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Retooling the ethanol industry : thermophilic, anaerobic digestion of thin stillage for methane production and pollution prevention

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Retooling the ethanol industry: Thermophilic, anaerobic digestion of thin stillage for methane production and pollution prevention

by

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ABSTRACT

Anaerobic digestion of thin stillage from a corn ethanol plant was tested at thermophilic temperature with a completely stirred tank reactor. Loading at 30, 20, 15, and 12 day hydraulic retention times (HRT) was tested. Ultrasonic pretreatment was used for one digester with another as a control. The influent thin stillage was a concentrated wastestream with 100 g/L total chemical oxygen demand and 60 g/L volatile solids (VS) typical. Significant reduction of VS was achieved with a maximum reduction (89.8%) at the 20 day HRT. Methane yield was also high with a typical yield of 0.6-0.7 L-CH_4/g-$VS_{removed}$ during steady state operation. Effluent VFAs were low for a thermophilic anaerobic digester with less than 200 mg/L as acetic acid for the 20 and 30 day HRTs. The influent thin stillage had a low pH (~4) and zero alkalinity, but biological regulation of alkalinity allowed for operation without alkalinity addition. Steady state operation was achieved at 30, 20, and 15 day HRTs, and digester failure occurred at a 12 day HRT. At the 20 day HRT, a sustained shock load with a 20% organic increase was easily handled by the system. Ultrasonic pretreatment did not significantly improve the operation of the system and is not recommended for future use with anaerobic digestion of thin stillage. The high VS reduction could improve water recycling within the ethanol production process. Substantial energy is produced from the system in the form of methane gas, and natural gas displacement is estimated at 43-59% for a dry grind ethanol plant. Energy production value is estimated at $7 to $17 million ($10 million likely) for a facility producing 95 million gallons of ethanol per year.

Keywords: ethanol, thermophilic anaerobic digestion, volatile fatty acids, methane

LITERATURE REVIEW

INTRODUCTION

Ethanol is a renewable fuel source that can be derived from a variety of biomass sources. In the United States, most fuel ethanol is derived from corn (Galitsky *et al.,* 2003). However, U.S. energy policy is highly politicized and continued efforts to enhance the resource reuse and recovery aspects of ethanol production will continue to make it more economically viable and therefore less dependent upon government subsidies. The goal of this research is to give overviews of current ethanol production methods and anaerobic digestion technologies and to show how thermophilic anaerobic digestion of thin stillage can enhance resource reuse and recovery in ethanol production.

Historical Ethanol Production

The fermentation of starches to ethanol is one of humankind's first value-added product techniques. From those humble (and likely accidental) beginnings thousands of years ago with hand harvested crops and wild yeast, a highly mechanized and large scale industry has developed to provide ethanol beyond consumptive beverage purposes. Current ethanol production capacity (as of February 2006) in the United States is 4,400 million gallons per year (MGal/yr) with 2,100 MGal/yr currently under construction (Renewable Fuels Association, 2006). The ethanol industry actually had a foothold in the late 1800s when more than 25 MGal/yr were produced for lamp oil in the United States (Weber, 2001). Large oil companies leveraged the government to place a tax on ethanol during the Civil War and nearly destroyed the industry. Ethanol use was not again prominent until after the Organization of Petroleum Exporting Countries oil embargo of 1973 (Weber, 2001). The ethanol industry received another boost in 1990 with the passage of the Clean Air Act amendments that require reformulated gasoline (of which ethanol is a viable additive) for reduction of air pollution by automotive tailpipe emissions (Singh *et al.*, 2001). Concerns with MTBE (the only additive used more than ethanol for reformulated gasoline) pollution of groundwater have also recently led to increased ethanol use (Hebert, 2005).

Political Support and Hindrance for Ethanol

Because ethanol production is part of the highly politicized energy sector, some of the political issues must be stated. The ethanol industry in the United States would not exist in its current form without tax breaks and incentives from various government agencies. The politics of ethanol have worldwide implications and are multifaceted within our own borders. One issue is bolstering the agrarian livelihood of the corn-belt by providing another outlet for corn production. Depending on where one resides in the US, this can be viewed as either positive or negative. The federal requirement for fuel oxygenates in non-attainment areas is also a political issue with ethanol use at its center. Fourteen states have already banned MTBE, the principal fuel oxygenate, in favor of ethanol. Four more states have passed bans that will take effect in coming years and two more have bans pending federal action (Renewable Fuels Association, 2005). Of course, ethanol's status as a renewable resource also places it squarely in the ongoing global warming debate.

Support for ethanol recently came in the form of a letter signed by 30 US governors and submitted to President Bush asking lawmakers to raise the requirement for ethanol use from five billion to eight billion gallons of ethanol per year by 2012. The governors argued that the risk of imported oil to the United States' energy, economic, and environmental security would best be mitigated in the "safest and cheapest way" by ethanol (Hebert, 2005).

Ethanol is not without its detractors, however. The politically influential American Petroleum Institute opposes ethanol expansion "into areas where it is uneconomical to be used," which roughly translates to anywhere that corn is not grown and excludes many heavily populated areas. Many in congress consider tax incentives for ethanol a welfare program for farmers (Hebert, 2005).

The United States can look to Brazil for how political support cultivated an ethanol industry. After the oil embargo of the 1970s, Brazil made a concerted effort to make itself less reliant on imported oil by supporting ethanol production from sugarcane. This effort has led to use of pure ethanol in 40% of Brazil's vehicles and a 24/76 ethanol/gasoline blend in the remainder of the fleet (Weber, 2001). Sweden has had similar success with oil consumption cut in half since 1980 even with increased demand (Weber, 2001).

Why Ethanol?

Part of the appeal of ethanol is that it is a renewable liquid fuel that can be dispensed in the same manner as conventional gasoline for use in transportation vehicles. Figure 1 illustrates a simplified version of how ethanol interacts in the carbon cycle. Ethanol does not have the problem of gaseous fuels like hydrogen that require pressurized tanks and a distribution network that is not established. Ethanol also burns much cleaner than conventional gasoline giving it an environmental advantage. A 100 million gallon per year ethanol facility also provides, directly and indirectly, approximately 2250 domestic jobs (Weber, 2001).

Although there are a myriad of other reasons for ethanol use, an advantage of production that is not often discussed will be demonstrated in this paper: the many byproducts and opportunities for resource recovery and reuse in the production of ethanol.

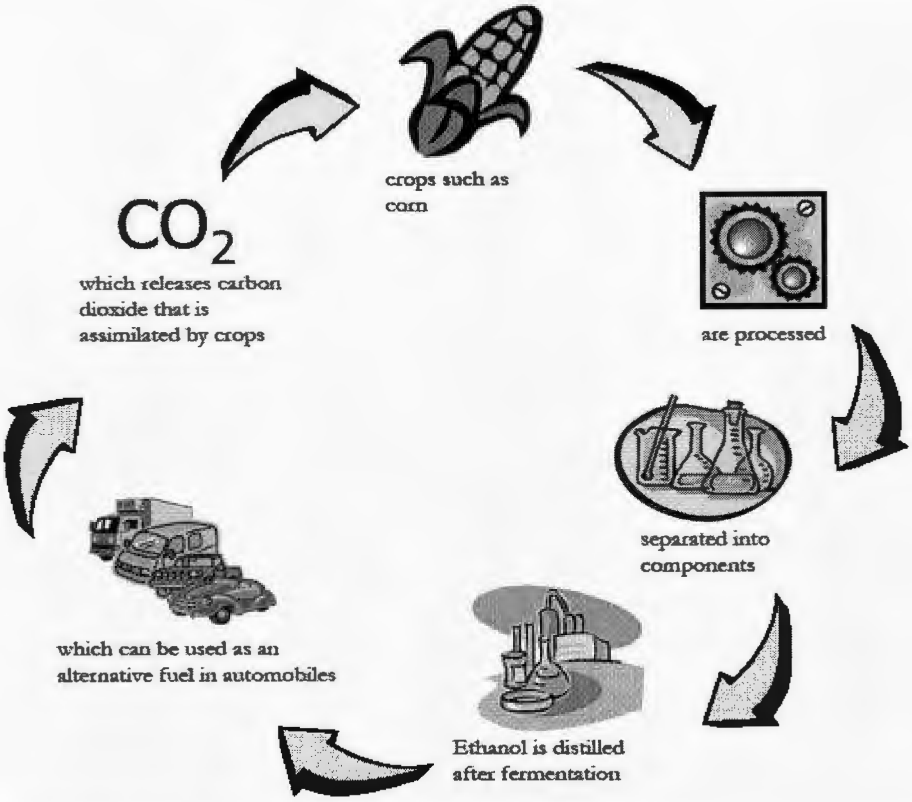

Figure 1: Ethanol and the Carbon Cycle (Singh *et al.*, 2001)

Ethanol Feedstocks

Although more ethanol is produced from corn in the United States than all other feedstocks combined (Galitsky *et al.,* 2003), there are other feedstocks that have the potential for future development. As mentioned, Brazil produces its ethanol almost exclusively from sugarcane, and much of the Caribbean and other areas of South America also utilize this feedstock. Already in the US, ethanol is produced exclusively from or in combination with corn using milo, barley, cheese whey, beer/beverage waste, wheat, and sorghum (Renewable Fuels

Association, 2005). Part of the competitiveness of ethanol production from corn, besides its political backing, is that many co-products are generated from the corn kernel during production. Recovery of these co-product resources underpins the ethanol industry and is a key to the future use of not only corn, but all other biomass feedstocks for ethanol production.

Ethanol Production Processes

Although several feedstocks can be converted into ethanol, corn is the main feedstock utilized in the United States and will be the only process discussed here in detail. Wet milling historically accounts for the majority of production in the United States (Galitsky *et al.,* 2003). The dry milling and modified dry grind processes make up the remainder of production with modified dry grind being a relatively new process that incorporates aspects of both the wet and dry mill technologies. Wet milling operations are usually larger (greater than 100,000 bushels per day operating capacity) because the large capital cost requires an economy of scale (Galitsky *et al.*, 2003). However, most new production facilities are of the dry grind type, which is the focus of this research.

Dry Milling

Singh *et al.* (2001) describe the dry milling process as more simplified and better suited to smaller scale ethanol production such as farmer's co-ops. The corn kernel is not separated before fermentation as in the wet mill process, which leads to more of the corn kernel staying in the stillage of dry grind ethanol plants.

Process Description

A dry mill process schematic is given in Figure 2. The corn kernels are first ground in a hammer-mill or roller-mill and then mixed with water and cooked. The cooked mash is cooled and mixed with enzymes to convert the starch to fermentable sugars. This converted mash is fermented with yeast to produce carbon dioxide and ethanol. Carbon dioxide is stripped and the remaining liquid undergoes distillation to produce 95% ethanol. Further dehydration of the ethanol uses molecular sieves, which preferentially retain the water while allowing the ethanol to pass. An ethanol purity of 99.95% is achievable with distillation and dehydration. After the ethanol is removed, the remaining fermentation residuals are referred to as whole stillage, which is centrifuged to remove the thicker solids. Distiller's dry grains (DDG) will be produced by drying the centrifuged solids. The liquid portion from the centrifuge is referred to as thin stillage and is typically evaporated to syrup and mixed on the DDG to form DDGS (distiller's dried grains with solubles).

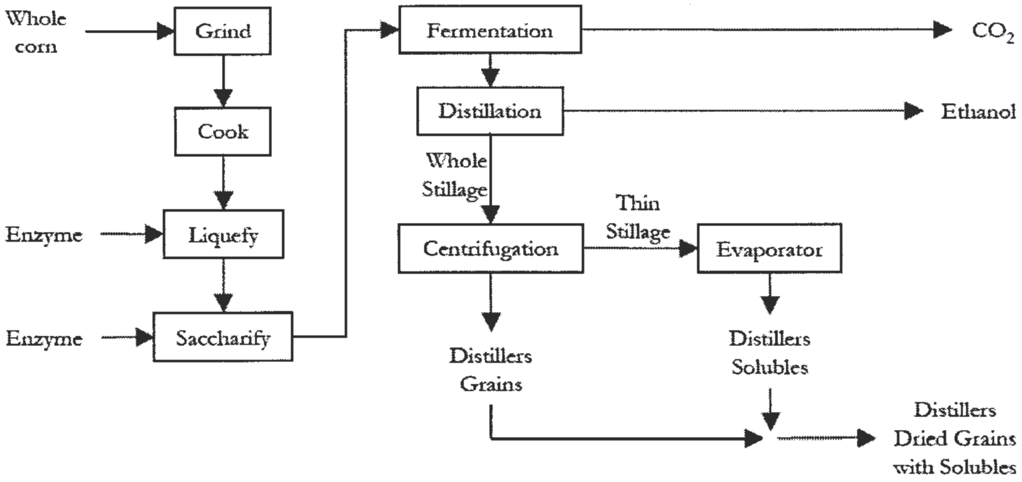

Figure 2: Schematic of the Conventional Dry Milling Ethanol Process (adapted from Singh *et al.*, 2001)

Principal Byproducts

Only three products are typical of the dry grind process: ethanol, DDGS, and carbon dioxide. Ethanol is sold primarily as a fuel, although beverage or industrial uses are also possible. Carbon dioxide can be sold for use in carbonated beverages, dry ice production, or other industrial uses. The DDGS is sold as a livestock feed.

