

A Process Study of the Biothermal Conversion of Water Hyacinths to Methane

Scientific Note

R. S. BUTNER*, D. C. ELLIOTT, L. J. SEALOCK, JR.,
AND D. P. CHYNOWETH

*Pacific Northwest Laboratory,** Richland, WA 99352; and University
of Florida, Gainesville, FL*

Index Entries: Biothermal; gasification; high-moisture feed-
stocks; biomass; wastes.

INTRODUCTION

The development of processes for the conversion of biomass materials to methane has historically followed two distinct and divergent paths. Biological conversion (anaerobic digestion) utilizes a complex but reasonably well understood biochemical route to produce methane from carbohydrates such as cellulose and hemicellulose. Digestion is generally carried out under mild (near ambient) conditions of temperature and pressure. The raw product gas is high in methane (typically 60 vol%) and needs relatively little downstream processing. The major drawbacks of anaerobic digestion are the relatively poor gas production rates and the incomplete conversion of lignin-containing materials.

Thermochemical gasification of biomass is carried out at much higher temperatures ($\geq 500^{\circ}\text{C}$) and takes advantage of an equally complex series of chemical reactions that occur between carbon-containing compounds, water, and oxygen. Reaction rates are several orders of

*Author to whom all correspondence and reprint requests should be addressed.

**Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO.

magnitude greater than those found in anaerobic digestion, and nearly total conversion of the biomass is possible. The raw product gases are typically low in methane content, however, and must be further processed to produce a methane-rich product gas. Some of the relative advantages and disadvantages of the two conversion routes are listed in Tables 1 and 2.

The concept of combining anaerobic digestion and thermochemical gasification operations to improve overall conversion efficiency was first proposed by Chynoweth et al. (1). The original concept used an oxygen-blown gasifier to produce synthesis gas from the unconverted biomass present in the effluent from an anaerobic digester. The effluent typically has a solids content of under 10 wt%; consequently, dewatering (and in most cases, drying) of the anaerobic effluent was required to permit efficient gasification of the effluent solids. This water removal was accomplished at the expense of process complexity, loss of organic material, and the need for additional mechanical and thermal energy input.

We have recently been exploring the concept of a hybrid process which uses a newly developed high-moisture biomass gasification system to improve the efficiency of the process. The two stage process is based on (1) anaerobic digestion of a water hyacinth/sewage sludge blend; this is followed by (2) pressurized catalytic gasification of the undigested residue to produce a high methane content gas. The use of this pressurized, aqueous gasification process eliminates the requirement for dewatering of the digester effluent.

In this paper we propose a flowsheet for such a two stage hybrid process, based on previous experience with anaerobic digestion and new experiments reported here on catalytic gasification. ASPEN-PLUS™ process simulation software was used to develop mass and energy balances around the conceptual hybrid process flowsheet. Process efficiencies and yields were determined for several cases, and the effect of key process variables was studied.

Table 1
Advantages and Disadvantages of Anaerobic Digestion

Advantages	Disadvantages
Works well with dry or moist feedstocks	Product requires compression prior to pipeline use or treatment
Produces a high-BTU gas stream with a high methane content	Limited carbon conversion results on most feedstocks
Simple reactor equipment operates at low temperatures and pressures, has low cost per unit volume	Slow kinetics requires large reactor volumes
	Supplemental nutrients may be required for some feedstocks

Table 2
Advantages and Disadvantages of Thermochemical Gasification

Advantages	Disadvantages
High conversion efficiency	Is generally limited to dry feedstocks (less than 60% moisture)
High conversion rate	Equipment is relatively complex, expensive
May be operated at elevated pressures	Generally requires downstream treatment of product gas to produce methane
Relatively insensitive to feedstock chemistry	

EXPERIMENTAL BASIS

The anaerobic digester used to obtain bioconversion yields is a key component of the Community Waste Research Facility, located at the Walt Disney World resort complex near Orlando, FL. The digester is operated jointly by the Institute for Gas Technology (IGT) and the University of Florida. The experimental test unit is a 4.5 m³ (160 ft³) jacketed reactor originally designed by IGT (2). The system was fed a mixture of water hyacinths and primary sewage sludge from the Reedy Creek Water Treatment Facility. The specific operating parameters used in obtaining the yield data are shown in Table 3.

