1812

Low-Temperature Conversion of High-Moisture Biomass

Topical Report January 1984 - January 1988

**L. J. Sealock, Jr.
D. C. Elliott**

**R. S. Butner
G. G. Neuenschwander**

October 1988

**Prepared for
the Biofuels and Municipal Waste
Technology Division
U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microtiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A10
226-250	A11
251-275	A12
276-300	A13

LOW-TEMPERATURE CONVERSION
OF HIGH-MOISTURE BIOMASS

TOPICAL REPORT
JANUARY 1984 - JANUARY 1988

L. J. Sealock, Jr.
D. C. Elliott
R. S. Butner
G. G. Neuenschwander

October 1988

Prepared for
the Biofuels and Municipal Waste
Technology Division
U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Pacific Northwest Laboratory (PNL) is developing a low-temperature, catalytic process that converts high-moisture biomass feedstocks and other wet organic substances to useful gaseous and liquid fuels. The advantage of this process is that it works without the need for drying or dewatering the feedstock. Conventional thermal gasification processes, which require temperatures above 750°C and air or oxygen for combustion to supply reaction heat, generally cannot utilize feedstocks with moisture contents above 50 wt%, as the conversion efficiency is greatly reduced as a result of the drying step. For this reason, anaerobic digestion or other bioconversion processes traditionally have been used for gasification of high-moisture feedstocks. However, these processes suffer from slow reaction rates and incomplete carbon conversion.

The PNL high-moisture gasification system, in which thermocatalytic conversion takes place in an aqueous environment, was designed to overcome the problems usually encountered with high-water-content feedstocks. The process uses a reduced nickel catalyst at temperatures as low as 350°C and pressures ranging from 2000 to 4000 psig--conditions favoring the formation of methane gas rather than hydrogen and carbon oxides. Tests have produced gases containing up to 55% methane. By comparison, gases produced by conventional thermal gasifiers typically contain only 5% to 15% methane. When compared with anaerobic digestion, the PNL-produced gases contain similar amounts of methane, but the reaction rate is 300 to 400 times faster. Furthermore, carbon conversion is nearly complete, whereas with anaerobic digestion it is only about 50% to 80%.

Over 180 tests have been conducted to evaluate the effectiveness of the process on feedstocks defined as high-moisture biomass. These tests also included 11 experiments at liquefaction conditions to determine oil product compositions and yields.

All experiments were conducted batchwise in a 1-L, bolted-closure, high-pressure autoclave (reactor), with a magnetically coupled stirrer. The reactor and associated sample lines were made of stainless steel to minimize

corrosion. The entire system, except for certain valves and the instrumentation, was housed in a 0.25-in.-thick plate steel barricade. Many other safety features were built into the system, including remotely controlled monitoring and sampling procedures.

During the tests, the complex gasification reactions were evaluated by several analytical methods. Among the results shown by these tests was that the heating value of the gas ranged from 450 to 550 Btu/scf, and if the carbon dioxide is removed, the product gas is pipeline quality. Conversion of the feedstocks was high; generally, greater than 90% of the carbon fed as high-moisture biomass was recovered as gaseous product.

Under alternate conditions, 350°C, alkali catalyst only, and reducing gas atmosphere, good yields of liquid products were obtained. The liquefaction results showed that the high-moisture biomass yielded biocrude oil in amounts comparable to oil produced from wood. The product oils were of similar or better quality based on oxygen content and hydrogen to carbon ratio.

Because the PNL process is applicable to a variety of wet biomasses, including grasses, aquatic plants, agricultural residues, and food processing wastes, it provides a versatile option for production of useful fuels from low-cost raw materials not commonly used in conventional conversion systems. Industrial and commercial interest is growing in specific applications such as the processing of grape pomace, brewer's spent grain, and other waste materials.

A patent is pending on the process, which was developed from basic research sponsored by the Gas Research Institute (GRI). Battelle Development Corporation (BDC) has purchased from GRI the rights and title to the invention and patents. Through PNL, BDC has subsequently entered a licensing agreement with Onsite*Ofsite, Inc., an engineering firm located in Pasadena, California. Onsite*Ofsite is assisting PNL in transferring the technology to the industrial sector. Onsite*Ofsite has completed initial design of a 5-wet-ton/day transportable research system and a 1.25-wet-ton/day skid-mounted system.

Process development is ongoing, and future work will concentrate on a continuous reactor system, which will provide more sophisticated engineering data needed to scale up the process. Specifically, this system will supply isothermal rate (conversion) data and allow catalyst effectiveness to be documented on a continuous basis. This work is currently sponsored by the U.S. Department of Energy's (DOE) Biomass Thermochemical Conversion Program managed by PNL. Additional spinoff work is being conducted for the Northwest Hazardous Waste Research, Development, and Demonstration Center (sponsored at PNL by DOE) to evaluate the process for catalytic conversion of hazardous organics in water to innocuous gases and a clean water stream.

ACKNOWLEDGMENTS

This project was performed by Pacific Northwest Laboratory (PNL) under Contract DE-AC06-76RLO 1830 for the U.S. Department of Energy (DOE), Conservation and Renewable Energy. The research was funded by the Biofuels and Municipal Waste Technology Division of DOE and managed through the PNL Biomass Thermochemical Conversion Program. Technical monitoring of the project for DOE was performed by Dr. Don J. Stevens of the Biomass Thermochemical Conversion Program, Technical Field Management Office at PNL. The Technical Field Management Office is managed by Gary F. Schiefelbein. This project is part of the DOE Thermochemical Conversion Program administered at DOE Headquarters by Simon Friedrich. The authors wish to acknowledge the guidance and support provided by Dr. Stevens and Messrs. Schiefelbein and Friedrich.

Analytical support for this project was provided at PNL by Richard T. Hallen, operation of the gas chromatograph-mass spectrometer and interpretation of the chromatographs and spectra; Frank T. Hara and coworkers, trace element analysis produced by inductively coupled plasma-atomic emission spectroscopy; and Ronald W. Sanders and coworkers, x-ray fluorescence spectroscopy. All experiments and analyses were performed at PNL except the sunflower feedstock analysis performed by Professor Olaf Theander of the Swedish University of Agricultural Science (Uppsala).

The authors also wish to acknowledge the contribution from two summer employees who participated in the research under the auspices of the Residence in Science and Technology program sponsored by DOE. Mary C. Johnson of the Detroit Country Day School, Birmingham, Michigan, performed the analytical work to determine the residual organic contaminants in the gasifier byproduct aqueous stream. Charles Wagner of Hanford High School, Richland, Washington, performed the analytical work to determine the dissolved ammonia content in the gasifier byproduct aqueous stream.

The authors thank Norman G. Banns and staff members at Onsite*Offsite, Inc., for their support, encouragement, and investment in helping to promote the concept and in developing preliminary designs for the 5- and 1.25-wet-ton/day processes.

The authors thank Dr. David P. Chynoweth, Director of the Bioprocess Engineering Research Laboratory at the University of Florida, Gainesville. Dr. Chynoweth provided several samples of anaerobic digestion effluent and water hyacinths, and collaborated with the authors on a technical paper dealing with a hybrid biochemical/thermochemical conversion process for wet biomass.

The authors express their gratitude to Eddie G. Baker of PNL for his encouragement, support, and technical insight regarding the gasification concept. As Project Manager for the "Catalytic Destruction of Hazardous Organics in Aqueous Solutions," funded by the PNL Northwest Hazardous Waste Research, Development, and Demonstration Center, he continues to contribute to the research effort described in this report.

Finally, the authors thank Sue Gano of PNL for her work on the editing and final review of this report and her help in the publication process.

CONTENTS

SUMMARY	iii
ACKNOWLEDGMENTS	vii
INTRODUCTION	1
CONCLUSIONS AND RECOMMENDATIONS	5
CONCLUSIONS	5
RECOMMENDATIONS	8
BACKGROUND	11
HIGH-PRESSURE AQUEOUS SYSTEMS	11
COMPARISONS OF LOW- AND HIGH-TEMPERATURE GASIFICATION	14
Kinetics	14
Thermodynamics	17
ANAEROBIC DIGESTION	17
HIGH-MOISTURE BIOMASS	21
FEEDSTOCK SOURCES	23
FEEDSTOCK ANALYSES	27
FEEDSTOCK PROCESSING	34
EXPERIMENTAL SYSTEMS AND PROCEDURES	37
BATCH REACTOR AND SAMPLING SYSTEM	37
EXPERIMENTAL PROCEDURES	42
ANALYTICAL PROCEDURES	44
Elemental Analysis	44
Ash	46
Moisture	46
Heat of Combustion	46

Gas Analysis	46
Calculation of Gas Composition and Carbon Conversion to Gas	47
Aqueous Byproduct Analysis	47
Analysis of Organics by Gas Chromatography-Mass Spectrometry	48
EXPERIMENTAL RESULTS	49
FEEDSTOCK EFFECTS	49
TEMPERATURE AND REACTION RATE	53
CATALYSTS - CONCENTRATION AND TYPE	56
BYPRODUCT COMPOSITION	63
LIQUEFACTION EXPERIMENTS	68
DISCUSSION OF RESULTS	75
FEEDSTOCK EFFECTS	75
PROCESS KINETICS AND THE ROLE OF CATALYST IN THE SYSTEM	78
Mechanism	78
Catalyst Contacting	82
GAS PRODUCT COMPOSITION	83
LIQUEFACTION TESTS	84
SYSTEM MODELING	87
COMPARISON WITH ANAEROBIC DIGESTION	87
TECHNOLOGY TRANSFER AND RELATIONSHIP TO OTHER PROJECTS	93
PATENT STATUS AND TECHNOLOGY TRANSFER	93
RELATIONSHIP TO OTHER PROJECTS	94
EVALUATION OF PROCESS ECONOMICS	94
FUTURE RESEARCH IN HIGH-MOISTURE BIOMASS GASIFICATION	97
HIGH-MOISTURE BIOMASS CONTINUOUS REACTOR SYSTEM	97

DESIGN OF THE CONTINUOUS REACTOR SYSTEM	98
CONTINUOUS REACTOR SUB-SYSTEMS	99
Feed Preparation and Handling	99
Pumping and Flow Control	101
Reactor	101
Reaction Product Recovery	102
Instrumentation and Control	103
Product Analysis	103
RELATED PUBLICATIONS	105
REFERENCES	109
APPENDIX - SUMMARY OF BIOMASS GASIFICATION EXPERIMENTS	A.1

FIGURES

1	Conceptual Flow Diagram of the Thermocatalytic Conversion Process	3
2	Comparison of Wood Flour Gasification in the Low-Temperature and High-Temperature Reactor Systems	15
3	Comparison of Methane Production from Wood Flour in the Low-Temperature and in the High-Temperature Reactor Systems	18
4	Yield and Moisture Content of Some High-Moisture Feedstocks	22
5	Schematic of 1-L High-Pressure Reactor Used for Biomass Gasification	38
6	Original Sampling System	39
7	Modified Sampling System	40
8	Schematic of Batch Reactor System	43
9	Catalyzed Carbon Conversion to Gases for High-Moisture Biomass	53
10	Higher Heating Value of Raw Product Gas from Catalyzed Gasification of High-Moisture Biomass	54
11	Energy Yield from High-Moisture Biomass by Catalytic Gasification	55
12	Time Versus Conversion Plot for Sunflower Stalks ~10% Solids Slurry, 1.2 g Ni Catalyst/g Dry Biomass	57
13	Effect of Nickel Catalyst Loading on Carbon Conversion in the Presence of Sodium Carbonate Co-catalyst	58
14	Effect of Nickel Catalyst Loading on Methane Yield in the Presence of Sodium Carbonate Co-catalyst	59
15	Effect of Nickel Catalyst Loading on Carbon Conversion	60
16	Effect of Nickel Catalyst Loading on Methane Yield	61
17	Effect of Sodium Carbonate Concentration on Methane Yield	62
18	Role of Catalysts in the High-Moisture Gasification System	79

19	Effect of Gasification Conditions on Product Quality	85
20	Model of Mobile Pilot Facility	95
21	Schematic of Continuous Reactor System	100

TABLES

1	Categories of Feedstocks Tested	24
2	Characterization of Feedstocks	28
3	Analysis of Sunflower Stalk Components	30
4	Trace Element Analysis in High-Moisture Biomass Feedstocks . .	32
5	Comparative Results of Drying Tests for Sorghum	33
6	Low-Temperature Gasification of High-Moisture Biomass Feedstocks	50
7	Carbon Balance for Low-Temperature Gasification of High- Moisture Biomass	52
8	Effect of Temperature of Catalytic Gasification of High-Moisture Biomass	55
9	Effect of Alkali Type on Catalytic Gasification of Cellulose	63
10	Experimental Details for Residual Aqueous Samples	64
11	Elemental Composition of Decanted Liquids from Residual Aqueous Byproducts	64
12	Analysis of Solids from High-Moisture Biomass Gasification . .	66
13	Product Distribution for High-Moisture Biomass Gasification . .	67
14	Summary of Analyses Using Ammonia-Selective Probe	68
15	Nitrogen Balance Around Reactor System - Experiment 159	69
16	Nitrogen Balance Around Reactor System - Experiment 161	69
17	Experimental Results for Liquefaction Experiments	71
18	Chemical Functional Groups in High-Moisture Biomass Oil Products	71
19	Liquefaction Results with Corn Stover at 350°C for 20 Min	73
20	Comparison of Estimated Equilibrium Gas Composition with Experimental Data	88

21	Methane Yield Comparisons	89
22	Comparison of Engineering Aspects of High-Moisture Gasification and Anaerobic Digestion	90
23	Parameter Ranges for the Continuous Reactor System Design . . .	99

INTRODUCTION

A significant need exists for an economical system that can be used to thermochemically convert high-moisture-content carbonaceous feedstocks to a useful form of energy. High-moisture feedstocks continue to be underutilized because of the high cost and amount of energy associated with drying the feedstocks and the technical problems associated with preparing the feedstocks so they can be fed to conventional thermochemical conversion systems. Biological conversion approaches, such as anaerobic digestion and fermentation, which have been used to convert high-moisture feedstocks, suffer from slow rates of conversion and the inability to convert the lignin fraction of the feedstock.