STILLAGE DIGESTION

The yeast fermentation to produce ethanol does not utilize all of the available organics, which results in a waste referred to as stillage. Older or smaller ethanol production facilities could dispose of stillage by direct feeding to livestock or discharge to a sewer. This is not an option on the larger scale that ethanol is now being produced. Dried livestock feed products are now the typical byproduct of the residual organics from dry mill ethanol plants.

The evaporator condensate (from the evaporation of thin stillage) is the single largest contributor to plant wastewater flow. Thin stillage is evaporated to syrup that is then applied to the distiller's dried grains (DDG) to produce distiller's dried grains with solubles, or DDGS (Anderson *et al.*, 1986). The evaporated thin stillage does not add any appreciable value to the final animal feed product but is a way to dispose of residual organics to achieve a "zero discharge" operation (Hunter, 1988). The use of thin stillage wastewater in this way is a loss of co-product and requires a significant amount of energy for evaporation. Anaerobic bacterial digestion of stillage represents an opportunity to recover energy in the form of methane (typical biogas is approximately two-thirds methane with the remainder as carbon dioxide) that can be utilized at the plant for heat in drying and distillation operations. The corn ethanol industry has attempted to develop this concept, but literature on full scale implementation is not available.

Stillage Characterization

The typical flowrate of stillage waste is 10 to 13 gallons per gallon of ethanol produced (Yeoh, 1997; Springer and Goissis, 1988). The chemical oxygen demand (COD) of stillage effluents can easily reach levels of 100 g/L (Olguin *et al.*, 1995). This represents both concentrated waste and a significant opportunity for energy recovery. Solids content is also important, however, because high suspended solids concentrations are not compatible with some digester configurations. Generalizations are difficult to make for this waste because plant operation has a significant influence on stillage composition. Nitrogen and phosphorus are generally sufficient for microbial growth, volatile fatty acids (VFAs) are moderately concentrated, and alkalinity is negligible because of a decreased pH due to VFAs.

Anaerobic Digestion of Corn Stillage

The literature is relatively devoid of studies involving corn stillage digestion by anaerobic digesters compared to other industrial-agricultural activities such as large-scale hog confinements and slaughterhouses. Wilkie *et al.* (2000) conducted a comprehensive review of ethanol stillage relating to anaerobic treatment and found limited information on anaerobic digestion of stillage from corn feedstocks. Because the ethanol industry in the United States is part of the private sector, anaerobic stillage digestion may be taking place that has not been published or referenced on the basis of "industrial secrets." Biothane, a leading supplier of industrial upflow anaerobic sludge blanket (UASB) digester equipment, has a number of corn related installations listed on its website and summarized in Table 1 (Biothane, 2005). Both expanded granular sludge bed (EGSB) and UASB digesters have been installed by Biothane for various corn waste treatment applications.

Table 1: Biothane (2005) Anaerobic Installations for Corn Waste

Industry	Country	Year of Installation	COD Load kg/d	Flow m^3/hr	Reactor Volume m^3	OLR kg/m^3-d	COD g/L
Biobed (EGSB)							
Corn Products	Turkey	1998	23,000	140	1,226	18.76	6.8
Corn Products	USA	1999	32,953	442	1,550	21.26	3.1
Corn Products	USA	1996	5,490	79	650	8.45	2.9
Corn Products	USA	1996	26,900	410	1,840	14.62	2.7
Biothane (UASB)							
Corn Starch Processing	Netherlands	1988	15,000	25	1,000	15.00	25.0
Corn Products	Spain	1998	4,032	7.2	535	7.54	23.3
Corn Products	Korea	1998	1,756	4.2	240	7.32	17.4
Ethanol from Corn	**USA**	**1988**	**20,000**	**55**	**2,400**	**8.33**	**15.2**
Corn	Mexico	1998	8,500	71	900	9.44	5.0
Ethanol from Corn	**USA**	**1986**	**20,000**	**227**	**2,000**	**10.00**	**3.7**
Corn Starch	Brazil	1996	16,000	190	1,800	8.89	3.5
Corn Products	Mexico	1996	8,200	114	650	12.62	3.0
Corn Starch Processing	Netherlands	1989	12,000	230	1,500	8.00	2.2

There are typically seven main wastewater streams in a large scale ethanol production plant practicing byproduct recovery: flash condensate; wash waters from the cleaning of process vessels, pumps, and piping; cooling tower blowdown; rectifier bottoms; evaporator condensate; scrubber blowdown; and general housekeeping wastes (Anderson *et al.*, 1986). The Biothane digesters could be treating any of these wastes, but evaporator condensate (from the evaporation of thin stillage) is the most likely because of its inherently low solids content.

Suspended Growth and Fixed-Film Digesters

The principle published research on anaerobic corn stillage digestion was conducted by Stover in the mid-1980s. These studies achieved positive results, but a number of fundamental problems may have limited the implementation of anaerobic digestion of corn ethanol waste. First, the studies were carried out at mesophilic temperatures, which would require more cooling of the stillage and also run at a lower rate. Second, the waste was typically diluted in the studies, which is impractical for implementation. Many of the published studies of anaerobic corn stillage treatment do not compare with current research because process recycling practices in the industry have increased the concentration of stillage waste. However, any comparison will aid in putting current research into context.

The first significant publication was by Stover *et al.* (1983). The study included mesophilic anaerobic digesters treating thin corn stillage from the Oklahoma State University Agricultural Engineer's 0.2 MGal/yr research facility and a 3.0 MGal/yr plant near Hydro, OK. The waste was settled by gravity and the supernatant used for the studies. Digesters were continuous flow suspended growth with 7.2 L mix tank and 3.5 L settling chamber capacities. The original research plan called for an aerobic polishing step, but the anaerobic treatment was better than anticipated and an aerobic step was eliminated. The high-strength influent was diluted for most of the study with, "all the systems except the 30-day SRT systems were operated at around one-third of the full strength stillage substrate concentrations." Two and four day SRT systems were operated as "once through" while the other SRTs were sludge recycle systems. The 30-day SRT runs were conducted at two-thirds and full strength for 30(a) and 30(b), respectively. The authors note that pH and temperature control were easier at longer SRT and higher wastewater strength operation. At 30-day SRT, only 200mg/L $CaCO_3$ alkalinity addition was required. The F/M ratios presented in Table 2 are based on MLVSS. With the diluted stillage, SRTs below four days were considered limiting.

Table 2: Summary of Continuous Anaerobic System Treatment Performance (Stover *et al.*, 1983)

		Soluble BOD_5		
		Influent mg/L	Effluent mg/L	Removal %
SRT (days)	F/M			
2	2.44	3,045	2,840	6.7%
4	1.50	2,315	650	71.9%
6	1.70	5,400	1,520	71.9%
10	0.85	6,120	180	97.1%
20	0.52	5,250	53	99.0%
30(a)	0.32	9,200	152	98.3%
30(b)	0.37	16,000	133	99.2%
		Soluble COD		
2	5.21	6,500	5,900	9.2%
4	2.25	5,200	1,200	76.9%
6	2.82	8,960	2,470	72.4%
10	1.29	9,300	850	90.9%
20	1.20	12,250	460	96.2%
30(a)	0.58	16,790	1,190	92.9%
30(b)	0.67	28,620	560	98.0%
		Soluble TOC		
2	1.96	2,450	2,130	13.1%
4	0.88	2,070	835	59.7%
6	0.83	2,650	1,290	51.3%
10	0.51	3,650	630	82.7%
20	0.38	3,820	320	91.6%
30(a)	0.27	7,800	230	97.1%
30(b)	0.29	12,280	430	96.5%

Stover *et al.* (1983) also presented similar batch studies, but the results mirrored the continuous studies fairly well and are not as significant to the current research. The research was considered successful with removal efficiencies of soluble waste well above 90% for long SRT systems.

Stover *et al.* (1984) continued research on anaerobic digestion of corn stillage with a more detailed evaluation of the thin stillage characteristics (Table 3) and a comparison of suspended growth and fixed film processes (Table 4).

Table 3: Raw Wastewater (Thin Stillage) Characteristics, mg/L (Stover *et al.*, 1984)

Parameter	Mean	Std Dev
TS	32,200	9,300
TDS	18,600	7,100
SS	11,800	3,700
VSS	11,300	3,500
CODt	64,500	12,600
CODs	30,800	6,200
BOD5t	26,900	800
BOD5s	19,000	2,100
TOCs	9,850	2,200
Total P	1,170	100
Soluble P	1,065	75
Total TKN	755	115
Soluble TKN	480	95
Soluble NH3-N	130	60
Total Protein	4,590	650
Soluble Protein	2,230	780
Total Carbohydrate	8,250	750
Soluble Carbohydrate	2,250	550
Soluble Glucose	<750	
pH (range)	3.3-4.0	

Table 4: Anaerobic Treatment System Performance in Terms of BOD (COD) (Stover *et al.*, 1984)

Suspended Growth Systems

Loading Rate F/M	Influent mg/L	Effluent mg/L	MLVSS mg/L	Methane %	Methane[a] Production ft^3/lb-BOD(COD)
0.22	2,300	15	3,380	78	21.1
(0.50)	(5,125)	(380)			(9.9)
0.23	4,100	28	5,380	71	20.7
(0.56)	(10,100)	(380)			(8.8)
0.31	8,880	35	8,500	70	15.7
(0.55)	(16,000)	(425)			(8.5)

Fixed-Film Reactor System

Loading Rate lbs/day/1000 ft^2	Influent mg/L	Effluent mg/L		Methane %	Methane[a] Production ft^3/lb-BOD(COD)
0.68	1,786	34		77	17.0
(0.95)	(2,512)	(131)			(12.6)
1.46	3,968	57		75	12.8
(2.10)	(5,696)	(215)			(9.2)
2.83	7,485	140		70	12.9
(4.01)	(10,100)	(271)			(9.6)
5.14	12,167	390		60	13.0
(7.68)	(18,445)	(756)			(8.7)

[a] Based on soluble BOD (COD) removed.

The suspended growth system showed similar performance to the fixed-film system, which should be attributed to the biomass recycle employed in the suspended growth system. The authors state an estimated scaled up methane production of 130,000 cubic feet of methane per day from 60,000 gallons per day of thin stillage, which is equivalent to 0.252 m^3-CH_4/kg-COD_{added} based on their average influent characteristics. Using the influent sCOD:tCOD ratio of 0.48 from Table 3, the calculated methane yields from Table 4 range from 0.25 to 0.37 m^3-CH_4/kg-$COD_{removed}$ with an average of 0.29 m^3-CH_4/kg-$COD_{removed}$.

Stover *et al.* (1984) continued by demonstrating the significance of methane recovery to the overall process. With respect to the energy required to produce ethanol, the authors estimated stillage evaporation to account for 28,400 BTU per production gallon of the total 97,850 BTU per production gallon consumed. If stillage evaporation were replaced with anaerobic treatment, they estimated that the methane produced by the anaerobic digesters could account for 60% of the daily BTU requirement for the ethanol plant. The analysis was based on the following parameters:

Influent
Flow – 60,000 gpd
sBOD – 10,000 mg/L (20,000 lb/d)
sCOD – 15,000 mg/L (30,000 lb/d)

Methane Production (based on soluble BOD (COD) removed)
Percent – 70%
Ft^3/lb BOD removed – 13
Ft^3/lb COD removed – 9

Digester Size – 545,000 gallons
HRT – 9.1 days
MLVSS – 10,000 mg/L
F/M – 0.22 (0.33)

Effluent Quality

sBOD – 35 mg/L
sCOD – 750 mg/L

This analysis disregards hydrolysis by basing the methane yield on soluble BOD (COD) removed. A portion of the total BOD (COD) is converted to soluble BOD (COD) in the digesters. The methane yield is therefore difficult but not impossible to compare. Also, the soluble COD loading assumed indicates an influent concentration of 60 g/L, which is much higher than the 2-18 g/L used in their experiments.

Previous studies had also considered aerobic treatment, but Stover et al (1984) state lower alkalinity and no nitrogen and phosphorus requirements as reasons to use anaerobic digestion. The authors also state that the anaerobic sludge could be dried and mixed with the DDGS although they never demonstrated that livestock would accept the sludge/DDGS and did not include sludge drying into their energy balance calculations.

Stover *et al.* (1985) also conducted shock loading studies for the anaerobic systems previously described. The fixed-film system was hydraulically and organically shock tested by doubling the flowrate (and therefore loading rate) for a 24 hour period. The system showed a 50% increase in gas production as well as increases in effluent COD, BOD, and VFAs. Levels of all parameters returned to normal levels when the shock load ceased. A temperature shock (drop from 36 to 26°C for four days) on the fixed-film system dropped gas production and elevated effluent parameters, but normal operation was reestablished after a return to normal operating temperature. The fixed-film digester was also tested for dormancy capabilities. Feeding ceased for 16 days and the temperature was dropped to 20 - 25°C during the dormancy period. Feeding resumed for seven days and then ceased for 11 days at mesophilic temperatures. In both instances of dormancy, the digester showed vigorous response to resumed feeding within 24 hours. The suspended growth system was also dormancy tested, and found to have similar restart capabilities to the fixed-film system. This should come as no surprise because during a dormancy period there is no difference in biomass retention between the two systems. Organic and hydraulic shock loads for the suspended growth system showed similar performance as the fixed-film system with pre-shock levels reestablished within 24 to 48 hours. The system also had the capability to withstand pH values as low as 6.5 but VFA accumulation occurred below 6.5, which the authors attributed to the VFA:Alk ratio rising above 0.5. COD for this study was in the range ~16-22 g/L. The authors further comment by stating that the F/M ratio is the best indicator for design basis and kinetic coefficient comparison, but they base these statements solely on their other papers.

