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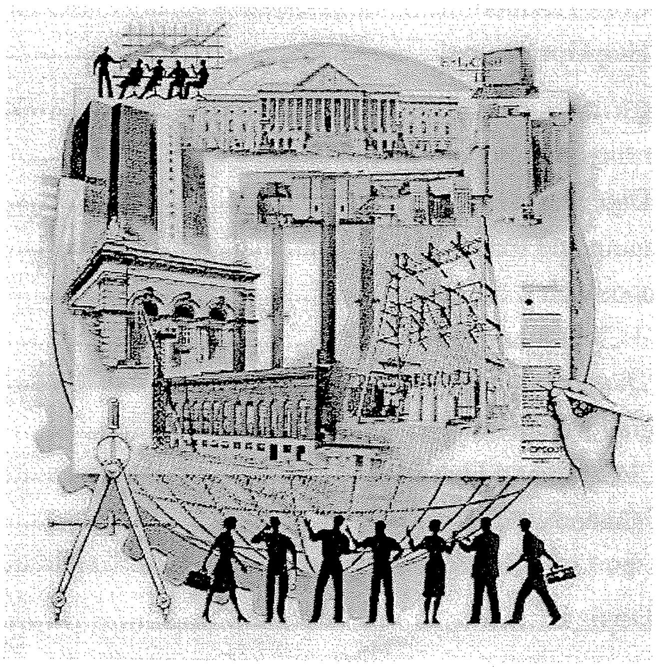
# Legislative Commission on Minnesota Resources



## Natural Gas Production from Agricultural Biomass

**Sebesta Blomberg Project No. 562500.00**

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Sebesta Blomberg & Associates, Inc.
2381 Rosegate
Roseville, MN 55113
Phone: 651.634.0775
Fax: 651.634.7400
Cecil Massie
Email: cmassie@sebesta.com

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# Executive Summary

The purpose of this study was to develop an engineering and economic model that would provide an economic incentive to hog operations to treat hog wastes by producing pipeline quality natural gas from blends of hog manure and biomass. The need for such an approach has arisen as hog operations have grown progressively larger and the concentration of odors and environmental impacts of hog operations has damaged neighbors and the environment.

At the same time, hog operations are intensely cost sensitive and even modest environmental costs are likely to damage the competitiveness of Minnesota hog production. The objective is to find a means of treating hog wastes that adds value to the operation and provides an incentive for hog farmers to manage their wastes in a more benign manner.

It is known that anaerobic digestion of hog manure will substantially reduce the odor from manure storage. Coupled with proper manure management in the barns, the odor from hog operations would be significantly reduced. Work done on hog manure digestion, however, has shown that the system does not produce enough energy to be self-funding. The objective, therefore, was to identify a process that would fund digestion of hog manure by increasing the energy output. It was proposed that co-digestion with various biomass sources found in abundance around hog operations would provide the increased energy output needed to justify the capital investment in the digesters.

The targeted biomass sources were beet pulp, wheat straw, green switchgrass, and corn stalks or stover. With the exception of switchgrass, these feedstocks are readily available in hog producing regions.

A limitation placed on this study that turned out to be particularly critical was a desire to avoid pretreatment of the biomass. Ideally biomass would be baled, transported to the site and fed to the digester after shredding. These unit operations are known at farm scale and would not pose a challenge to farmers who are, after all, not in the biogas business as their primary activity.

A further rationale for this approach is that if the pretreatment becomes complicated or expensive, then it is likely to be more effective to simply haul in wood wastes.

Anaerobic digesters are typically linked to power production but the history of these projects is that they are uneconomic due to low output and high capital cost. Small scale on farm digestion to produce natural gas is also capital intensive and uneconomic.

# Natural Gas Production from Agricultural Biomass

## *Executive Summary*


This study set out to consider a model for producing biogas in quantity and refining it to pipeline quality natural gas. This approach is in use on both human wastes at Renton, Washington and on dairy wastes near Baldwin, Wisconsin.

Natural gas production is preferred over electricity because "green gas" commands a substantial premium in the market. The value chain for green gas includes the energy content, a substantial federal tax credit, greenhouse gas credits and potentially production tax credits if the gas is used to produce electricity in central generators. Collectively these provide a greater return than electricity is able to produce.

Literature searches for comparable approaches failed to turn up any similar to the proposed approach. The literature is replete with gas production values from various biomass sources but do not indicate what if any pretreatment method was used. Based on the results of this study, it seems likely the biomass samples were hydrolyzed chemically before they were fed to the digester.

In the end, beet pulp, wheat straw and switchgrass produced no measurable gas. The samples were effectively inert. Corn stover showed very modest gas production. Of 1.3 kilograms fed to the digester, about 200 grams appear to have been converted to gas.

These results, while obviously discouraging suggest that further work may provide an economic option for biomass gasification by digestion. Work by DOE on fungal composting to break down biomass for ethanol fermentation is a potential solution. An alternative approach offered by research by Dr. Roger Ruan at the University of Minnesota has demonstrated liquefaction of corn stover as a preparatory step to making polyols. These polyols are plausibly digestible and could provide the bridge to natural gas needed.

It is remarkable how little stover would be required to meet the biomass needs of even very large hog operations. As little as 2300 tons per year would be sufficient to supply a 20,000 animal operation. This raises the further possibility that a central pretreatment plant could economically supply substrate to multiple locations.

The estimated capital costs for small operations are not attractive but larger ones may prove attractive. The estimated capital investment per standard cubic foot per hour (SCFH) of pipeline gas production ranged from over $2000 per SCFH at the low end to $363 at the higher gas production rates. At projected gas prices, there is potentially a five year simple payback on the capital investment for the larger hog operations.

## Conclusions

For the natural gas production approach to work additional work is needed on pretreatment technologies to facilitate the conversion of biomass by digestion.

Such work is being advanced by various parties including private companies, the University of Minnesota and the Department of Energy. Once the barrier is overcome, this process has potential to be economic in larger hog operations.

It now seems likely the preferred model will centralize the pretreatment of biomass and distribute substrate to the farms but this will await the development of a workable pretreatment process. Once such a process is identified, the hog industry should return to this report for a roadmap to an economic method of treating its wastes.

# *Introduction*

## Natural Gas in Minnesota

Minnesota used 359,685 million cubic feet of natural gas in 2004 and in December of 2006 Minnesotans paid an average of $12.53 per thousand cubic feet for delivered gas. Overall natural gas consumption sends over $4 billion annually to energy suppliers outside of the state.