Pacific Northwest Laboratory (PNL)^(a) is developing a proprietary thermochemical system that has important technical and economic potential as a method for converting high-moisture feedstocks to methane. This report, the first formal report documenting the progress in developing the concept, is based on tests in a 1-L autoclave (reactor) conducted from January 1984 to January 1988. The project titled "Low-Temperature Thermochemical Conversion of High-Moisture Biomass Feedstocks to High-Valued Fuels" is sponsored by the U.S. Department of Energy (DOE), Conservation and Renewable Energy through its Biofuels and Municipal Waste Technology Division.

The process chemistry described in this report was first identified under a separate basic science research study for the Gas Research Institute (GRI) (Sealock, Elliott, and Hallen 1982). During that time, a low-temperature, high-pressure catalytic system was recognized as a means to address the basic dilemma hindering the development of processes for the direct production of methane from carbonaceous solids (Elliott and Sealock 1985). Specifically, at the high temperatures currently used for gasification (typically, greater than 600°C), methane formation is limited by thermodynamic equilibrium; however, if the temperature of the gasification is reduced to temperatures where methane is favored (~400°C), then the rate of carbon conversion to gas is too slow to be useful. This dilemma has been

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute.

addressed by using a low-temperature environment to shift reaction equilibrium toward the production of methane while employing catalysts and high-pressure water to obtain practical reaction rates for the conversion of carbon to gas.

As a result of the progress described in this report, this processing system has demonstrated the potential for expanding the range of biomass feedstocks that can be utilized in thermochemical systems. Feedstocks such as aquatic plants and herbaceous plants, which may have moisture contents in excess of 75 wt%, are readily converted to fuel gas at high efficiency. Crop residues and many other biomass feedstocks have also shown high rates of conversion and excellent methane yields.

Due to the inherent ability of the system to work with relatively dilute streams, the concept also has broad applicability to a number of nonbiomass uses. Given the current national emphasis on waste utilization and waste reduction, the system is being viewed (in another PNL project) as a more general means of recovering energy (as medium-Btu gas) from byproduct or waste streams containing dilute organics (1% to 20%) in water. In that project, the low-temperature catalytic system is being investigated as a means of hazardous waste destruction (Baker and Sealock 1988a,b). The concept also has potential as a means of recovering useful energy while substantially reducing the chemical and biological oxygen demands (COD and BOD) of solid and aqueous waste streams in several food processing applications. While the application of the system for energy production from biomass is mid term, the application of the technology to waste stream processing is near term.

Results are presented in this report for more than 170 batch reactor tests using the novel thermochemical catalytic gasification system. During these tests, high-moisture biomass was efficiently converted to medium-Btu fuel gas. The gasification system operates at low temperatures (350°C to 450°C) and high pressures (2000 to 4000 psig) to attain high rates of conversion and high methane yields. Results are also presented for 11 batch reactor experiments at liquefaction conditions for several high-moisture feedstocks. In addition to experimental results, the report includes a compilation of analytical data for the various high-moisture biomass

feedstocks tested. A discussion of the results is provided, along with an overview of future work and technology transfer applications.

Because of the many features of the PNL gasification system, it is referred to as low-temperature, high-moisture, or catalytic. These designations are used interchangeably throughout this report according to the context of individual sections. A simplified flow diagram of the conversion process is given in Figure 1.

FIGURE 1. Conceptual Flow Diagram of the Thermocatalytic Conversion Process

CONCLUSIONS AND RECOMMENDATIONS

The results of the work described in this report have led to the following conclusions and recommendations.

CONCLUSIONS

Pacific Northwest Laboratory is developing an important proprietary catalytic gasification process. The concept is not just another gasification concept but a system that can convert unconventional, hard-to-handle, high-moisture feedstocks to methane. The system avoids the large energy penalty of drying feedstocks, which is associated with other thermochemical systems, by efficient use of waste heat and by employing catalysts and high pressure to convert aqueous slurries of the high-moisture biomass at relatively low temperatures. The concept has developed significant industrial interest and has numerous potential spinoff applications. Onsite*Ofsite, Inc., a private turnkey engineering design and construction management firm located in Pasadena, California, has obtained the license for the technology and is assisting PNL in transferring the technology to industry. Technology transfer of the process to industry is expected to be an important part of future research efforts.

The term "high-moisture biomass" includes a wide range of materials but is generally applied in this report to feedstocks containing more than 60 wt% moisture at harvest. The current interest in DOE is greatest for the herbaceous terrestrial plants such as sorghum or napier grass. Aquatic biomass sources, such as kelp and water hyacinths, are of lesser interest but are certainly high-moisture biomasses. The term is also applicable to many agricultural field residues such as corn stover and sunflowers. Food processing wastes such as spent grain, grape pomace, and potato waste are also considered as high-moisture-biomass-derived materials, as are the residues derived from biochemical conversion of biomass and animal manures.

High-moisture biomasses were found to represent a wide range of materials as evidenced by differences in ash amount and composition, structural component composition, and heteroatom content. As a result, a range of

reactivities was observed when working with these materials. The herbaceous species were found to be quite reactive, although not as reactive as refined cellulose. The aquatic species were generally less reactive. The food processing wastes demonstrated good conversions but were the least reactive of the biomass feedstocks tested.

Excellent conversions of high-moisture biomass feedstocks were obtained in the 1-L batch reactor. Carbon conversions ranging from 90% to 100% of the carbon contained in the feedstocks were often achieved after 15 min at 400°C. Gas compositions usually ranged from 40% to 50% CH₄ (methane), 40% to 45% CO₂ (carbon dioxide), 5% to 10% H₂ (hydrogen), and contained only trace amounts of CO (carbon monoxide). The heating value of the gas produced was typically in the range of 450 to 550 Btu/scf. The product gas is pipeline quality upon the removal of the CO₂.

Good catalyst contacting, obtained by high loading of nickel metal catalysts to the batch reactor, was determined to be very important. High nickel loading resulted in faster and more complete carbon conversion to gas and led to higher yields of methane in the product gas. Good contacting of the solid catalyst with the gaseous products and solid/liquid biomass feedstock was not a primary design consideration in the batch reactor, and recent results demonstrate the importance of adequate contacting and the need for additional study. Slow carbon conversions (for some feedstocks) and continuing formation of methane following cessation of the carbon gasification reactions are additional evidence of inadequate catalyst contacting within the reaction environment.

The effect of temperature within the range of this study (350°C to 450°C) can be significant, particularly in less-effective catalytic and non-catalytic cases. A reaction temperature of 400°C appears to be near the optimum for high catalyst loading cases with the more reactive feedstocks (herbaceous biomass). Operation at higher temperature (450°C) did not markedly increase the rate of reaction and actually reduced the yield of methane. Temperatures higher than 400°C may be useful for less-reactive feedstocks, such as some food processing wastes. However, lower-temperature operation may be possible with improved catalyst contacting.

The addition of alkali carbonate catalyst was superfluous for high-ash biomass feedstocks in cases using high nickel loadings. Previous research with low-ash biomass has shown that alkali has catalytic gasification activity by itself, and enhances nickel catalytic activity for gasification when the nickel is used at low loadings (Sealock, Elliott, and Hallen 1982). More recent results have demonstrated that with good nickel catalyst contacting (high nickel loading) the addition of alkali carbonate may actually reduce methane yield from high-ash biomass without significantly improving the rate of gasification.

The batch reactor system, which used a cold feed and was equipped with a sample recovery system, was a useful means for determining relative rates of reaction and the extent of reaction during heatup. The data obtained with the batch system provided excellent baseline information needed to document the relative rate of conversion and the product quality that can be expected from the various high-moisture biomass feedstocks. However, no isothermal kinetics data were obtained with this type of system because of the large thermal inertia of the reactor and its contents. Conversion rate data are required for any potential scaleup of the system, and a 1-L continuous reactor system (CRS) is being built to provide the required rate information and to document the reaction chemistry on a continuous basis.

Under typical liquefaction conditions (~350°C, 3000 psig, and CO reactant gas), the yields of biocrude oil produced from high-moisture biomass were comparable to the amounts produced from wood. The quality of the high-moisture biomass liquefaction products falls in a general range similar to that reported for wood liquefaction products. However, certain examples of high-moisture biomass product oils had elemental compositions (H/C ratios, oxygen contents) indicating a higher-quality liquid product. A major difference from wood-derived oils was that a higher nitrogen concentration remained in the oils produced from high-moisture feedstocks initially containing a large amount of nitrogen. Examples of these feedstocks include spent grain and aquatic biomasses.

Low-temperature, high-pressure, catalytic gasification appears to be a useful means of energy recovery from many types of biomass. This approach requires significantly less reactor volume and residence time and produces significantly less solid byproduct than does anaerobic digestion.

RECOMMENDATIONS

Batch reactor tests should be continued as new feedstock materials are identified so that relative reactivities and methane yields can be determined and compared with other feedstocks. Additional tests to establish the effect of cellulose, lignin, and protein content on conversion should also be performed as part of the baseline tests. Further testing is also needed to determine required feedstock pretreatment and slurry preparation procedures for various high-moisture biomass feedstocks to be used in high-pressure reactor systems. Results of batch reactor tests should be used to suggest appropriate experimental parameters to be used in the 1-L CRS. Additional testing in the liquefaction mode should be conducted.

The CRS now under construction^(a) should be operated with high-moisture biomass as the feedstock to provide valuable chemical and engineering data regarding the process concept. The data should include reaction rates and product yield and quality data as functions of reactor temperature and pressure, as well as catalyst lifetimes. In particular, further testing should be conducted to evaluate the nickel-catalyzed, steam-cracking model suggested by this research. These tests should include model compound experiments to test specific mechanisms of reaction. The information developed in the CRS should be used for future scaleup of the process, and a technical and economic assessment of the concept should be made based on the results of the CRS tests.

An independent, detailed, and objective comparison between anaerobic digestion and low-temperature, high-pressure, catalytic gasification should

(a) The CRS was brought online in May 1988, after preparation of this text.

be made to determine the relative costs and benefits of the two process approaches for the production of methane from high-moisture biomass. The comparison should evaluate product yield, economics, and environmental impact, as well as the compatibility of the process with downstream users of the product gas. As part of this comparison, further consideration should be given to the combined bio/thermal process evaluated in this project.

BACKGROUND

While several research areas are relevant, this study centers on two distinct research fields and process approaches to biomass conversion. These areas are 1) high-pressure aqueous systems, including catalytic gasification of wood and wood components and aqueous catalyzed water-gas shift and 2) more conventional, high-temperature gasification of biomass and other carbonaceous solids. For comparison, conversion of high-moisture biomass to methane by anaerobic digestion is also considered. A further comparison of the PNL conversion process and anaerobic digestion is made in the Discussion of Results section.