Fluidized-Bed Digesters

Kothari *et al.* (1986) treated waste from a wet-mill ethanol plant with a two-stage mesophilic anaerobic system. However, the wastewater exhibits very different characteristics from the current research:

• Total COD:	9,028
• Soluble COD:	6,428
• Total BOD_5:	5,900
• Soluble BOD_5:	4,691
• TSS:	2,181
• VSS:	1,986
• Total Alkalinity ○ As $CaCO_3$	0
• TKN	41
• TP	48

All in mg/L.

The less concentrated wastewater allowed for use of a fluidized bed with acidogenesis and methanogenesis digesters comprising the two phases. This anaerobic system was evaluated for use as a pretreatment step before aerobic activated sludge treatment. The system achieved 83% BOD_5 removal at loadings up to 25.4 kg COD/m^3-day. Methane yield varied from 0.21 to 0.31 m^3/kg COD. This system is well suited for this application and would significantly reduce the load on the activated sludge system while simultaneously recovering energy. A two-phase fluidized bed digester is not practical for high solids loading, however.

UASB Digesters

Another published study on anaerobic treatment of corn-ethanol wastewater was conducted by Lanting and Gross (1985). A Biothane UASB digester was tested at South Point Ethanol in Ohio, which produces ethanol from corn. The basis of the study was to investigate an anaerobic pretreatment step for the plant's trickling filters, which were treating the plant wastewater. Average influent total COD was about 3,600 mg/L, which is significantly lower than wastes from other ethanol plants. Mainly due to the less concentrated waste, the authors state that "…the feasibility of anaerobic digestion for the treatment of corn-ethanol wastewater was not really an issue." Results of the study are summarized in Table 5.

Table 5: Average Performance Characteristics during Pilot Study (Lanting and Gross, 1985)

Average Performance Characteristics During Pilot Study			
	Influent	Effluent	Removal
TCOD, mg/L	3,627	874	76%
SCOD, mg/L	2,889	416	86%
TBOD, mg/L	2,441	288	88%
SBOD, mg/L	1,910	181	91%

Volumetric Loading	9.3 $kg/m^3/d$
HRT	9.4 hr
Biogas Methane Content	83%
Methane Yield	0.33 m3/kg-TCOD removed

Shock loading tests were also conducted by Lanting and Gross, and the UASB pilot could handle loadings of three to four times the average flow.

Packed-Bed and Gas-Fluidized Digesters

The final applicable study found was by Hunter (1988). This study compared two types of anaerobic digesters for the treatment of ethanol stillage. The ethanol production facility was located in Colwich, KS and utilized a mix of corn and milo as fermentation substrate during the study (proportions unspecified). Hunter's research was plagued by weak initial planning and poor operation of the digesters. The author had held the lofty goal of anaerobic treatment without alkalinity addition. Unfortunately, he included the initial start-up of the digesters within the scope of operation without alkalinity addition and subsequently appears to have never established a viable population of anaerobic biomass. Apparently, other reviewers felt the same as a publication of this work could not be found outside of Hunter's PhD dissertation.

The two digester types were a packed-bed system (corrugated plastic medium, 530L net capacity between three digesters) and a gas-fluidized system (sand as medium, 265L net capacity between three digesters). Table 6 summarizes the two system's performance. Feeding was initiated in both digesters when approximately 70% COD destruction was achieved in either digester. Because the digesters were not run independently, the gas fluidized digester was never operated in a way that would give useful data. A 20 day HRT was average for the batch fed systems.

Hunter calculated that an HRT of 23.3 days would be required to achieve a pH of 7.0 in the packed bed digesters and 44.6 days in the gas fluidized digesters. These calculations were extrapolated, however, and a neutral pH was never actually achieved.

Table 6: Summary of Average Performance Data (Hunter, 1988)

		Effluent		Percent Removal	
Parameter	Influent	Packed-Bed	Gas Fluidized	Packed-Bed	Gas Fluidized
COD	53,737	13,951	29,175	74.0%	45.7%
BOD5	39,840	11,200	19,577	71.9%	50.9%
BOD:COD	0.69	0.57	0.60	-	-
Temp	36.5	32.9	32.7	-	-
pH	4.1	6.6	5.4	-	-
Volatile Acids	1,332	362	605	72.8%	54.6%
Total Non-Filt. Res.	30,492	9,041	18,749	70.3%	38.5%
Volat. Non-Filt. Res.	25,392	7,090	14,785	72.1%	41.8%
Alkalinity	0.0	6.5	0.0	-	-

Hunter lists 0.395 L-CH_4/g-$COD_{removed}$ as the theoretical methane potential and that many other studies come close. He also stated that full scale digesters exhibit typical COD removal efficiencies of 65-85%.

In Hunter's literature review, he noted on page 20 that, "At least one ethanol production facility is presently using an anaerobic treatment system colonized by granule-forming microbes. The organisms are reportedly incapable of tolerating full-strength wastewater from the production process, and the digester influent must be diluted to a maximum COD of 15,000 mg/L." Cited: Personal Communication, David Vandegren, Plant Manager, High Plains Ethanol Corp, May, 1988. He also notes that thin stillage has no known commercial value.

Corn Ethanol Summary

The need for ethanol production to reduce dependence on fossil fuels is apparent. The treatment of ethanol production wastes to produce more energy would improve both the energy balance and economics of ethanol production. Many studies investigated the possibility of digesting the ethanol waste anaerobically in the early to mid 1980's, but limited success was realized. The fundamental understanding of anaerobic processes has advanced significantly over the past 20 to 25 years and is now offering a fresh examination of anaerobic digestion of corn ethanol waste with thermophilic anaerobic digestion.

THERMOPHILIC ANAEROBIC DIGESTION

Treatment of wastestreams by anaerobic digestion is a slow, complex process that degrades organic material and yields energy in the form of methane gas. Mesophilic anaerobic digestion is far more common than thermophilic digestion (35-37°C and 55°C, respectively). However, digestion at thermophilic temperatures offers many advantages over mesophilic digestion. Paulo *et al.* (2001) summarized the principal advantage by stating that, "thermophilic treatment is an alternative to mesophilic digestion due to the higher metabolic rates of the bacteria involved and, consequently, the higher specific methanogenic activities." The methanogenic activity ratio of thermophilic to mesophilic is generally considered to be approximately two to one. This roughly correlates to a thermophilic digester that is half the size of a mesophilic digester of similar configuration. The other advantages of thermophilic digestion are the enhanced deactivation of pathogens, increased volatile solids destruction, and enhanced liquid-solids separation. Disadvantages are the increased heat requirement for waste streams of ambient temperatures and reduced supernatant quality (Buhr and Andrews, 1977). This overview will cover digester designs, digestion pathways, nutrient requirements, and inhibitory compounds as related to thermophilic anaerobic digestion. Ahring (1995) claims that thermophilic digesters are as stable and operable as their mesophilic counterparts, but early problems due to lack of experience gave them a bad reputation. Ahring *et al.* (2002) give the advantages of thermophilic digestion as better sanitizing effect, lower retention time, and better lipid disintegration.

Digester Configurations

The fundamental differentiation in anaerobic digester configurations is whether the hydraulic and sludge retention times are equal. Although digester designs that uncouple the hydraulic and sludge retention times (UASB, EGSB, anaerobic filter, etc.) exhibit higher loading rates and efficiencies than a CSTR, the uncoupled systems cannot handle high solids wastes as well as the CSTR. Attached growth systems do not necessarily differentiate between the desired accumulation of biomass and the undesirable accumulation of suspended solids, which leads to clogging. A granular biomass retention system can clog with high suspended solids, which leads to biomass washout. Also, substrate transport into the granule is a limiting factor for high suspended solids wastestreams. Inorganic granules can also replace biomass granules for wastestreams with high calcium and magnesium, which leads to decreased methanogenic activity (Tagawa *et al.*, 2002). Granular biomass is also not necessarily the most active methane producing population. Hwu *et al.* (1997) compared granular biomass, crushed granular biomass, and washed-out (non-granular) biomass degrading oleate (a long-chain fatty acid). For this system, the non-granular biomass performed best in subsequent batch tests indicating that the granules did not include the balanced microbial population for optimum treatment. Although this is a very specific instance of washout in a granular sludge application, it is an example of the inability of granular sludge to cope with a relatively complex substrate.

Organic Loading Rate

The digester configuration greatly affects the viable organic loading rate. As van Lier (1996) states, "conventional digester systems can be used without any problems if thermophilic treatment is applied for other reasons than aiming at the highest possible loading rate." Conventional, meaning non-granular, systems have a lower loading rate but can be operated effectively if their limitations are recognized.

Ahring (1995) studied a full scale experiment at the Vegger, Denmark Biogas Plant. The experiment consisted of four digesters of 200 m^3 each. The VS loading was increased by increasing the percentage of industrial waste added as the industrial waste was more concentrated than the cattle manure that makes up the balance of the influent. The results of this study are summarized in Table 7.

Table 7: Operational Parameters and Results of the Vegger Biogas Plant, Denmark (Ahring, 1995)

	Run 1	Run 2	Run 3	Run 4
Organic Load (kg VS/day/m^3)	6.3	6.7	8.5	10.3
Industrial Waste (%)	20	22	35	42
Industrial Waste (VS %)	43	47	63	70
Gas production (m^3 gas/day/m^3)	4.1	4.5	6.8	10.1
Biogas yield (m^3/kg-VS)	0.65	0.67	0.80	0.99
VFA (g/L as acetate)	3.5	3.0	1.0	0.5
Ammonia conc. (g-N/L)	2.7	3.0	2.3	2.2

Although the substrate was significantly different than stillage, the digester configurations were the same, and organic loading rates were relatively high. The significant finding here is that the thermophilic system operated much more efficiently at high loading rates. This is contrary to intuition in that the harder the system was pushed, the better it worked. The most impressive aspect is that the VFA concentrations were significantly lower at the highest VS loading. Many factors could have contributed such as the higher VS loadings also being on the good side of an ammonia toxicity breakpoint (if ammonia inhibition for the system was at 2.5 g-N/L for instance).

Digestion Pathways

Anaerobic treatment is dependent upon a complex interrelation of several inter-dependent microbial populations for complete degradation. This contrasts with aerobic treatment, which has interrelations but is based principally on singular bacterial communities acting independently. The following equations exhibit that aerobic pathways yield greater than seven times more energy from the same carbohydrate.

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad (\Delta G^{\circ\prime} = -2{,}870\ \mathrm{kJ \cdot mol^{-1}})$
$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \qquad (\Delta G^{\circ\prime} = -390\ \mathrm{kJ \cdot mol^{-1}})$ Schink (1997)

However, the low energy yield in methanogenesis for the bacteria is why a great deal of potential energy is stored in the methane, which can then be used by humans for heating purposes. Figure 3 shows the generally accepted reaction pathways that occur during anaerobic digestion.

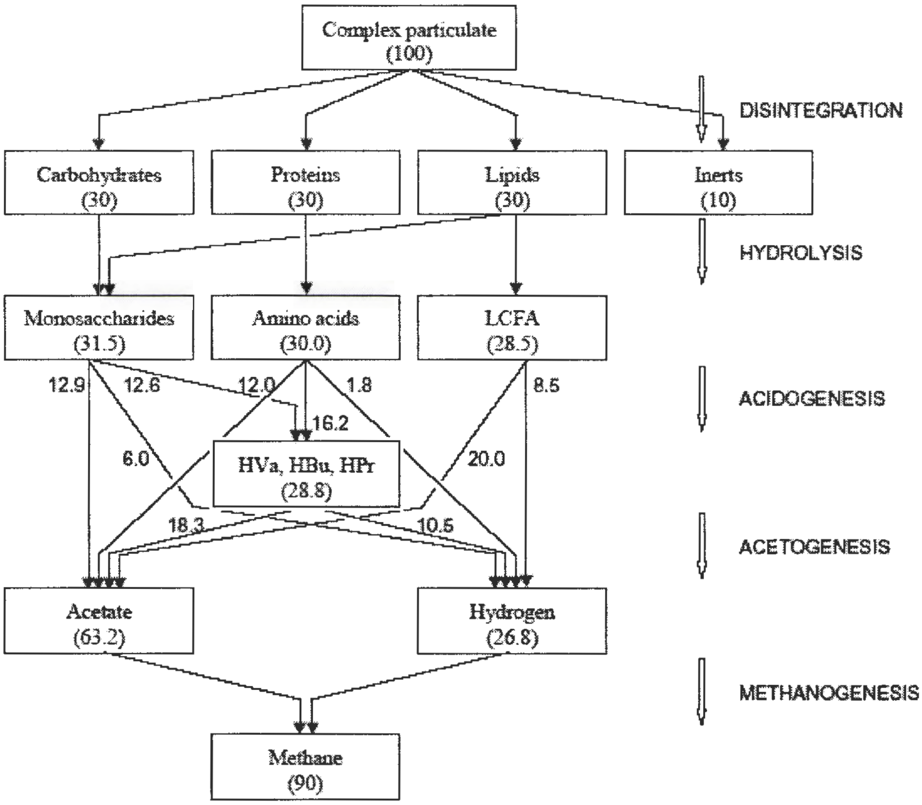

Figure 3: Flow-Diagram for the Anaerobic Degradation of a Composite Particulate Material, as Implemented in ADM1 (Batstone *et al.,* 2002). Valerate (HVa), Butyrate (HBu), and Propionate (HPr) are grouped for Simplicity. Numbers in Parenthesis Indicate COD Fractions.