Of particular significance to Minnesotans is the fact that 68% of all the homes in Minnesota are heated with natural gas. The next largest fuel source for home heating is electricity followed closely by LPG. Any increase in natural gas prices or supply interruption strikes directly at the population with few if any alternatives.

Finally, several key industries are dependent on a reliable source of natural gas for process heat and reagents. The 17 ethanol plants in Minnesota use an estimated 17, 500 million cubic feet of natural gas and natural gas is a key component in oil refining at the two oil refineries in Minnesota.

Collectively, therefore, Minnesota is heavily dependent on natural gas for the health and comfort of our population and industry. If sources of natural gas within the state could be developed, it would be a significant strategic gain for the state.

## Hog Production in Minnesota

Hog production is a major value added industry in Minnesota. Hog growth and finishing contributes $2.0 billion to the state GDP directly and supports an additional $5.6 billion in further processing and economic activity.

Minnesota typically has a hog population on the order of 6.5 million animals in the state at any given time producing around 1 gallon of manure wastes per day per animal. Owing to limitations on land application to the fall and spring, large scale hog manure storage has become a required practice. Unfortunately, this large scale storage is accompanied by large scale odor problems that have besieged rural communities in some cases with stifling pollution. For many communities keenly aware of the link between hog operations and economic vitality, the choice has come down to clean air or prosperity.

The problems associated with manure storage and land application are not unique to Minnesota. For example, in 1997 Iowa considered legislation to require hog operations to cover hog storage lagoons and basins for odor containment. As recently as March 2007 Blue Earth County in Minnesota considered requiring installation of biofilters to knock down odor from barns. Even such simple steps are considered too costly by some farmers. A white paper prepared by Iowa State University in 1997, for example, opined that requiring covered manure storage could drive the hog business out of Iowa.

Anaerobic digestion of hog manure is a well studied topic and there is little doubt that widespread use of anaerobic digesters would substantially reduce the odor and emission problems related to hog operations. Any mandate to use digestion technology would present the same competitiveness issues raised by the Iowa study in 1997. What this program set out to do was to demonstrate an economically attractive method for converting corn stalks into saleable natural gas using a process that cleaned up hog manure incidentally to the main purpose of energy production.

For this purpose we selected anaerobic digestion of mixtures of hog manure and corn stalks or other biomass as the preferred process. Digestion is the preferred process for several reasons:

- Digestion is a proven process for destroying hog manure odors.

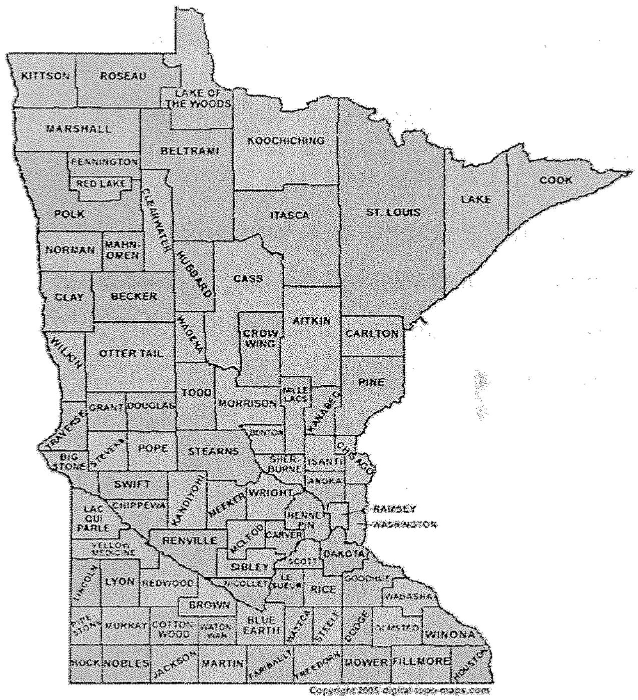
# Natural Gas Production from Agricultural Biomass

## *Introduction*

- Digestion is known to convert residual solids in manure to gas and based on literature searches was believed to convert various biomass sources to methane.
- The process is economic at scales consistent with farm-scale operation.
- The technology and know-how to operate a digester can be readily learned and applied by farm personnel.

The productivity of biomass/hog manure blends is largely unknown and the first portion of the study focused on obtaining basic yield and gas production rate data from lab scale digesters. Following this, the data was converted into engineering flow sheets and process design for gas production and refining.

## Minnesota Corn Production




United States corn production is from 11.1 to 11.8 billion bushels per year. The largest corn producing states are in order; Iowa, Illinois, Nebraska and Minnesota. In 2005 Minnesota produced about 1.2 billion bushels of corn from nearly 7.5 million acres of corn.

Corn is a significant crop in nearly every county in Minnesota with 25 counties producing in excess of 20 million bushels in 2006. The four largest producers, Renville, Redwood, Martin and Faribault Counties, produce about 15% of the states total corn output. These counties are also major hog producing regions. Corn is an unusual crop in that the stalk and root systems are large and extensive. In fact, the mass of the stalks, roots and grain are nearly equal. Up to this time, there has been little incentive to recover value from the stalk portion of the corn plant and with few exceptions, the stalks are chopped or disked back into the soil in the fall. Corn is so widely grown, however and the mass of stalks produced per acre is so great that corn stalks are the largest potential source of biomass for renewable energy production available in the United States, accounting for nearly 2/3rds of all the biomass available annually.

# Natural Gas Production from Agricultural Biomass

## *Introduction*

Corn stalk production is typically on the order of four dry tons of biomass per year per acre. The extent of stalk removal permissible is related to the soil type, the grade and the expected wind and water erosion potential. On average across Minnesota approximately one-half of the stalk production is believed available for harvest and use as a renewable fuel.

Corn stalks are a difficult fuel to harvest and use. Firstly there is a short harvest season between corn maturation, corn picking and winter weather. In about the northern half of Minnesota it is generally accepted that corn stalks cannot be reliably harvested every year. The preferred method of harvest is round bales with a plastic over wrap as shown in the picture.

Each bale contains approximately 1000 pounds of dry solids and can be stored for extended periods with minimal loss of fuel value when stored on ground arranged in north-south lines. It is best to avoid stacking the bales as this promotes water retention and spoilage. North-south alignment is preferred because it allows maximum solar heating which reduces moisture retention and spoilage.