The thermochemical reactor is a 1-L batch reactor used for laboratory studies of the catalytic low-temperature gasification of biomass. The system is operated by Pacific Northwest Laboratory (PNL) and has been used to test the gasification of nearly a dozen different high-moisture

Table 3
Operating Specifications of IGT Anaerobic Digester

Parameter	Reported value
Reactor Configuration	unmixed, top feed solids concentrating
Reactor h/d ratio	2.0
Reactor residence time	
HRT, hydraulic residence time	7 d
SRT, solids residence time	14 d
Reactor temperature	58°C
Solids content of feed	4.4 wt%
pH in reactor	7.0–7.9
Solids content of effluent	1.3–7.2 wt%
Volatile solids, % of total solids	60–83 %
Average daily loading rate	5 kg volatile solids/m ³ , .3 lb VS/ft ³

biomass feedstocks. For the purpose of this study, the reactor was fed with the effluent obtained from the IGT bioreactor. Operating conditions for the low-temperature gasifier are shown in Table 4. The experimental apparatus and methods used in obtaining product yield and conversion data for the moist-biomass gasifier have been described in detail in previous publications (3).

Several hundred grams of digester effluent were shipped frozen in plastic sample bottles to PNL. The material was thawed prior to use and an elemental analysis was obtained using a Perkin-Elmer 240B elemental analyzer. The analysis obtained is presented in Table 5. The analysis was done on the wet material to avoid carbon losses during drying. This analysis was used to calculate total carbon conversion during the thermal gasification experiments. Estimation of the composition of the dried material is shown and is based upon 7.2 wt% dry solids. Data from the analysis of a dried sample taken from the same reactor at a different time is shown for comparison.

The thawed effluent was gasified in a 1-L batch autoclave. Gas samples were taken every 15 min after the reactor had reached a temperature of 250°C. Ultimate carbon conversion to gas, as determined by the gas chromatographic analysis of the gas samples, reached 65–75 wt% within 15–20 min of reaching final reaction temperature. The results of the two experiments performed with the material are shown in Table 6.

Analysis of the aqueous material remaining in the reactor after gasification experiments with similar feedstocks indicates that most of the unconverted carbon is present as water-soluble organic material, principally phenol derivatives and fatty acids (4). Some carbon also remains as a solid material. This solid typically is deposited on the outside of the reactor liner. Analysis of the solids filtered from the reactor contents indicate that they contain approximately 3 wt% carbon, with the balance consisting of powdered catalyst. The filtrate which remains is a single liquid phase.

Table 4
Operating Conditions of Moist-Biomass Gasification System

Parameter	Reported Value
Reactor type	Stirred batch autoclave, with stainless steel liner
Reactor volume	.001 m ³ , 1 L
Reactor temperature	380–400°C
Reactor pressure	27.6–34.6 MPa, 4000–5000 psia
Solids content of feed	5–10 wt%
Catalyst type	Harshaw 1404-T methanation catalyst, 68 wt% nickel on alumina support
Catalyst loading	1.6–1.7 g/g biomass solids
Biomass loading	typically 300 grams, wet
Residence time	20–30 min at temperature

Table 5
Ultimate Analysis of Anaerobic Digestion Effluent

Element	As received	Corrected	Dried Material
Carbon	3.1	43.1	44.3
Hydrogen	11.6	—	6.0
Nitrogen	.3	4.2	3.1
Oxygen	not determined	—	28.5
Ash	not determined	—	18.1

The compositions of the gaseous products of both the biological conversion and the thermochemical conversion steps are shown together in Table 7. In both cases, the composition is shown on a dry gas basis. Gas yields are also shown for each of the conversion steps. These yields are expressed in total gas volumes produced per unit mass of dry feedstock.