The fundamental reason for the symbiosis is that the intermediate product pool must be kept small to allow for favorable energetics. The living cell needs at a minimum -20 kJ per reaction to make an ATP conversion, which happens to be where most anaerobic synergistic reactions occur (Schink, 1997). At least four groups of bacteria are required: primary fermenting bacteria, secondary fermenting bacteria, and two types of methanogens. Each group corresponds to a step in the anaerobic process as described below.

Hydrolysis

Hydrolysis is described by Schink (1997): "Polymers (polysaccharides, proteins, nucleic acids, and lipids) are first converted to oligomers and monomers (sugars, amino acids, purines, pyrimidines, fatty acids, and glycerol), typically through the action of extracellular hydrolytic enzymes." The "classical" primary fermentative bacteria hydrolyze most of the organic molecules through these extracellular enzymes. Hydrolysis reactions can be slow and are often rate limiting for complex substrates (Christ *et al.*, 2000). Bacterial cells cannot assimilate polypeptides and polysaccharides consisting of more than six or seven monomer units. Larger molecules must therefore be hydrolyzed outside of the cell. Confer and Logan (1997) offered a theory of hydrolysis whereby the macromolecules diffuse to near the cells and are hydrolyzed. These hydrolyzed fragments release from the cell surface back into the bulk solution and are further hydrolyzed until they are small enough to be assimilated by the cells able to metabolize the products. The important part of this theory is that hydrolysis is cell associated and there are not enzymes in the bulk solution that are randomly hydrolyzing macromolecules, although not all hydrolysis is tightly cell associated either. Confer and Logan speculated that the intermediates must be released back into the bulk solution because an individual cell may not have all of the enzymes required to hydrolyze a given macromolecule.

Particulate hydrolysis is governed by particulate surface area (Sanders *et al.*, 2000). This is reasonable because a higher surface area will allow more of the particulate to be covered with bacteria. Sanders *et al.* (2002) concluded that for dissolved polymeric substances (starch and gelatin), the initial hydrolysis rate is linearly related to the sludge concentration. Therefore, for dissolved substrate, the hydrolysis is limited by enzymatic activity of sludge. So for a mixture of particulate and dissolved polymers, the most rapid hydrolysis will take place with a combination of smaller initial particulates and high bacterial concentrations.

Acidogenesis and Acetogenesis

Acidogenesis uses the products of hydrolysis to produce short-chain fatty acids (also called volatile fatty acids or VFAs). Most acetate is produced directly from hydrolysis products and is therefore considered acidogenesis. However, acidogenesis also produces VFAs larger than acetate, which must be converted to acetate by acetogens. This is accomplished by the so-called secondary fermentative bacteria, obligate proton reducers, which are required for "fatty acids longer than two carbon atoms, alcohols longer than one carbon atom, and branched-chain and aromatic fatty acids (Schink, 1997)." Once acidogenesis and acetogenesis have converted polymers into acetate, methanogens convert the acetate to methane.

Methanogenesis

The final step in anaerobic digestion is methanogenesis, which is probably the most studied step in the anaerobic pathway. Methanogens are a definitely non-diverse group. Methanogens are from the Archaea (archaebacteria) group as opposed to the more common microbial designations of Bacteria (eubacteria) and the Eukarya (eukaryotes).

Methanogens are fairly uniform in physiology, and they only utilize a few substrates: H_2 + CO_2, formate, methanol, methylamines, and acetate (Blaut, 1994). The principal substrate is acetate with hydrogen also playing a significant role. The equations for these main methanogen substrates are:

$CH_4COO^- + H^+ \rightarrow CH_4 + CO_2$ ($\Delta G° = -32 kJ/mol CH_4$)
$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ ($\Delta G° = -130 kJ/mol CH_4$) Blaut (1994)

Acetate is utilized by only two genera of methanogens: *Methanosarcina* and *Methanosaeta* (formerly *Methanothrix*) (Ferry, 1993). Methanogens thrive at mesophilic and thermophilic temperatures with the first thermophilic methanogen isolated (*Methanobacterium thermoautotrophicum*) by Jeikus and Wolfe in 1972.

Ahring (1995) found that increasing the loading rate generally increased the process stability in a thermophilic digester (based on lower effluent VFA concentrations). The majority of methanogens were *Methanosarcina* spp. single cells, and no activity was indicated for the *Methanothrix* spp. tested. Approximately 1.0 mM (60 mg/L) of acetate was the breakpoint between methane production pathways with greater than 1.0 mM of acetate favoring the aceticlastic pathway where methane is formed from the methyl-group of acetate. Less than 1.0 mM favored a two step methane production involving the oxidation of acetate into hydrogen and carbon dioxide and then conversion to methane by a hydrogen-utilizing methanogen. The second pathway is termed syntrophic acetate oxidation. Acetate oxidizing cultures therefore dominated the niche usually associated with *Methanothrix* in mesophilic systems (<1 mM of acetate). When the numbers of the methanogens are compared, the digester with the highest loading rate and SMA also had a significantly higher hydrogen-utilizing methanogen population as well as an acetate-utilizing population rivaled only by the stable pilot scale digester.

Nutrient Requirements

Osuna *et al.* (2003) experimented with UASB granules from distillery wastewater at 30°C and a 12 hour HRT. One digester received trace metal addition and one no addition. The lack of trace metals showed incomplete conversion of VFAs, especially propionate. Cobalt and manganese were listed as the most important for development of a propionate degrading population. Also, tests involving direct addition of trace metals to batch vials for methanogenic activity tests did not give a higher methanogenic activity than no nutrient addition. This implies that the addition of trace elements did not stimulate activity because the long term depravation of trace elements did not allow for maintenance of bacteria that need the trace elements for enzymatic activity.

Inhibitions

Anaerobic microorganisms are sensitive to many different compounds if encountered in sufficient quantities.

Volatile Fatty Acids

Ahring (1995) concluded that the unstable digesters could not respond to substrate addition because the terminal microbes (methanogens) were already working at full capacity and therefore could not utilize any more VFAs leading to a VFA accumulation. Lab study also showed that methane potential (methane evolved plus potential methane from effluent VFAs) dropped with increasing VFA concentration. This indicates that hydrolysis is affected by high VFA concentrations.

Ahring *et al.* (1995) studied a CSTR with manure as substrate at thermophilic temperatures. They summarized by stating that, “Under conditions of unstable operation, intermediates such as volatile fatty acids and alcohols accumulate (Gujer and Zehnder, 1983) at different rates depending on the substrate and the type of perturbation causing instability (Allison, 1978).” Common causes listed were: hydraulic or organic overload, organic or inorganic toxins, and substrate changes. Ahring *et al.* (1995) stated that pH, VS reduction, and gas composition were slow indicators of upset. VFA accumulation indicates an imbalance in anaerobic digesters between VFA producers and consumers. Tests for combined butyrate and isobutyrate showed imbalances in the digester faster than other tested parameters while propionate/acetate ratio was slow to detect changes. Total VFA is also a good indicator of digester stability. Butyrate and isovalerate also detected imbalances.

Ahring *et al.* (1995) estimated VFA toxicity guidelines:

- Up to 50 mM of all VFA tested (individually) does not inhibit methane production and actually increases methanogenesis up to this level
- Acetate or butyrate were inhibitory at 200 mM
- Propionate or valerate were inhibitory at 100 mM

Their evaluation based only on methane yield is suspect because the small differences were not shown to be tested for significance. Yield also requires a real-time estimation of the VS concentration, which would have been logistically difficult to conduct.

The study suggests that relative changes in VFAs are of importance and not the absolute concentrations because all systems run differently.

Tagawa *et al.* (2002) found that the propionate degradation rate was significantly lower under thermophilic conditions than other low molecular weight fatty acids (especially acetic and butyric acid), which confirmed the findings of others. For a healthy system, the propionate/acetate ratio should be below 1.4 (Hill, 1982).

Ammonia

Nitrogen is a very important nutrient for bacterial growth, but too much nitrogen in the form of ammonia can cause toxicity. Liu and Sung (2002) stated that ammonia is the main hydrolysis product of an organic proteineous substrate such as animal or food processing wastewater, which can cause high ammonia levels. Ammonia concentrations of about 200 mg/L are beneficial as ammonia is an essential nutrient of anaerobes. Lethal total ammonia nitrogen concentrations are above 10,000 mg/L regardless of acclimation. They also stated that pH has a significant effect on ammonia inhibition. A range of 7.0-7.5 showed the least inhibition. Biomass appeared to be capable of acclimating at ammonia concentrations of up to 4,000 mg/L, although performance was degraded. Acclimation also reduced pH effect.

Temperature

Dispersed sludge, crushed granules, and intact granules were tested by van Lier *et al.* (1996) for relative stability during temperature changes. Temperature effects were greatest with dispersed sludge and crushed granules. Granular sludge exhibited the least temperature effects although it also had a lower conversion rate. Crushing the granules showed a maximum activity increase of two to three fold over intact granules. Temperature disturbances are more pronounced with granular sludge at higher loading rates. A loading rate of 20 kgCOD/m^3-d was thermostable, but at loading rates of 40-90 kgCOD/m^3-d the UASB exhibited higher effluent VFA concentrations with fluctuating temperatures. The easy explanation to this research is that the granule structure is not as effective in regard to instantaneous treatment capacity, but the granules protect the microbial biomass from adverse conditions.

In a related study, van Lier (1996) stated that, “the effect of temperature fluctuations on the process stability of thermophilic wastewater treatment systems is most severe if CSTR and/or batch digesters are used. These types of systems may be characterized by a very narrow temperature range for methanogenesis. While a temperature decrease immediately affects the conversion capacity of a high loaded CSTR system, an increase in the process temperature may result in complete digester failure." Adverse effects caused by high temperatures were also observed by Ahring (1995), although acclimation was shown to be possible. Ahring's temperature effect tests showed that higher temperature operation was possible, but that hydrolysis was likely the inhibited step at higher temperatures. Propionate degradation is inhibited at increased temperatures, although results were similar at 61°C as at 55°C after significant acclimation to the elevated temperature. Ahring *et al.* (1995) showed, however, that a rapid temperature change (from 55°C to 59°C in this case) caused a cessation of methane production that did not recover within 10 days. Zinder *et al.* (1984) attributed the inhibition to aceticlastic methanogens. Their experiment involved a temperature shift from 58°C to 64°C for a 24 hour period, which caused a significant increase in acetic acid and a large drop in biogas production. This indicates that the aceticlastic methanogens were severely inhibited by the temperature shift. In summary, an abrupt increase in temperature inhibits many thermophilic anaerobic subpopulations and will trigger inhibition or cessation of anaerobic degradation. This observation is critical in future digester designs involving thermophilic systems treating influent substrate with temperatures greater than thermophilic levels.

Sulfate/Sulfide

Although sulfate does not inhibit organic degradation, it does inhibit methane production because organic material will be utilized to reduce sulfate before methane will be produced. Sulfate reducing bacteria dominate at COD:sulfate ratios below 1:1, and methanogens dominate at ratios above 10:1 under mesophilic conditions (Colleran and Pender, 2002). Most wastewaters are between these extremes. Sulfate reducing bacteria reduce sulfate to sulfide, which can be inhibitory to methanogens (Metcalf and Eddy, 2003).

Other Inhibitions

Khanlil *et al.* (1988) studied the effects of selected detergents on anaerobic digestion. The non-ionic detergent Tergitol (nonyl phenyl polyethylene glycol ether) and soap did not inhibit mesophilic digestion. The anionic detergent sodium dodecylbenzene sulphonate reduced mesophilic degradation by approximately half and VFAs accumulated. Thermophilic digestion was less affected, and the authors suggest thermophilic digestion over mesophilic if such detergents will be a present.

Ghosh *et al.* (2001) used a two-stage configuration to pre-acidify toxicants because the substrate (peat-water effluent) contained furfural, phenol, etc., which are inhibitory to methanogens.

ULTRASOUND

The goal of ultrasonic pretreatment is enhanced hydrolysis, which is often the rate limiting step in anaerobic digestion. Tiehm *et al.* (1997) paraphrase Alchley and Crum (1988) by stating:

> Ultrasound frequencies range from 20 kHz to 10 MHz. Particularly at low frequencies from 20 kHz to 40 kHz, cavitation occurs when the local pressure in the aqueous phase falls below the evaporating pressure resulting in the explosive formation of small bubbles. These bubbles oscillate in the sound field over several oscillation periods, grow by a process termed rectified diffusion, and collapse in a nonlinear manner. Cavitation is accomplished by high pressure gradients, an extreme

> increase of the temperature inside the bubble, and in the region around the bubble. Therefore, cavitation leads to strong mechanical forces.

Tiehm *et al.* (1997) studied ultrasonic pretreatment of sewage sludge as an anaerobic digestion enhancement. Studies previous to this were small scale and had a maximum ultrasound power supply of 500 W. The concept is that cell lysis by ultrasonic disintegration will yield better anaerobic digestion. They tested the COD increase in sludge supernatant (basically soluble COD) and found an increase of up >6,000 mg/L with 96 seconds of ultrasonic treatment. However, they never discuss the raw supernatant COD, so the percentage increase may be minimal. The study used 150 liter digesters and a 3.6 kW ultrasound system to treat a municipal sludge consisting of 53% primary and 47% waste activated sludge on a dry solids weight basis.