Woodford Custom Inc. operates from Redwood Falls, Minnesota and provides custom baling services for corn stover harvest. The experience of Woodford Custom is that stover yields are consistently at or above 5300 pounds per acre at 15% moisture or less. Bales weigh 1250 pounds. Field preparation to cut and chop the corn stalks ranged from $10 to $12 per acre in 2006 or $2.80 per bale. Balers can harvest five acres per hour and in 2006 the average cost to custom bale was $12.50 per bale including net wrap. Hauling costs are estimated to be 11 cents per bale per loaded mile. Therefore, the delivered cost for baled stover to the hog operation from five miles away is estimated to be $15.85 per 1250 pound bale or about $25 per ton. Dry matter loss occurs with round bales during storage and over the course of a year, the expected loss is 7.75% pushing the cost per usable ton to $27.

## Minnesota Hog Operations

Minnesota is the third largest producer of hogs in the United States ranking only behind Iowa and North Carolina. Minnesota hog producers raised 15.4 million hogs with an average weight of 270 pounds when they went to market. Hog operations produce $2 billion of on-farm income and support an additional $5.6 billion in economic activity in the state annually

Hog operations are a major user of other Minnesota commodities especially corn and soybeans. A typical pig eats 10.5 bushels of corn and 3.8 bushel of soybeans before being sent to market. Collectively this accounted for 57 million bushels of soybeans and 157.7 million bushels of corn in 2005. In 2005 this represented respectively 14% and 19% of the corn and soybean output of the state. According to the Minnesota Pork Producers Association, feed accounts for about 65% of the operating expense of hog production so hog operations provide a significant added value to the crops on which they are based.

# Natural Gas Production from Agricultural Biomass

## *Introduction*

Population surveys by the USDA put the hog population at about 6.6 million hogs at any given time. This is an increase of nearly 1 million hogs over the last decade. Each hog produces approximately 1 gallon of manure per day. This manure is rich in nutrients essential to crop production and numerous studies by the University of Minnesota have shown benefits of manure application for fertilizers including up to 8 bushels per acre of additional yield for corn crops fertilized with hog manure. It is believed that using manure enhances soil tilth and recycles vital micronutrients back to the soil.

There has been a relentless march toward very large hog operations in the last 15 years. As shown in the table below, the number of operations has decreased nearly two-thirds while the number of very large operations (more than 2000 animals) has increased from 260 in 1992 to over 1100 by 2006.

Table: 1 Growth of Large Scale Hog Operations Since 1993

| Year | Total Operations | 2,000 to 4,999 | 5,000+ head |
|---|---|---|---|
| 1993 | 12,500 | 210 | 90 |
| 1999 | 7,500 | 580 | 220 |
| 2006 | 4,800 | 800 | 300 |

National Agricultural Statistics Service data for Minnesota hog operations are shown in the table below. While there are a very large number of small producers with less than 100 animals, 89% of all the animals are in operations of more than 1000 animals. This indicates that focusing digestion on very large operations is a practical approach to dealing with the manure from hog operations in Minnesota.

Table 2: Registered Hog Operations by Number of Animals

| Operation size based on animal count | Number of registered operations | % of total hogs in operations this size | Cumulative % of total hog population |
|---|---|---|---|
| Over 5,000 | 300 | 46% | 46% |
| 2,000 to 4,999 | 800 | 32% | 78% |
| 1,000 to 1,999 | 600 | 11% | 89% |
| 500 to 999 | 700 | 6% | 95% |
| 100 to 499 | 1200 | 4.5% | 99.5% |
| 1 to 99 | 1200 | 0.5% | 100.0% |

Reference: www.nass.usda.gov /QuickStats/PullData_US.jsp accessed 4-5-07

In fact, the largest hog operations are larger than this table indicates because for 300 operations to have 46% of the 6.6 million hogs in Minnesota, the average operation must have more than 10,000 animals.

The practical significance of this analysis for this report is that in sizing digester options, the sizes of interest are those corresponding to 10,000 animals, 5,000 animals and 1,000 animals.

The hog population in Minnesota is co-located with the corn producing regions in the three tiers of counties stretching across Minnesota from the Iowa border north to a line from the Twin Cities metro area west to the South Dakota border. About 87% of the hogs in Minnesota are located in this region with Martin County topping the list with over 700,000 hogs in that county alone. This co-location of hogs and corn operations presents the opportunity explored in this study for co-digestion of manure and corn stalks.

# Process Design

## Corn stover requirement and cost

In developing a process for the conversion of corn stalks to natural gas using hog manure as a media the process engineering is necessarily limited by the realities of farm scale operations. Therefore the process design was built around these guiding principles:

- The scale of operation must be consistent with the scale of the hog operations where the process is to be located. On the other hand, the scale of operation must not be so large as to exceed known digester design.
- The process must fit into the hog operation without disrupting the fundamental business or diverting resources away from the farm without compensation.
- The unit operations and equipment used in the process should be the same as equipment currently in use or commonly in use in agriculture.
- Failing at that, the equipment should be of a type compatible with farming operations in general.
- The conversion process must contain steps that are operable by farm staff with a minimum of outside technical support. The process scale must be economic to operate.

Scale of Operation:

As noted in the discussion of hog operations, Minnesota hog populations are highly concentrated in large operations. The three typical sizes of operation may be broadly classified as 10,000 hogs, 5,000 hogs and 1,000 hogs.

If we assume that a hog produces 1 gallon of manure per day per animal, then the flow thru the respective operations would match these sizes. Allowing for up to 35 day residence time in the digester gives us the first estimate of the size of the digesters.

Table 3: Design Manure Flows

| Hog Population (Animal count) | Daily Manure Flow (Gallons per Day) | Digester Working Volume Gallons/Cubic Feet |
|---|---|---|
| 1,000 | 1,000 | 35,000 / 4,678 |
| 5,000 | 5,000 | 175,000 / 23,394 |
| 10,000 | 10,000 | 350,000 / 46,788 |

The manure production and digester sizing shown in Table 3 are comparable to those of large dairy operations. Milking herds of 1,000 to 2,000 head are common in Wisconsin and Minnesota. A typical 950 pound dairy cow will produce about 10 gallons of manure daily. Residence time in dairy digesters is commonly 28 to 30 days so the digester volume of a 10,000 hog operation is about the same as a 1,000 head dairy operation. Since digesters are being constructed for farms with up to 5,000 head, there is no concern that these digesters are beyond the scale of available technology.

As shown in the experimental section, the mixture of corn stover and hog manure was fed to the digester at 7.8% solids. This was the highest concentration considered mixable/flowable with conventional design.