HIGH-PRESSURE AQUEOUS SYSTEMS

Some of the earliest work in the field of high-pressure aqueous systems includes Modell, Reid, and Amin (1978); Amin, Reid, and Modell (1975); and Modell (1985). Much of this work consisted of reforming glucose and wood flour in water at supercritical conditions ($>374^{\circ}\text{C}$, density $>0.31\text{ g/mL}$). The work presented some interesting results, which were attributed to the unique properties of the supercritical water system; the use of some catalysts also was described. Examination of the results given by Modell and others showed that only limited gasification occurred in their system, and almost no methane was formed. The catalysts tested by these researchers had almost negligible effect. Although glucose conversion in the experiments was high (approaching 100%), the yield of gas was low. Only small amounts (18%) of the carbon present were converted to gas, with the balance of the carbon remaining in the aqueous byproduct as low molecular weight organics. Methane concentration in the product gas was only 1.5%. Results obtained with maple sawdust (without catalyst) were somewhat better, achieving a 39% carbon conversion to gas with a methane concentration of 5% in the product gas after 60 min at 377°C . None of the work reported by Modell and others involved the use of alkali catalysts.

In an earlier study in our laboratory, the pressurized aqueous system was used to examine the gasification of biomass (Sealock, Elliott, and Hallen 1982). Various combinations of alkali metal and alkaline earth carbonates

and supported metal catalysts were studied as catalyst systems for the gasification of four biomass feedstocks: cellulose, holocellulose, lignin, and Douglas fir wood flour. Highlights of these initial findings in the low-temperature gasification of biomass are presented in the following paragraphs.

The use of a nickel catalyst was shown to play a substantial role in the production of methane from biomass. The catalytic effect increased with temperature over the range studied. The highest yield of methane was achieved using a wood flour feedstock in the presence of a nickel catalyst (without alkali) at 450°C. Methane yields of 10% to 20% of the mass of the wood flour feed were obtained at temperatures from 400°C to 450°C. Methane concentrations in the product gas ranged from 23% to 27%, with the remainder of the gas primarily hydrogen and carbon dioxide. There was evidence that the nickel served a hydrogenation function in converting ethylene to ethane. The nickel catalyst facilitated production of carbon dioxide as well. On the basis of these limited results, nickel was judged to be a more active catalyst than cobalt, which was also tested, in the low-temperature gasification system.

The alkali metal carbonates were more effective catalysts than the alkaline earth carbonates in all cases studied. The alkali metal carbonates of cesium, potassium, and sodium all functioned at a similar level of catalytic activity in the system. A qualitative ranking of catalytic activity was established ($K > Na > Cs$), although the differences were not great at the temperatures tested (350°C to 450°C).

The presence of alkali carbonate catalysts increased the conversion to gaseous carbon compounds in all cases studied except with lignin at 450°C. The alkali carbonates catalyzed the production of carbon dioxide and hydrogen at the expense of carbon monoxide, methane, and probably water. The production of ethylene at the expense of ethane was also noted, but both these products were inhibited by the alkali. The alkali and nickel appeared to have an additive effect in most cases, which resulted in greater methane production, higher methane concentration, and increased carbon conversion to

gases. In the presence of the combined catalyst, total carbon conversion to gas in excess of 90% was demonstrated for wood flour after 1 h at 450°C.

Cellulose was the most reactive feedstock studied in the batch reactor system as measured by the rate of carbon conversion to gases. It generally reacted two to three times faster than lignin over the range of catalysts and temperatures studied. Methane production from cellulose was generally greater than that of lignin when the feedstocks were converted in the presence of the nickel catalysts. Experiments using holocellulose produced results similar to the cellulose tests, but the presence of hemicellulosic material appeared to slightly decrease the reactivity.

Lignin was generally the least reactive feedstock studied. However, lignin was shown to be a major source of methane. Sodium carbonate and nickel catalysts individually had only a slight effect on the rate of conversion of lignin. However, the combination of the two catalysts resulted in a marked increase in the conversion rate. Wood flour was also less reactive than cellulose, apparently because of the contribution of the lignin fraction in the whole wood. Due to this lignin fraction, the wood flour also produced greater amounts of methane when compared with cellulose.

More recent work has been reported by Antal et al. (1987). Experiments were performed in supercritical water (385°C to 400°C, 5000 psig) to study acid- and base-catalyzed reactions in a continuous flow reactor. Ethanol, propanol, and ethylene glycol underwent acid-catalyzed dehydration to the corresponding alkene. Substantial conversion of these compounds was observed after reaction times of less than 1 min. Base catalysis was almost undetectable. In these experiments, supercritical water enabled acid-catalyzed ionic reaction pathways to supplant the free radical pathways existing at higher temperatures. The acid catalyst had negligible effect on acetaldehyde under the same conditions. The yield of gas was not reported for a single noncatalyzed test with glucose (Simkovic et al. 1987) under the same conditions (24 s residence time). Acetol, glyceraldehyde, and formaldehyde were identified as the major products remaining in the aqueous byproduct, while the gas product consisted of 55.7% CO₂, 34.5% H₂, 9.3% CO, 0.2% CH₄, and 0.4% C₂.

COMPARISONS OF LOW- AND HIGH-TEMPERATURE GASIFICATION

The low-temperature gasification system investigated in this and in earlier studies differs from conventional gasification in two important respects: reaction mechanism and thermodynamics. The mechanistic differences can be traced to the catalytic enhancement of reaction rates in the low-temperature system and result in comparable reaction rates even though the operating temperatures differ widely. The thermodynamic differences manifest themselves in the dramatically different product gas distributions despite basic chemical similarities among feedstocks. These differences and their respective causes are discussed below.

Kinetics

An important characteristic of the low-temperature, high-pressure, catalytic gasification system is that rates of gasification can be achieved which are comparable to those for conventional high-temperature, steam-blown gasification. In addition, much higher yields of methane are possible with the low-temperature system. Although enhanced methane production in the low-temperature, high-pressure system was expected on the basis of thermodynamic considerations, it was not considered likely in our earlier research that the pressurized aqueous medium would greatly influence the kinetics of carbon conversion to gases, nor the mechanistic pathways of gasification (Sealock et al. 1981). However, a comparison of the carbon-to-gas conversion data with results of higher temperature gasification experiments (shown in Figure 2) demonstrates that overall residence time requirements of the two types of reactor systems are quite similar. While the role of the nickel catalyst in obtaining the unexpectedly high conversion rates is discussed in detail elsewhere in this report, some consideration must be given to whether the increased conversion is due to the changes in chemical mechanisms or changes in the transport phenomenon.

The high water to carbon ratios in the low-temperature, high-pressure system could enhance the mass transfer of reaction products and intermediates from biomass particles, thus explaining the higher rates of conversion observed in the system. Whether this enhancement is a result of the solvent properties of the water or is due to the higher diffusivity of the fluid is

FIGURE 2. Comparison of Wood Flour Gasification in the Low-Temperature and High-Temperature Reactor Systems

not clear. Earlier experiments to determine the extent of mass transfer limitations in high-temperature gasification indicated no increase in the rate of carbon conversion resulting from variations in steam flow in the system (Sealock et al. 1981). Apparently, the small increase of water vapor partial pressure within the reactor, which was caused by increased steam flow, did not approach the effect of a saturated water atmosphere found in the low-temperature, high-pressure system. In fact, a decline in conversion rate at very high steam flow was noted in the high-temperature experiments. This finding implied an effect caused by the short residence time of the water molecules. In the low-temperature, high-pressure batch system, where water is sealed within the reactor, there is constant contact of the catalyst and biomass with the aqueous environment.

Sealock et al. (1981) concluded that there appears to be little reason to believe that the difference in operating conditions would have enough effect on the chemical mechanisms of biomass gasification to explain the differences in apparent rates of reaction. They suggested that the much larger amount of water vapor present in the low-temperature, high-pressure system could cause a shift in equilibrium concentrations and, thereby, change the relative importance of various reaction mechanisms. However, it is unlikely that any reactions are near enough to equilibrium concentrations that such a consideration would be important except for some gas phase reactions ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$; $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$). The fluid medium may also influence char formation by increasing the rate of transfer of products away from the feedstock. This transport effect may tend to reduce char formation by minimizing intermolecular condensation reactions. The change in transport would affect the various decomposition reactions to the same extent. Minimization of char formation does not introduce a new mechanism, per se, but only accentuates the gasification reactions.

Other experimental results (Sealock et al. 1981) have shown an increase in reaction rates and carbon conversion to gas with pressures of only 150 psig. Conceivably, the even higher pressure of the water vapor used in the low-temperature, high-pressure system could be part of the explanation of the increased rate of carbon conversion. It appears that this system may

more than compensate for the lack of thermal energy by increasing the frequency of molecular collisions within the reactor.

Thermodynamics

Because a reliable method does not exist for predicting reactor equilibria in polar systems operating near their critical point, thermodynamic effects on product distribution could not be examined in detail during this study. However, based solely on consideration of LeChatelier's principle, it is expected that the product distribution in biomass gasification would be shifted strongly towards methane by the combination of low temperature and high pressure found in the aqueous gasification system. In fact, this shift towards methane production has been observed (Sealock et al. 1981), as illustrated in Figure 3. The increase in methane concentration resulting from process conditions is dramatic and has a significant impact on the potential applications of the high-moisture biomass gasification system.

ANAEROBIC DIGESTION

Unlike the thermally induced pyrolysis/reforming reaction model assumed for the high-moisture biomass gasification process, anaerobic digestion is a series of low-temperature, enzymatically catalyzed reactions that ultimately proceed via the production of methane from volatile organic acid intermediates (Stafford, Hawkes, and Horton 1980). These volatile organic acids, which include acetic, formic, butyric, and other short-chain organic acids, are metabolized to methane by a group of organisms known as methanogens. These organisms (principally bacteria) exist together with other (acid producing) organisms as an "anaerobic consortium," which effects the conversion process.

The anaerobic conversion process is highly selective, both with respect to product (methane and carbon dioxide essentially are the sole products) and with respect to feedstocks. The selective nature of the process results in a strict upper limit to the gas yields that can be expected from anaerobic conversion of biomass to methane. Conversion is limited for the most part to the carbohydrate fraction of the biomass, which can include structural (i.e., cellulose) and nonstructural (i.e., pectins and free sugars) components.

FIGURE 3. Comparison of Methane Production from Wood Flour in the Low-Temperature and High-Temperature Reactor Systems

Conversion of noncarbohydrates (particularly lignin) generally does not take place in anaerobic systems. The high-moisture biomass reactor does not have this limitation, although the presence of lignin does appear to affect product gas composition and reaction rate.

Conversion of noncatalytic (partially) generally does not take
place in anoxic system. The high-pressure process does not have
this limitation, although the pressure of liquid does appear to affect
product gas composition and reaction rate.

HIGH-MOISTURE BIOMASS

The goal of this research has been to investigate the feasibility of utilizing high-moisture feedstocks in a thermochemical conversion process. High-moisture feedstocks have been defined to include a number of terrestrial and aquatic plants, as well as some biomass-derived materials such as food processing wastes and bioconversion residues (Milne 1986). Some of these feedstocks are quite attractive as potential energy crops because they exhibit high growth rates, are relatively easy to harvest, or perform some beneficial ancillary function (water hyacinths, for example, can be used to reduce the organic and heavy metal content of sewage water streams).

For many high-moisture feedstocks, the primary incentive for their use is the high per-acre yield that can be obtained. While not all high-moisture feedstocks exhibit high growth rates, the converse is generally true that nearly all high-growth feedstocks have high moisture contents during their active growth stages. This rule is an outgrowth of the biological importance of water as a transport medium for plant nutrients. In general, plants that grow rapidly need very efficient transport systems for providing nutrients from the soil to new growth, and this results in higher moisture contents. Figure 4 illustrates this point by indicating some typical annual biomass yield data versus average moisture content of the freshly harvested feedstock.

Recognizing the potential of these feedstocks, DOE is sponsoring a program to develop and study herbaceous crops for biomass energy (Cushman, Turhollow, and Elmore 1986), as well as a program for short rotation woody crops (Ranney and Dawson 1987). The Department of Agriculture has also studied a number of plants that can be grown on marginal soils to produce chemicals and energy (Butler 1982).

In addition to biomass crops, high-moisture biomass also includes biomass-derived residues such as food processing wastes (potato steam peeling waste; cranberry, grape, and apple pomace; brewer's spent grain). Utilization of these feedstocks has spurred industrial interest in potential processing systems both as a means of energy recovery and as a waste disposal

FIGURE 4. Yield and Moisture Content of Some High-Moisture Feedstocks

technique. These feedstocks may provide more near-term application of processing technology designed for high-moisture biomass.

Despite their abundance, many high-moisture feedstocks are not utilized to the extent possible. One reason is the difficulty associated with converting the high-moisture biomass to a useful form of energy. While many of the feedstocks under investigation have been successfully converted to methane in anaerobic digesters or to ethanol via hydrolysis/fermentation processes, the overall energy yields of these biochemical processes are low in comparison to thermochemical gasification or combustion. These low conversions for bioconversion processes are primarily due to the presence of lignin and other unreactive biomass components. As a result, residues from bioconversion are included as a high-moisture biomass feedstock for this project.

