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BIOTHERMAL GASIFICATION OF BIOMASS

by

David P. Chynoweth
Vipul J. Srivastava
Michael P. Henry
Paul B. Tarman

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Institute of Gas Technology
Chicago, Illinois 60616

ABSTRACT

The BIOTHERMGAS Process is described for conversion of biomass, organic residues, and peat to substitute natural gas (SNG). This new process, under development at IGT, combines biological and thermal processes for total conversion of a broad variety of organic feeds (regardless of water or nutrient content). The process employs thermal gasification for conversion of refractory digester residues. Ammonia and other inorganic nutrients are recycled from the thermal process effluent to the bioconversion unit. Biomethanation and catalytic methanation are presented as alternative processes for methanation of thermal conversion product gases. Waste heat from the thermal component is used to supply the digester heat requirements of the bioconversion component. The results of a preliminary systems analysis of three possible applications of this process are presented: 1) 10,000 ton/day Bermuda grass plant with catalytic methanation; 2) 10,000 ton/day Bermuda grass plant with biomethanation; and 3) 1,000 ton/day municipal solid waste (MSW) sewage sludge plant with biomethanation. The results indicate that for these examples, performance is superior to that expected for biological or thermal processes used separately. The results of laboratory studies presented suggest that effective conversion of thermal product gases can be accomplished by biomethanation.

BIOTHERMAL GASIFICATION OF BIOMASS

INTRODUCTION

Numerous studies have concluded that biomass and organic residues represent a renewable energy resource that, in the United States, could amount to several quads per year. Because of large variations in their physical and chemical characteristics, no single process developed to date is suitable for conversion of all types of organic feedstocks to synfuels.

This paper describes a process developed at the Institute of Gas Technology (IGT), referred to as the BIOTHERMGAS Process,* which combines biological and thermal processes into a system that can efficiently convert the full spectrum of biomass or waste feedstocks to SNG or other fuel products with minimum process residues.

If a particular biomass species or organic residue is abundant and economical to collect or harvest and transport to an energy conversion facility, the following criteria are of major importance in the selection of a conversion process:

- Energy product desired (SNG, steam, liquid fuels)
- Feedstock characteristics (moisture content, nutrients, biodegradability)
- Thermal efficiency
- Effluent streams (by-products, wastes)
- Environmental Impact
- Economics
- Time available for development to commercial state

In developing the BIOTHERMGAS Process, our goal was the production of substitute natural gas (SNG). Known processes under development for conversion of biomass to SNG are either biological or thermal. Each of these has advantages and limitations, which are illustrated dy data presented in Table '.

In a typical biological gasification scheme, biomass containing 90% to 95% water is added on a continuous or semicontinuous basis at a loading of 0.1 lb VS/cu ft-day and a retention time of 15-20 days. In this continuously mixed reactor, which is kept anaerobic at 35°C, a mixed population of anaerobic bacteria effect the conversion of 50% of the organic matter to methane and carbon dioxide, at a ratio of 60/40. This is equivalent to a methane yield of 4 SCF/lb of organic matter added, and a methane production rate of 0.4 volumes per volume of culture per day.

The main advantages of anaerobic digestion for biomass conversion are as follows:

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* IGT has filed a patent application for the BIOTHERMGAS Process.

- Wet or dry feeds can be processed
- Product gas is methane and carbon dioxide
- Process is operated at low temperature and pressure
- Design and operation is simple and inexpensive.

The main disadvantages include –

- Conversion efficiencies are low.
- There is a large output of unreacted residues with high water content
- Conversion and gas production rates are low.
- Need for sufficient nutrients (e.g., nitrogen and phosphorus) in feed to support microbial growth.

Table 1. COMPARISON OF ANAEROBIC DIGESTION AND THERMAL GASIFICATION FOR CONVERSION OF ORGANIC MATTER TO SNG

	Anaerobic Digestion	Thermal Gasification
Loading, lb organic/ft^3-day	0.1	3070*
Retention Time	10-20 days	10-20 minutes
Output, 10^3 Btu/ft^3-day	0.3-4.0	14,440*
Reactor Temperature, ^{o}C	35-55	750-950*
Thermal Efficiency, %	40	60
Organic Residues, % of feed	50	5
Feed Water Requirement, %	20	50
Feed Nutrient Requirement	Balance of C, N, and P	None
Product Gas	CH_4, CO_2	CH_4, CO, H_2, CO_2, hydrocarbons

* Two-stage char and hydrogasifier.

In a typical thermal gasification scheme, biomass is mixed with oxygen and steam under conditions of high temperature and pressure at a loading of 3070 lb/cu ft-day and a residence time of 10 to 20 minutes. The products are hydrogen, carbon monoxide, carbon dioxide, methane and other hydrocarbon gases, ammonia, liquids, char and ash. The hydrogen and carbon monoxide can be passed through a shift reactor and methanated catalytically. A typical methane yield and production rate for this scheme is 5 SCF/lb organic matter added and 14,440 SCF/cu ft per reactor-day. Although conversion of organic matter is almost complete, some undesirable organics may appear in liquid and gaseous streams. The thermal efficiency of this scheme is typically 50% to 60%. The major advantages of thermal gasification for biomass conversion are –

- High conversion efficiencies
- High conversion rates

The principle disadvantages include –

- Requirement for feeds with low moisture content
- High temperature and pressure
- Complex and expensive design and operation.

Some of the variability in physical and chemical characteristics of biomass and organic wastes is illustrated in Tables 2, 3, and 4. The moisture data in Table 2 suggests that sewage sludge, Bermuda grass, kelp, and water hyacinth might be more suitable for biological conversion, while drier feeds such as municipal solid wastes (MSW), and trees might be more suitable for thermal conversion. Table 3 illustrates that the nutrient content of biomass is quite variable. Generally, a carbon/nitrogen (C/N) ratio less than 15, and carbon/phosphorous ratio less than 75 is required for good biological conversion.(6,8). Thus, many of these feedstocks would require supplementary nutrients for biological conversion.

Table 2. MOISTURE CONTENT AND HEATING VALUE OF VARIOUS BIOMASS FEEDSTOCKS

	Moisture, %	Heating Value, Btu/Dry lb
Wastes		
Sewage Sludge	89-97	7800
MSW	20-60	5447
Grasses		
Bermuda Grass	20-40	7955
Bamboo	16	8381
Trees	5-50	9130
Aquatic Biomass		
Kelp	88	4708
Water Hyacinth	95	6535

Table 4 illustrates that the nutrient content can vary from sample to sample. Nutrient variability related to changes in growth conditions may seriously affect digester performance in a way that could be disastrous on a large scale. Data obtained in our laboratory demonstrated that kelp Lots 26, 37, and 48 were not nutrient-limited for digestion, but Lots 41 and 42 with high C/N ratios resulted in significantly reduced performance, (3, 4). It is conceivable that biomass produced on a large scale for conversion to SNG may be too moist for thermal conversion, and lack sufficient nutrients for biological conversion.