Table 4: Corn Stover Demand by Hog Operations Size

| Operation Size<br>Hog Population<br>Gallons per day | Pounds of manure<br>per day | Pounds of Stover per day for 7.8% solids | Tons of Stover per year | Acres Harvested @<br>5300 lbs/acre |
|---|---|---|---|---|
| 1000 | 8,000 | 624 | 113.9 | 43 |
| 5,000 | 40,000 | 3,120 | 569.4 | 215 |
| 10,000 | 80,000 | 6,240 | 1138.8 | 430 |
| 20,000 | 160,000 | 12,480 | 2,277.6 | 860 |

The above stover demand demonstrates that for even the largest operations, stover supply and handling is practical. The total material handled is well within the capabilities of existing farm systems and for the largest operation the expected travel is less than 5 miles in any direction. Commercial auctions such as the hay and straw auction at Pipestone, Minnesota routinely handle 1200 tons in a single day.

Recently proposals have surfaced to use forage choppers to harvest and haul corn stover to a central site much like corn silage is prepared. As envisioned in this process, the chopped stover would be stored in large plastic bags and held until use. This approach holds merit if the chopped stover can be stored at or near the point of use. Preliminary estimates are that this approach is up to $10 per ton cheaper than the round bale process. The limitation of this process, however, is that trucking to the end user must be available at the time of harvest.

Corn stover removal carries out with it nutrients that should be recycled to the next crop. The estimated nutrient content of stover is shown in the table below.

Table 5: Estimated nutrients in corn stover

| Nutrient | Lbs per ton |
|---|---|
| Nitrogen (N) | 15.0 |
| Phosphate (P2O5) | 5.9 |
| Potash (K2O) | 25.0 |
| Organic matter (C )<br>After decomposition | 260 |

Source: Iowa State University Fact Sheet BL-112, December 2002

Collectively these add up to $10 per ton to the value of corn stover if the nutrients are leaving the farm of origin. However, if the stover is digested on the same farm and reapplied as part of the manure, then this cost is not a factor.

## Anaerobic Digestion Alternatives

Anaerobic Digestion is a biological process for the decomposition of organic matter in which complex organic molecules are converted to carbon dioxide and methane. The process depends on the exclusion of oxygen from the reaction mass during the digestion process because the microorganisms die on contact with oxygen.

Digestion is known to attack and destroy the volatile compounds found in manure that produce the objectionable odor associated with hog operations. Low molecular weight organics and volatile organic acids are particularly labile to destruction by digestion.

The optimum conditions for conversion of organic solids depend on the preferred temperature for the organisms doing the digestion and are broadly classified as mesophilic (middle temperature) or thermophilic (high temperature) loving bacteria. Mesophilic bacteria prefer temperatures around 90 to 100°F while thermophilic bacteria prefer perform best at temperatures from 120 to 140°F.

As it comes from the hog barn, hog manure has very low solids content, usually around 2%. By contrast, dairy manure is typically 8 to 10% solids. The flow properties and the potential gas yield from dairy manure is very much different from hog manure. Depending on the flow characteristics, a digester may have more or less mixing.

## Completely Mixed Digester (Mesophilic and Thermophilic)

The most common form of an anaerobic digester is the completely mixed reactor. Completely mixed reactors are tanks that are heated and mixed. The majority of completely mixed reactors are operated in the mesophilic range of temperature (90-100 degrees F). Some completely mixed digesters are operated at thermophilic temperatures (120-140 degrees F). Thermophilic digesters operate at a higher rate of conversion of solids to gas, but the cost of operation is also higher. High energy costs are associated with mixing and heating the waste. A high cost of installation is also associated with this process. Although the cost is high, completely mixed digesters are a proven technology that achieves reasonable conversion of solids to gas.

## Two-Stage (Temperature Phased Reactor)

A temperature phased reactor is a two-stage system. The initial digester is operated in the thermophilic range, which is followed by a second digester operated in the mesophilic range. The first digester destroys pathogens. In the second digester, bacteria consume the organic acids created in the first stage. The system consists of two tanks, one for each stage. The tanks can be mixed or unmixed; mixing adds operation costs to the system. Temperature phased digestion has been used to digest dairy manure. One example is Tinedale Farms in Wisconsin. This system has been in operation since 2001.

## Plug Flow

Plug flow is one of the simplest and least expensive forms of anaerobic digestion. Waste enters one side of the reactor and exits the other. Bacteria are not conserved, so a portion of the waste must be converted to new bacteria. Since the plow flow digester is a growth based system, it is less efficient than a retained biomass system and it converts less waste to gas. Solids must periodically be removed from the reactor. The plug flow reactor is a simple, economic system. Applications are limited to concentrated manure containing a minor amount of sand and silt.

There are several farms across the country that is currently operating plug flow systems for digestion. Some examples are: AA Dairy in New York, Craven Farm in Oregon (1994), and Haubenschild in Minnesota (1999).

## Contact Digester (Mesophilic and Thermophilic)

An improvement on the plug flow digester is the contact digester in which a portion of the solids leaving the digester carrying bacteria is recycled to the front end of the plug flow digester. A contact digester retains bacterial biomass by separating and concentrating the solids and returning the solids into the influent. More of the degradable waste can be converted to gas since a substantial portion of the bacterial mass is conserved. Contact digesters can be completely mixed or plug flow reactors and can be operated at either mesophilic or thermophilic temperatures. Influent passes through the initial tank, mixed or plug flow, which is followed by a separator tank. Contact digesters can handle dilute and concentrated waste. Gravity-settling techniques are effective with dilute waste, but not for concentrated waste. Mechanical separation and gas floatation are other methods of separation techniques that can be applied during contact digestion. Gas floatation separation is referred to as anoxic gas floatation (AGF) and is effective for concentrating the biomass from actively fermenting digester liquors with out the need for degassing.

### Operating Experience Favors Plug Flow Design

In many respects this project is built around the idea of getting hog manure to act like dairy cow manure in the digester. Dairy manure has higher solids and these solids are the source of additional gas production. While mixed systems have been applied to higher solids wastes, the plug flow digester is the best technology for this project.

It is the objective of this project to minimize the grinding and preparation of the biomass before entering the digester. Since some of the biomass sources under consideration are long with tendency to wrap, the most preferred design will have make the most of use of gravity and pressure to move the solids through the digester. A simple box flow plug flow digesters seems most likely to achieve this end.

## Biogas cleaning and transport

Digestion of biomass and manure wastes produces a wet, low heating value biogas. In order to export this gas from the farm it must be refined and transported either by truck or by pipeline to an end user. This section of the report addresses how this is to be accomplished.