Five digesters were tested: a 22 day control digester and 22, 16, 12, and 8 day ultrasound pretreated digesters. Ultrasonic pretreatment improved VS destruction from 45.8% to 50.3% at the 22 day HRT while other VS destructions were: 16 day – 49.3%; 12 day – 47.3%; and 8 day – 44.3%. Although VS destruction was enhanced, the biogas production was the same for the 22 day digesters. This may indicate that the ultrasound actually mineralizes some of the VS (otherwise the mass balance would not close). The sludge was possibly directly mineralized to CO_2.

Chyi and Dague (1994) studied the acidogenesis phase of a two-stage mesophilic system using cellulose at various constant pH, HRT, particle size, and loading rate combinations. A pH of 5.6 was found to have optimal conversion and was used for the remainder of the tests conducted. Table 8 summarizes the results of this study.

Table 8: Effect of Particle Size on Acidification (Chyi and Dague, 1994)

	Conversion Percentage, % (effl. SCOD/Inf. COD) x 100	
HRT, hrs	20 μm cellulose	50 μm cellulose
36	33%	20%
48	40%	28%
60	49%	36%
72	54%	39%

They concluded that the larger the particle size, the longer the required hydrolysis time. Hydrolysis was determined to be rate limiting in the acidogenesis digester (hydrolysis is slower than acidogenesis). This is significant to ultrasound pretreatment because just a few broken bonds in organic polymers that reduce particle size can significantly increase hydrolysis rates. Since most other ultrasound studies focus on municipal sludge and theorize that improvements are made based on cell lysis, this study reveals a potential for enhanced digestion of a waste such as thin stillage by ultrasound even if there is no cell lysis occurring.

RESEARCH

OBJECTIVE

The primary objective of this study was to determine if full strength thin stillage could be digested anaerobically to produce methane and reduce VS. Secondary objectives included determining:

- The optimum HRT for methane production and VS reduction
- Average effluent concentrations for total COD, soluble COD, TS, VS, TSS, VSS
- Methane production potential (yield)
- Alkalinity and trace element addition requirements
- Effect of ultrasound pretreatment
- The potential impact of an anaerobic digester system to ethanol production

METHODS AND MATERIALS

The methods and materials utilized in this research follow very closely to traditional anaerobic digestion research over the past few decades. The only new element to this experimental design was to use thermophilic temperatures and ultrasonic pretreatment to digest ethanol plant stillage.

Experimental Setup

Digester Configuration

Two CSTR thermophilic digesters were used. Both vessels were of acrylic construction and had a working liquid volume of 10 liters with approximately three liters of headspace. Large bore peristaltic pumps (Masterflex I/P 7591-00) were used for the influent and effluent pumping. Mechanical mixers (Eastern Mixer Brand) were used to mix both digesters continuously and to mix the influent substrate. One timer (ChronTrol) controlled the influent mixers and pumps, and another controlled the effluent pumps. An agitated water bath (Fisher Scientific 7305) was used to control the digester temperature. The gas collection and measurement was pressure regulated by a round flexible vinyl ball approximately 20 cm in diameter. Steel wool in a glass vessel was used to remove H_2S from the digester gas followed by a glass flowrate observation bubbler and a glass sampling port with a rubber septum. Oil filled (Schlumberger) gas meters were used to record volumetric biogas production. Figure 4 shows a schematic of one full digester configuration.

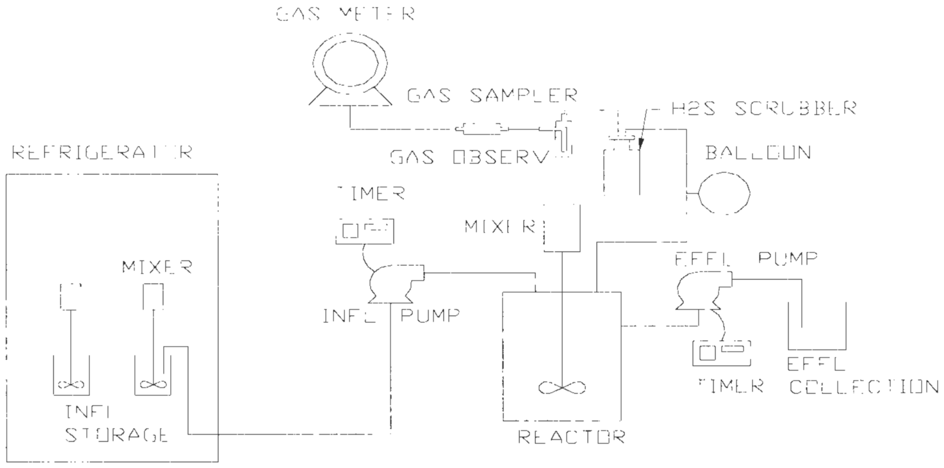

Figure 4. Thermophilic Digester Schematic

Substrate

Thin stillage from the Midwest Grain Processors (MGP) ethanol plant located in Lakota, IA was used in all experiments. Substrate was overnight shipped from MGP once per week and kept refrigerated at 4°C prior to use. MGP is a dry grind ethanol plant with a production capacity of 50 MGal/yr that will be expanded to 95 MGal/yr within a few years. After distillation, the whole stillage is centrifuged into thick and thin stillage. The thin stillage substrate was sampled directly from the effluent piping of the centrifuge by MGP staff and was as representative as possible. Trace element solution (composition in Table 9 based on Zehnder et al, 1980) was added periodically at a rate of approximately one milliliter of trace element per 20 grams of influent total COD.

Table 9: Trace Element Composition (Zehnder et al, 1980)

Chemical	Concentration mg/L
$FeCl_3 \cdot 4H_2O$	10,000
$CoCl_2 \cdot 6H_2O$	2,000
EDTA	1,000
$MnCl_2 \cdot 4H_2O$	500
Resazurin	200
$NiCl_2 \cdot 6H_2O$	142
Na_2SeO_3	123
$AlCl_3 \cdot 6H_2O$	90
H_3BO_3	50
$ZnCl_2$	50
$(NH_4)_6Mo_7O_{24} \cdot 6H_2O$	50
$CaCl_2 \cdot 2H_2O$	38
HCl, ml/L	1.0

Experimental Variables

Only two variables were used throughout this study. Several experimental runs were conducted at various hydraulic retention times. The original experimental plan called for tests at HRTs of 20, 15, 12, and 9 days, however, digester failure at 12 days eliminated the 9-day run and added a 30-day HRT run. The other variable was pretreatment of the influent thin stillage with ultrasound.

Operation

The two digesters were operated in semi-continuous mode with feeding occurring multiple times per day as shown in Table 10. Feeding was controlled by large bore peristaltic pumps that were operated by a timer. The timer cycle operated such that the influent substrate mixers would turn on for 30 seconds before influent pumping began and did not turn off until after the pumping cycle was finished. Pumps were calibrated to deliver 166 ml per pumping cycle for each digester, which was generally accomplished in 11 seconds. Originally, the pumps on the effluent were set up with a timer, but a timer malfunction that pumped all of the biomass out of the digesters prompted manual decanting of the digesters. This manual decantation was conducted once per day just after the gas meter reading was taken. Mixers were run continuously throughout the experiment for both digesters. Stable thermophilic temperatures were achieved by use of an agitated water bath that was heated to maintain the internal temperature of the digesters at 55°C. The biogas was vented to the building exhaust piping from the exit of the volumetric gas meters. The entire experimental setup was contained in a controlled temperature room at 37°C to further encourage stable temperatures.

Table 10: Digester Feeding Cycles

HRT, Days	Cycle Time, hrs
30	12.0
20	8.0
15	6.0
12	4.8

Thermophilic Digester Startup

Because of the stillage characteristics of low pH and zero alkalinity, the startup of thermophilic digester was a great challenge. The startup period was initiated by seeding the two thermophilic digesters with sludge from the thermophilic digesters at the Newton Water

Pollution Control Facility, Newton, IA. Thin stillage was added to achieve an F/M ratio of 0.5, followed by adding deoxygenated tap water to bring the liquid level of digesters to 10 L. The pH of the mixed liquor in the digesters was adjusted to 7.0 prior to operation. The digesters were sealed and purged with nitrogen gas for two minutes each to remove oxygen from the headspace. The initial startup consisted of long acclimation periods in batch operation to cultivate a viable population of thermophilic biomass. Biogas production, biogas composition, pH, and VFAs were monitored during the startup period. Additional substrate was added when biogas production either stabilized or dropped and VFAs were stable or declining.

Ultrasonic Pretreatment

The influent thin stillage for the sonicated digester was pretreated by a Maxonics ultrasonic unit provided by Etrema Products, Inc., Ames, IA. The sonication vessel was water jacketed with a direct connection to a cold water tap and could sonicate 1.4 L of stillage in batch operation. Stillage was circulated continuously during sonication using a Cole-Parmer Model 7593-00 large bore peristaltic pump. The 1.5 kW ultrasound unit was operated at a frequency of 20 kHz. Pretreatment was conducted throughout the CSTR study with fresh stillage pretreated every one or two days for 4.0 minutes after the ultrasound unit reached resonance. The relatively long sonication time of four minutes was selected because the stillage was more concentrated than previous studies with municipal sludge.

Analytical Methods

Sampling Frequency

On a daily basis, volumetric biogas production and pH were recorded. Biogas composition was measured approximately once per week during steady operation and more frequently during startup periods with a gas chromatograph (GOW-MAC Series 350, carrier gas 100% helium and standardized gas 70% CH_4, 25% CO_2, and 5% N_2). Gas was sampled with a Hamilton 1.0 mL (No 1001) graduated syringe. The pH was analyzed with a Fisher Scientific Accumet AR25 pH meter, which included a temperature probe. The pH was analyzed immediately after withdrawal of the effluent to minimize pH changes from CO_2 release and cooling of the sample. VFAs were measured weekly during stable operation and more frequently (often daily) during startup periods. The distillation procedure from Standard Methods (1995) was used for total VFA analysis.

In general, all other parameters were only tested after steady state was reached, although COD and TS/VS were tested periodically to help with operation of the digesters. Standard Methods (1995) was followed for COD, soluble COD, TSS/VSS, TS/VS, and alkalinity analysis procedures. The filter papers utilized were Fisher Scientific G4 (1.2 micron retention, 90 mm diameter) glass fiber filter circles for TSS/VSS and Osmonics MAGNA LIFT nylon transfer membranes (0.45 micron retention, 82 mm diameter) for the soluble COD determination.

Steady State Analysis

Three hydraulic retention times (i.e. 45 days operation for a 15 day HRT) with stable gas production was considered to be quasi-steady state for this experiment and was used as the determination for when intensive data collection would take place. A minimum of four consecutive days of data collection was conducted at each HRT with the exception of the 12 day HRT because of system failure. Influent characteristics were tested at least twice, but were not considered part of the dynamic system and were therefore not sampled every day. All effluent parameters were tested every day during the intensive testing. The alkalinity determination of the effluent was conducted immediately after the sample was withdrawn to minimize the effect of CO_2 loss.

Statistical Analysis

Standard statistical procedures were used including standard deviation and mean averaging. If significant difference analysis was required, a one sided *t*-test was used with $p<=0.05$ considered significantly different. No new equations were derived from the data collected, so complex statistical analysis was not a large part of this effort. Volumetric biogas production was corrected to STP using the ideal gas law.

RESULTS

Although the thermophilic system proved difficult to start up, robust treatment of thin stillage at steady state and shock loading conditions was achieved.

Steady State Operation

Significant pollutant reduction was achieved at all HRTs tested when steady state operation was achieved. Table 11 summarizes the quasi-steady state analysis conducted at several HRTs for the ultrasound pretreated and control digesters. Note that steady state operation was not achieved at the 12 day HRT. This non-steady state data represents a single day of sampling taken prior to digester failure after one week of operation at the 12 day HRT loading rate.

Table 11: Summary of Anaerobic Digestion of Thin Stillage (mg/L unless indicated)

			Sonicated				Control			
		HRT	30	20	15	12	30	20	15	12
COD										
	Influent	Total	102,000	121,000	96,100	87,700	97,100	121,000	96,100	90,700
		Soluble	61,200	74,900	49,500	N/A	59,000	76,000	51,000	N/A
	Effluent	Total	17,300	14,700	15,400	20,600	17,500	14,000	18,000	26,400
		Soluble	1,810	2,170	3,410	8,440	2,010	2,130	5,920	13,000
Solids										
	Influent	TS	70,100	89,600	67,400	66,400	68,900	90,300	65,900	72,200
		VS	63,200	82,900	61,900	61,900	61,900	83,500	59,100	52,300
		TSS	27,600	33,800	24,700	27,100	27,700	34,200	25,400	29,500
		VSS	26,500	32,400	24,200	25,000	26,700	32,900	24,800	27,100
	Effluent	TS	18,800	16,300	17,300	20,500	16,800	14,800	16,500	23,200
		VS	11,000	9,600	9,500	11,600	10,900	8,500	9,300	14,800
		TSS	14,600	11,600	12,300	14,100	11,600	10,200	11,300	13,300
		VSS	10,700	9,190	9,070	10,200	10,000	8,590	9,370	11,000
VFA, as acetic			150	170	760	4,200	160	200	2,400	6,300
Alkalinity, as $CaCO_3$			5,800	4,000	5,300	5,000	4,500	4,000	3,900	4,400
pH			7.48	7.24	7.31	6.91	7.44	7.17	7.09	6.86
Loading Rate, g-COD/L/d*			3.4	6.1	6.4	7.3	3.2	6.1	6.4	7.6
Methane Yield, $m^3/kg\text{-}VS_{added}$			0.566	0.571	0.616	0.485	0.617	0.567	0.621	0.462
Methane Yield, $m^3/kg\text{-}VS_{removed}$			0.685	0.645	0.728	0.596	0.748	0.631	0.737	0.644
Methane Percentage			59.5%	57.2%	57.9%	52.6%	60.3%	56.8%	57.3%	52.6%

*Multiply by 62.4 for lb-COD/1000 ft^3/d

Pollutant Removal

One objective of anaerobic digestion is pollutant removal. Figures 5, 6, 7, 8, and 9 representing COD, TS, VS, TSS, and VSS, respectively, show the influent and effluent pollutant concentrations for these parameters. The influent and effluent concentrations of FS and FSS are shown in Figures 10 and 11, respectively, and will be discussed separately in the following section. Error bars represent one standard deviation for Figures 5 through 11.