Table 3. CARBON/NITROGEN, AND CARBON/PHOSPHORUS RATIOS OF VARIOUS BIOMASS FEEDSTOCKS

	C/N	C/P
Wastes		
Sewage Sludge	8	50
MSW	76	204
Grasses		
Bermuda Grass	40	194
Bamboo	177	710
Trees		
Pine Wood	518	--
Aquatic Biomass		
Kelp	15	84
Water Hyacinth	10	94

Table 4. VARIATION IN C/N RATIOS OF KELP (*Macrocystis pyrifera*)

Kelp Lot	C/N
26	17.1
37	15.1
41	23.5
42	24.0
48	13.5

The BIOTHERMGAS Process, conceived and under development at IGT with in-house funds, combines biological and thermal gasification processes for total conversion of the organic components of biomass (regardless of water or nutrient content), and provides sufficient ammonia contained in or synthesized from the product gas to supply the needs of the biomethanation process. Phosphorus and other inorganic nutrients are recycled to maximize their retention within the process. This combining of processes broadens the spectrum of feeds suitable for conversion, increases net energy recovery, and reduces the quantity of undesirable process residues.

DESCRIPTION OF THE BIOTHERMGAS PROCESS

A generalized process scheme for the BIOTHERMGAS Process is shown in Figure 1. Biomass, organic wastes, or other types of natural residues such as peat, are chopped, ground, and mixed with water and nutrients derived primarily from process streams. The biodegradable component of the biomass is converted to methane, carbon dioxide, and bacterial cells via anaerobic digestion. Gases from the digesters are purified to remove carbon dioxide and traces of hydrogen sulfide. Effluent from the digester is mechanically dewatered to a water content of less than 50% and transferred to the thermal gasification unit. Supernatant from dewatering is used for feed slurry dilution, as needed, and represents one possible point of nutrient recycle. Dewatered solids are gasified to hydrogen, carbon monoxide, carbon dioxide, hydrocarbons, and ammonia (if solids contain nitrogenous matter). Gases may be utilized to synthesize ammonia if needed for the anaerobic digestion process. Process gases are used for catalytic or biological synthesis of methane. Although initial supplements of phosphorus or other inorganic nutrients may be necessary, these compounds are recovered in the ash from the thermal gasification unit and recycled to the feed as needed by the biological gasification process.

The BIOTHERMGAS Process is a hybrid of well established unit operations. However, their application in the manner proposed here needs evaluation. Anaerobic digestion has been demonstrated as an effective method for the gasification of a variety of organic wastes and biomass feedstocks. However, the conversion of refractory components (typically 50% to 60% of the feed organic matter) does not occur, and some feeds lack a suitable complement of nutrients for support of rapid conversion with high yields. In general, anaerobic digestion improves the dewatering characteristics of sewage sludges; its effect on most other types of biomass has not been evaluated. In order for the effluent to be a suitable feed for thermal gasification, however, dewatering to about 50% or less will be necessary.

Recycle of water derived from sedimentation and dewatering processes should minimize external water requirements and result in maintenance of soluble nutrients within the anaerobic digestion process. The effect of recycled water on the digestion process should be favorable but needs further investigation.

Several approaches have been developed and evaluated for thermal gasification of biomass.(9) Energy penalties associated with dewatering of feedstocks with high water content often rule out that conversion process, but in the BIOTHERMGAS Process, the anaerobic digestion component permits conversion of feeds with a high water content. Although the water content of digester effluent will also have to be lowered prior to thermal gasification, it is assumed that improvement in dewatering characteristics resulting from anaerobic digestion will reduce the associated energy penalties. The success of the overall process will depend significantly on evaluation of this step.

Although aerobic incineration of digester effluent sludges is practiced commercially, we believe that combination of thermal gasification for production of SNG from digester sludges is unique to the BIOTHERMGAS Process and has not been previously investigated. This treatment should result in conversion of refractory organics to hydrocarbon gases, carbon monoxide, hydrogen, and carbon dioxide. Decomposition of nitrogenous matter should result in production of ammonia, which can be recycled back into the digestion process if needed. Otherwise, ammonia represents a valuable by-product. Ash from the thermal conversion may contain nutrients that could be utilized by the bioconversion process. Accordingly, ash will be recycled either directly or following chemical separation.