PROCESS SIMULATION

The process flowsheet was based on earlier design studies of the original biothermal process concept (5) and on a techno-economic study of the high-moisture biomass gasification process (6). A simplified schematic diagram is shown in Fig. 1. The actual input file which was used to simulate the process contained more than 20 unit modules, including heat exchangers, filters, mixers, reactors, flash vessels, pumps, and power recovery turbines.

The reactors were simulated using the RSTOICH process block, which is a module in a ASPEN-PLUS[™] unit operations library. This module allows the user to specify the stoichiometry of the conversion process in mass or mole units. An empirical reaction stoichiometry for each reactor was developed from the experimental data.

The simulation was based on a feed rate of 10 kg (wet) biomass/sec at 10 wt% solids (i.e., 1 kg/s solids). The elemental composition used to model the biomass solids was based on available laboratory determination of the ultimate analysis of the reactor effluent.

Table 6
Summary of Gasification Experiments Using Anaerobic Sludge

run # ^a (a)	% solids in sludge	Temperature	Carbon conversion	Methane yield (b)	Carbon recovery	Gas HHV
163	7.2	400°C	69.7 %	0.29 m ³ /kg	83.1 %	20.5
167	7.2	380°C	73.5 %	0.27 m ³ /kg	94.9 %	19.9

^aHigher heating value (HHV) reported in MJ/m³

^bYields are reported on the basis of volume of methane (at standard conditions) per dry mass of feed.

Table 7
Gas Analysis and Yield from Conversion Steps

Conversion step	Gas composition, vol%				Gas yield (m ³ /dry kg)
	[CH ₄]	[CO ₂]	[H ₂]	[C ₂ H ₆]	
Anaerobic digestion	59.1	40.9	—	—	.50
Thermal gasification	48.3	41.5	7.0	1.2	.53

A summary of process inputs and outputs is shown in Table 8. No recycle of the aqueous stream from the thermal reactor was included in the simulation, since conversion data on this material is not yet available. Two product gas streams were produced. The first product stream is a high-BTU gas containing the bulk of the methane produced in the process, and has a higher heating value (HHV) of 22.7–24.9 MJ/m³ (611–670 BTU/scf). The product stream is available at 6.91 MPa (1000 psia). In the base case, this stream was produced at a rate of .66 m³/sec, with an energy equivalent of 15.8 MW. A much smaller second stream (.09 m³/sec) (containing principally CO₂) with a HHV of 2.3–6.5 MJ/m³ (65–175 BTU/scf) was produced at much lower pressure (.35 MPa) and was assumed to be used in-plant as a fuel gas. Downstream processing of either stream to increase the HHV or remove impurities was not factored into the design.

As in most processes operating at elevated temperatures, the recovery of the sensible heat from process streams was an important factor in the design. Because of the extensive use of heat recovery, the only significant heat load on the process is the final heating of the feed to the thermal reactor temperature. In designing the process flowsheet, it was assumed that this high-grade heat requirement was met by a fired heater