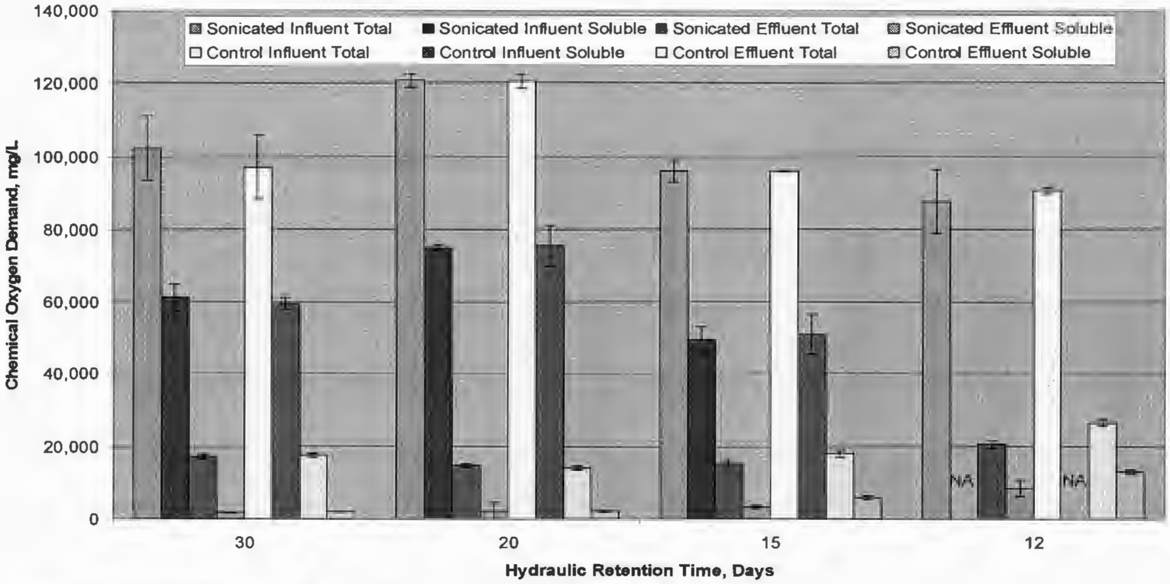

Figure 5: COD Sampling Results

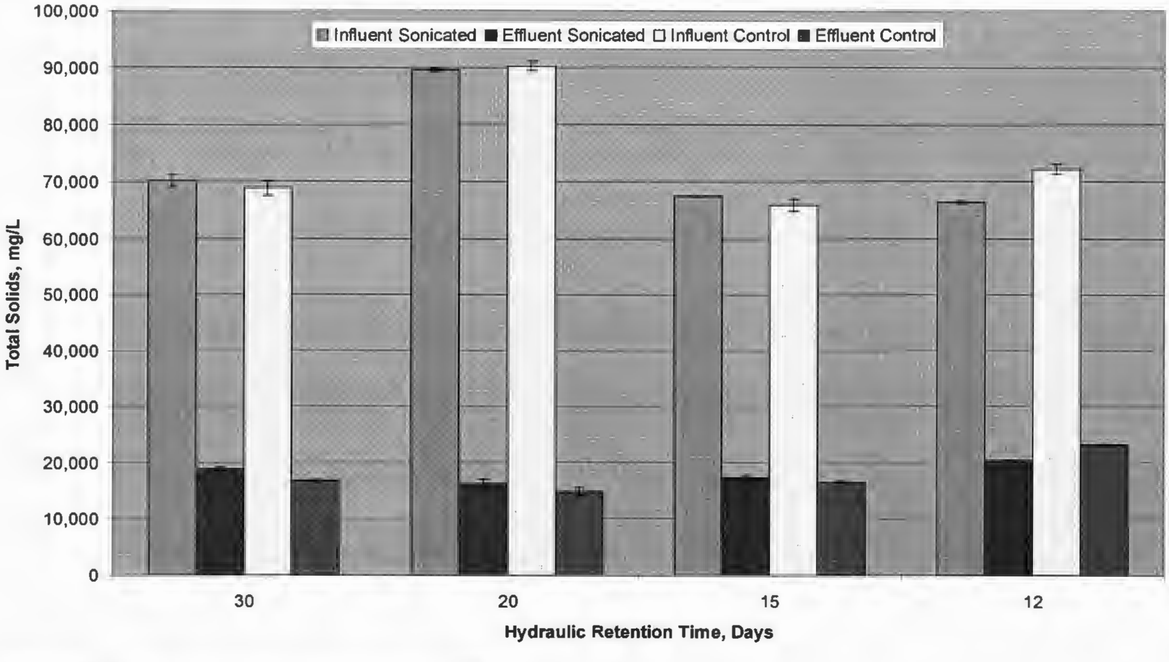

Figure 6: Total Solids Sampling Results

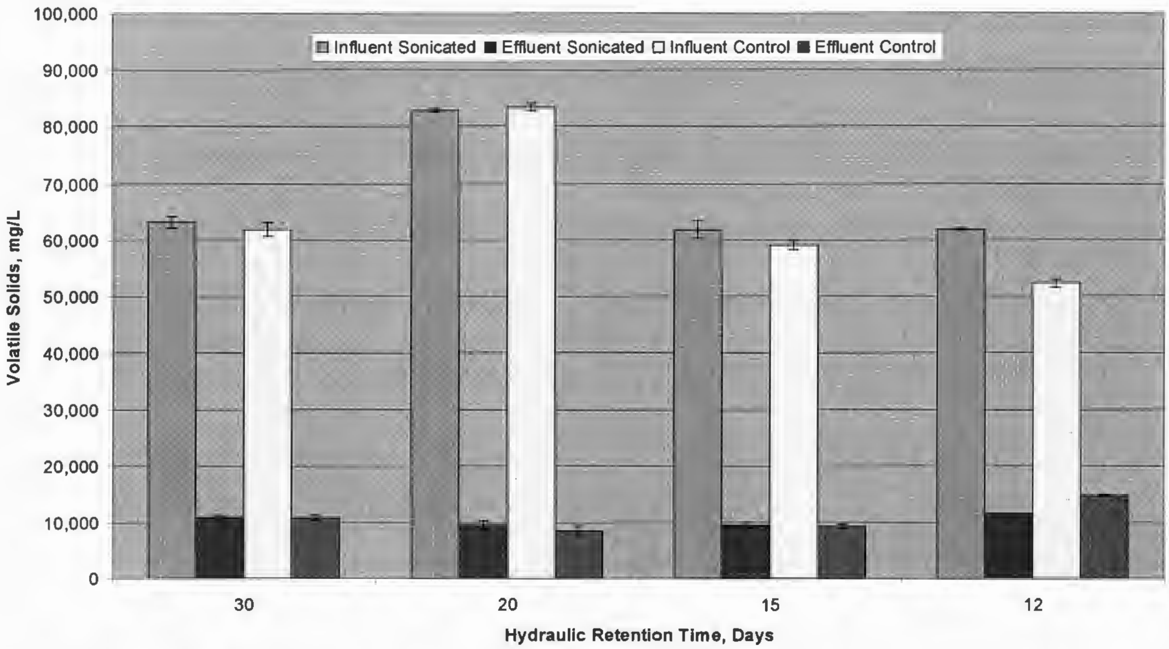

Figure 7: Volatile Solids Sampling Results

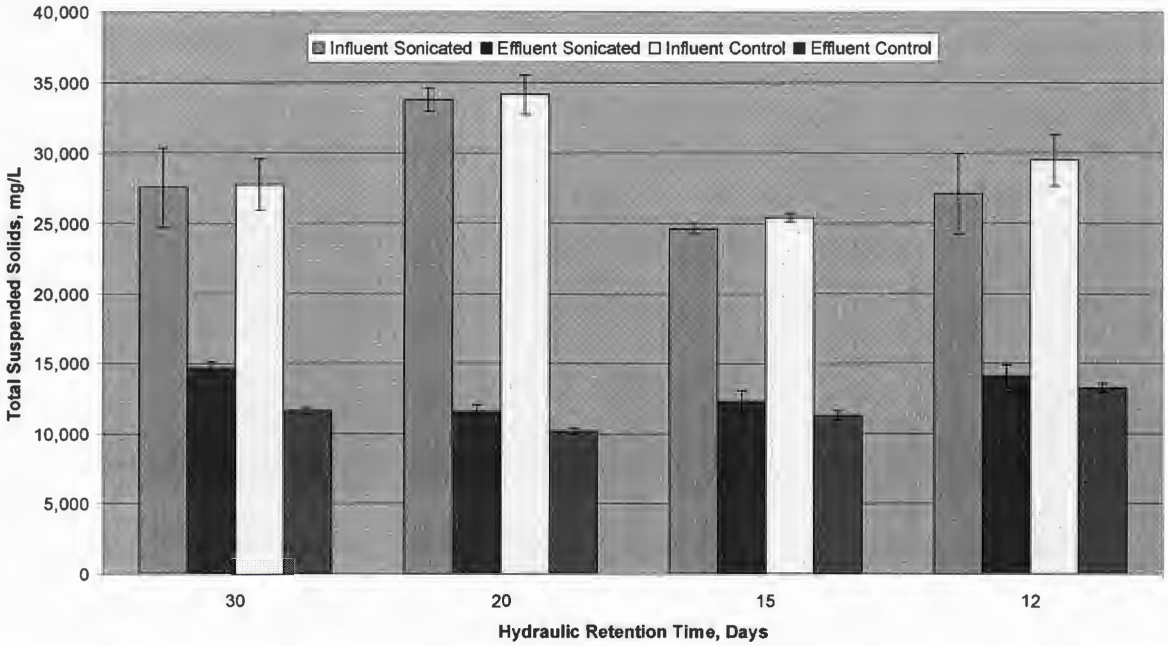

Figure 8: Total Suspended Solids Sampling Results

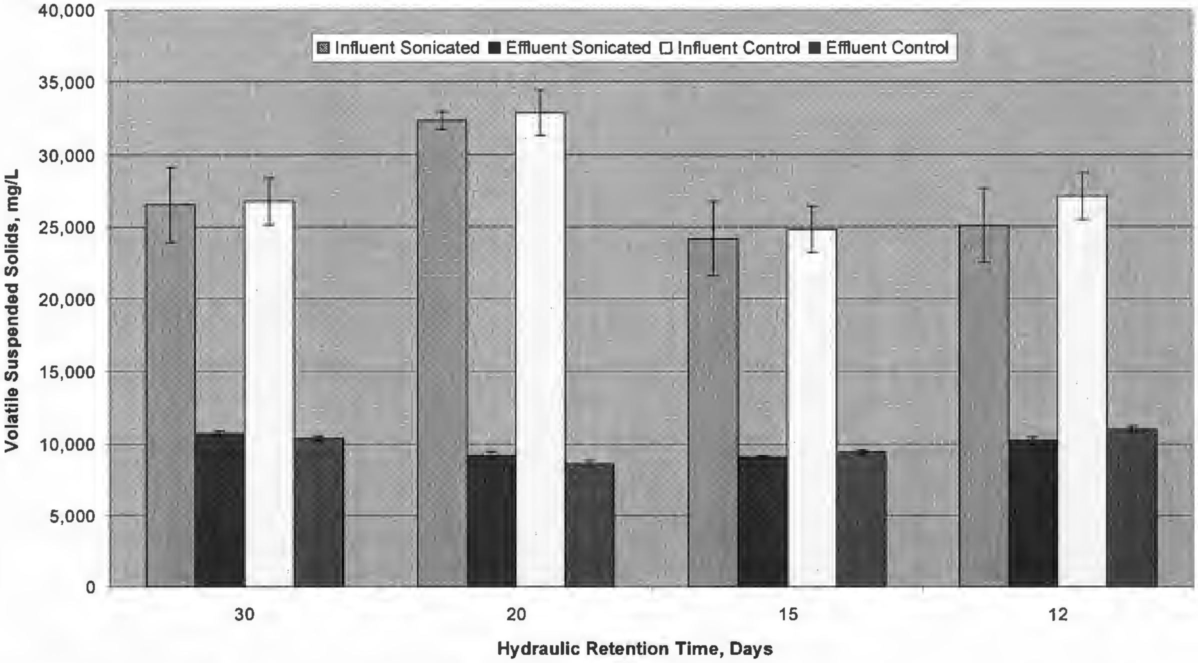

Figure 9: Volatile Suspended Solids Sampling Results

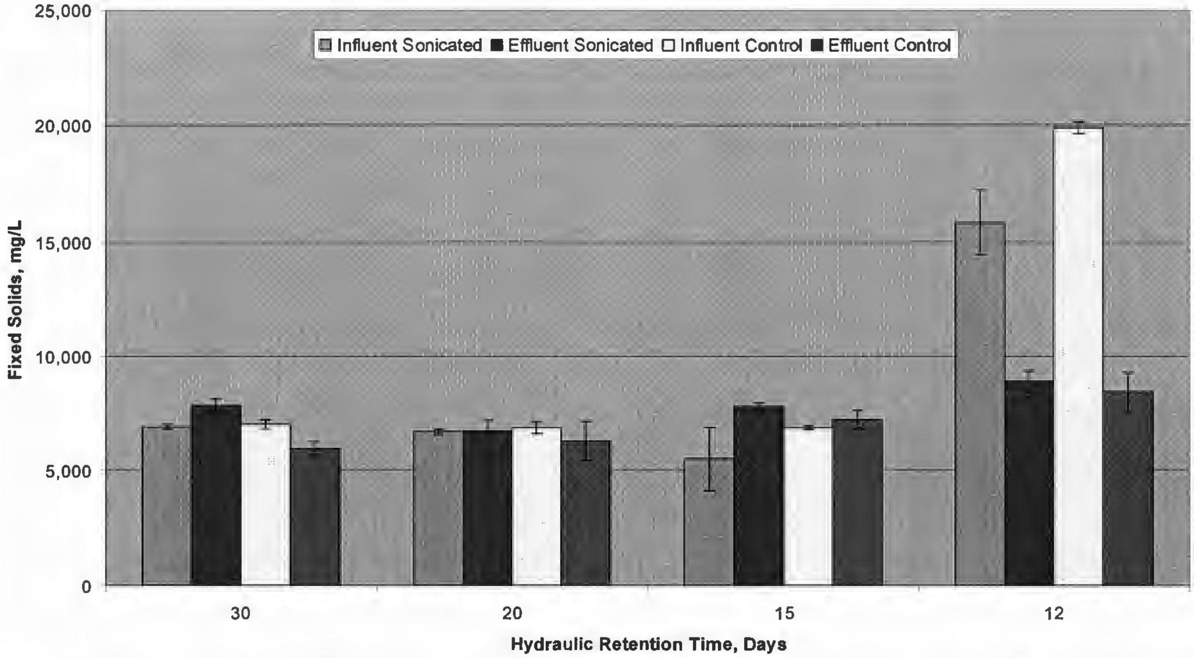

Figure 10: Fixed Solids Sampling Results (Alkalinity Addition in 12 Day Influent)

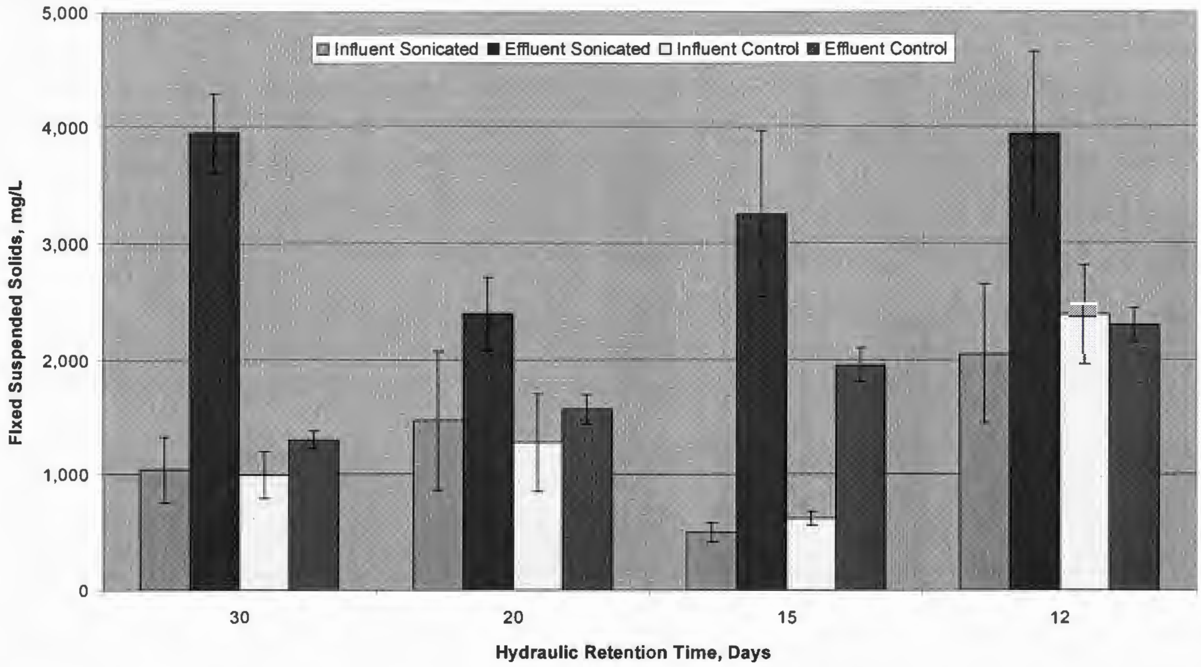

Figure 11: Fixed Suspended Solids Sampling Results

System Stability

Other parameters besides pollution indicators are used to gauge the general health of the digesters. VFAs and alkalinity are good indicators of the relative stability of an anaerobic system. Low VFA:Alk ratios indicate stable operation. Figure 12 illustrates the increasing instability of the digesters with decreasing HRT.

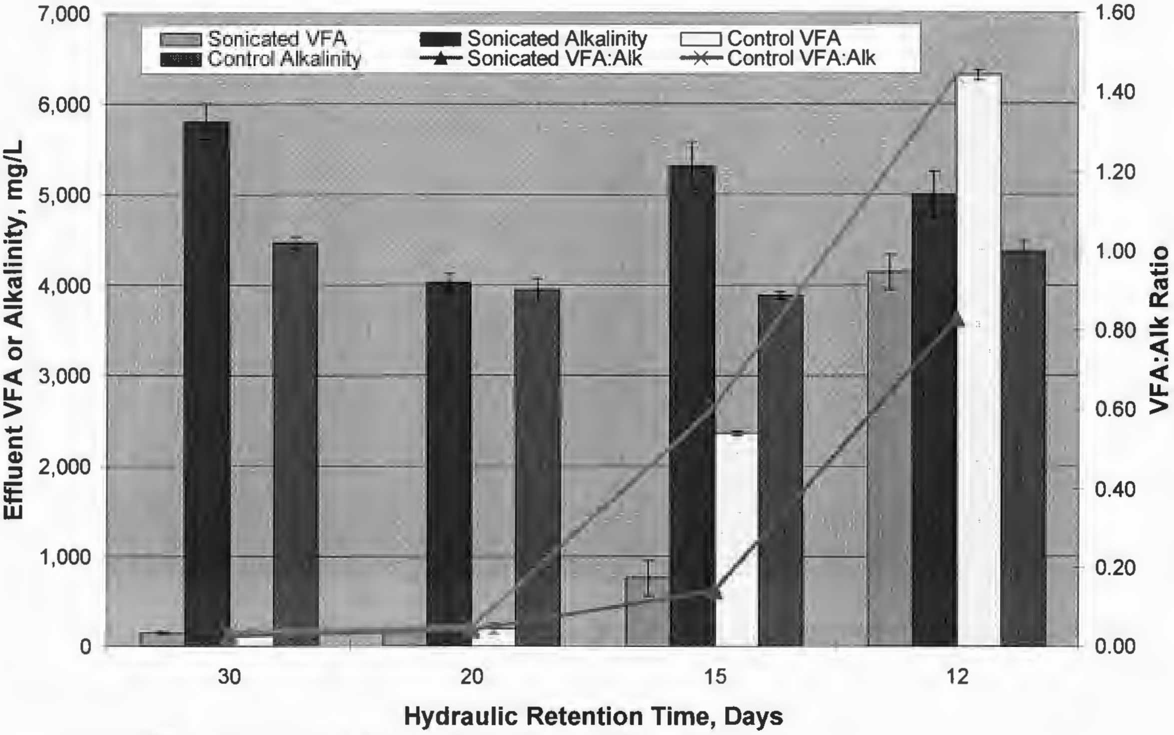

Figure 12: Effluent VFA and Alkalinity Sampling Results

The methane yield is another indicator of system stability. Figure 13 shows methane yield with respect to COD removal.