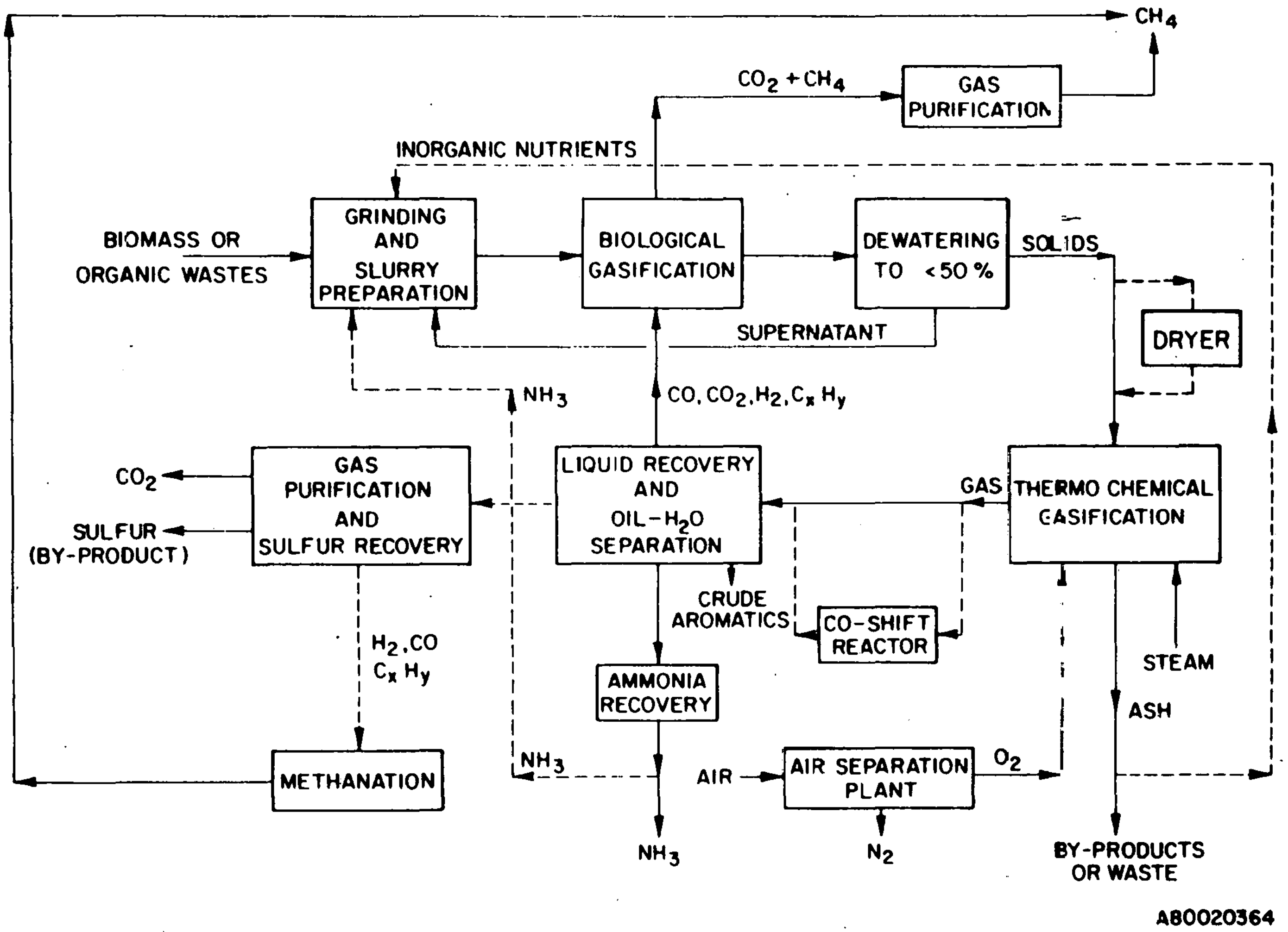

Figure 1. BIOTHERMGAS PROCESS SCHEME

The BIOTHERMGAS Process includes two methods for conversion of thermal process gases to SNG – catalytic methanation and biomethanation. Catalytic methanation employs conventional techniques for gas purification, shift, and chemical synthesis. Biomethanation involves cooling of the thermal gases and sparging through the same anaerobic digester used for feed conversion. The gases will not only be converted to methane, but also can be used to supply heating and mixing for the digestion operation. Biomethanation of coal gasification gases by mixed methanogenic bacterial cultures and conversion of hydrogen, carbon dioxide, and carbon monoxide has been demonstrated in pure culture.(10,5) The reactions involved are presented below:

$$CO_2 + 4\ H_2 \quad CH_4 + 2\ H_2O$$

$$CO + 3\ H_2 \quad CH_4 + H_2O$$

$$4\ CO + 2\ H_2O \quad CH_4 + 3\ CO_2$$

We believe that purging the anaerobic digester with hydrogen or other gases will improve the kinetics of the methanogenic reaction by –

- Reducing the methane concentration in solution and thus favoring the equilibrium toward its production
- In the case of hydrogen purge, providing a substrate on which methanogenic bacteria thrive.

In summary, it can be said that the BIOTHERMGAS Process appears to have the following advantages over the separate anaerobic digestion or thermal gasification processes:

- Wet or dry feeds can be processed
- Nutrients required for biological conversion can be minimized by recycle from the thermal conversion process
- The overall thermal efficiency is high because the thermal process supplies heat requirements for biological conversion
- Thermal process gases can be biomethanated and may result in improved biological kinetics
- Process residues are minimal
- It allows greater flexibility in feed requirements and operating conditions.

Although the BIOTHERMGAS Process conceptually appears to show promise for conversion of organic matter to methane, the following aspects need further investigation before a valid analysis can be made:

- Preliminary systems and economic analysis
- Dewatering characteristics of digester effluent
- Effect of digester supernatant recycle on biological gasification
- Thermal gasification characteristics of digester effluent

- Effect of recycle of thermal process ash on biological gasification
- Biomethanation potential of thermal product gases
- Effect of thermal product gases on biological process kinetics.

The results from laboratory and bench-scale experiments on the above basis will permit development of a preliminary design scheme and a more accurate energy and economic evaluation of the process.

We have initiated a preliminary systems and bench-scale analysis of the BIOTHERMGAS Process using in-house funds at IGT. Some of the results of this work are presented below.

PRELIMINARY SYSTEMS ANALYSIS

A systems analysis of the BIOTHERMGAS Process was initiated in order to obtain an estimate of the materials and energy balance for the process. Although preliminary estimates of process economics were made, the available data base is limited, and formal presentation will thus be deferred.

Systems studies of materials and energy balances for three applications of the BIOTHERMGAS Process were conducted as outlined in Table 5. The first two examples represent a probable upper size limit for a biomass-fed plant with a capacity of 10,000 dry ton/day and corresponding SNG output of 100 billion Btu/day. Assuming a biomass productivity of 20 tons/acre-year, an area of 182,000 acres would be required for growth of the feed for this plant. Bermuda grass was selected as the feedstock because it is a prime candidate for biomass energy farms and we have detailed data on its composition and anaerobic digestion.(7) The major difference in Examples 1 and 2 is the use of catalysis versus biomethanation for conversion of the thermal product gases to SNG. Example 3 is an order of magnitude smaller and represents the application of the BIOTHERMGAS Process for conversion of the MSW and sewage generated by a population of about 500,000.

Table 5. SYSTEMS ANALYSIS STUDIES

	Example 1	Example 2	Example 3
Feed	Bermuda Grass	Bermuda Grass	MSW/Sewage Sludge
Loading, dry tons/day	10,000	10,000	1,000
Gasifier	Two-Stage, O_2-Steam	Two-Stage, O_2-Steam	Single Stage, O_2-Steam
Methanation of Thermal Product Gases	Catalytic	Biomethanation	Biomethanation
Approximate SNG Output, 10^9 Btu/day	120	111	7

<u>Example 1. Bermuda Grass – Catalytic Methanation</u>

Table 6 summarizes the physical and chemical properties of Bermuda grass. The operating and performance parameters used for the Example 1 systems study are listed in Table 7. Data presented for gasification of peat(1) were used as a basis for thermal conversion of digester effluent solids. Grass slurry is fed to the anaerobic digester operating at 35°C with a loading of 0.15 lb VS/cu ft-day and a retention time of 12 days. A methane yield of 3.50 SCF/lb VS added was assumed, with a methane content of 60 mol percent in the total digester gas. For stable digestion it was assumed that the feed should have a C/N ratio of less than 12. Although nitrogen must be added initially, it accumulates via recycle and ultimately becomes a by-product. The gas produced is purified to pipeline quality SNG by carbon dioxide and hydrogen sulfide.