In conventional high-temperature gasification, the same moisture content that facilitates rapid growth during the production cycle becomes a liability. Thermochemical gasification of biomass feedstocks has conventionally

been limited to relatively dry feedstocks, i.e., less than 50 wt% moisture (and in most cases, below 15 to 30 wt%). Use of higher-moisture feedstocks reduces conversion efficiency, in part because of the large energy penalty paid to overcome the latent heat of vaporization. High-moisture feedstocks can also lead to reduced gasification temperatures, lower conversion efficiency and reaction rates, and the production of a lower-quality product gas. In addition, the ash contents of some high-moisture feedstocks are relatively high and can pose slagging and other ash-removal problems in a high-temperature gasification system where reactor temperatures often exceed the softening or fusion temperatures of the ash components. Direct combustion routes for recovering energy from high-moisture biomass are similarly constrained, since the moisture content of the biomass directly affects the net heating value of the fuel.

Because of the practical limitation on moisture content, the range of feedstocks used for thermochemical processing has been narrow. Wood has been the primary feedstock, although various crop residues and byproducts have been tried. While open-air drying of high-moisture biomass feedstocks is feasible in some instances, climatic conditions, harvesting conditions, and the high susceptibility of many herbaceous species to rapid deterioration often prevents the use of this method. Force drying of these materials has the effect of reducing the net energy produced by the conversion system.

For all of the problems associated with high-moisture feedstocks, the high growth rates and ready availability of some of these feedstocks makes them potentially valuable additions to the resource base, provided that an efficient system for recovering their stored energy can be developed. The catalytic, low-temperature gasification system described in this report shows strong potential to fill this need.

FEEDSTOCK SOURCES

Since the usual constraint of low moisture content could be eliminated when selecting a thermochemical conversion feedstock, a wide variety of potential feedstocks were considered. The scope of this project did not allow for an exhaustive study of all feedstocks; however, representative

materials from several broad categories were selected. The selection of these feedstocks was based on availability, chemical makeup, and estimated potential for large-scale use. Some preference was given to feedstocks for which bioconversion data were available so that direct comparisons of process yields and efficiencies could be made. Table 1 lists the types of feedstocks tested in this project. In addition to these feedstocks, other materials were tested to provide reference points for the process. These other feedstocks were microcrystalline cellulose, Douglas fir wood flour, peat, and lignite coal.

TABLE 1. Categories of Feedstocks Tested

<u>Type of Biomass</u>	<u>Feedstocks Tested</u>
Terrestrial	Napier Grass, Sorghum, Sunflower, Corn Stover
Aquatic and Marine	Water Hyacinth, Kelp
Waste Material	Potato Waste, Spent Grain, Grape Pomace, Anaerobic Digestion Sludge, Black Liquor

The feedstock sources and descriptions of handling procedures are given below:

- Napier Grass (Provided by Dr. W. H. Smith, University of Florida) - The sample consisting of stems and leaves was collected shortly after harvest, chopped and bagged, and packed in an insulated container with dry ice for shipment to PNL. The shipment was still cold when received, and the bags of material were placed in a freezer for storage until used.
- Sorghum (Provided by Dr. W. H. Smith, University of Florida) - The sample consisting of stems and leaves was collected shortly after harvest of the grain head, chopped and bagged, and packed in an insulated container with dry ice for shipment to PNL. The shipment was still cold when received, and the bags of material were placed in a freezer for storage until used.

- Silage Sorghum (Provided by Dr. C. G. Coble, Texas A&M University) - A second sample of chopped sorghum was obtained and shipped in plastic bags inside 55-gal drums. The material had been placed in these containers shortly after harvest and had been stored at ambient conditions for several weeks. As a result of this type of storage, the material appeared to be more representative of a silage sorghum. The material samples indicated a relatively high ash content, most likely foreign material collected during handling. The sorghum had undergone substantial biological decay. This material was sent offsite for feedstock grinding tests.
- Sunflowers (Provided by D. C. Elliott, Richland, Washington) - The sample consisting of stems and leaves was recovered after harvest of the seed head. The sample was chopped, bagged, and frozen at PNL.
- Corn Stover (Provided by D. C. Elliott, Richland, Washington) - The sample consisting of stalks and leaves was recovered after field drying following harvest. The material was a hybrid, sweet corn variety. The sample was chopped, bagged, and frozen at PNL.
- Water Hyacinth (Provided by Dr. D. P. Chynoweth, Reedy Creek Experimental Sewage Treatment Facility at Walt Disney World located near Orlando, Florida) - Samples were obtained from both the primary and secondary treatment lagoons. The samples were uprooted, packed in ice, and flown to PNL where they were frozen as a block inside a double layer polyethylene bag.
- Kelp (Purchased from Neushul Mariculture, Goleta, California) - The sample was freshly harvested macrocystis kelp from Pacific Ocean sea beds off the El Capitan Beach in the Santa Barbara Channel. The sample was packed in ice and flown to PNL where it was divided into several polyethylene bags and frozen.
- Potato Waste (Provided by Lamb-Weston, Richland, Washington) - The sample was derived from frozen french fry manufacture. It is a combination of wash water from the unpeeled potatoes and the

wastewater from the steam peeler and includes peel waste, potato flesh, cull potatoes, and cull fries. The sample was transported to PNL where it was frozen.

- Spent Grain (Obtained from the Blitz-Weinhard Brewery, Portland, Oregon) - The sample was the residue following malting of barley (thermally forced sprouting) and water extraction of the sugars formed during malting. The material had been partially dewatered by allowing the liquid to drain away from the solids while piled on the floor of the brewery. The sample was collected at the brewery and transported at ambient conditions to PNL where it was divided into several lots, bagged, and frozen.
- Grape Pomace (Provided by Gallo Wineries, California) - The sample was recovered from an outdoor storage pile which had been in existence for approximately 9 months. The sample included skins, seeds, and stems resulting from the grape squeezing process.
- Anaerobic Digestion Sludge (Provided by Dr. D. P. Chynoweth, Reedy Creek Water Treatment Facility at Walt Disney World located near Orlando, Florida) - The sample consisted of the undigested effluent from the experimental anaerobic digester operated by the Institute of Gas Technology for the Gas Research Institute. The digester was fed a mixture of water hyacinths (which were grown in adjacent ponds and used to treat water from the nearby Walt Disney World complex) and primary sewage sludge in a typical ratio of 2:1. Typical residence times in the anaerobic digester were 10 to 14 days. The samples were sent as bottled slurries, which were stored frozen at PNL.
- Black Liquor (Provided by H. M. Folster, Weyerhaeuser Corporation, Federal Way, Washington) - The sample was from the black liquor stream of a Kraft pulping plant. The material was the partially dewatered stream, which is fed to the chemical recovery furnace. It is an aqueous, lignin salt solution containing the dissolved

lignin portion of the wood and the sodium compounds used in the pulping process. The sample was stored at ambient conditions at PNL.

- Cellulose (Purchased from the J. T. Baker Chemical Company) - The sample consisted of a microcrystalline cellulose.
- Wood flour (Obtained from DOE's Biomass Liquefaction Experimental Facility, formerly in Albany, Oregon) - The sample consisting of Douglas fir wood flour (-40 mesh) was produced from paper-grade wood chips by drying and hammer-milling.
- Peat (Unknown origin) - The sample was a low-grade sphagnum-moss peat.
- Lignite Coal (Provided by the Savage Mine, Richland County, Montana) - The sample consisting of low-sulfur (typically 0.5%) lignite coal (approximately 6500 Btu/lb) was ball milled and sieved (-20 mesh) at PNL and stored in a sealed can at ambient conditions.

FEEDSTOCK ANALYSES

The feedstocks used in the batch reactor tests were characterized to document moisture, ash and heat content, and elemental analysis for carbon, hydrogen, nitrogen, and oxygen, as well as for trace elements. Examination of the feedstock characterization data illustrates the extreme variability of these biomass resources. The composition of these feedstocks is tabulated in Table 2. Ash content and nitrogen content in particular are subject to a great deal of variability. Moisture content ranged from 50% to 95%.

A terse review of existing information regarding the structural composition of high-moisture biomass feedstocks was also undertaken in this project. The goal of this effort was to establish a database depicting both the elemental composition (including ash) and the main structural units of the biomass feedstocks being studied in the gasification and liquefaction experiments. This information, in conjunction with the experimental results, contributed to an increased understanding of the conversion pathways and helped to foster improved processing approaches.

TABLE 2. Characterization of Feedstocks

Feedstock	Mass Percent, dry basis					Percent Moisture	HHV, (a) Btu/dry lb
	C	H	N	O	Ash		
Napier Grass	45.2	6.0	<0.1	42.3	5.7	84.4	7870
Sorghum	44.4	5.8	0.4	38.3	7.9	77.0	8040
Sunflower I	40.2	5.3	0.7	38.6	11.7	83.0	7420
Sunflower II	40.6	5.3	1.0	39.2	9.8	82.2	7630
Corn Stover	43.0	5.5	1.2	37.8	10.8	41.2	7450
Water Hyacinth	43.0	5.8	5.6	29.5	15.3	94.9	7730
Kelp	26.9	4.0	1.2	30.2	38.4	89.0	7150
Potato Waste	44.7	6.6	<0.1	44.5	3.7	88.0	7870
Spent Grain	48.6	6.8	3.4	35.3	3.4	80.5	9170
Grape Pomace	52.5	6.0	1.8	33.7	5.4	52.5	--
Anaerobic Digestion Sludge	44.3	6.0	3.1	28.8	18.1	96.5	8400
Digestion Sludge II ^(b)	3.1	11.7	0.5	--	--	92.8	--
Black Liquor ^(b)	18.7	7.3	<0.1	52.6	--	--	--
Cellulose ^(b)	42.4	6.1	<0.1	47.3	--	--	--
Wood Flour	52.0	6.3	<0.1	40.5	0.1	2.0	8190
Peat	58.0	4.7	0.5	31.0	4.6	32.9	--
Lignite	56.6	3.8	0.1	25.8	9.0	12.0	--

(a) HHV = Higher heating value.

(b) Not dried; characterization on an as-received basis.

The feedstocks evaluated in the project were similar in many aspects to those reported in the literature but could differ significantly with respect to growing conditions, location, or variety. In the case of sorghum, for example, there are many different varieties grown and their composition depends on growing conditions and end use of the plant or parts of the plants.

The parameters of most interest for the limited database evaluation performed in this investigation consisted of a description of the main sources of carbon contained in the feedstock, how the carbon structures differed, and the concentration and composition of the inorganic material

present in the biomass. Much of the information available regarding biomass characteristics lists elemental compositions and, in some cases, expresses the main structural components as percentages of cellulose, hemicellulose, and lignin. Since the composition of cellulose is consistent among plant types, direct comparisons can be made based on cellulose content. The structural polysaccharides of hemicellulose vary from species to species; these differences in structures still require identification, and their role in the conversion process is not understood. The monomers that make up the lignin in the feedstocks tested also vary, although generalizations can be made for similar plant types.

Kelp has a completely different structural component from the other feedstocks studied. The main cell wall component of kelp is alginic acid, which is composed of D-mannuronic acid units $\text{CHO}(\text{HCOH})_4\text{COOH}$. The alginic acid differs from cellulosic structures, which are made up of β -D-glucose monomers. The major difference is the presence of carboxyl groups in the kelp structure.

Potato waste also has a somewhat different structure from the cellulose-, lignin-, and hemicellulose-based feedstocks. The potato waste (peel waste, potato flesh, cull potatoes, and cull fries) appears to consist predominantly of starch. The exact form of the starch is not known at this time, but in general, potato starch is composed of amylose/amylopectin polymers, which differ from cellulose primarily in conformation of the monomeric glucose units and the presence of side chains in the amylopectin fraction.

Further definition of the sunflower feedstock was provided through collaboration with Professor Olaf Theander of the Swedish University of Agricultural Sciences (Uppsala). First, samples of sunflower stalks were fractionated into a pith fraction and an outer stem fraction. From five samples each, it was determined that $28.8\% \pm 3.9\%$ of the stalk mass was contained in the pith and $66.4\% \pm 5.1\%$ of the mass was contained in the outer stem. The pith was further characterized to contain 8.8% dry solids, while the outer stem contained 24.8% dry solids. Based on this information, the dry matter

of the sunflower stalk was calculated to be divided into a 1:7 ratio between the pith and the outer stem. These dry samples were then analyzed at the Uppsala laboratory (Table 3).