## Biogas composition

Biogas is the generic term applied to the mixture of methane, carbon dioxide and trace gases produced during the anaerobic digestion of manure and other substrates. The closely related landfill gas has similar composition but in addition to the contaminants formed during manure digestion, landfill gas is known to contain trace levels of other contaminants such as vinyl chlorides and siloxanes.

Biogas typically has a composition from 55 to 60% methane with the balance as carbon dioxide and trace contaminants of hydrogen sulfide as shown.

Table 6: Typical Biogas Characteristics

| | |
|---|---|
| Methane | 60% by volume |
| Carbon Dioxide | 40% by volume |
| Hydrogen sulfide | 1000 to 4000 parts per million by volume |
| Water vapor | Saturated |

## Pipeline and CNG Standards

Biogas in its raw form cannot be transported via conventional pipeline or in compressed gas cylinders. While some landfill gas is transported in dedicated pipelines to single use points such as at the High Plains ethanol plant in York, Nebraska, the presence of water vapor and acid forming gases (hydrogen sulfide and carbon dioxide) would cause the pipe or cylinder to corrode rapidly. To avoid these conditions pipeline tariffs and the Federal Department of Transportation have specified the composition of gases that can be transported. The comparative allowable compositions are shown below.

Table 7: Comparison of Pipeline and Compressed Natural Gas Specifications

| Component/Property | Units of Measure | FERC Tariff Spec[1] | CNG Spec per DOT[2] |
|---|---|---|---|
| Water vapor | Lbs per mmscf (million std cu ft) | Less than or equal to 6 | Less than 0.5 |
| Hydrogen sulfide | Grains per Ccf | Less than or equal to 0.25 | Less than or equal to 0.10 |
| Total sulfur | Grains per Ccf | Less than 20 | Less than 0.1 |
| Heating value | Btu per Cubic Foot | 950 or greater | |

| | | | |
|---|---|---|---|
| Temperature | Degrees Fahrenheit | Less than 120 | |
| Oxygen | Per cent by volume | Less than 0.2 | Less than 1.0 |
| Carbon dioxide | Per cent by volume | Less than 2.0 | Less than 3.0 |
| Non-hydrocarbon gases | Per cent by volume | | Less than 4.0 |

[1] Issued May 1, 2003 Northern Natural Gas Company FERC Tariff

Fourth revised sheet 281

[2] DOT regulations DOT-E-8009 13th revision

Note in particular that the specification for water and hydrogen sulfide are much more stringent for CNG than for pipeline gas.

## Successful Biogas to Natural Gas Projects

Purification of biogas to pipeline standards has been studied extensively primarily in Europe. Sweden and Holland in particular have implemented renewable energy projects built around purified biogas. At least 30 projects of this type have been identified including the wastewater treatment plant for King County in Seattle, Washington.

Typical European projects are described in the following articles:

Jan K. Jensen et al. "Biogas and Natural Gas Fuel Mixture for the Future", Danish Gas Technology Centre

Owe Jonsson, "Biogas Feeding to the Natural Gas Grid and Digestate Use in the Swedish Biogas Plant of Laholm", Swedish Biogas Institute

## Biogas Upgrading Techniques

Four different processes for cleaning biogas have been used and their effectiveness evaluated by the Swedish Gas Centre. (Marareta Persson, "Evaluation of Upgrading Techniques for Biogas", School of Environmental Engineering, Lund University, Lund Sweden)

The four techniques used in Sweden are:

- Pressure swing absorption with molecular sieves
- Water washing
- Scrubbing with Selexol polyglycol ether
- Chemical reaction with alkanolamines

The reported results from Sweden have strongly favored the water washing process and that is also the process in use in King County Washington. A farm scale unit for such a process is in use in Wisconsin with expansions of that process planned near Baldwin, Wisconsin.

Water washing is the preferred technique because it is rugged and reliable. The process depends on the higher solubility of carbon dioxide in water compared to methane. When biogas is compressed to a pressure around 150 to 200 psig, the carbon dioxide can be effectively scrubbed from the methane. The solubility of carbon dioxide is still low at these pressures and water flow rates must be very high to achieve the purity required. The gas emerging from the water scrubbing step will be saturated with water vapor and must be dried either by refrigeration or by desiccant dryers.

Water used in the scrubber can be regenerated for reuse by being fed to the top of a stripper column and allowed to degas as it passes over the column packing. Blowing air up the column increases the efficiency of water recovery but introduces a limited amount of oxygen back into contact with the gas. The equipment used for this purpose is commonly called a "decarbonator" and several commercial versions are in use for degassing water for boiler feed water and reverse osmosis applications.

Pressure swing absorption with molecular sieves is a commonly used technique that sorts molecular entities based on their affinity to zeolites and molecular size. Zeolites are a class of compounds that form small spheres with tightly controlled openings. Zeolites are typically sold in form of small pellets and are used in beds of varying widths and depths. The openings allow some molecules to enter while rejecting larger ones and molecules are bound to the zeolite by the affinity of the molecule to the surface of the zeolite molecule. The bonding is very similar to hydration and there is an appreciable exotherm on bonding and the equivalent endothermic process when the attached molecule is removed.

As used in this application the zeolites selectively remove carbon dioxide from the methane while allowing the methane to pass thru. When a zeolite bed becomes loaded with carbon dioxide a vacuum is applied to the bed causing the trapped carbon dioxide to come back out of the zeolite. Because the pressure on the bed "swings" from high pressure to low pressure during a use and regeneration cycle, this approach is called "pressure swing absorption". To avoid poisoning the zeolite, all the hydrogen sulfide and most of the water must be removed before the absorption bed.

Scrubbing with Selexol polyglycol ethers is similar to water washing in that the gas is compressed and contacted in a scrubber. As with the pressure swing absorption process, the ether is sensitive to hydrogen sulphide and it must be removed upstream of the glycol stripper. Selexol has a greater affinity for the carbon dioxide which allows operation at lower pressures or with lower liquid flow rates. On the other hand, the increased affinity for the carbon dioxide makes regeneration more difficult. Conversations with the Swedish Gas Centre have confirmed that the process is very sensitive to water accumulation in the polyglycol ether and loses effectiveness as the solvent becomes diluted.