Table 6. PHYSICAL AND CHEMICAL CHARACTERISTICS OF BERMUDA GRASS

Total Moisture, ~ total wt.	33.0
Total Solids, % total wt.	67.0
Volatile Solids, % dry wt.	95.0
Ash, % dry wt.	5.0
Heating Value, Btu/lb dry	8180
Total Carbon, % dry wt.	47.1
Total Hydrogen, % dry wt.	6.04
Total Oxygen, dry wt.	39.6
Total Nitrogen, % dry wt.	1.96
Total Sulfur, dry wt.	0.21

The effluent is collected anaerobically in a sedimentation tank for gravity settling at atmospheric temperature with a retention time of 3 days. It has been observed in the laboratory experiments that Bermuda grass effluent has good gravity settling characteristics.(7) It was assumed that 5% of volatile solids present in the effluent will be converted to 60% methane and 40% carbon dioxide. The thickened slurry is mechanically dewatered from 10-12% to 50% solids. The supernatant and associated nutrients from the sedimentation tank and dewatering process are recycled into the feed slurry tank.

The composition of the solids in digester cakes is similar to that of Minnesota peat which has been the subject of extensive thermal gasification at IGT under the sponsorship of DOE and Minnesota Gas Company.(1) Hence, IGT's PEATGAS™ process* was selected as a basis for our preliminary calculations on thermal gasification of effluent solids. This is a two-stage steam-oxygen gasification process with a drier and feed preheating unit located between the lockhopper feed system and the hydrogasifier. The hot gas from the hydrogasifier, at about 1475°F and 510 psig, is used in the drier to dry the feed cake. The solid and liquid effluent (char and ash) is fed into the char gasifier and is gasifed at 1700°F and 520 psig. Gas produced in the char gasifier is fed into the hydrogasifier and exits through the drier. The components in the product gas phase are carbon monoxide, carbon dioxide, hydrogen, steam, methane, ethane, ammonia and traces of higher hydrocarbons. The gas is passed through a venturi

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* IGT offers PEATGAS research and development, engineering and technical services related to the PEATGAS process.

Table 7. OPERATING PARAMETERS FOR GASIFICATION OF BERMUDA GRASS THE BIOTHERMGAS PROCESS

A. Anaerobic Digestion	
Temperature	35°C (95°F)
Culture Volume	126.7×10^6 cu ft
Loading	0.15 1b VS/cu ft-day
Retention Time	12 days
Assumed Methane Yield	3.50 SCF/1b VS added-day
Methane Content in Digester Gas	60 mol %
B. Thermal Gasification (Steam-Oxygen)	
Two-Stage Reactor:	
<u>Stage One</u>	
Temperature	1475°F
Pressure	530 psig
Solids Residence Time	1-5 sec
<u>Stage Two</u>	
Temperature	1700°F
Pressure	545 psig
Solids Residence Time	10 min
C. Chemical Methanation	
Temperature	830°F
Pressure	410 psig
Methane Content	94 mol %

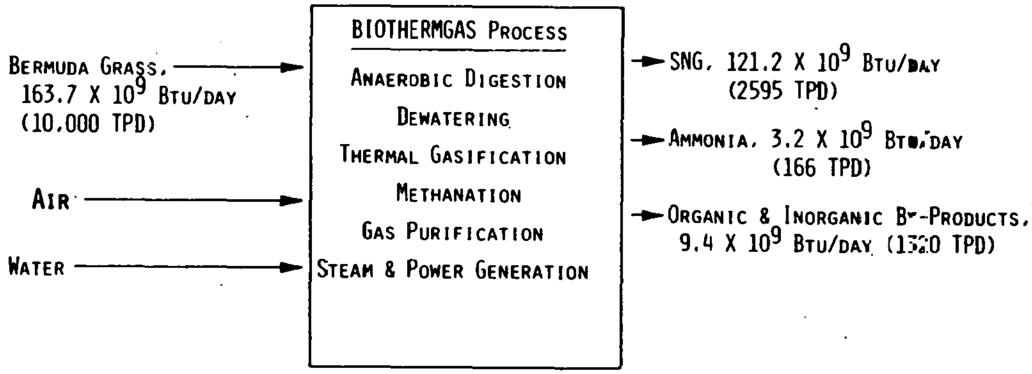
scrubber (dust removal) unit; about 30% of it is then used as transport gas and pressurizing gas for preheating the feed. Of the remaining 70%, about two-thirds goes through a CO-shift reactor to increase the hydrogen/carbon monoxide ratio to about 3.67; one-third is by-passed. The combined gas stream is passed through gas upgrading processes including liquid recovery, oil-water separation and acid-gas removal processes. The processed gas then passes through a catalytic methanation unit and emerges as pipeline-quality SNG.

The results of the systems analysis of Example 1 are summarized in Figure 2, and more detailed information on the materials and energy balance are presented in Tables 8 and 9. The BIOTHERMGAS Process with catalytic methanation produces 121 billion Btu/day of SNG from 10,000 tons/day of Bermuda grass. This represents a cold gas efficiency of 74% – a significant improvement over efficiencies of about 40% and 60% which are typical for mesophilic digestion and the PEATGAS process, respectively.

Table 8. OVERALL MATERIALS BALANCE FOR BIOTHERMAL GASIFICATION OF BERMUDA GRASS TO SNG

Input, ton/day (dry)		Output, ton/day (dry)	
A. Using Catalytic Methanation			
Bermuda Grass	10,000	SNG	2,595
Oxygen	790	Sour Gas	6,505
		By-Products	850
		Waste Water	840
	10,790		10,790
B. Using Biomethanation			
Bermuda Grass	10,000	SNG	2,390
Oxygen	790	Sour Gas	6,475
		By-Products	845
		Waste Water	1,080
	10,790		10,790

In the biological gasification, the total volatile solids (organic matter) reduction is 42%, leaving 58% as refractory organic matter in the digester effluent. An additional 5% of the remaining volatile solids is converted in the sedimentation tank, another 1% is recycled with the supernatant from sedimentation and mechanical dewatering. Following dewatering, the solids cake contains 57% of the total feed solids, which accounts for 54% of total feed energy. About 58% of the energy in the digester effluent cake is recovered as SNG; 16% energy is recovered as by-products. The remaining 26% is the unrecovered energy for which a use may be found with additional study of the process. The total plant efficiency, which is defined as total recovered energy divided by feed energy, is about 82%.