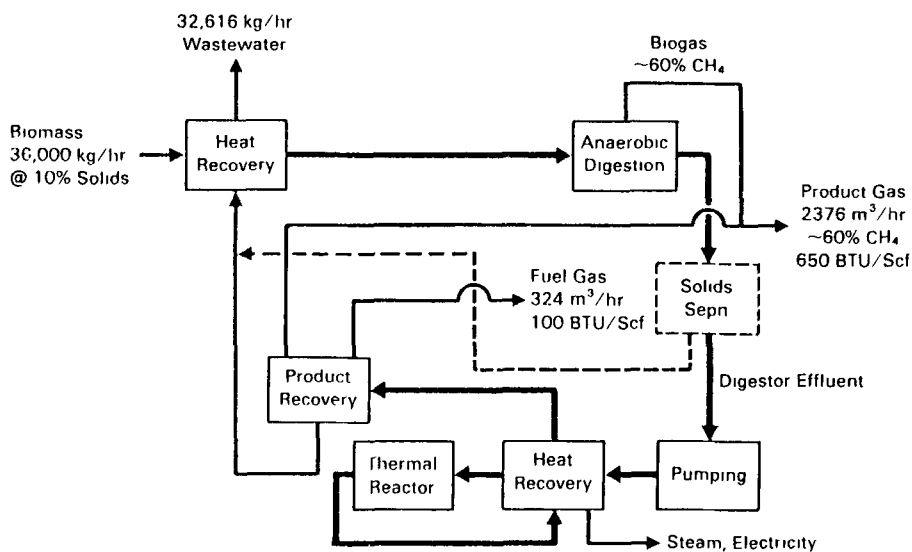


Fig. 1. Simplified process schematic of biothermal process.

Table 8
Summary of ASPEN-PLUS™ Material and Energy Balance Around Hybrid
Process, base case

Total feed rate	10 kg/sec (@ 10 wt% biomass solids)
Product stream	.79 kg/sec (.66 m ³ /sec) 63.2 vol% CH ₄ , 34.4 vol% CO ₂ , 2.4 vol% H ₂
Fuel gas	.15 kg/sec (.09 m ³ /sec) 9.2 vol% CH ₄ , 88.9 vol% CO ₂ , 1.9 vol% C ₂ H ₆
Wastewater	9.06 kg/sec 96.7 wt% H ₂ O, 2.0 wt% solids, .9 wt% dissolved organics; balance, .4 wt% dissolved gases
Heat requirements	3.76 MW (@ 400°C)
Cooling requirements	1.83 MW (@ 35–80°C)
Electrical requirements	.66 MW, 890 hp
Electrical production	.16 MW, 214 hp

using the low-BTU gas stream (along with supplemental product gas) as fuel. Some of this energy was assumed to be recovered in a waste heat boiler producing superheated steam at 4.13 MPa (600 psia) which was expanded through a turbine to produce electricity and .34 MPa (50 psia) steam for use onsite. Mechanical energy was also recovered by relieving process stream pressure through expansion turbines. As a result, approximately 25% of the mechanical energy requirements of the process could be met with power recovered from the process fluids.

Only initial attempts were made to optimize process variables such as the temperature approach in heat exchangers or the pressure and temperature of the three flashes. Six simulation cases were performed to determine the effect of varying the degree of conversion taking place in the bioreactor and the effect of partially dewatering the bioreactor effluent. The results of the six cases are summarized in Table 9.

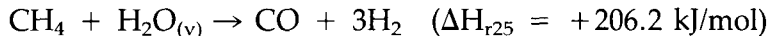
Table 9
Summary of ASPEN-PLUS™ Simulations

CASE #	BASE	CASE1	CASE2	CASE3	CASE4	CASE5
Digester efficiency	51.5%	51.5%	30%	70%	51.5%	51.5%
Solids content in digester effluent	6.1%	11.0%	7.8%	4.6%	19.8%	7.6%
Overall thermal efficiency	83.3%	88.8%	78.2%	87.7%	94.1%	85.1%
Cold gas efficiency	102.8%	100.7%	97.9%	107.1%	100.7%	100.7%
Product HHV (MJ/m ³)	24.2	23.4	24.9	23.4	22.7	22.7
(BTU/scf)	(649)	(630)	(670)	(628)	(611)	(611)
Product yield (m ³ /sec)	.6647	.6788	.6127	.7158	.7048	.7048
(MMscf/h)	(.0845)	(.0863)	(.0779)	(.0910)	(.0896)	(.0896)

DISCUSSION

The results of the modeling of the hybrid biothermal process are useful in identifying key behaviors and limitations of the process. Since equipment costs were not estimated for this study, process efficiency was selected as the main criterion for comparing the different cases. However, there are many ways of defining efficiency; therefore, we will briefly define the approach used at PNL.