The ash content and composition are important components of the feedstocks being used in the PNL catalytic conversion system. Ash contribution to the conversion sequence and pathway has potential to directly influence (either positively or negatively) the amount of catalyst required and can influence carbon conversion, rate of reactions for water-gas shift and methanation, total gas production, and final composition of gases produced. Currently, only generalizations can be made regarding the effect of these inorganic substances, as information on the mineral content of the plants is dependent on the plant's growth media and can vary significantly even within the same feedstock type. Only a limited amount of data are available regarding either the catalytic effects of ash components in thermochemical

TABLE 3. Analysis of Sunflower Stalk Components

<u>Composition</u>	<u>Pith</u>	<u>Outer Stem</u>
Extractable w/80% Ethanol	2.3	21.9
Extractable w/Further Hexane	0.2	traces
Polysaccharide-anhydro Components(a)		
Glucose	30.7	26.9
Mannose	1.9	1.0
Galactose	1.2	1.0
Xylose	1.9	13.1
Arabinose	1.5	1.0
Uronic Acid	traces	5.9
Klason Lignin	1.3	12.2
Ash(b)	22.6	7.2

(a) Approximately; anhydro-glucose represents cellulose; uronic acid, the pectins; and the other anhydro-sugars, the hemicellulose.

(b) Determined at PNL.

systems or their toxicity or nutrient value relative to various bioconversion methodologies. Trace element analysis for several of the feedstocks is presented in Table 4.

Although processing variability due to changes among feedstock types was an important consideration in this project, variability due to inconsistencies in sampling a given feedstock must also be considered. For example, four samples of water hyacinths were obtained and analyzed from the frozen block in which they were stored. The samples ranged from 94.3% to 95.4% moisture (5.7% to 4.6% dry solids) and had an average moisture content of 94.9%. The moisture content reported in Table 4 represents the combined dry mass recovered from these samples. Other samples of water hyacinth were rinsed with distilled water, dried, and ashed. The rinsed hyacinth samples had a moisture content of 93.6% ($\pm 0.9\%$) and an ash content of only 10.5% ($\pm 0.2\%$) compared with 15.3% ($\pm 1.0\%$) unwashed. Rinsing the hyacinths appears to have removed some inorganic material (apparently some of the sediment in which the hyacinth was rooted). However, all experiments using hyacinths in this project used as-harvested (unwashed) water hyacinths.

In another case, kelp was analyzed in both the as-received and water-washed state. The difference was less dramatic than with the hyacinths. The ash content was reduced from 38.4% ($\pm 0.3\%$) to 36.9% ($\pm 0.7\%$) apparently as a result of washing sea sand or salt from the kelp. The kelp also absorbed some water during the rinsing as the moisture content increased from 88.9% ($\pm 0.4\%$) to 90.5% ($\pm 0.3\%$).

Tests to determine the dry solids content of the high-moisture biomass feedstocks showed that this procedure was a major source of scatter in the data. Sampling the high-moisture biomass or the heterogeneous slurry of biomass solids in water was an imprecise procedure and difficult to replicate. Added to the sampling problem was the difficulty of drying the high-moisture biomass feedstocks to constant weight without degrading the feedstock. The relatively reactive nature of many of the herbaceous feedstocks (which contain free sugars and other easily pyrolyzed components) led to scorching of the dried samples, even at drying temperatures of 100°C to 110°C.

TABLE 4. Trace Element Analysis in High-Moisture Biomass Feedstocks, wt% (dry basis)

Element	Napier ^(a)		Sunflower ^(b)	Corn ^(b)		Kelp ^(c)	Spent ^(c) Grain	Grape ^(b) Pomace	Orchard Leaf ^(d)	
	Grass	Sorghum ^(a)		Stover	Hyacinth ^(b)				PHL ^(d)	NBS
K	0.97	2.04	4.71	2.63	0.81	6.05	0.077	1.46	0.151	0.147
Ca	0.32	0.42	2.10	0.48	1.26	1.11	0.259	0.61	2.085	2.090
Na	0.010	0.020	NA	NA	0.91	2.65	0.57	NA	NA	NA
Mg	0.22	0.14	NA	NA	0.21	0.57	0.175	NA	NA	NA
S	0.102	0.112	0.266	0.12	NA	NA	0.002	0.227	0.207	0.230 ^(e)
Cl	0.272	0.862	0.588	0.42	NA	NA	NA	0.022	0.079	0.070 ^(e)
Fe	0.28	0.105	0.023	0.150	0.11	0.008	0.024	0.047	0.030	0.030
P	0.195	0.172	0.24	0.47	0.57	0.23	0.513	0.30	0.15	0.021
Si	0.60	1.62	0.74	1.73	0.70	0.04	0.760	0.17	<0.08	0.05
Mn	0.125	0.010	0.002	0.004	0.002	0.001	0.004	0.002	0.010	0.009
Al	0.008	0.058	NA	NA	0.055	0.008	0.006	NA	NA	NA
Zn	0.004	0.003	0.002	0.002	0.017	<0.001	0.001	0.001	0.003	0.003
Ti	0.001	0.005	0.002	0.017	0.015	0.001	<0.001	0.001	0.004	0.002
Ni	0.004	0.015	0.003	0.010	0.019	<0.001	0.001	0.003	<0.001	<0.001
Cu	0.001	0.001	0.001	0.001	0.010	<0.001	0.001	0.002	0.001	0.001
Cr	0.001	0.016	0.001	0.003	<0.001	<0.001	<0.001	<0.001	0.001	<0.001 ^(e)
Li	0.001	0.001	NA	NA	0.002	0.005	0.001	NA	NA	NA
Ba	0.001	0.001	NA	NA	0.002	0.001	0.001	NA	NA	NA
Sr	0.007	0.001	NA	NA	0.006	0.050	0.002	NA	NA	NA
B	<0.001	<0.001	NA	NA	<0.001	0.013	<0.001	NA	NA	NA

(a) Average of inductively coupled plasma-atomic emission spectrometry and x-ray fluorescence analysis.

(b) X-ray fluorescence analysis only.

(c) Inductively coupled plasma-atomic emission spectrometry only.

(d) Orchard Leaf is a National Bureau of Standards (NBS), Standard Reference Material 1571 with certified analyses for specified elements.

(e) Not certified value, for reference only.

NA = not analyzed.

A number of tests with different drying environments were performed to determine a preferred route that could be replicated with some consistency. In the process of this testing, the configuration of the drying oven (particularly the exposure of the heating elements) and the drying temperature were shown to have potential impact on determining the amount of dry solids, as well as the elemental composition of the dry solids. Scorching of some biomass (exposed fibrils and thin leaves) was observed in drying to constant weight with air temperatures measured at only 100°C to 110°C. The results of some comparative drying tests are given in Table 5. These results

TABLE 5. Comparative Results of Drying Tests for Sorghum

<u>Drying Tests</u>	<u>Dry Solids, wt% $\pm\sigma$</u>	<u>Carbon Content in Dry Solids, wt% $\pm\sigma$</u>	<u>Carbon Content of High-Moisture Biomass, wt% $\pm\sigma$</u>
Filter Dried, 23°C	31.25 $\pm$ 1.33	42.54 $\pm$ 0.56	13.3 $\pm$ 0.5
Vacuum Dried, 58°C	24.38 $\pm$ 0.62	43.50 $\pm$ 0.23	10.6 $\pm$ 0.3
Oven Dried, 100°C	25.22 $\pm$ 1.43	44.78 $\pm$ 0.49	11.3 $\pm$ 0.8
Oven Dried, 100°C w/Exposed Elements	21.82 $\pm$ 2.12	45.46 $\pm$ 0.34	9.9 $\pm$ 0.9
Oven Dried, 103°C(a)	23.9	44.8	10.7

(a) Only one test was conducted.

provide insight into the range of error involved in just the drying step. The filter drying of the biomass was the least severe procedure and resulted in the highest level of reported carbon for the high-moisture biomass feedstocks. This procedure gave a number that was wholly inconsistent with any of the oven-drying techniques. Although the several oven-drying techniques produced widely varying results, the standard deviations (σ) at the four conditions (shown in Table 5) overlapped in the range of 10.7%. The variations in the procedures suggest that a relative error of up to 10% should be expected in the sampling, drying, and carbon determination process.

Due to the implications of significant losses of carbon during oven drying of high-moisture biomass (as suggested by the low-temperature filter drying result), an experiment was performed to attempt to quantify the losses of carbon during drying at $\sim$ 100°C. Sorghum was placed in a sealed vessel and heated to 100°C with a continual nitrogen purge. The purge gas was passed through a condenser and then analyzed and measured volumetrically. After a period of 70 h at 85°C to 100°C, 211 L of off gas had been recovered and analyzed. The sorghum feedstock had been dried down to 35.9% of the original moist mass. Condensate water totaling 117.6 g and having a pH of 3.32 was recovered along with 3.8 g of water in the reactor outside the liner. The mass balance was not particularly good for the experiment, only 92.0%. Carbon dioxide appeared to be the only gas product, ranging from 0.1 to 0.5 vol% in the purge gas. The carbon dioxide identified in the off gas

(2.02 g) and that calculated to be in the condensate water (0.15 g CO₂/100 g H₂O at 24°C sat'd, pH 3.8 = 0.18 g) amounted to a carbon loss of less than 1% by weight from the carbon in the sorghum. This amount is insignificant and does not account for the difference between the oven-drying and filter-drying results reported in this study.

FEEDSTOCK PROCESSING

High-moisture biomass feedstocks generally cannot be fed to the high-pressure reactor in their "as-received" state. Because of the low bulk density and fibrous nature of the feedstocks, further processing is required to reduce particle size and produce a "slurry." The feedstock slurry requirements for feeding to the batch reactor system was not an important consideration in this study. The major feed material requirement was that the slurry could be stirred by the turbine propeller in the reactor. In addition, the reactor internals (thermowell, cooling coils, and stirrer) had to move into the slurry during assembly of the reactor. In a continuously fed reactor, the rheological properties required of the slurry would likely be determined by the mechanical limitations of the high-pressure feeding system. Further expansion to full-scale operation will require slurry preparation sufficient for the high-pressure feeding system and will likely require multiple feedstock capability.

Biomass slurries were prepared for experiments in this study by using a common household blender (600 W). Differences in the mechanical properties of the feedstock quickly became apparent in the slurry preparation process. For example, water hyacinths, kelp, potato waste, and spent grain were all quite easy to blend into a homogeneous mixture containing approximately 10% solids by weight. The slurries appeared to be fairly stable with respect to sedimentation. However, the drier and more fibrous feedstocks (napier grass, sorghum, and sunflowers) required considerable effort to blend. The slurries prepared from these more fibrous feedstocks were also quite heterogeneous in texture and consisted primarily of small (less than 0.5 in. in length) strands of plant fiber. The difficulty in preparing a slurry from these more fibrous materials led to the use of excess water to aid in preparing the slurry. The excess water was drained before the mixture was placed into the

reactor. Slurries prepared in this fashion typically had a solids content of approximately 7% to 10%. Analysis of the discarded excess water showed that it contained several thousand ppm of carbon, representing approximately 1% of the original carbon in the feedstock. The dissolved carbon lost from the feed is likely to be low molecular weight carbohydrates.

Changes in slurry properties as a function of temperature have been of interest in this project since its inception. A series of early tests were made by heating the biomass slurries at atmospheric pressure. In these experiments, water hyacinth and potato waste slurries were heated to their boiling points (near 100°C) and "cooked" under reflux for several hours while the feedstocks were monitored for changes in color and pH, and for gas evolution. These tests were made with and without catalyst (Na_2CO_3) present. Changes in fluid properties (surface tension and viscosity) of the slurry upon addition of the catalyst were noted. These changes may have been due to the solubilization of long chain acid segments from the biomass. Darkening of the slurry and gas evolution were also noted in the presence of the Na_2CO_3 .

Additional tests were made by heating biomass slurry (without catalysts) to intermediate temperatures of 150°C, 200°C, 250°C, and 300°C in the reactor. For the experiments at less than 300°C, ball-milled sorghum slurries containing approximately 12 to 15 wt% solids were used. No substantial degradation of the feedstock was noted for the 150°C and 200°C experiments; however, at 250°C, the physical structure of the biomass was completely destroyed and a low-viscosity suspension of very fine particles and oil-like material was produced. For the experiment conducted at 300°C, a mixture of coarsely chopped napier grass and sunflower containing approximately 10 wt% solids was converted to an aqueous suspension of a fine black powder. This experiment suggests that pyrolytic (as well as hydrolytic) reactions occurring at 300°C and below change the biomass structure significantly in the high-pressure water environment. These changes are important to the low-temperature gasification reactions for biomass and will influence the design of larger-scale feeding systems for continuous gasification units.