Cold Gas Efficiency = 74%

Total Plant Efficiency = 82%

Figure 2. ENERGY AND MATERIALS FLOW OF BIOTHERMAL GASIFICATION OF BERMUDA GRASS TO SNG USING CATALYTIC METHANATION

Table 9. ENERGY BALANCE FOR BIOTHERMAL GASIFICATION OF BERMUDA GRASS TO SNG USING CHEMICAL METHANATION
(Feed Input: 10,000 ton/day)

Input, 10^9 Btu/day		Output, 10^9 Btu/day	
A. For Biological Gasification of Feed			
Feed to the Digester	163.7	Methane Gas	66.5
		Solids in Effluent	92.9
		Heat Loss With the Liquid Stream and Other Radiation Losses	4.3
	163.7		163.7
B. For Dewatering of Digester Effluent			
Solids in Effluent	92.9	Methane Gas	3.4
		Solids in Cake	87.8
		Solids Leaving With Liquid Stream	0.8
		Heat Loss Associated With Liquid Stream	0.9
	92.9		92.9
C. For Thermal Gasification of Cake and Chemical Methanation			
Solids to Gasifier	68.5	Pipeline Gas	50.7
Solids to Boiler	19.3	Higher Hydrocarbons (oil, tar, benzene, etc.)	8.1
		Ammonia and Sulfur	3.3
		Char and Ash	1.2
		Cooling Water and Air Cooling Losses	16.9
		Flue Gas From Boiler	4.2
		Heating Value of Assumed Vent Gases, Sensible Heat of Vent Gases, Waste Heat Recovery and Product Losses	1.9
		Motive Power	1.5
	87.8		87.8

Table 10. ENERGY BALANCE FOR BIOTHERMAL GASIFICATION OF BERMUDA GRASS TO SNG USING BIOMETHANATION
(Feed Input: 10,000 ton/day)

Input, 10^9 Btu/day		Output, 10^9 Btu/day	
A. For Biological Gasification of Feed			
Feed to the Digester	163.7	Methane Gas	66.5
		Solids in Effluent	92.9
		Heat Loss With the Liquid Stream and Other Radiation Losses	4.3
	163.7		163.7
B. For Dewatering of Digester Effluent			
Solids in Effluent	92.9	Methane Gas	3.4
		Solids in Cake	87.8
		Solids Leaving With Liquids Stream	0.8
		Heat Loss Associated With Liquid Stream	0.9
	92.9		92.9
C. For Thermal Gasification of Cake and Biomethanation			
Solids to Gasifier	68.5	Methane Gas	41.5
Solids to Boiler	19.3	Higher Hydrocarbons (oil, tar, benzene, etc.)	8.1
		Ammonia and Sulfur	3.3
		Char and Ash	1.2
		Cooling Water and Air Cooling Losses	16.9
		Flue Gas From Boiler	4.2
		Heat Losses Associated With Vent Gases, Unaccounted Heat of Formation of Methane, WHR and Other Losses	11.1
		Motive Power	1.5
	87.8		87.8

Example 2. Bermuda Grass Biomethanation

This example is identical to Example 1 up to dust removal and the venturi-scrubber unit. Of the total thermal effluent gas, 70% is passed to the liquid recovery and oil-water separation unit without going to the CO-shift reactor. The remaining 30% is utilized within the plant. The gas stream coming out of the liquid recovery unit is cooled and purged into the anaerobic digester for biomethanation. The bacteria methanate hydrogen, carbon monoxide, and carbon dioxide by reactions that are presented on page 8.

The product gases are methane and carbon dioxide, which are the same gases produced from digestion of the organic feed. The final gas is purified to pipeline quality by removing carbon dioxide and hydrogen sulfide.

The operational parameters for biological and thermal gasifiers are the same as in Example 1. (See Table 7.)

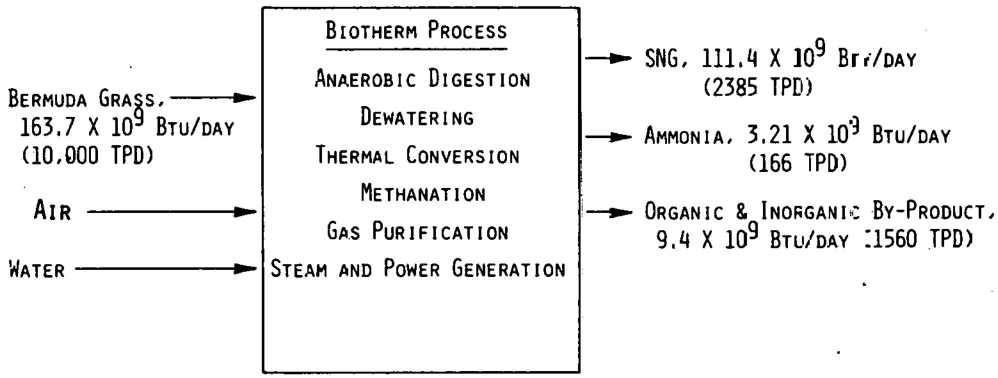
The results of the systems analysis of Example 2 are summarized in Figure 3, and details on the materials and energy balance for the two examples are presented in Tables 8 and 10. The BIOTHERMGAS Process with biomethanation produces 111 billion Btu/day of SNG from 10,000 tons/day of Bermuda grass. This represents a cold gas efficiency of 68%, which is higher than efficiencies of biological or thermal gasification used separately. Many unknowns exist for the use of biomethanation in this manner, such as gas conversion efficiencies and the effect of purging on anaerobic digestion of the organic feed.

The energy and materials balance up to dewatering is the same as for Example 1. However, the balances in the final steps are different. About 48% of the total energy in the cake is recovered as pipeline gas. The loss of about 10% compared with Example 1 might be attributed to reaction heat emitted during biomethanation, and lower steam and power requirements related to elimination of the shift reaction and catalytic methanation steps. The heat of formation of methane amounts to about 2% to 3% of the feed energy and would provide the heat needed for anaerobic digestion.