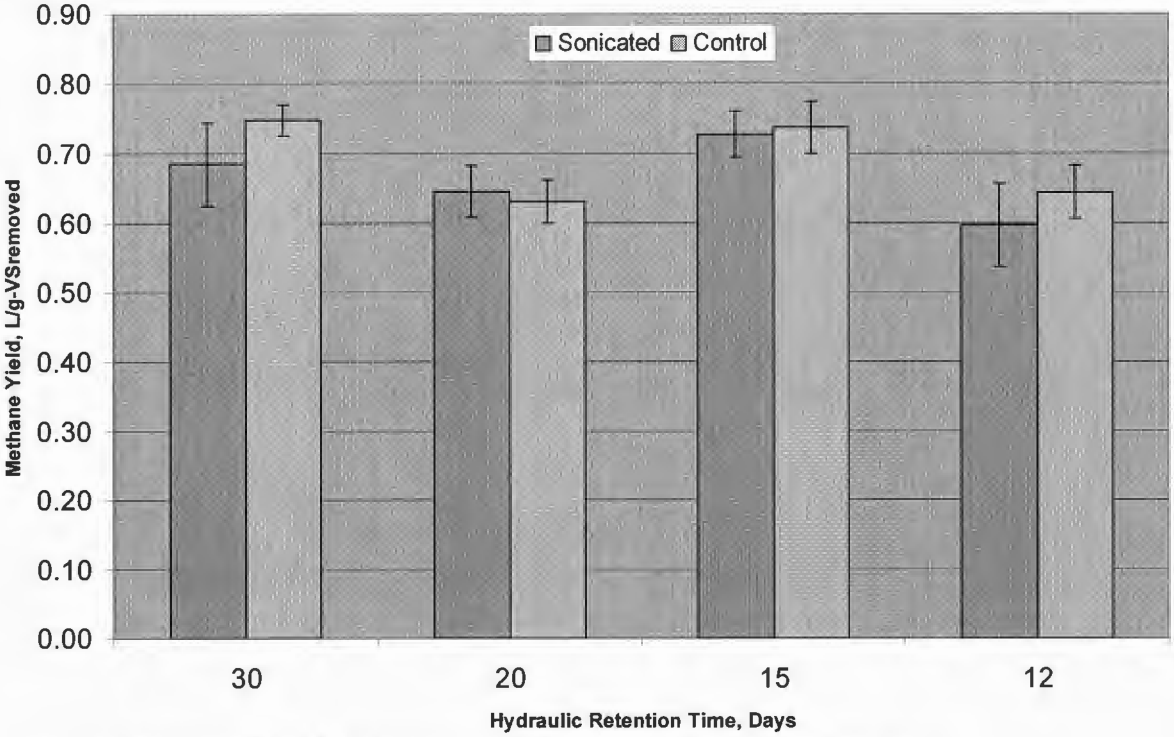

Figure 13: Methane Yield Relative to VS Removed Sampling Results

Shock Loading Performance

During the scheduled testing for the 20 day HRT, the thin stillage sent from MGP was more concentrated with respect to organic pollutant parameters than the other batches of thin stillage. This was presumably due to a temporary drop in efficiency of the centrifuges at the ethanol plant that separate the thin and thick stillage. Regardless of the cause of the spike, a shock loading condition was encountered during data collection that allows for some insight into how well the system could adapt to an organic shock load. Figure 14 shows the response and recovery of the digesters to an organic shock load of approximately 20%.

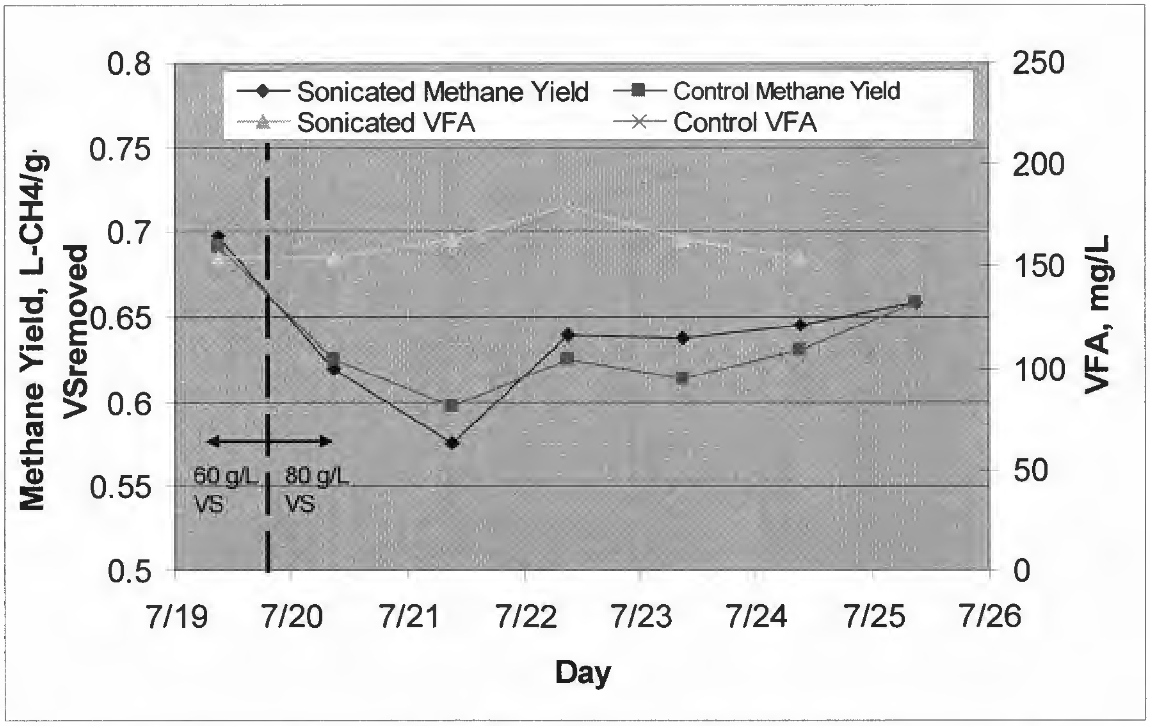

Figure 14: Methane Yield and Effluent VFA during a Sustained Shock Load

Sonication Effect

Methane yield and VS reduction were considered the most important operating factors and were used to determine significant difference. Table 12 shows the P-values for a one-sided *t*-test of paired data (one pair per day) from the Sonicated and Control digesters during steady state analysis.