EXPERIMENTAL SYSTEMS AND PROCEDURES

Performing the high-pressure experiments described in this report demanded the careful development of the experimental reactor system and safe operating procedures. Before the experimental program was initiated, the high-pressure reactor system and the laboratory facility (where it is located) underwent an Operational Readiness Review, including evaluation of the equipment by staff members responsible for safety and pressure systems engineering. A Safety Evaluation Document was prepared, as were Safe Operating Procedures. In addition, operators were trained specifically to operate the high-pressure system. A description of the experimental system and procedures is given below.

BATCH REACTOR AND SAMPLING SYSTEM

Gasification of high-moisture feedstocks was carried out batchwise in the 1-L, Inconel[®], bolted-closure, high-pressure autoclave (reactor). A schematic representation of the reactor is shown in Figure 5. The reactor vessel was fabricated by Autoclave Engineers, Inc., who also manufactured the magnetically coupled stirrer assembly and the reactor furnace. The reactor and the associated sample lines were constructed of stainless steel to minimize corrosion, which is a potential problem when dealing with hot alkali solutions. The system had the capability to operate at temperatures up to 450°C and pressures up to 6000 psig. Pressure and temperature were monitored remotely, the pressure by means of an Autoclave Engineers pressure transducer system. The temperature inside the reactor was monitored by a Type K thermocouple; the output was sent to a digital thermocouple monitor as well as a chart recorder/temperature controller.

The entire experimental system, except for certain valves and the instrumentation, was located inside a 0.25-in.-thick plate steel barricade, which was built to ensure the safety of the operators while the system was at working pressure. A rupture disk was located on a line leading from the reactor to a 1-in. pipe, which served to vent the reactor contents to the

[®]Trademark of Huntington Alloys, Inc., Huntington, West Virginia.

FIGURE 5. Schematic of 1-L High-Pressure Reactor Used for Biomass Gasification

outside of the laboratory in the case of reactor overpressure. The system was also configured with pressure and temperature monitoring devices (alarms), which turned off the furnace if the pressure or temperature exceeded preset limits.

The reactor was equipped with sampling ports, which allowed the contents to be sampled at any time during experimental operation. The sampling ports were configured such that samples were withdrawn from either the top or the

bottom of the reactor vessel. The valve on the reactor end of the sample line was a remotely controlled air-operated valve, which allowed samples to be taken from outside the protective barricade without operator exposure to the pressurized reactor.

The remotely controlled sampling system as originally configured is shown in Figure 6. Samples were taken by opening the pneumatically operated valve (A), allowing the sample line between Valve A and Valve B to fill with gas. Typical pressures in this line were 500 to 1000 psig. Valve A was then closed and Valve B was opened. This operation allowed the sample to fill a previously evacuated 100-mL sample bulb (C). Valve B was then closed, and the sample was analyzed by withdrawing a small portion of the stored gas in C. Typical pressures in the sample bulb were 200 to 400 psig. Approximately 10 to 20 mL of aqueous material were carried over into the sample bulb with each sample.

To improve experimental reproducibility, the sampling system was modified to reduce the sample size withdrawn from the reactor. The modified sampling system is shown in Figure 7. Valves B' and C' were opened, and the system evacuated with a small vacuum pump. All valves were then closed. A

FIGURE 6. Original Sampling System (All tubing shown is 1/4-in. OD, 0.035-in. wall, 316 SS.)

FIGURE 7. Modified Sampling System (All tubing shown is 1/4-in. OD, 0.035-in. wall, 316 SS.)

sample was withdrawn by opening the manually operated control valve (A') until the pressure in the sample line (between A' and B') was approximately 50 psig. Valve A' was then closed and Valve B' opened, filling the syringe port to a pressure of approximately 15 psig. A sample was withdrawn by inserting a syringe through a Teflon® septum on the sampling port. After the samples were withdrawn, the system was once again evacuated. A Drierite® column packed with desiccant was used to trap any moisture in the gas. The column and the desiccant were weighed before and after the experiments, and the difference was recorded.

®Trademark of E.I. duPont de Nemours and Company.

®Trademark of W.A. Hammond Drierite Company.

The following key changes should be noted:

- The volume of the sample holding loop was reduced from approximately 23 mL to about 2.6 mL. The volume of the system was not known precisely, since the dead volume of valves and fittings could not easily be calculated.
- The volume of the dead space in front of the sampling valve was reduced from approximately 10.4 mL to about 1.3 mL.
- The new sampling system allowed the entire sample loop to be evacuated prior to taking a sample, avoiding cross contamination of samples.
- The new system was equipped with an absorbent column to collect any water in the samples. This column was weighed before and after an experiment, permitting quantitative determination of the mass of water collected.
- The combination of a manually operated sampling valve and a pressure transducer on the sample loop allowed the collection of very carefully controlled sample volumes. Typically, the sample loop was filled to a pressure of 50 psig, as opposed to the old system, which was filled to 300 to 500 psig. Thus, the reduction in sample volume was actually much greater than indicated by the reduction in loop volume.

The sampling system modifications resulted in a dramatic reduction in sample volume (estimated volume reduction from about 150 mL to a volume of about 10 mL). The actual reduction in sample volume was even more pronounced than these figures indicate, since the samples were generally taken at several hundred psig. Whereas the sampling procedure during gasification experiments had originally resulted in a temporary loss of several hundred pounds of pressure from the reactor (and an accompanying reduction in temperature), the sampling procedure developed for the new system resulted in negligible pressure drop and no discernible change in temperature. The

improved system increased the reliability and precision of the sampling process. The complete batch reactor system with the modified sampling system is shown in Figure 8.

EXPERIMENTAL PROCEDURES

Prior to each experiment, enough frozen biomass was taken from the freezer to prepare a slurry consisting of approximately 10% biomass solids (5% in the case of water hyacinths). Distilled water was used to bring the moisture content up to the desired level. A small portion of the slurry was withheld for a precise determination of its moisture content. The observation of slight variations in the solids content of the slurry made this step necessary. The slurry was blended in a small laboratory blender until no further change in consistency could be observed.

For experiments conducted at 400°C, approximately 330 g of this slurry mixture were measured into a stainless steel liner along with measured amounts of reagent-grade anhydrous sodium carbonate and a commercially supplied silica/alumina-supported nickel metal methanation catalyst (Harshaw Ni 1404), as required. The Ni 1404 catalyst was first ground into a powder to improve its dispersion in the reactor. For experiments performed at 450°C, a lower loading of biomass (220 g nominal loading) was fed to the reactor, along with a proportionately smaller amount of each catalyst. This reduced loading was necessary to compensate for the higher pressures and increased gas production experienced in the closed reactor system at this higher temperature.

The liner and its contents were inserted into the reactor, which was then sealed. The reactor was purged, leak checked, and pressurized with nitrogen. The stirrer was started, and the reactor and its contents were heated to the desired temperature with a 1.7-kW electrical heater. Typically, about 90 min were required to heat the 300 mL of aqueous feedstock and catalyst to 400°C. The aqueous biomass, reaction gases, and catalyst were rapidly mixed inside the reactor by the stirrer. An analog temperature controller maintained the temperature at the desired level once the contents reached the correct temperature. A typical sampling schedule might specify

FIGURE 8. Schematic of Batch Reactor System

that the first gas sample be withdrawn when the reactor reached the target temperature. The reactor would then be held at temperature for 1 h, and samples of the contents would be taken every 15 min. Other sampling schedules were used, as required, to monitor the reactions. Samples could also be removed during heatup or cooldown and at shorter or longer time intervals. At the end of the experiment, the contents of the reactor were rapidly cooled by running cold water through a cooling coil of stainless steel tubing attached to the inside of the reactor lid (see Figure 5).

After the reactor contents were fully cooled, the volume of the gas remaining in the reactor was determined by venting the gas through a wet test meter. A 1-cm³ gas sample of the reactor contents was taken for analysis. All gas samples were analyzed using a Carle AGC-S (automatic gas chromatograph) in conjunction with a Spectra-Physics SP4000 data processing station. The quantity of biomass-derived product gas (and thus the carbon conversion) was calculated based on the fraction of nitrogen in the gas sample. Since this fraction decreased as the nitrogen was diluted with product gas, its concentration allowed the material balance to be calculated and the progress of the reaction to be determined at each sample time. This method of following the gasification reaction had been used successfully in previous work (Sealock, Elliott, and Hallen 1982). The liquid and solid materials left in the reactor were also examined and weighed so that a mass balance around the entire reactor could be made.

ANALYTICAL PROCEDURES

A wide range of analytical support was required in this project to understand the complex gasification reactions occurring during the testing of these high-moisture feedstocks. The analytical procedures used are detailed below.

Elemental Analysis

Perkin-Elmer (P-E) 240 and 240B analyzers were used for analysis of carbon, hydrogen, nitrogen, and oxygen. The P-E 240 determines carbon, hydrogen, and nitrogen by detecting and measuring their combustion products (CO₂, H₂O, and N₂). Combustion occurs in pure oxygen under static conditions, and

the products are analyzed by thermal conductivity. Helium is used to carry the combustion products from the combustion furnace through the reduction tube (which reduces any NO_x) and through the series of detectors and traps. For oxygen analysis, a separate sample must be pyrolyzed in helium over platinized carbon so that oxygen is converted to carbon monoxide. The carbon monoxide is scrubbed free of acid gases and then oxidized and measured as carbon dioxide. In all cases, the instrumental readout was in millivolts, which was used to calculate the composition based on reference compounds. Because sulfur concentrations were so low in most feedstocks, the P-E analyzers could not be used for sulfur analysis. The concentration of nitrogen for most feedstocks was also at or below the limit of detectability.

Sulfur and other trace elements were determined by either X-ray fluorescence (XRF) or inductively coupled plasma-atomic emission spectrometry (ICP-AES). The energy dispersive XRF used a combination of titanium and zirconium excitation sources. A dual-spectrum backscatter parameter matrix correction method was used in the analyses to provide increased sensitivities over a wider range of elements (Sanders et al. 1983). With this dual source system, the suite of elements measured extended from aluminum to strontium (excluding germanium, scandium, and the noble gases) and also included mercury and lead.

Although the dried biomass could be analyzed directly with the XRF system, significant sample preparation was required prior to the ICP-AES analysis. Known masses of the biomass were first processed by an alkali fusion to facilitate dissolution of the metallic elements and removal of the organic elements. Two different fusions were used for comparison, sodium peroxide in a zirconium crucible and potassium hydroxide in a nickel crucible. In each case, the fusing alkali metal and the crucible metal flooded the spectrum for zirconium and potassium, and those two elements could not be determined. As a result, the sodium and zirconium could only be measured in the potassium hydroxide fusion, and the potassium and nickel could only be determined in the sodium peroxide fusion. Both fusion systems were used because the alkali metals were important elements in the biomass. After the fusions, the samples were diluted with water to a known volume and acidified. The solution was then analyzed with the ICP-AES (Jarrell-Ash Model 96-965), and the concentrations of the elements in the dry biomass calculated.

Ash

Ash was determined by combustion in a muffle furnace similar to ASTM method D-1102-84. This method covers determination of ash from wood. Porcelain crucibles with lids were used throughout.

Moisture

Moisture determinations were a crucial part of this research. Extra time was spent on method development. The methods studied were described earlier in the Feedstock Analyses section of this report.

Heat of Combustion

Heats of combustion were obtained by burning the dry biomass in a Parr oxygen bomb calorimeter as in ASTM method E-711-81. An adiabatic system was maintained through the use of a controlled-temperature water jacket. The biomass was compacted into a tablet prior to the test to keep the sample in the crucible and to obtain complete combustion and consistent results.

Gas Analysis

Gas analysis was performed by gas chromatography (GC) using a Carle AGC. The AGC configuration No. 0158A was used to detect low molecular weight gases including hydrogen. This AGC uses a set of three columns (80% Porapak N + 20% Porapak Q, 50/80 mesh; Molecular Sieve 13X, 80/100 mesh; and 8% OV-101 on Chromosorb W AWDACS, 80/100 mesh) with automatic switching controls to separate hydrogen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, oxygen, and nitrogen. Thermal conductivity detectors are used in the AGC. Hydrogen was determined through the use of the Carle hydrogen transfer system, a metallic membrane for hydrogen separation by diffusion. The GC signal was processed in a Spectra-Physics 4000 data processor, which plotted the signal, integrated peaks, and determined retention times; it then printed a table of data including peak identifications and gas composition based on previously analyzed standard gas mixtures.