Example 3. Municipal Solid Waste – Biomethanation

Table 11 summarizes the physical and chemical properties of the municipal solid waste and sludge blend. Table 12 presents the operating parameters of the biological and thermal gasifier used for the systems study of Example 3. The front end of the plant, which separates metals and other heavy matter from the organic fraction of refuse and reduces particle size of the digester feed, was taken from the IGT BIOGAS® Process.(6) A single-stage steam-oxygen gasifier was used for thermal conversion of digester effluent solid, and biomethanation was used for conversion of thermal process gases to SNG.

The raw MSW goes in the primary shredder and the metals and heavy materials in the shredded raw material are removed in the magnetic and air separator. The clean and shredded MSW is fed into the hammer mill, then to the fiberizer to process the feed. The fiberized raw material goes into the blender where it is mixed with the sewage sludge and the supernatant obtained from dewatering the digester effluent. The anaerobic digester is fed at a loading of 0.20 lb VS/cu ft-day and retention time of 15 days. Methane yield was assumed to be 3.50 SCF/lb VS added per day with a methane content of 60 mol % in the total digester gas. The effluent is conditioned by adding flocculants such as ferric chloride and lime, and then set for gravity thickening. As mentioned earlier, the supernatant is recycled to make feed slurry, and the thickened slurry of 10% to 12% solids is dewatered mechanically to about 50% solids. Our recent laboratory



Cold Gas Efficiency = 68%

Total Plant Efficiency = 76%

Figure 3. ENERGY AND MATERIALS FLOW FOR BIOTHERMAL GASIFICATION OF BERMUDA GRASS TO SNG USING BIOMETHANATION

Table 11. PHYSICAL AND CHEMICAL CHARACTERISTICS OF MSW/SLUDGE BLEND (90% MSW + 10% Sludge, dry wt.)

Total Moisture, % total wt.	31.1
Total Solids, % total wt.	68.9
Volatile Solids, % dry wt.	81.5
Ash, % dry	19.1
Heating Value, Btu/lb dry	7480
Total Carbon, dry wt %	42.2
Total Hydrogen, dry wt %	5.6
Total Oxygen, dry wt %	31.9
Total Nitrogen, dry wt %	1.2

Table 12. OPERATING PARAMETERS FOR GASIFICATION OF MSW/BLEND BY BIOTHERMGAS PROCESS WITH BIOMETHANATION

A. Anaerobic Digestion	
Temperature	35°C
Culture Volume	5.07 X 10^6 ft^3
Loading	0.20 lb VS/cu ft-day
Retention Time	15 days
Methane Yield (assumed)	3.50 SCF/lb VS added
Methane Content in Digester Gas	60 mol %
B. Thermal Gasification (Steam Oxygen)	
Single-Stage Reactor Temperature	1700°F
Reactor Pressure	350 psig
Carbon Conversion	95%
Solids Residence Time	10-20 min.

experiments have resulted in a cake with about 38% solids from a slurry of 2% solids without addition of any flocculant.

The digester effluent solid cake is gasified thermally in a single-stage steam-oxygen gasifier at 1700°F and at a pressure of 350 psig. Since the size of the plant is small and the digester effluent solid composition different than those of Bermuda grass digester effluent, it was decided to use a cheaper, simpler, single-stage reactor. The feed is dried from the thermal gasifier effluent gas using heat recovered from the gasifier waste heat recovery unit. The gaseous stream is upgraded in the dust removal and venturi scrubber unit. It is then processed in the liquid recovery and oil-water separation unit. The effluent gas is cooled and purged into the anaerobic digester to methanate the gases as described in Example 2.

The results of the systems analysis of Example 2 are summarized in Figure 4, and more detailed information on energy balance and overall material balance is presented in Tables 13 and 14. The BIOTHERMGAS Process with biomethanation produces 7 billion Btu/day of SNG from 1,000 tons/day of municipal solids waste. This represents a cold gas efficiency of 60%. The lower efficiency compared with that obtained in Examples 1 and 2 can be attributed to the higher ash content of MSW/sludge compared with Bermuda grass.

Table 13. OVERALL MATERIALS BALANCE FOR BIOTHERMAL GASIFICATION OF MSW/SLUDGE BLEND TO SNG USING BIOMETHANATION

Input, tons/day (dry)		Output, tons/day (dry)	
MSW (Unprocessed)	1,000	SNG	149
Sludge	112.5	Sour Gas	510
Oxygen	101	Materials Recovered in Feed Processing	334
		Waste Water	124
		By-Product	96.5
	1213.5		1213.5

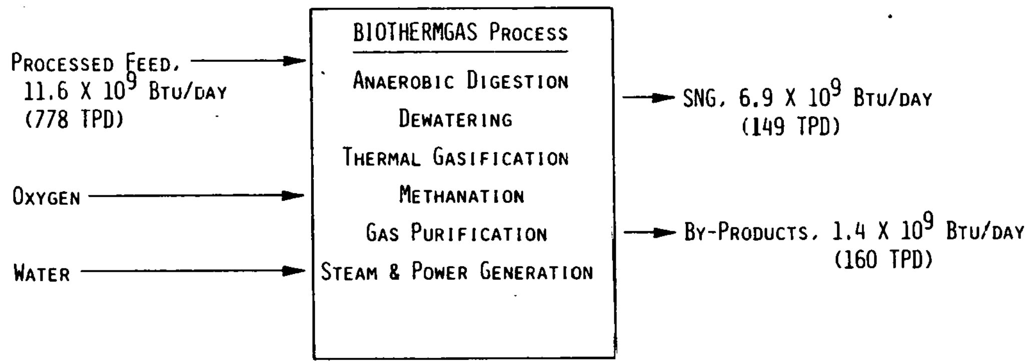
Of the total processed feed, 80% is fed to the digester and 20% is directly utilized for power and steam generation. In biological gasification, the volatile solids (organic matter) reduction is about 42%, leaving 58% of the volatile solids in the digester effluent. Following dewatering, the cake contains 55% of digester feed energy. Total energy recovery after thermal gasification and biomethanation is 46% of the energy input into the thermal gasifier. About 18% is recovered in the form of by-products; the remaining 35% energy is unrecovered heat of formation of the methane. The total cold gas efficiency of the process is 60.3%, and the total plant efficiency is 71.6%

EXPERIMENTAL STUDIES ON BIOTHERMGAS PROCESS

The following describes experimental work conducted thus far on the BIOTHERMGAS process. The initial objectives were as follows:

- To evaluate potential for biomethanation of thermal product gases by a biomass-fed digester
- To determine effects of thermal product gases on kinetics of methanogenic and non-methanogenic phases of anaerobic digestion.