Chemical reactions can also be used to remove carbon dioxide from biogas. For example, at Haubenschild farms in Princeton, Minnesota a fuel cell project has a small caustic scrubber to remove carbon dioxide before the methane reformer. Alkanolamines can be used to chemically react with carbon dioxide and then dissociated by heating with steam. Chemical reaction processes cannot be reasonably expected to compete with a water scrubbing system on an economic basis and find application only in small or experimental applications.

The UOP system for membrane purification depends on the relative permeability of carbon dioxide and methane. Carbon dioxide is the more mobile component but a significant portion of the methane co-diffuses to the permeate. To reduce the methane loss systems usually operate in at least two stages where the permeate is re-filtered to recover methane back to the first stage. The system has been used successfully to produce pipeline quality natural gas from gas wells. In addition, a UOP membrane system was installed on a digester project at Seneca Foods in Minnesota but was taken out of service when the digester failed to produce adequate gas to feed the unit.

Water Scrubbing Processes

A number of processes built around water scrubbing have been proposed. Early equilibrium data for the multi-component system of carbon dioxide, methane, hydrogen sulfide and water were published in 1964. The article also presents a block diagram showing what has come to be essentially the process in use today. (Hydrocarbon Processing & Petroleum Refiner, April 1964, Vol. 43, No 4, Froning et al.)

US patent 4,409,102 shows a process for water scrubbing of biogas at an operating pressure of 300 psig. This system follows the Froning process fairly closely and is distinguished from it primarily in that the treated gas is biogas where Froning was treating sour natural gas.

A significant deviation from the earlier work appears in US patent 3,981,800 where the inventor pressurizes the entire digester. Carbon dioxide is solubilized in the digester mass while the less soluble methane continues to be released. This process is not likely to be economic owing to the high cost of building pressure vessels for the entire digester volume.

Water scrubbing systems with end of pipe dehydration and final cleaning for a 3,000 head herd will cost approximately $500,000 in equipment with an additional $250,000 of installation and piping costs. Approximately half of the equipment cost is compressors with the balance distributed among pumps, pressure vessel scrubbers and controls. There is a very strong economy of scale in compressor cost and a centralized gas cleaning system is strongly favored over multiple smaller units.

## Final Gas Cleaning and Dehydration

Gas emerging from the scrubbing step is saturated with water vapor and may contain trace levels of hydrogen sulfide and other contaminants. Water vapor can be removed either by a desiccant drying system using alumina, molecular sieves or silica gels. Natco group is a large manufacturer of this type of drying system. (www.natcogroup.com)

An alternative to desiccant beds is mechanical refrigeration. When methane gas is cooled to –20F the residual moisture content is less than 5 pounds per million Btu at 100 psig which is adequate for pipeline quality but not for CNG.

Siloxanes are formed from silicon, oxygen and methane to form a volatile form of silicon. Silicon containing ingredients are used in shaving creams, deodorants, shampoos and sealants as dispersing agents. When siloxanes decompose during compression and handling, the resulting silicon dioxide powder is extremely damaging to close tolerance equipment such as compressors and generators. Pioneer Air Systems (www.pioneerair.com) has patented a gas treatment skid for removal of siloxanes, hydrogen sulfides, sulfur dioxide and water from biogas and landfill gas. The claim is 99% removal of these contaminants with their system.

## Transfer of Custody/Pipeline System

When gas is clean, dry and ready for transfer from the point of origin to the natural gas pipeline it will pass through a transfer of custody point. In physical layout this is usually a small shed containing the gas analyzer, the gas meter, an odorizer and necessary pressure regulation and pressure relief valves. According to Xcel, a natural gas distributor in Wisconsin, a typical transfer of custody facility will cost $125,000. Odorization of natural gas is an essential safety feature. By regulation, gas must be odorized to be detectable at 20% of the lower explosion limit. To make the gas detectable, tertiary methyl mercaptan is added to gas at the rate of 0.5 to 1.0 pounds per million standard cubic feet of gas. In a typical arrangement, the odorant is added by passing a side stream of gas through a tank of mercaptan. The odorized portion is then blended back with the main stream of gas for transfer to the pipeline.

Continuous gas analysis is provided to assure the gas composition and heating value. Modern gas chromatographs are not much larger than a pressure reducing station but are capable of measuring gas with great accuracy and reliability. The Yamatake Corporation Model HGC303 is typical of these new instruments. Yamatake Specification SS2-HGC100-0100F attached describes this instrument.

The Wobbe Index is a measure of compatibility of a gas with equipment burning natural gas. The Index is defined to be the Gross Caloric Value (as Btu per cubic foot) divided by the square root of the specific gravity. Only gases with the same or similar Wobbe indexes are typically considered direct substitutes.

The Wobbe Index is most commonly used in preparing mixtures of LPG, butane and air to make synthetic natural gas. Some literature has indicated methane from biogas has been adjusted to increase the Wobbe Index for gas lines in Europe by adding propane to refined biogas. In many cases, local gas distribution pressures are less than the pressure used in the scrubbing process and injection into the local pipeline would involve pressure reduction. In some cases, however, additional pressure will be required and then a booster pump will be used to put the gas in the pipeline. For this purpose either a multi-stage piston compressor or a diaphragm compressor would be suitable.

## Truck Transport of Biogas Methane

Truck transport of compressed methane to either an end user or a pipeline transfer of custody facility is an option for dispersed digesters. In general, if a pipeline can be constructed and used for the life of the line, it will be cost effective to do so. Truck transport is useful when a pipeline has not been built or cannot be built due to easement limits or when the gas is being directed to end users not connected to a pipeline system. Truck transport requires much higher compression than for a typical pipeline transport but the cost of the compressor and trailer are an offset to the fixed cost of a pipeline.

A truck transport trailer is comprised of multiple high pressure tubes on the order of 2 feet in diameter and up to 34 feet long. A leading manufacturer of these trailers is FIBA Technologies, Inc of Westboro, Massachusetts (www.fibatech.com) whose super jumbo trailer is capable of carrying up to 144,000 standard cubic feet of compressed natural gas. Operating pressures for this unit are up to 3200 psig.

# Conceptual Design

The purpose of this section is to present a conceptual design for a regional biogas to natural gas process. The process consists of multiple local digesters tied to a central refinery and gas injection point on the natural gas pipeline.

This configuration is favored because while digester capital cost and connecting pipeline is essentially linear with capacity, the cost of the refinery per unit of capacity decreases dramatically as the scale increases.

Round bales of corn stover will be disaggregated using a farm style bale grinder/feeder such as the BaleBuster 2800 shown below. This unit operates from the tractor power take off (PTO) and will grind 10 to 12 bales per hour of corn stover. The list price for this equipment is $28,500.

