental Science and Technology 2007, 37(4):277-313.

[3] Chyi YT and Dague RR. Effects of particulate size in anaerobic acidogenesis using cellulose as a sole carbon source. Water Environment Research 1994; 66(5): 670-678.

[4] Nickel K, Neis U. Ultrasonic disintegration of biosolids for improved biodegradation. Ultrasonics Sonochemistry 2007, 14:450-455.

[5] Tiehm A, Nickel K, Zellhorn M, Neis U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. Water Research 2001, 35(8):2003-2009.

[6] Wang F; Wang Y and Ji M, Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration, J. Hazar. Mater 2005, 123: 145–150.

[7] Benabdallah EI-Hadj T, Dosta J, Marquez-Serrano R, Mata-Alvarez J. Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene removal. Water Research 2006, 41(1):87-94.

[8] APHA. Standard methods for the examination of water and wastewater. 15th ed. New York: American Public Health Association Inc., 1980.

[9] AOAC. Association of Official Analytical Chemists. Official methods of analysis. 14th ed. Assoc. Off. Anal. Chem., Washington, DC.

[10] Wei-Haan W, Burns RT, Moody LB, Hearn CJ, Grewell D. Characterization of ultrasonic pretreatment on biogas production potential from corn ethanol by-products. Biomass and Bioenergy. In review.

[11] Owens WF, Stuckey DC, Healy JB, Young LY, Mc Carty PL, Biomass for monitoring biochemical methane potential and anaerobic toxicity. Water Research 1979, 13:485-492.

[12] Walsh JC, Ross C, Smith M, Harper S, Wilkins W. Handbook on biogas utilization. Prepared for U.S. Department of Energy, Southeastern Regional Biomass Energy Program. Prepared by Georgia Institute of Technology, Engineering Technology Branch. Atlanta, GA; 1988.

[13] SAS Institute. 1990. SAS User's Guide: Statistic. Version 6.3 ed. SAS Inst. Inc., Cary, NC.

[14] Bougrier C, Carrere H, Delgenes JP. Solubilization of waste-activated sludge by ultrasound treatment. Chem. Eng. J. 2005, 106:163-169.

[15] Rai CL, Struenkmann G, Mueller J, Rao PG. Influence of ultrasonic disintegration on sludge growth and its estimation by respirometry. Environmental Science Technology 2004, 38:5779-5785.

[16] Grönroos A, Kyllönen H, Korpijärvi K, Pirkonen P, Paavola T, Jokela J, Rintala J. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. Ultrasonic Sonochemistry 2005, 12(1):115-120.

[17] Tiehm A, Nickel K. Neis U. The use of ultrasound to accelerate the anaerobic digestion of sewage sluge. Water Science and Technology 1997, 36 (11): 121-128.

[18] Khanal SK, Isik H, Sung S, and van Leeuwen J. Effects of ultrasound pretreatment on aerobic digestibility of thickened waste activated sludge. In *proceedings of 7th specialized conference on small water and wastewater systems,* March 7-10, 2006, Mexico City, Mexico.

[19] Lafitte-Trouqué S, Forster CF. The use of ultrasound and γ-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures. Bioresource Technology 2002, 84:113–118.

[20] Wang Q, Kuninobu M, Kamimoto K, Ogawa HI, Kato Y. Upgrading of anaerobic digestion of waste activated sludge by ultrasonic pre-treatment. Bioresource Technology 1999, 68: 309-313.

[21] Dewil R, Baeyens J, Goutvrind R. Ultrasonic treatment of waste activated sludge. Environmental Progress 2006, 25: 121-128.

CHAPTER 5. GENERAL CONCLUSIONS

General Discussion and Suggestions for Future Research

Chapter 3-Evaluation of ultrasonic pretreatment on methane production potential from corn ethanol by-products

The current study demonstrated that ultrasonic pretreatment can increase methane yield from anaerobic digestion of corn ethanol co-products. Ultrasonic pretreatment was shown to increase methane production by 25, 12, and 19% from anaerobic digestion of DDGs, centrifuge solids and thin stillage, respectively. These findings are in agreement with many other researches (Table 1) that have used ultrasonic pretreatment to enhance the degradability of anaerobic digestion of wastewater sludge.