Calculation of Gas Composition and Carbon Conversion to Gas

Following the analysis of the gas samples from the experiments, calculations were made to determine the composition of the actual gas product and to determine the conversion of biomass to gases as a function of time. The gas sample was first calculated to an air-free composition to correct for air leakage into the sample during transfer from the sample line into a syringe and then through the septum into the GC. The correction was straightforward based on the subtraction of all the oxygen in the analytical result and subtraction of a portion of the nitrogen in a mole ratio of 78/21 to the oxygen as is found in air. The gas composition was further corrected to a nitrogen-free basis to determine the actual composition of the gas generated from the biomass. Subtraction of the nitrogen was necessary because it resulted from the nitrogen pressurization of the reactor prior to the experiment.

The air-free gas composition of the samples was used to determine the carbon conversion to gas. Based on the known amount of nitrogen added to the reactor at the beginning of the experiment, the gas production was determined by the amount of dilution of the nitrogen from its initial 100%. For example, if the initial amount of nitrogen in the reactor was 1 L and after 15 min the nitrogen concentration in the reactor had dropped to 40%, then the amount of product gas produced in that time must have been 1.5 L (1 L N₂/1 + 1.5 total L = 40%). Subsequent calculations were made for each of the gas samples recovered during the experiment. Carbon conversion to gas was then calculated on a mass basis for the carbon in the product gases as a percent of the carbon in the feedstock.

Aqueous Byproduct Analysis

The aqueous byproducts were analyzed for ammonia, COD, and dissolved organics. The ammonia analytical procedure is described in the Experimental Results section, along with the recovery procedure for the dissolved organics. The gas chromatography-mass spectrometry (GC-MS) methods used for qualitative and quantitative analysis are described in the next paragraph. The COD method used was the dichromate reflux method, No. 508 (American Public Health Association 1980).

Analysis of Organics by Gas Chromatography-Mass Spectrometry

Essentially the same GC-MS technique was used for both the aqueous byproduct extracts of the gasification experiments and the oil products from the liquefaction experiments. The GC column was a 60 m x 0.25 mm ID, DB-5 wall-coated, open tubular, silica capillary purchased from J&W Scientific, Inc. The column was contained in a Hewlett-Packard (HP) 5890 GC directly coupled with an HP5970 mass selective detector. The HP splitless injection system was used with an injector temperature of 300°C and an injection port pressure of 5 psig with helium carrier gas. The column temperature was programmed to 300°C at 10°C/min with a starting temperature of 40°C. The portion of the column passing through the transfer zone between the GC and the MS was maintained at 300°C. The 70-ev electron impact spectra were recorded from 20 to 300 m/e at a scan rate of 250 amu/s. One-microliter injections were used for these analyses.

EXPERIMENTAL RESULTS

This section presents the results of the experimental tests conducted with high-moisture biomass feedstocks at PNL from January 1984 to January 1988. In addition to the feedstock characterization described earlier in this report, more than 180 batch reactor experiments were performed. Raw data for many of these experiments are included in the appendix.

The specific operating conditions and sampling procedures used in this study were changed as work on the experimental system progressed. Initial experiments were performed at temperatures up to 450°C and with a combined charge of supported nickel metal and sodium carbonate catalysts at concentrations previously identified in a research project on the gasification of wood (Sealock, Elliott, and Hallen 1982). Subsequently, lower temperatures (380°C to 400°C) were found to be sufficient; the sodium carbonate catalyst was often unnecessary or detrimental; and a higher nickel catalyst concentration was useful in increasing carbon conversions and methane yields.

In addition to changes in reaction conditions, improvements were also made to the reactor sampling system. The gas sample recovery system was modified to reduce sample volumes and to minimize the errors in gas sample composition. Also, methods were developed for more accurate accounting of the carbon recovery in the system and for analysis of dissolved organics and ammonia in the byproduct aqueous stream. As a result of these changes during the experimental program, important caveats are applied to some of the data regarding perceived accuracy and to comparability among some experiments.

FEEDSTOCK EFFECTS

Results of this experimental program demonstrated the wide range in reactivity for high-moisture biomass feedstocks. However, this is expected based on the wide range of feedstocks tested in the project, as shown in Table 6. Even so, when only native biomass feedstocks (i.e., the whole plant samples and agricultural wastes) are considered, the differences between the rates of reactivity (as measured by carbon conversion to gas after 15 min at

TABLE 6. Low-Temperature Gasification of High-Moisture Biomass Feedstocks

Feedstock	Conversion of Carbon to Gas, %		Methane Yield @ 45 min, scf CH ₄ /dry lb feed	Expt. No.
	15 min	45 min		
Cellulose	98	93	5.5	162/4/5
Sorghum	100	95	5.4	160/149
Sunflower	88	91	5.4	159
Napier Grass ^(a)	101	90	5.3	90
Corn Stover ^(a,b)	--	102	1.7	136
Anaerobic Digestion II	70	72	5.2	163
Water Hyacinth ^(c)	73	80	4.5	175
Kelp	79	78	3.0	176
Douglas Fir ^(a,b)	50	51	2.7	45
Grape Pomace	41	92 ^(d)	6.9 ^(d)	177
Spent Grain	56	83	6.6	174
Potato Waste ^(a,b)	46	53	2.0	38
Peat	22	58 ^(d)	4.5 ^(d)	190
Black Liquor	11	23	0.4	151

Test Conditions: 400°C, 45 min heatup from 250°C to 400°C, Ni metal catalyst (1.2 g/g dry solids), 8 to 12 wt% dry solids

(a) Large sample bulbs and Na₂CO₃ co-catalyst.

(b) Low nickel catalyst loading (0.17 g catalyst/g dry solids).

(c) 5 wt% dry solids.

(d) 60 min.

temperature) and the product yields (expressed in units of standard cubic feet of methane per dry pound of biomass) show interesting variations.

The data in Table 6 were derived primarily from experiments conducted late in the project that were performed with the low-volume gas sampling system, a high nickel catalyst loading, and without the addition of sodium carbonate as a co-catalyst (which was determined in some cases to inhibit methane production). However, some data (Douglas fir, corn stover, and potato waste, in particular) are not comparable because of the lower level

of nickel catalyst used in the earlier experiments. Also, the use of the original gas sampling system, as with napier grass, for example, typically led to less consistent results.

The results in Table 6 demonstrate a rather typical conversion of herbaceous biomass (cellulose, sorghum, sunflower, corn stover, napier grass) at a high rate such that 90% to 100% conversion was achieved in 15 min or less after the temperature reached 400°C. The initial conversion of the biomass began at temperatures of 300°C or less. The total residence time needed at 400°C for an isothermal experiment is expected to be somewhat longer than 15 min. The formation of methane gas appeared to lag behind the total gas production and was maximized at about 45 min of residence time at 400°C. This finding indicates that a significant portion of the methane was not formed as pyrolysis (gasification) and/or hydrolysis products, but was produced as a result of a secondary gas phase reaction. This reaction, which appears to be rate limiting, is catalytic, implying that the rate of methane production could be limited by nonkinetic factors (i.e., mass transfer). The mass transfer limitations could be a result of interphase resistances (from the gas phase into the liquid) or could be more directly catalyst-related (i.e., limited mass transfer from the liquid or gaseous phase to/from the catalyst surface). The uncertainty surrounding phase relationships in the near-critical system makes a reliable determination difficult; however, any mass transfer limitations on rate likely are a result of the interphase mass transfer resistance. In either event, an improvement in rate should be expected in a well-designed, continuous stirred-tank reactor (CSTR) or packed-bed reactor.

The variation in the carbon conversion numbers has been a concern throughout the experimental program. During a typical experiment, the carbon conversion appeared to rise during the initial stages as the biomass was gasified, leveled off as the reaction neared completion, and then often dropped off toward the end of the experiment. No experimental basis for this anomalous fall-off in carbon conversion to gas could be identified; however, a check on the carbon conversion to gas could be made by analysis of the aqueous and solids residues remaining after the experiment. As shown in Table 7, these data suggest that the 90% to 100% carbon conversions found by

gas analysis were substantiated by the carbon balance when the vent gas yield was normalized to obtain a carbon balance closure.

Other feedstocks listed in Table 6 exhibited different processing characteristics. The aquatic biomass, kelp and water hyacinth, showed a good rate of reaction but a lower total conversion; i.e., the aquatic biomass gasified as readily but to a limited degree (~80%). The residual, non-gasified material is represented by the high yields of solids and dissolved organics in the aqueous byproduct, as shown in Table 7. The anaerobic digestion residue showed similar results that may be reflective of the source of the residue, which was a digester feedstock containing 50% water hyacinths and 50% sewage sludge.

The food processing materials, grape pomace and spent grain, exhibited a different type of activity, a relatively low rate of reactivity, which suggested the need for a longer residence time at temperature. These materials also produced a larger amount of methane product gas even at lower levels of total conversion compared with the herbaceous biomass.

The black liquor feedstock appeared to have low reactivity under normal conditions and with the nickel metal catalyst. The apparent cause of the low

TABLE 7. Carbon Balance for Low-Temperature Gasification of High-Moisture Biomass

Feedstock	Carbon in Feed, g	Carbon in Products, g (%)				Carbon Balance
		Vent Gas	Aqueous	Solids	Catalyst	
Cellulose	12.7	12.4 (97.5)	0.0 (0.0)	0.3 (2.3)	-0.7 (-5.3)	94.5
Sorghum	11.1	10.0 (90.2)	0.2 (1.9)	0.2 (2.0)	-0.1 (-0.8)	93.3
Sunflower	12.0	10.0 (83.4)	0.3 (2.3)	0.4 (3.1)	0.2 (1.6)	90.4
Anaerobic Digestion II	9.4	6.5 (69.1)	0.7 (7.4)	0.3 (3.5)	0.0 (0.0)	80.0
Water Hyacinth	7.0	4.4 (62.1)	0.5 (7.3) ^(a)	0.4 (6.3)	0.3 (4.4) ^(a)	80.1
Kelp	7.6	5.9 (76.9)	0.8 (10.3) ^(a)	0.4 (5.3)	-0.1 (-0.7) ^(a)	92.6
Grape Pomace	15.8	11.5 (73.0)	0.2 (1.3)	0.7 (4.2)	0.4 (2.5)	81.0
Spent Grain	14.9	11.2 (74.9)	0.8 (5.1)	0.2 (1.6) ^(a)	0.1 (0.7)	82.3

(a) Estimated.

reactivity is the high sulfur content of black liquors; however, no studies were conducted to determine if the nickel catalyst had been poisoned by the sulfur. Further studies are required to determine if black liquor or high-sulfur feedstocks can be adequately gasified in the PNL system.

TEMPERATURE AND REACTION RATE

The effect of temperature was studied only to a limited degree. Most experiments were performed at either 400°C or 450°C. A series of early tests demonstrated the temperature effect over the 400°C to 450°C range in a non-optimal catalytic system (sodium carbonate and low nickel concentration). The results of these tests are shown in Figures 9 and 10. The temperature effect on carbon conversion is significant, whereas the temperature effect on the heating value of the product gas is not as pronounced in most cases. However, the result of these two functions, as shown in Figure 11, is that

FIGURE 9. Catalyzed Carbon Conversion to Gases for High-Moisture Biomass

FIGURE 10. Higher Heating Value of Raw Product Gas from Catalyzed Gasification of High-Moisture Biomass

temperature has a major effect on the energy yield. As will be seen in the next section, the effect of catalyst on reaction rate and product quality can be even more dramatic.

Subsequent tests conducted with the higher nickel concentration (>1.0 g catalyst/g dry biomass) also demonstrated the effect of temperature between 380°C and 400°C . The data in Table 8 are for two feedstocks. The more reactive cellulose exhibited almost no temperature effect. The less reactive feedstock, grape pomace, showed a consistent increase in carbon conversion and methane production through the temperature range. It is important to note that the temperature-induced increase in methane yield is not directly proportional to the increase in carbon conversion. In other words, as temperature increases, the carbon conversion increases faster than the methane yield. This is a result of a shift in gas composition as temperature increases, with higher temperatures resulting in a lower methane mole fraction in the product gas but more total methane being produced.

FIGURE 11. Energy Yield from High-Moisture Biomass by Catalytic Gasification

TABLE 8. Effect of Temperature of Catalytic Gasification of High-Moisture Biomass

Feedstock	Temperature, °C	Conversion of Carbon to Gas, %		Methane Yield @ 45 min, scf CH_4 /dry lb feed	Expt. No.
		15 min	45 min		
Cellulose	400	98	93	5.5	162/4/5
Cellulose	380	93	89	5.8	156
Grape Pomace	400	41	77	6.4	177/171
	390	21	45	5.5	173
	380	11	35	4.2	172

Test conditions: except for temperature, same as in Table 6.