Two measures of process efficiency were used. Overall thermal efficiency is defined as the total energy available from the process (as product, by-product, steam, and mechanical power) divided by the total energy fed to the process in the form of heat and feedstock. In all cases, the HHV of the gas was used to estimate the energy available in product streams, and the energy available in the feedstock was taken as 19525 kJ/kg (8400 BTU/dry lb), a value which was obtained experimentally in a bomb oxygen calorimeter. The other efficiency used was the cold gas efficiency. Cold gas efficiency is the ratio of the energy contained in the product to the energy contained in the feedstock. Although overall thermal efficiencies can never exceed 100%, cold gas efficiency may actually exceed 100%. An example of a process in which the cold gas efficiency exceeds 100% is the steam reforming of methane to product synthesis gas



In an idealized system with 100% conversion, the cold gas efficiency of the steam reforming of methane would be 128%. In general, a cold gas efficiency of more than 100% indicates that the process involved is endothermic.

Steam reforming is a particularly appropriate process to use as an example, because the thermal portion of the process is in many ways analogous to steam reforming of biomass (3). Examination of the cold gas efficiency of the biothermal process for the six cases studied indicates that cold gas efficiencies for the process exceed 100% in some cases, indicating that the process is net endothermic.

The independent variables in the six cases were the conversion in the bioreactor and the percent solids fed to the thermal reactor. The effects of these variables are shown in Figs. 2 and 3. These results illustrate two of the determining factors in selecting operating conditions for the biothermal process.

As seen in Fig. 2, both the thermal efficiency and the cold-gas efficiency are directly related to the conversion in the bioreactor. At higher levels of conversion in the bioreactor, a greater fraction of the feedstock is converted directly to the desired product (methane). The limits imposed by the biodegradability of the feedstock are not necessarily reflected in the upper limit of this graph. It is unlikely that 70 wt%

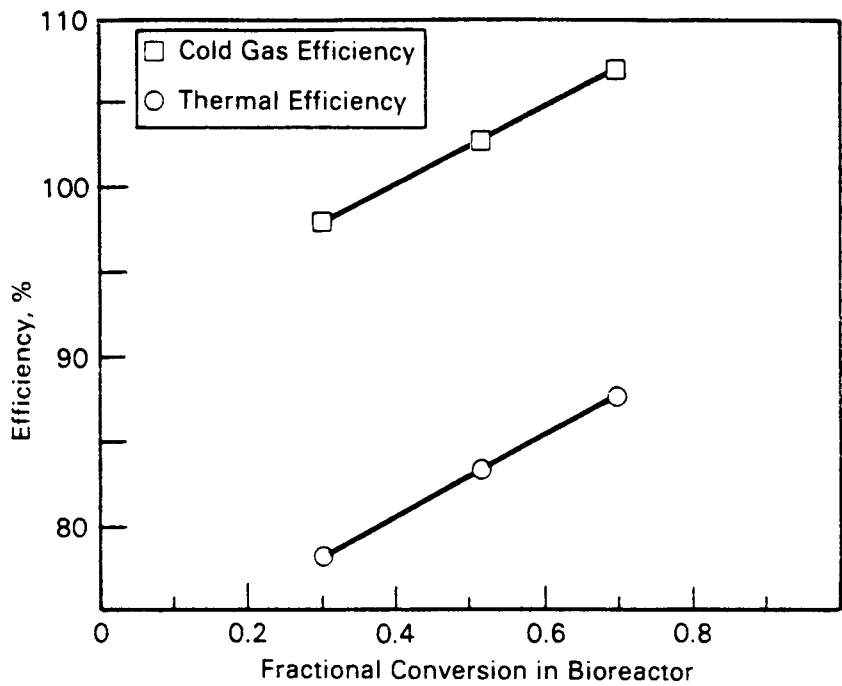


Fig. 2. Effect of bioreactor conversion on process efficiency.