Table 1. Ultrasonic pretreatment studies

Reference	Ultrasonic condition	Comments
Foster et al. [1]	Frequency: 23 kHz Time: 4 min	Increased biogas production by 15%
Bien et al. [2]	Frequency; 20 kHz Time: 60 s	Increased biogas production by 20-24%
Wang et al. [3]	Frequency: 9 kHz Time: 30 min	Increased biogas production by 64%

In contrast, Schaefer et al. [4] found no significant improvement in the anaerobic digestion of corn ethanol thin stillage when treated at a thermophilic temperature (55°C) in a completely stirred tank reactor with an ultrasonic pretreatment. The better results shown in the current study is possibly due to better ultrasonic conditions (such as frequency, amplitude, and treatment time) being selected for our experiment.

In comparison to chemical and thermo-chemical pretreatment method, ultrasonic treatment was shown to be effective and, is not hazardous to the environment. A study conducted by Kim et al. [5] evaluated the effects of various pretreatment methods (thermal, chemical, ultrasonic, and thermo-chemical) on the biogas production from anaerobic digestion of waster water sludge. They found that methane production was significantly increased by the four pretreatments. However, thermo-chemical pretreated WAS produced greatest amount of biogas. Ultrasonic frequency utilized in this study was 42 kHz. Operating frequency is an important factor that impacts the efficiency of ultrasonic systems. The cavitation effect generally decreases at high frequency range and increases at lower frequency range [6]. Therefore, nearly all sludge disintegration tests are conducted at the lower frequency range of 20 kHz. Therefore it is hard to make a statement that thermo-chemical pretreatment is more effective than ultrasonic pretreatment since ideal ultrasonic frequency was not utilized in their study. In addition, ultrasonic pretreatment is a physical process which means no secondary chemical compounds are generated. Therefore, when compared to chemical or thermo-chemical pretreatments, ultrasonic pretreatment is more environmental friendly.

Comparing with thermophilic treatment, ultrasonic pretreatment seems to be more effective at increasing methane yield from anaerobic digestion of corn thin stillage. In the current study, methane production from ultrasonic pretreated and untreated thin stillage were 411 and 346 ml/g VS_{added}, respectively. A study conducted by Agler et al. [7] tested the applicability of an integrated method of thermophilic anaerobic digestion of thin stillage from dry mill corn grain- to- ethanol plants by utilizing anaerobic sequencing batch reactors (ASBRs). They estimated the methane yield by total COD loading rates and removal rates was 245 ml/g COD_{added} (approximately equal to 350 ml/g VS_{added}) after reaching sustainable operating performance. The data suggested that ultrasonic pretreatment methods are more effective than thermophilic pretreatment; and a better methane yield could be obtained under thermophilic conditions than mesophilic conditions. Anaerobic digestion of ultrasonic pretreated corn thin stillage under thermophilic condition may further improve methane production. However, a combination of ultrasonic and thermophilic pretreatment methods will require more energy input. In consequence, energy consumption and economic return should be evaluated as well.

Methane generated from stillage digestion could partially replace fossil fuels (often natural gas, sometimes coal) as energy inputs for the ethanol production process. Agler et al. [7] estimated that methane generated from thermophilic anaerobic digestion of corn thin stillage could replace 51% of natural gas consumed at a conventional dry mill ethanol facility and improve the net energy balance ratio from 1.26 to 1.70. Using integrate data obtained by Agler et al.[7], in theory, using ultrasonic pretreatment prior to anaerobic digestion of corn thin stillage could possibly replace more than 60% of natural gas consumed at a conventional dry mill ethanol facility and improve the net energy balance ratio up to 2. Indeed, if ethanol co-products are solely used for energy production, it makes more sense to anaerobicaly digest whole stillage than thin stillage, since additional energy used for drying could be eliminated. Therefore, further investigation is needed to evaluate the effect of ultrasonic pretreatment on anaerobic digestion of whole stillage.

Corn ethanol co-products are traditionally used for animal feed. Historically, market prices of corn ethanol co-products are similar to market prices of corn and soybean meal. However, supply and demand play an important role in ethanol co-product prices and the economics of producing a certain type of ethanol co-product, such as DDGs. As the ethanol industry has rapidly expanded across the nation, the supply of various corn co-products has become more abundant and the price of co-product may drop in the future. Additionally, natural gas prices most likely will continue to increase in the future. Optimization of methane yield by ultrasonic pretreatment could make recovery of energy from corn ethanol co-products more economically feasible than selling co-products as animal feed.