Table 12: One Sided *t*-test P-values

HRT, days	30	20	15
Methane Yield	0.193	1.97E-05	0.005
VS Reduction	0.088	1.73E-05	0.159

DISCUSSION

Overall, the anaerobic digesters performed much better than expected. When this project started, there was doubt as to whether the full strength waste was amenable to anaerobic digestion. Although the required retention times for stable operation were longer than desired, the VS destruction and methane production were excellent. Also, the digesters operated without the need for external alkalinity addition, which will help the real world viability of the process.

Steady State Operation

Steady state operation was achieved to an HRT as low as 15 days and an organic loading rate as high as 6.4 g-COD/L/day. The digesters began to show signs of instability at the 15 day HRT, but operation for 45+ days without failure indicated that at least a quasi-steady state was achieved. When a transition to the 12 day HRT rate was attempted, the digesters only ran for a few days at the higher loading rate before effluent VFAs spiked severely and certain failure was evident. Based on operational stability, the 20 day HRT is recommended for further study.

Organic Pollutant Removal

Initial estimates of VS destruction were 60% because the waste had already been through a biological process (alcoholic yeast fermentation) that would have presumably utilized the best organic portions of the corn slurry. Therefore, VS destruction in the 80-90% range was astounding, especially for a CSTR with no solids retention. Figure 7 illustrates the high rate of VS destruction. The 20 day HRT exhibited both the lowest effluent VS and the highest percent destruction at 88.5% and 89.8% for the sonicated and control digesters, respectively.

COD removal was similar to VS removal and is another indication of the organic pollutant potential removed by the system. Figure 5 shows similar results at the 20 and 30 day HRTs with very low effluent soluble COD in each case. Effluent soluble COD began to rise in the 15 day HRT, which appears to be mostly due to an increase in VFAs.

VSS was reduced significantly as well, but VSS is not necessarily a good indicator of overall CSTR performance. A relatively high VSS is desirable in the digester because it is an indication of a significant biomass population, which is required for digestion. In the CSTR, the effluent concentration is equal to the mixed liquor concentration, so differentiation between desirable biomass and what is actually destroyed from the influent VSS is difficult. In other words, a digester with higher effluent VSS could actually be healthier (more stable) than a digester with low effluent VSS.

System Stability

One of the best indications of system stability is VFA:Alk ratio. A low VFA indicates that the methanogens are fully utilizing the VFA substrate, and a relatively high alkalinity indicates that the pH is stable enough for the pH sensitive microbes. As shown in Figure 12, the 30 and 20 day HRTs exhibited very low VFA:Alk ratios. The 15 day HRT began to show signs of instability with increased levels of effluent VFAs in both digesters indicating that the methanogens were not able to fully utilize the VFA substrate before it was washed out. The 12 day HRT data was taken shortly before system failure due to elevated VFA and rapidly declining pH and biogas production.

Methane yield also indicates system stability. The 30, 20, and 15 day HRTs had stable methane yield as shown in Figure 13. The 12 day HRT showed a reduced methane yield even before system failure.

Initially, these thermophilic digesters were being tested to be part of a temperature phased anaerobic digester (TPAD) system. In the TPAD system, a thermophilic digester is followed by a mesophilic digester and the combination of both temperature levels gives a more stable system overall because the advantages of one temperature balance with the disadvantages of the other temperature. This thermophilic system was stable enough that a TPAD system may not offer significant advantages, especially because these thermophilic digesters have exhibited the ability to produce an effluent with very low VFAs.

Shock Loading Performance

Although the shock loading at the 20 day HRT was not intended, the data set gives insight into the capability of the system to handle increased organic loading. Influent VS and COD spiked from an average of 61g/L to 83g/L and 100g/L to 120g/L, respectively. This sustained increase replicates what would happen in a real ethanol plant during a problem with solids separation in the stillage centrifuges.

A slight decrease in methane yield was observed following the shock load (Figure 14), but full recovery was observed in two to three days. Effluent VFA showed only a slight increase but never reached levels indicative of system instability (compared to VFA levels at the 15 and 12 day HRT in Figure 12).

Comparison to Other Digesters

Although no information in the literature for a direct comparison could be found, several studies investigated anaerobic digestion of waste from corn ethanol production. Table 13 compares methane yield and VS reduction. Influent COD concentrations and loading rates are also given to put the other studies into context.

Table 13: Operational Parameter Comparison

Methane Yield $m^3/kg\text{-}COD_{removed}$	Methane Yield $m^3/kg\text{-}VS_{removed}$	VS Reduction Percent	Loading Rate g-COD/L-d	Loading Rate g-VS/L-d	Temperature	Notes	Reference
-	0.68	82.6%	3.4	2.1	Thermophilic	Sonicated CSTR	This Study
-	0.65	88.5%	6.0	4.2	Thermophilic	Sonicated CSTR	This Study
-	0.73	84.6%	6.4	4.1	Thermophilic	Sonicated CSTR	This Study
-	0.75	82.5%	3.2	2.1	Thermophilic	CSTR	This Study
-	0.63	89.8%	6.0	4.2	Thermophilic	CSTR	This Study
-	0.74	84.2%	6.4	3.9	Thermophilic	CSTR	This Study
0.25	-	-	4.7	-	Mesophilic	Suspended Growth	Stover et al. (1984)
0.26	-	-	5.2	-	Mesophilic	Fixed Film	Stover et al. (1984)
0.25	-	-	17.4	-	Mesophilic	Two Stage Fluidized Bed	Kothari et al. (1986)
0.33	-	-	9.3	-	Mesophilic	UASB	Lanting and Gross (1985)
-	-	72.1%	2.7	-	Mesophilic	Packed Bed	Hunter (1988)
-	-	42.8%	2.7	-	Mesophilic	Gas Fluidized	Hunter (1988)
-	0.65	-	-	6.3	Thermophilic	CSTR	Ahring (1995)
-	0.67	-	-	6.7	Thermophilic	CSTR	Ahring (1995)
-	0.80	-	-	8.5	Thermophilic	CSTR	Ahring (1995)
-	0.99	-	-	10.3	Thermophilic	CSTR	Ahring (1995)

The methane yield of the thermophilic digesters was greater than that of the mesophilic digesters in all cases for corn waste digestion. Reduction of VS was also higher with the thermophilic system where data was available.

Sonication Effect

The effect of sonication was not as pronounced as expected. Many other studies have shown that ultrasonic pretreatment improves anaerobic digestion, but most of these also involve municipal waste activated sludge, which contains bacterial cells that are presumably lysed by sonication. Initially, the stillage was expected to be very difficult to degrade, and a pretreatment would be required. Ultrasonic pretreatment was chosen as the pretreatment method for investigation.

The data showed mixed results for the effect of sonication. Using a one-sided *t*-test, significant difference was determined on the basis of P-values of less than 0.05. No significant difference was detected at the 30 day HRT. The 20 day HRT showed a significant difference for both methane yield and VS reduction. The sonicated digester had a higher methane yield, although the difference was small (significant difference only tests if there is a difference, not the magnitude of the difference). However, the control digester had a better VS reduction. Hypothetically, this could be due to more biomass growth in the sonicated digester, but regardless of the reason, the ultrasonic pretreatment did not improve VS destruction for thin stillage. The 15 day HRT showed a significant difference for methane yield with the sonicated digester again producing more methane, but no significant difference was detected in VS destruction. VS destruction may have been confounded by the fact that VFAs are not included in the VS test because the VFAs evaporate along with the water during the TS determination. Significant difference was not tested at the 12 day HRT because data was limited.

Overall, any improvements that may have been gained by use of ultrasonic pretreatment were minimal for this anaerobic system. The thermophilic anaerobic system works well on this wastestream (>80% VS reduction at all steady-state HRTs) even without pretreatment. The added complexity of a pretreatment step is certainly not warranted based on tests with this ultrasound unit.

Internal Ethanol Plant Recycling

Ethanol production is an energy intensive process and also requires a significant amount of water for production. This research has demonstrated a thermophilic, anaerobic system to address both of these concerns within the ethanol production process.

Energy Recycling

Distillation and drying alone require a significant amount of heat within the ethanol production process. Assuming a conservatively low full scale methane yield of 0.5 m^3-CH_4/kg VS_{added}, anaerobic digesters would have a methane production potential of about 35 million m^3 from a 95 million gallon per year ethanol facility. This represents 1.2 million Decatherms per year of heating potential. Current operation with stillage evaporation requires 2.8 million Decatherms per year, and without stillage evaporation would require 2.1 million Decatherms per year (Leegard, 2006). Methane produced by anaerobic digestion would therefore conservatively represent between 43% and 59% of the current natural gas usage by a facility similar to MGP. Potential natural gas cost savings would range from $7 to $17 million with a likely savings of $10 million or about a dime per gallon.

Water Recycling

Currently, the thin stillage is evaporated to low value syrup that is mixed with the distiller's dried grains as a disposal method. The evaporation of this quantity of water represents a significant energy requirement (about one quarter of natural gas requirement). The organic and inorganic concentrations of the thin stillage are too high for further water reuse in the ethanol production process. Essentially, there is not enough "room" in the water to add additional raw milled corn. The anaerobic system addresses this limitation of water reuse in two ways. First, most of the VS is destroyed, which makes the anaerobic effluent more organically suitable for reuse than the raw thin stillage. Second, the inorganic portion of thin stillage is changed in the anaerobic digesters. The FS are essentially equal in the influent and effluent as shown in Figure 10 (the 12 day HRT is based on only one day of sampling at non-steady state with the influent containing additional FS from alkalinity addition and should be disregarded) indicating that total FS are conserved. However, Figure 11 indicates that the FSS are consistently higher in the effluent than the influent. This indicates that salts are precipitating in the anaerobic process, which would make for easy removal of precipitated salts with a liquids-solids separation process. The precipitation of these salts is likely due to the increase in pH (4 to 7) in the digesters and subsequent increase in alkalinity. More analysis will be required to confirm the composition of the salts, but easy removal of precipitants will make the effluent more attractive for internal ethanol plant recycling and reduce subsequent bleed-off rates.

CONCLUSION

Ethanol is a domestic, renewable energy source that will prove to be a major player in the United States' path to energy independence. Production is heavily influenced by political forces, but continued developments in byproduct recovery and reuse will lead to more favorable economics. Effective developments in utilization of more feedstock options are also important to future ethanol production. Eventual depletion of non-renewable resources will also help to make the economic situation more favorable.

The current production of ethanol in the United States is from corn. Significant capital investment in the ethanol industry is underway with current production capacity at 4,400 MGal/yr and another 2,100 MGal/yr in construction.

Anaerobic digestion is a complex process involving several subgroups of anaerobic bacteria. Thermophilic anaerobic digestion of the waste thin stillage from corn ethanol production offers a method for both significant energy recovery and waste minimization as an internal ethanol plant process.

Reduction of thin stillage VS from corn ethanol production was achieved with a thermophilic, anaerobic CSTR. Maximum VS reduction (89.8%) was observed at the 20 day HRT and an organic loading of 6.0 g-COD/L/day. Methane yield was also high with a typical yield of 0.6-0.7 $L\text{-}CH_4/g\text{-}VS_{removed}$ during steady state operation. Effluent VFAs were low for a thermophilic system with levels less than 200 mg/L as acetic acid typical for the 20 and 30 day HRTs. The influent thin stillage had a low pH (~4) and zero alkalinity. The digesters were able to produce significant alkalinity by ammonification to give a pH (7.0-7.5) ideal for biological methane production.

Steady state operation was achieved at 30, 20, and 15 day HRTs. Digester failure occurred at a 12 day HRT. For future pilot scale studies on thin stillage, a 20 day HRT is recommended because of lower effluent VFAs and more stable operation. The selection of a 20 day HRT also leaves a buffer for differences in mixing etc. for scaled-up systems. At the 20 day HRT, a sustained shock load with a 20% organic increase was easily handled by the system. Ultrasonic pretreatment did not significantly improve the operation of the system and is not recommended for future use with anaerobic digestion of thin stillage.

The VS reduction by anaerobic digestion lends to improved water recycling within the ethanol production process. Substantial energy potential is produced from anaerobic digestion in the form of methane gas. Because ethanol production requires significant heat for distillation and drying, anaerobic methane production will reduce the use of natural gas within the ethanol production process and insulate the ethanol industry from volatile natural gas markets. Estimated natural gas displacement is 43-59% for a dry grind ethanol plant. Energy production value is estimated at $7 to $17 million ($10 million likely) for a facility producing 95 million gallons of ethanol per year.

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