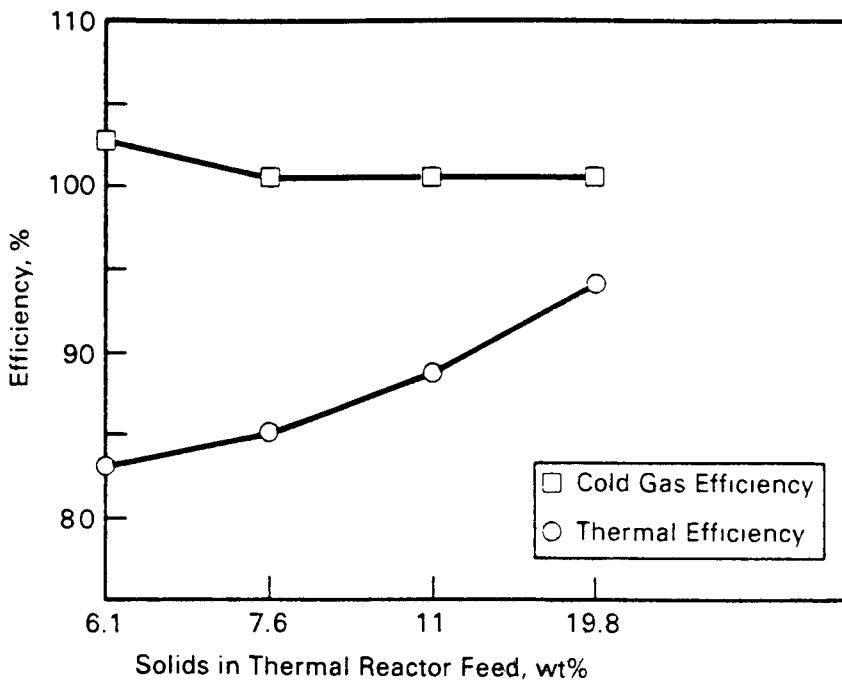


Fig. 3. Effect of solids concentration on thermal efficiency.

carbon conversion can be achieved in an actual digester operating on water hyacinth/sludge blends.

From an efficiency standpoint, as much of the conversion of biomass as possible should be performed in the biological reactor. This is true because of the greater efficiency of biochemical processes in general, and because of the greater selectivity to the desired product (i.e., methane). Realistically, maximum conversions are limited by the biodegradability of the feedstock and by the long residence times required for high conversions. For the water hyacinth/sludge blend used in the IGT reactor, conversion was limited to approximately 40 wt% after a solids residence time (SRT) of 14 d, increasing to 62 wt% after a SRT of 30 d. The thermal gasification step, on the other hand, is relatively insensitive to feedstock biodegradability and operates at gas production rates that are several orders of magnitude greater than those obtained in the digester. Thus, optimum design becomes a matter of determining an upper limit for practical conversions in the bioreactor. This limit is set by the relative cost per unit volume of the two reactors and by the biodegradability of the feedstock.

Figure 3 illustrates the effect of solids content of the feed to the low-temperature gasifier. This variable was manipulated in the simulation by the use of a stream splitter module placed immediately after the bioreactor. This module is a rough simulation of a filter, and creates a high solids stream and a low solids stream (filtrate). A fixed percentage (5%) of the biomass solids were assumed to be lost to the filtrate, and the ratio of total filtrate to solids flowrates was varied. The effect of this change on the cold gas efficiency is negligible (the slight drop results from the filtrate losses). The thermal efficiency, on the other hand, is strongly dependent upon the solids content of the feed to the thermal reactor. This result can be anticipated by considering that the process heating requirements essentially reduce the heat needed to raise the reactants the final 20°C or so to reaction temperature. By varying the feed solids ratio, one directly affects the amount of heat which must be supplied to the process. Again, one is faced with a theoretical trend which must be balanced with the engineering constraint posed by pumping high-solids streams to high pressure. Practical considerations probably limit the solids content in this stream to approximately 25–30 wt% (6).

Examination of the case results also points out other design variables which one would expect to be important. Certainly, the temperature approach in heat exchangers used to preheat the feed is a critical design variable. For this study, a value of 20°C is used; but in actual practice, this value would have to be optimized against the cost of building high-pressure heat exchangers for close approaches. Any decrease in the temperature approach would reduce the heat load on the process, increasing the overall efficiency.