In addition, the recover of post-digestion nutrients (such as N, P, and Mg) will be challenging given that these nutrients are in a soluble form. Nutrients (such as N, P, and Mg) after anaerobic digestion could possibly be recovered by precipitated struvite which could be sold as high value fertilizer. This may further improve the economically feasible to anaerobic digestion of corn ethanol. However, additional research is need to investigate the possibly to recover of co-products nutrients.

Ultrasonic pretreatment has limitations as well. One of major issues facing ultrasonic pretreatment is high energy consumption. The optimization of energy consumption is essential for the use of ultrasonic as a pretreatment to anaerobic digestion for the process to be economically feasible. An extremely basic energy balance was prepared in this study. It 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 centrifuge solids produced only 55% of the energy required to operate the process. A complete evaluation of the energetic efficiency and potential economic return on the use of ultrasonic as a pretreatment method for anaerobic digestion of ethanol stillage needs to be done in future studies.

In summary, the application of anaerobic digestion technology to recover energy from corn ethanol stillage has great potential and optimization of methane yield by ultrasonic pretreatment will potentially make recovery of energy from corn ethanol co-products more economically feasible than selling co-products as animal feed.

Chapter 4 - Evaluation of ultrasonic pretreatment on anaerobic digestion of different animal manures

The study presented in chapter 4 demonstrated that ultrasonic pretreatment increased methane yield from anaerobic digestion of animal manure. In this study, average methane yield from ultrasonic pretreated swine slurry, beef feedlot manure, dairy manure slurry, and solids separated dairy manure effluent was shown to increase by 14, 55, 37 and 8%, respectively.

González-Fernández et al. [8] evaluated the effect of three pretreatment methods (mechanical, chemical, and thermal) on methane production and anaerobic biodegradability of swine wastes. The mechanical pretreatment was performed by separation of liquid and solid of swine slurry by a 0.25 mm pore size screen. For the chemical pretreatment, flocculant agent (polyacrylamide) and alkali (NaOH) were added. The thermal pretreatment was applied at 170 °C for 30 min. They reported that methane production was enhanced by flocculation pretreatment (11%), alkali (13%), and thermal treatment (35%). No mechanical pretreatment improvement of methane yield was observed. Comparing results reported by González-Fernández et al. [8] with data generated in current study; ultrasonic pretreatment appears to be more effective when applied to anaerobic digestion of animal manure. A combination of ultrasound with thermophilic pretreatment may further enhance method yield. Again, energy consumption and economic return should be evaluated since more energy is required for pretreatment process.

Methane yield on per gram VS basis from solids separated dairy manure effluent was greater than those from dairy manure without separation as a result of poor digestibility of fibers. This result is in agreement with pervious study [10] [11]. A study conducted by Lo et al. [10] evaluated the effect of liqid-solids separation pretreatment on methane production from mesophilic digestion of dairy cattle manure and found that the methane production rate from screened waste (0.5 L CH_4/L/day) was approximately double that obtained from unscreened slurry at 6 days hydraulic retention time (HRT). Later, Liao et al. [11] conducted a similar study and found similar results that screening out the coarse solids from the manure before digestion increased total methane production and methane content of biogas. However, cattle manure slurry contains a large fraction of particulate matter and most of the biologically degradable component of the slurry is contributed by the particulate matter [12]. Therefore, overall methane production could possibly be decreased, when liquid-solids separation method is used, due to a loss of carbon rich particulate matter.

The current study showed that an increase in ultrasonic amplitude and the length of exposure to ultrasonic treatment results in an overall increase in methane production and greatest methane production was obtained with the highest power and longest treatment time utilized. However, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with shortest treatment time used. An increase in ultrasonic amplitude and treatment time resulted in a reduction of energy efficiency. The optimization of energy consumption is essential for the use of ultrasonic as a pretreatment method prior to anaerobic digestion for the process to be economically feasible. Therefore, determining the ideal ultrasonic amplitude and treatment time is the key to maximize energy efficiency. In addition, many other factors including ultrasonic intensity, ultrasonic density, and power input are also important parameters that can affect the ultrasonic disintegration. Future investigation is needed to determine ideal ultrasonic time, amplitude, intensity, density, and power input to optimize animal manure ultrasonic pretreatment efficiency.