Once a day, four cultures under study were fed a mixture of activated and primary sewage sludges at an organic loading of 0.15 lb VS/cu ft-day. Three of the cultures were continuously purged with various air-free mixtures of hydrogen, carbon monoxide, carbon dioxide and helium; as a control the fourth system was operated without gas purging. The data presented below were obtained at a hydraulic retention time of 15 days. In the future we plan to operate the fermentation at hydraulic retention times of 10, 7, 5, and 3 days in order to define the effect of gas purging on process kinetics.



Cold Gas Efficiency = 60%

Total Plant Efficiency = 72%

Figure 4. ENERGY AND MATERIAL FLOWS OF BIOTHERMAL GASIFICATION OF MUNICIPAL SOLID WASTE AND SLUDGE BLEND TO SNG USING BIOMETHANATION

Table 14. ENERGY BALANCE FOR BIOTHERMAL GASIFICATION OF MSW/SLUDGE BLEND TO SNG USING BIOMETHANATION
(Feed Input: 1000 ton/day MSW + 112.5 ton/day Sludge)

Input, 10^9 Btu/day		Output	
A. For Biological Gasification of Processed Feed (80% of Total)			
Feed to the Gasifier	9.3	Methane Gas	3.6
		Solids in Effluent	5.2
		Heat Loss With Liquid Stream	0.5
	9.3		9.3
B. For Dewatering of Digester Effluent			
Solids in Effluent	5.2	Solids in Cake	5.1
		Solids Leaving With Liquid Stream and Other Heat Losses	0.1
	5.2		5.2
C. For Thermal Gasification of Cake and Biomethanation			
Solids to Gasifier	5.1	Methane Gas	3.4
Solids to Boiler (20% of total feed)	2.3	Higher Hydrocarbons and Other Organic By-Products	0.5
		Char and Ash	0.3
		Inorganic By-Products	0.5
		Cooling Water and Air Cooling Loss	1.2
		Heat Losses from Vent Gases, Unaccounted Heat of Formation of Methane, Waste Heat Recovery, and Other Losses	1.5
	7.4		7.4

Materials and Methods

Digester Design

All experimental runs were conducted in 4-inch outside diameter cylindrical plexiglas reactors having a total volume of 3.0 liters and a working volume of 1.5 liters. The reactors were each equipped with four internal vertical baffles spaced at ninety degrees to promote efficiency mixing of the cultures. Sewage sludge feed slurries were charged to the reactors through 1/2-inch feed ports at the top of the reactors and effluent was withdrawn through 1/2-inch ports near the bottom of the reactors. In addition, each reactor was fitted with a 1/4-inch gas dispersion tubing which extended through the head plate and to within 1/2-inch of the bottom of the culture for purging of selected gases directly into the culture.

Inocula, Digester Feeds, and Purge Gases

The inoculum for these runs was obtained as digester draw-off from an active sewage sludge digester at the West-Southwest Sewage Treatment Plant of the Metropolitan Sanitary District of Greater Chicago (MSDGC). Sewage sludge digester feeds were also obtained from MSDGC and consisted of a mixture of 24% activated sludge and 76% primary sludge on a dry solids basis. Purge gases were obtained as primary standards from Mattheson Company.

Digester Operation

All of the runs were fed with a sewage sludge feed slurry in the semicontinuous mode according to the operating conditions presented in Table 15. The sewage sludge organic loading was maintained at 0.15 lb VS/day with a hydraulic retention time of 15 days. Run 601 was operated without gas purging to serve as an experimental control, while the other three runs were continuously purged with gases having the compositions presented in Table 16.

Prior to introduction into the cultures, the purge gases were passed through heated copper tubings to remove any traces of oxygen. Purge gas flow rates were monitored daily with a soap film bubble meter and adjusted to 60 ± 2 ℓ/day.

Analytical Procedures

Daily gas production from the control, Run 601, was monitored by fluid displacement from a gas burette. The fluid consisted of a solution of 75 wt % water, 20 wt % sodium sulfate, and 5 wt % sulfuric acid. Once a week the volume of gas purged into each of the purged runs was monitored with a wet test meter and the resultant product gas was collected over a 24-hour interval in an inverted drum gas collector. All reported gas volumes and flow rates were converted to a dry basis at 60^{o}F and 30 in. Hg. Samples of total product gas were analyzed for hydrogen, carbon dioxide, oxygen, nitrogen, methane and carbon monoxide with a Fisher Hamilton Gas Partitioner and a Carle AGC III H gas chromatograph.

Samples of digester effluent were monitored daily for pH and weekly for volatile acids. When steady-state performance was achieved, effluents were analyzed twice for total alkalinity, elements (carbon, hydrogen, nitrogen, sulfur and phosphorus) and heating value, and once for ammonia nitrogen. Analyses for elements and heating value were performed on 8-day composite samples.

Chemical analyses of raw feeds and effluent slurries were performed according to standard analytical procedures listed in Table 17, except for the following procedures that were developed at IGT:

- Carbon-hydrogen analysis
- Heating value
- Volatile fatty acids

Carbon-hydrogen analysis was conducted by the ASTM coal and coke procedure D3178-73.

Heating values were determined using a Parr Model 1241 automatic adiabatic calorimeter system. The unit is standardized to meet ASTM D2015 requirements. A check for completeness of combustion was made by plotting Btu/lb versus percent carbon in the samples. A straight line was obtained with minimal scatter.

Table 15. DIGESTER OPERATING CONDITIONS

Feed: Mixture of 24% Activated Sewage Sludge and 76% Primary Sewage Sludge (Total Solids Basis)

Culture Volume	1.5
Temperature	35°C
Feeding Frequency	Daily, Semicontinuous
Loading	0.15 lb VS/ft-day
Retention Time	15, 10, 7, 5, 3 days
Gas Purge Rate	60 /day in all runs except Control

Table 16. COMPOSITION OF PURGE GASES

RUN	Purge Gas Composition, mol %			
	H_2	CO_2	CO	H_2
601 (Control)	--	--	--	--
602	30	40	30	0
603	30	40	0	30
604	0	40	30	30

Volatile fatty acids concentrations were determined by flame ionization gas chromatography using a Hewlett-Packard Model 5840A gas chromatograph (GC) equipped with an automatic injection system. Samples were prepared for analysis by addition of 0.3 ml of 10 N sulfuric acid per 2-ml sample and centrifuging at 20,000 rpm for 30 minutes. GC operating conditions were as follows: 6 ft X 1/4 in. (O.D.) glass column packed with Chromosorb 101