The digester design includes a manure metering system, a circulating warm water heating system including in-floor heating of the digester, cover and all necessary controls. Based on experience in the dairy industry and furnished by a confidential client, the installed capital cost including all heating and mixing systems is approximately $1.00 per gallon of nominal hydraulic capacity. Since each gallon entering the digester may be held from 20 to 30 days, the digester capital cost will range from $20 to $30 per gallon per day of flow capacity.

Digester sizing and cost based on these factors for different sized hog operations are shown in the table below.

Table 8: Process Design Basis

| Hog Population | Daily Manure Flow<br>Gallons per day | Digester Volume<br>25 day retention<br>In gallons | Digester Cost<br>US Dollars |
|---|---|---|---|
| 1000 | 1,000 | 25,000 | $25,000 |
| 5,000 | 5,000 | 125,000 | $125,000 |
| 10,000 | 10,000 | 250,000 | $250,000 |
| 20,000 | 20,000 | 500,000 | $500,000 |

At each site the gas will be de-sulfurized and dried to remove water vapor that could condense in the transfer line. This primary treatment has an estimated capital cost for each digester location of $70,000 consisting of $10,000 for the sulfur removal, $30,000 for dehydration and $30,000 for compressors to boost the gas to 150 psig.

Tying the individual digesters to the central refinery are pipelines. For the purpose of this study the pipelines are either 2 inch nominal HDPE or 4 inch nominal HDPE. For budgetary purposes the installed costs for these lines running up to five miles are:

Table 9: Installed Gas Line Cost

| Line size | Capacity<br>Standard Cubic Feet per day | Installed cost |
|---|---|---|
| 2 inch HDPE | 1,472,021 | $5.70 per linear foot |
| 4 inch HDPE | 8,432,768 | $9.72 per linear foot |

The cost of refining capacity decreases drastically as scale increases as shown in the following table of gas output capacity versus initial capital cost. These figures are based on budgetary pricing from Questair, a supplier of pressure swing absorption refineries.

Table 10: Questair Capital versus Capacity

| Nominal Gas Output Capacity<br>Standard Cubic Feet of Methane per hour<br>(SCFH) | Initial Capital Cost<br>US Dollars | Dollars per SCFH of capacity |
|---|---|---|
| 700 | $90,000 | $128 |
| 35,000 | $450,000 | $12.8 |
| 70,000 | $580,000 | $8.28 |

Source: Questair Inc.

# *Summary of Capital Costs*

Table 11: Summary of Capital Costs

| Line Item | 1,000 Hogs | 5,000 Hogs | 10,000 Hogs | 20,000 Hogs |
|---|---|---|---|---|
| Methane Gas output SCFH | 130 | 650 | 1,300 | 2,600 |
| Stover prep | $28,600 | $28,600 | $28,600 | $28,600 |
| Digester | $25,000 | $125,000 | $250,000 | $500,000 |
| Pre-treatment | $70,000 | $70,000 | $70,000 | $70,000 |
| Pipeline | $150,000 | $150,000 | $150,000 | $150,000 |
| Gas refining | $20,000 | $90,000 | $166,000 | $195,000 |
| Total | $293,730 | $463,600 | $664,600 | $943,600 |
| Total capital per SCFH | $2,135 | $713 | $511 | $363 |

Green gas is estimated to have a market value of $10 to $13 per thousand cubic feet. Assuming production runs 8000 hours per year; the potential gross revenue would be $104 per SCFH of capacity. Assuming pretreatment allows gas production of 10,000 cubic feet of natural gas per ton of biomass, the raw material cost to produce that gas would be about $3 per thousand cubic feet or $24 annually. This leaves about $80 per year to recover the capital investment and reward the farmer with about a five year simple payback.

# *Experimental Results*

The experimental protocol called for testing the gas production potential of blends of hog manure with the following biomass sources:

- Corn stalks
- Wheat straw
- Sugar beet pulp
- Green chopped switchgrass

## Reactor design/construction

The reactors for the digester experiments are constructed of molded high-density polypropylene. They were tested for oxygen permeation and showed high flux of oxygen into the reactor volume.

Oxygen flux was measured by placing a mixture of methylene blue indicator in a solution of sodium bisulfite in water. The sodium bisulfite is an oxygen scavenger oxidized methylene blue is a pico-mole oxygen detector. Oxidized methylene is blue. Therefore, a change from colorless to blue indicates that oxygen is passing through the wall into the reactor. During the testing, the methylene blue turned blue within four days indicating a high rate of oxygen permeation.

To seal the polypropylene tanks, they were coated with twice with epoxy paints and then sealed with a polyurethane cover coat. Retesting the vessels showed the oxygen permeation had been blocked.

All metal surfaces in the reactor are epoxy coated then polyurethane sealed.

The agitators for the reactors are hydraulic drives to assure agitation even in thick slurries. The drive fluid is glycerin.

Temperature controls are installed on each vessel and the tanks wrapped with insulation to maintain isothermal operation.

## Experimental Procedure

The moisture content of the stover was 5% water from the field. Deionized water was added to bring the moisture content to 50% water by weight. Then the mixture was allowed to soak for one week in a water tight (but not air tight) container.

19 liters (5 gallons) of deionized water was added to 4600 grams of the pre soaked corn stover at 50 % moisture ending up with a mixture of 90 % moisture (10% solids). 11 liters (3 gallons) of hog manure at 3% solids was added to the corn stover mixture for a operation solids of 7.8%.

15 gallon heated, insulated, and air tight tanks were used for the reactions.

Tedlar gas sampling bags were used to collect the biogas from the tanks.

Tank contents were mixed daily using a hydraulic motor with an attached mixing paddle.

A control with only corn stover was setup and operated the same way without adding hog manure.

Another control was also setup and operated that contained only hog manure without corn stover.

All reactors where maintained at 33 degrees Celsius (91 degrees Fahrenheit) with an automatic heating control system.

## Experimental Data

A first set of tests was conducted for blends of the hog manure and samples. In addition samples of hog manure alone and corn stover mixed with water were tested.

The first battery produced no gas production from beet pulp, wheat straw and switchgrass. Gas production from the corn stover sample produced unexpected results and was repeated.