In addition, total solid (TS) content of animal manure could affect the ultrasonic pretreatment performance [13] [14] due to the nature of cavitation. Cavitation is the phenomenon where micro-bubbles are formed in the liquid phase and expand to unstable size, and then rapidly collapse [15]. During collapse, the adjacent cell walls and membranes can be disrupted by extreme shear forces due to cavitation. Ultrasonic pretreatment is more commonly used for treating wastewater sludge, the TS content of sludge used for those studies was diluted to less than 5%. Unlike wastewater sludge, animal manure usually contains higher TS content (8-20%). Therefore, additional water was added in current study to achieve uniform and efficient ultrasonic pretreatment. Before applying ultrasonic pretreatment in the field, further study should be conducted to determine the effects of TS content (range from 8- 20%) on the performance of ultrasonic efficiency.

Literature Cited

[1] Forster CF, Chacin E, Fernandez N. The use of ultrasound to enhance the thermophilic digestion of waste activated sludge. Environmental Technology 2000, 21(3): 357-362.

[2] Bien JB, Malina G, Bien J, Wolny L. Enhancing anaerobic fermentation of sewage sludge for increasing biogas generation. Journal of Environmental Science and Health 2004, 39 (4):939-949.

[3] Wang Q, Kuninobu M, Kakimoto K, Ogawa H, Kato Y. Upgrading of anaerobic digestion of waste activated sludge by ultrasonic pretreatment. Bioresource Technology 1999, 68(3): 309-313.

[4] Schaefer SH, Sung, S. Retooling the ethanol industry: Thermophilic anaerobic digestion of thin stillage for methane production and pollution prevention. Water Environment Research 2008, 80(2):101-108.

[5] Kim J, Park C, Kim T, Lee M, Kim S, Kim S, and Lee J. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. Journal of Bioscience and Bioengineering 2003, 95 (3): 271-275.

[6] Khanal SK, Grewell D, Sung S, van Leeuwen J. Ultrasound applications in wastewater sludge pretreatment: A review. Environmental Science and Technology 2007, 37(4):277-313.

[7] Agler M, Garcia ML, Lee ES, Schlicher M, Angenent. Thermophilic anaerobic digestion to increase the net energy balance of corn grain ethanol. Environ. Sci. Technol. 2008, 42(17):6723-6729.

[8] Gonzalez-Fernandez C, Leon-Cofreces C, Garcia-Encina A. Different pretreatments for increasing the anaerobic biodegradability in swine manure. Bioresource Technology 2008, 99(18):8710-8714.

[9] Ardic I, Taner F. Effects of thermal, chemical and thermochemical pretreatments to increase biogas production yield of chicken manure. Fresenius Environmental Bulletin 2005, 14:373–380.

[10] Lo KV, Bulley PH, Whitehead AJ. The effect of solids-separation pretreatment on biogas production from dairy manure. Agricultural Wastes 1983, 8(3):155-165.

[11] Liao PH, Lo KV, Chieng ST. Effect of liquid-solids separation on biogas production from dairy. Energy in Agriculture 1984, 3:61-69.

[12] Ong HK, Greenfield PF, Pullammanappallil PC. An operational strategy for improved biomethanation of cattle-manure slurry in an unmixed, single-stage digester. Bioresource Technology 2000, 73: 87–89.

[13] Grönroos A, Kyllönen H, Korpijärvi K, Pirkonen P, Paavola T, Jokela J, Rintala J. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. Ultrasonic Sonochemistry 2005; 12(1):115-120.

[14] Wang F, Wang Y, Ji M. Mechanisms and kinetic models for ultrasonic waste activated sludge disintegration. J. Hazard. Mater. 2005, B123: 145-150.

[15] Khanal SK, Grewell D, Sung S, van Leeuwen J. Ultrasound applications in wastewater sludge pretreatment: A review. Environmental Science and Technology 2007, 37 (4): 277-313.