Table 17. LIST OF STANDARD ANALYTICAL PROCEDURES FOR KELP

Test	Standard Procedure	Reference
Ash	Ignition, gravimetric	APHA-AWWA-WPCF Standard Methods, 14th Edition, Part 208G
Alkalinity	Titrimetric Method	Standard Methods, 14th Edition, Part 403
Carbon Dioxide	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
Conductivity	Conductance Cell and Wheatstone Bridge	Standard Methods, 14th Edition, Part 205
Hydrogen	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
Methane	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
Moisture	Evaporation, Gravimetric	Standard Methods, 14th Edition, Part 208G
Nitrogen (ammonia)	Specific Ion Probe	Standard Methods, 14th Edition, Parts 418 and 413J
pH	Electrometric Method	Standard Methods, 14th Edition, Part 424
Phosphorus	Colorimetric	AOAC Official Method of Analysis, 12th Edition, Section 3.062
Solids (total)	Evaporation, Gravimetric	Standard Methods, 14th Edition, Part 208G
Solids (volatile)	Ignition, Gravimetric	Standard Methods, 14th Edition, Part 208E
Sulfur	Combustion, Gravimetric	ASTM, D3177-75

(80/100 mesh); nitrogen carrier gas, 30 ml/min; hydrogen, 30 ml/min; air, 250 ml/min; injector, 200°C; oven, 180°C; and detector 250°C. Baseline separation of acetic, propionic, isobutyric, butyric, isovaleric, valeric, and caproic acids is affected by this procedure in 15 minutes. Every 10 samples is followed by a 10 N sulfuric acid rinse and a standard containing all seven acids.

Results and Discussion

The results of laboratory experiments on the effect of continuous gas purging of the anaerobic digestion process with thermal conversion product gases are presented in Tables 18 and 19. It is apparent from these data that the reduced gases (hydrogen and carbon monoxide) either separately or in combination with carbon dioxide, could be biomethanated by the microbial population involved in anaerobic digestion of sewage sludge. The gas conversion efficiencies were highest for the run purged with a mixture of hydrogen and carbon dioxide. The recovery efficiency of energy from the feed gas in this case was 30%. This efficiency could be easily improved by various methods of increasing the gas-culture contact, e.g., gas recycle or reducing bubble size.

Table 18. EFFECT OF GAS PURGING ON METHANE PRODUCTION RATES

	Run No.			
	601	602	603	604
Purge Gases	None	H_2, CO_2, CO	H_2, CO_2, He	CO_2, CO, He
Methane Production, / culture-day				
Total	0.753	1.65	1.95	1.12
From Sludge	0.753	0.77	0.79	0.79
From Purge Gases	--	0.88	1.16	0.33

Table 19. EFFECT OF GAS PURGING ON FEED ENERGY RECOVERIES AS METHANE

	Run No.			
	601	602	603	604
Purge Gases	None	H_2, CO_2, CO	H_2, CO_2, He	CO_2, CO, He
Feed Sludge Energy Recovery, %	48.2	49.4	50.2	50.6
Feed Gas Energy Recovery, %	--	12.0	29.5	8.46

It is interesting to note that gas purging with hydrogen did not adversely affect conversion of sludge. Recent literature on anaerobic metabolism suggests that hydrogen could reduce the rates of acid-phase and the acetate-to-methane reaction.(11,2) If this were the case in our experiments, concentrations of fermentation products would have accumulated in these runs (602 and 603) and conversion efficiencies would have been lower than those in the control. Effluent-quality data in Table 20 indicate that volatile acids concentrations were low in these runs and sludge conversion efficiencies similar to those of Runs 601 and 604, which were not purged with hydrogen. The effect of hydrogen on this fermentation needs additional research to resolve the conflicting observations.

Table 20. EFFLUENT QUALITY OF SLUDGE DIGESTERS PURGED WITH VARIOUS GAS MIXTURES

	Feed	Run No. 601	602	603	604
Purge Gases	--	--	H_2, CO_2, CO	H_2, CO_2, He	CO_2, CO, HE
Total Volatile Acids, mg/ℓ as acetic	--	56	20	12	26
Total Alkalinity, mg/ℓ as $CaCO_3$	--	7920	7100	7070	7100
No. of Retention Times in Operation					
pH	--	7.29	7.18	7.20	7.20
NH_3-N at mg/ℓ	--	1150	1240	1210	1180
Total Solids (TS)	5.35	3.59	3.42	3.40	3.33
Volatile Solids, wt % of TS	67.4	56.0	58.1	57.0	57.8
Heating Value, Btu/dry lb	7130	5820	6010	5940	5960
Elements, wt % of TS					
C	38.7	31.7	32.2	32.1	32.4
H	5.46	4.45	4.63	4.56	4.60
N	4.35	3.96	4.21	4.14	4.19
S	0.77	1.13	0.98	0.99	1.07
P	1.40	1.85	1.90	2.00	2.00

The effect of gas purging on the kinetics of methanogenesis will become apparent when the retention time is reduced and the system becomes kinetically limited by the methanogenic reactions. We anticipate that hydrogen purging will increase the rate of methanogenesis and hence the overall process kinetics.

CONCLUSION

A preliminary evaluation of IGT's BIOTHERMGAS Process has shown that combining biological and thermal gasification results in a process with a higher conversion efficiency and greater choice of feedstocks that can be processed, than either biological or thermal processes used separately. The biological gasification component can receive high moisture feeds, effect low temperature and low pressure conversion of a major portion of the feed, and can be used for methanation of thermal process gases. The thermal gasification component gasifies refractory organic residues from the biological component, provides heat, ammonia and other nutrients for recycle to the biological component, and provides gases that can be used for heating, mixing, and stimulating methanogenesis in the biological component.

Research planned for further demonstration of the technical and economic feasibility of the process is presented in Table 21. This work includes evaluation of the process at the laboratory scale, a more detailed systems and economic study, and process design and scale-up.

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Table 21. FUTURE RESEARCH

- Dewatering Characteristics of Digester Effluent
- Effect of Recycling Digester Supernatant on Biological Processes
- Thermal Gasification of Digester Effluent
- Recycle of Nutrients in Thermal Process Ash to Biological Processes
- Biomethanation of Thermal Product Gases
- Effect of Thermal Product Gases on Biological Process Kinetics
- Evaluation of Different Biomass Species, Organic Wastes, and Peat
- Process Design and Scale-up

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