Another determining factor is the treatment of the waste heat boiler. Depending upon the demand for process heat elsewhere on site, consid-

erably higher power recoveries could be expected by operating the power recovery turbine with an atmospheric or subatmospheric exhaust. Although this would have no influence on cold gas efficiency, the overall efficiency of the process would be improved slightly.

CONCLUSIONS

Biological conversion and thermal gasification are often seen as competing technologies. In actuality, each has advantages which complement each other. The modeling of a hybrid process which uses both conversion processes to improve the overall system efficiency demonstrates that basic process limitations and engineering constraints both affect the optimum design of the process. Optimum efficiency is obtained when most of the conversion of biomass is carried out in the biological reactor, but that conversion is limited by the biodegradability of the feedstock and the relatively poor kinetics of biological processes. The efficiency of the process is also improved by increasing the solids concentration in the feed to the thermal reactor, but pumping constraints place an upper limit (25–30 wt%) on solids concentration.

The use of the high-moisture biomass gasification system to gasify the effluent from an anaerobic digester provides an opportunity for efficient utilization of biomass which is not fully biodegradable. Careful design of the thermal gasification process can insure high process efficiency despite the low solids content of the feed.

FUTURE WORK

Additional study of the biothermal process concept is planned. Further investigations are expected to include bioassays on the aqueous material leaving the low-temperature gasifier. This stream is known to contain phenolic compounds, which are potentially toxic to digester cultures. If this stream is biodegradable, it could be recycled back to the anaerobic digester. Recycle to the thermal reactor is also a possibility which will be evaluated. A continuous-feed thermal reactor is being built and will be used to determine catalyst lifetime and effects of several process variables. Studies of process economics will address the engineering tradeoffs which must be made in determining the optimum process configuration.

ACKNOWLEDGMENTS

The authors would like to acknowledge their respective sponsors for the generous support of the research on which this study was based. The high moisture biomass gasification process is being developed by Pacific

Northwest Laboratory under the sponsorship of the Biomass Thermochemical Conversion Program of the Division of Biofuels and Municipal Waste Technology, United States Department of Energy. The Pacific Northwest Laboratory is operated for the US Dept. of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO.

The Community Waste Research Facility is operated by IGT and the University of Florida in cooperation with Walt Disney World. Sponsorship of the research is provided by the Gas Research Institute (GRI).

REFERENCES

1. Chynoweth, D. P., Srivastava, V. J., Henry, M. P., and P. B. Tarman. (1980), "Biothermal Gasification of Biomass", *Proceedings of Energy from Biomass and Wastes IV*. pp. 527-554. Published by Institute of Gas Technology, Chicago, IL.
2. Chynoweth, D. P., Biljetina, R., Srivastava, V. J., and T. D. Hayes. (1985), "Biogasification of Water Hyacinth and Primary Sludge in an Experimental Digester", *Energy from Biomass and Wastes IX*, pp. 695-722. Published by the Institute for Gas Technology, Chicago, IL.
3. Butner, R. S., Elliott, D. C., and L. J. Sealock, Jr. (1986), "Effect of Catalyst Type and Concentration on Thermal Gasification of High-Moisture Biomass," *Biotechnology and Bioengineering Symposium No. 17*. pp. 169-177. Wiley, NY.
4. Butner, R. S., Elliott, D. C., and L. J. Sealock, Jr. (1986), "Energy Recovery from Aquatic Biomass in a Thermochemical Gasifier," in the proceedings of *Aquatic Plants for Water Treatment and Resource Recovery*, Orlando, FL, July 20-24, 1986. In press.
5. Chynoweth, D. P., and V. J. Srivastava. (1983), "Biothermal Conversion of Biomass and Wastes to Methane," *Biotechnology and Bioengineering Symposium No. 13*. Wiley, NY.
6. Pack, G. E., Desrosiers, R. E., and K. Kamali. (1985), *Low Temperature Thermochemical Biomass Gasification Techno-Economic Evaluation—Final Report*. GRI-85/0058. Gas Research Institute, Chicago, IL.