Table 12: Biogas Composition

| Sample Date | N2 % | CH4 % | CO2 % | Ethane % | Propane % | i-Butane % | n-Butane % |
|---|---|---|---|---|---|---|---|
| 05/29/07 | | 58 | 29 | | | | |
| 06/03/07 | | 49 | 33 | | | | |
| 06/04/07 | | 39 | 32 | | | | |
| 06/05/07 | 6 | 11 | 34 | 0.3 | 0.2 | | |
| 06/25/07 | 14 | 15 | 76 | | | | |
| 06/26/07 | 18 | 17 | 66 | | | | |
| 06/28/07 | 18 | 20 | 68 | | | | |
| 06/29/07 | 16 | 24 | 66 | | 0.7 | | |
| 06/30/07 | 17 | 22 | 62 | | | | |
| 07/02/07 | 14 | 24 | 66 | | 0.7 | | |
| 07/03/07 | 19 | 25 | 59 | | 0.7 | | |
| 07/05/07 | 9 | 32 | 72 | | 0.7 | | |
| 07/06/07 | 7 | 34 | 71 | | 0.8 | | |
| 07/06/07 | 6 | 37 | 23 | 0.3 | | 0.2 | 0.2 |
| 07/08/07 | 16 | 36 | 50 | | 0.8 | | |
| 07/09/07 | 12 | 46 | 50 | | 0.7 | | |
| 07/10/07 | 6 | 47 | 17 | | | | |
| 07/11/07 | 5 | 56 | 17 | | | | |
| 07/13/07 | 4 | 56 | 16 | | | | 0.5 |
| 07/16/07 | | 55 | 14 | | | | 0.5 |
| 07/18/07 | | 55 | 14 | | | | 0.5 |
| 07/19/07 | 2 | 53 | 18 | | | | |
| 07/20/07 | 2 | 53 | 17 | | 0.6 | | |
| 07/22/07 | 3 | 53 | 15 | | | | |
| 07/23/07 | 4 | 55 | 15 | | 0.6 | | 0.4 |

| | | | | |
|---|---|---|---|---|
| 07/25/07 | 3 | 58 | 14 | 0.7 |
| 07/28/07 | 3 | 61 | 14 | 0.8 |
| 07/31/07 | 2 | 63 | 18 | 6.8 |

Table 13: Daily Gas Production

| Sample Date | Day | Biogas Liters Per Day | Methane Liters Per Day | CO2 Liters Per Day | Total Methane | Days | Total CO2 |
|---|---|---|---|---|---|---|---|
| 05/29/07 | 0 | 1.3 | 0.8 | 0.4 | | | |
| 06/03/07 | 5 | 0.6 | 0.3 | 0.2 | 1.4 | 5.0 | 1.0 |
| 06/04/07 | 6 | 0.9 | 0.3 | 0.3 | 0.3 | 1.0 | 0.3 |
| 06/05/07 | 7 | 1.0 | 0.1 | 0.3 | 0.1 | 1.0 | 0.3 |
| 06/25/07 | 27 | 0.9 | 0.1 | 0.7 | 2.7 | 20.0 | 14.1 |
| 06/26/07 | 28 | 0.5 | 0.1 | 0.4 | 0.1 | 1.0 | 0.4 |
| 06/28/07 | 30 | 0.5 | 0.1 | 0.3 | 0.2 | 2.0 | 0.7 |
| 06/29/07 | 31 | 0.8 | 0.2 | 0.5 | 0.2 | 1.0 | 0.5 |
| 06/30/07 | 32 | 2.5 | 0.6 | 1.6 | 0.6 | 1.0 | 1.6 |
| 07/02/07 | 34 | 1.9 | 0.5 | 1.3 | 0.9 | 2.0 | 2.5 |
| 07/03/07 | 35 | 2.7 | 0.7 | 1.6 | 0.7 | 1.0 | 1.6 |
| 07/05/07 | 37 | 1.7 | 0.5 | 1.2 | 1.1 | 2.0 | 2.5 |
| 07/06/07 | 38 | 3.2 | 1.1 | 2.3 | 1.1 | 1.0 | 2.3 |
| 07/06/07 | 38 | 11.4 | 4.2 | 2.6 | 0.0 | 0.0 | 0.0 |
| 07/08/07 | 40 | 9.4 | 3.4 | 4.7 | 6.7 | 2.0 | 9.4 |
| 07/09/07 | 41 | 12.0 | 5.5 | 6.0 | 5.5 | 1.0 | 6.0 |
| 07/10/07 | 42 | 10.7 | 5.0 | 1.8 | 5.0 | 1.0 | 1.8 |
| 07/11/07 | 43 | 7.6 | 4.2 | 1.3 | 4.2 | 1.0 | 1.3 |
| 07/13/07 | 45 | 7.4 | 4.2 | 1.2 | 8.3 | 2.0 | 2.4 |
| 07/16/07 | 48 | 4.8 | 2.7 | 0.7 | 8.0 | 3.0 | 2.0 |
| 07/18/07 | 50 | 9.6 | 5.3 | 1.3 | 10.5 | 2.0 | 2.6 |
| 07/19/07 | 51 | 12.0 | 6.3 | 2.2 | 6.3 | 1.0 | 2.2 |
| 07/20/07 | 52 | 14.4 | 7.6 | 2.5 | 7.6 | 1.0 | 2.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 07/22/07 | 54 | 8.3 | 4.4 | 1.3 | 8.8 | 2.0 | 2.6 |
| 07/23/07 | 55 | 10.2 | 5.6 | 1.5 | 5.6 | 1.0 | 1.5 |
| 07/25/07 | 57 | 10.1 | 5.8 | 1.4 | 11.7 | 2.0 | 2.9 |
| 07/28/07 | 60 | 4.9 | 3.0 | 0.7 | 9.1 | 3.0 | 2.1 |
| 07/31/07 | 63 | 5.1 | 3.2 | 0.9 | 9.5 | 3.0 | 2.7 |
| | | | | | 116.4 | | 69.5 |

## Mass Balance

Total mass at the start and end of the test was measured. The total gas production was 230.3 grams which corresponds almost exactly to the observed dry mass loss of 230 grams.

Table 14: Mass of Gas Produced

| Gas Type | Liters Produced | Gram moles | Grams |
|---|---|---|---|
| Methane | 116.4 | 5.19 | 83.0 |
| Carbon Dioxide | 69.5 | 3.10 | 136.4 |
| Nitrogen | 8.7 | 0.39 | 10.9 |
| | | Total gas | 230.3 |

Table 15: Mass Lost on Digestion

| | | |
|---|---|---|
| Starting solids | 1,480.00 | grams |
| Ending solids | 1249.68 | |
| Loss | 230.32 | |