In the batch reactor system, isothermal kinetic data could not be produced because of the large thermal inertia of the reactor system. Therefore, all effects evident between operating at a lower and a higher temperature are magnified by the amount of reaction occurring during the finite amount of time (in the range of minutes) required for preheating from the lower to the higher temperature. The amount of reaction occurring during the heatup cycle is significant. As an example, Figure 12 illustrates the rapid conversion of the feedstock by showing the conversion versus time plot for sunflower stalks treated at 400°C in the presence of approximately 1.2 g Ni catalyst/g dry biomass and a slurry concentration of ~10 wt% solids. In the figure, the data indicate that conversion begins at temperatures as low as 250°C to 280°C, and is reaching maximum rate before the reactor reaches its final temperature. Similar results are seen for all of the high-moisture biomass feedstocks tested. The non-isothermal conditions made extraction of useful rate data difficult. The development of isothermal rate data is a principal objective of the CRS studies scheduled for FY 1988-89.

CATALYSTS - CONCENTRATION AND TYPE

The two basic types of catalyst used for this study were nickel metal (reduced and stabilized on a silica-alumina support) and alkali and alkaline earth carbonates (usually sodium carbonate). Early tests were performed at a nominal loading of 1 g Na_2CO_3 and 0.17 g Ni catalyst/g of biomass solids. These loadings were selected on the basis of earlier gasification studies conducted with wood and wood constituents (lignin, cellulose, and hemicellulose) as feedstocks (Sealock, Elliott, and Hallen 1982). The principal nickel catalyst used was Harshaw Ni 1404-T, which is reported by the manufacturer to have a surface area of 125 m^2/g and to contain 68 wt% nickel metal. This catalyst was supplied in the form of 3/16-in. tablets, which were later crushed to form a loose powder and thus provide better dispersal within the stirred reactor vessel. Catalyst loadings ranged from 0.17 g catalyst/g biomass solids up to 1.7 g catalyst/g biomass solids. Most of the later runs were made with a nominal loading of 1.2 g Ni/g dry biomass solids. The data

FIGURE 12. Time Versus Conversion Plot for Sunflower Stalks ~10% Solids Slurry, 1.2 g Ni Catalyst/g Dry Biomass

show that increased levels of nickel catalyst are advantageous and, in most cases, the carbonate catalyst is not necessary for gasification and actually works to limit methane yields.

A broad comparison of catalyst effect for a number of high-moisture biomass feedstocks can be found in comparing Table 6 with Figure 9. The results in Table 6 are achieved with a high nickel catalyst loading (1.2 g Ni/g dry biomass solids), without sodium carbonate, at only 400°C; whereas, the data in Figure 9 are from experiments with a lower amount of nickel (typically 0.17 g Ni/g dry biomass solids) with sodium carbonate at 400°C and 450°C. The change to the high nickel loading in the absence of sodium carbonate greatly improves the activity when compared at 400°C and more than

compensates for a 50-degree increase in temperature as well. This conclusion generally can be applied to all the high-moisture biomass feedstocks listed.

Three specific catalyst concentration relationships were studied in detail. These relationships are 1) the effect of nickel concentration at constant alkali concentration; 2) the effect of nickel concentration in the absence of alkali catalyst; and 3) the effect of alkali concentration at constant nickel concentration.

Figures 13 and 14 present the data for napier grass gasification with various loadings of nickel catalyst with the sodium carbonate co-catalyst. The temperature effect from 400°C to 450°C for napier grass is not really discernible over this series of experiments. The increased nickel catalyst loading, however, has a significant effect, resulting in an increase in carbon conversion of 30% and a 100% increase in methane yield. The data from Figure 14 also suggest that methane yield may be limited at 450°C to some level below that attainable at 400°C. Such a limitation could be due to the influence of temperature on thermodynamic equilibrium.

FIGURE 13. Effect of Nickel Catalyst Loading on Carbon Conversion in the Presence of Sodium Carbonate Co-catalyst

FIGURE 14. Effect of Nickel Catalyst Loading on Methane Yield in the Presence of Sodium Carbonate Co-catalyst

Figures 15 and 16 have similar format and contain data for experiments with sorghum over a range of nickel catalyst loading without the sodium carbonate co-catalyst. In Figure 15, the temperature effect is quite obvious in the noncatalyzed case and is not significant for high nickel loading. In fact, there may be little temperature effect at the lower catalyst loading cases, as seen in Figures 13 and 14 for napier grass, but no 400°C experiments for sorghum were conducted for comparison. Similarly, in Figure 16, a strong temperature effect was measured in the noncatalyzed case; however, again for the high nickel loading, an inverse effect is noted. The thermodynamic limitation on methane production at higher temperature is again the reasonable explanation. The high carbon conversions to gas (in excess of 100% in Figure 15) at high nickel concentration are due to a poor material balance on these experiments and cast some doubt on the accuracy of the estimated methane yields shown in Figure 16. Normalization of the carbon

FIGURE 15. Effect of Nickel Catalyst Loading on Carbon Conversion

conversion data to a nominal 95% results in a reduction of the estimated methane yields (4.6 scf at 450°C and 6.6 scf at 400°C).

The effect of alkali concentration on nickel-catalyzed methane production from sorghum is shown in Figure 17. These experiments were all performed with a high nickel catalyst loading. The data clearly show the higher methane yield achieved at 400°C compared with 450°C. In addition, there is a slight inhibition of methane production with increasing sodium carbonate concentration in the system. The sodium carbonate concentration listed on the horizontal axis describes the addition of sodium carbonate to the reaction medium. Furthermore, there is alkali in the sorghum itself equivalent to 0.052 g $\text{Na}_2\text{CO}_3/\text{g}$ dry sorghum. There is no companion plot of carbon conversion for these experiments as all of these experiments resulted

FIGURE 16. Effect of Nickel Catalyst Loading on Methane Yield

in carbon conversions in excess of 100%. Therefore, to plot the data shown in Figure 17, the experimental data have been normalized to a common basis (100% carbon conversion). The linearity of the corrected data suggests that the assumption inherent in the correction is appropriate. This correction results in a different view of the data than was reported earlier (Butner et al. 1986).

Alternatives to the Ni 1404 catalyst and sodium carbonate co-catalyst have received little attention in this experimental program. While other nickel catalysts or other metals could be as active or more active than the nickel for low-temperature gasification of high-moisture biomass, this possibility is not promising in light of results of related model compound studies with alternative noble and transition metal catalysts (Baker and Sealock 1988a,b). Alternative alkali compounds were tested in the past with cellulose as the feedstock without the nickel catalyst (Sealock, Elliott, and Hallen 1980).

FIGURE 17. Effect of Sodium Carbonate Concentration on Methane Yield

A series of tests were performed with five different carbonates to determine relative activity in the presence of nickel catalyst. For these tests, cellulose was used as the feedstock to eliminate cross effects from other alkali or alkaline earth components contained in biomass ash. The results of these tests are given in Table 9. The experiments represent a relatively narrow band of reactivity, as suggested by percent carbon conversion to gas. The methane production varies somewhat more, and the alkaline earths appear to be particularly amenable to good methane production based on mass yield and concentration in the product gas. However, due to the low level of nickel catalyst loading, the carbon conversion and methane yields are low in all cases. These alkali effects may be due more to interaction with carbonaceous buildup on the nickel catalyst than interaction with actual gas production from biomass.

TABLE 9. Effect of Alkali Type on Catalytic Gasification of Cellulose

Carbonate Catalyst	Mol Catalyst/ g Cellulose	g Catalyst/ g Cellulose	Carbon Conversion to Gas, %		Methane Yield, scf/g dry biomass		Methane, vol% product gas
			15 min	45 min	15 min	45 min	
Na	0.0032	0.34	65.5	66.9	2.62	2.76	26-27
			64.3	64.1	2.47	2.58	
K	0.0032	0.44	68.7	61.2	2.57	2.30	26-24
			72.1	63.9	2.92	2.55	
Cs	0.0032	1.07	58.4	57.6	2.55	2.33	26-28
			86.1	79.9	3.66	3.28	
Mg ^(a)	0.0032	0.30	71.9	67.2	3.48	3.39	32-36
			72.5	69.7	3.36	3.50	
Ca	0.0032	0.32	69.8	60.9	2.70	2.75	26-32

Test Conditions: 0.167 g Ni Catalyst/g Cellulose, 400°C.

(a) $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

BYPRODUCT COMPOSITION

The primary form of data generated from the experimental system has been gas composition and yield analyses. In all the experiments, visual inspection indicated there was a small amount of unconverted solid carbonaceous residue as well as dissolved organics (in most tests). Also, the residual aqueous byproduct was recovered and weighed following the gasification of the biomass. The composition and appearance of this material was highly variable depending on the amount and type of catalyst used in the experiment. In noncatalyzed experiments, the residual aqueous byproduct was dark yellow with a substantial amount of black powder and fibrous solid, which was assumed to be partially pyrolyzed biomass. In the nickel-catalyzed tests, the residual aqueous was often clear or light blue-green and the solid was a powdery, dark-gray material.

A detailed analysis of the aqueous byproduct was made for several experiments (Tables 10 and 11). Prior to solids filtration, decanted liquids were recovered from the experimental samples. Carbon, hydrogen, and nitrogen

analyses were performed using the P-E 240B instrument. Other, heavier elements were measured using ICP-AES. Chemical oxygen demand measurements for these liquids were also made.

The experiments with added catalyst are distinguished by their elevated levels of nickel and/or sodium. The dissolved sodium in the catalyzed cases accounts for about half of the sodium in the carbonate catalyst added. The dissolved nickel ranges from a few hundredths of a percent up to 1% of the nickel added as catalyst. One cause of higher nickel dissolution could be

TABLE 10. Experimental Details for Residual Aqueous Samples

<u>Expt. No.</u>	<u>Feedstock</u>	<u>Catalyst</u>	<u>Temperature, °C</u>
129	Sorghum	None	450
113	Sorghum	35 g Ni	400
115	Sorghum	35 g Ni 5 g Na ₂ CO ₃	400
134	Napier Grass	None	450
90	Napier Grass	38 g Ni	400
137	Spent Grain	35 g Ni	400

TABLE 11. Elemental Composition of Decanted Liquids from Residual Aqueous Byproducts

<u>Expt. No.</u>	<u>Elements</u>														<u>COD, mg/L</u>
	<u>C, %</u>	<u>N, %</u>	<u>H, %</u>	<u>Ni, ppm</u>	<u>Na, ppm</u>	<u>K, ppm</u>	<u>Si, ppm</u>	<u>Ca, ppm</u>	<u>Mg, ppm</u>	<u>P, ppm</u>	<u>Zn, ppm</u>	<u>Fe, ppm</u>	<u>B, ppm</u>	<u>pH</u>	
129	0.33	1.5	12.2	0.7	46	560	43	47.2	2.1	2	0.4	0.3	0.2	8.84	3305
113	0.05	0.8	12.2	43	110	870	36	14	--	--	--	0.1	--	9.88	341
115	0.24	1.0	11.9	150	4900	1210	15	65	--	3	--	--	--	9.59	3214
134	0.67	1.0	11.9	46	26	610	60	190	46	140	0.7	0.3	0.1	4.67	20484
90	0.30	0.12	12.0	77	7000	250	45	14	1.1	--	--	0.1	--	9.86	3283
137	0.14	0.65	12.2	1110	410	140	11	8.3	2.2	--	--	0.1	--	9.12	492

higher operating temperature. Also, the concentration of nickel in the aqueous byproduct appears to increase with the use of the sodium carbonate co-catalyst. Dissolved nickel concentration may also be related to feedstock type, based on the range of concentrations obtained from the noncatalytic experiments. For example, the spent grain may cause higher nickel loss due to complexation of the nickel with the nitrogen-containing components resulting from the protein in the spent grain (see discussion on composition of liquefaction products).

The solids were vacuum-filtered from the residual aqueous byproduct and washed with approximately three 20-mL portions of boiling water and a similar amount of acetone until the filtrate was colorless. Air was pulled through the solids for 10 min, followed by oven drying at 110°C to constant weight (approximately 1 to 2 h). Analysis of these solids, given in Table 12, shows that the residue was primarily composed of catalyst except in the noncatalyzed tests (129 and 134) where a substantial amount of carbonaceous solids remained. The solids recovered from the catalyzed tests were more hydrogen-rich when sodium carbonate was not used in the catalyst system. Apparently, some of the carbon on the nickel catalyst was hydrogenated in the absence of the alkali catalyst.

Following filtration of the solids, the undiluted aqueous phase was weighed and subjected to an acid/base extraction procedure. This extraction procedure was based on U.S. Environmental Protection Agency (EPA) water analysis techniques for phenolics and polycyclic aromatic hydrocarbons. In fact, the techniques used are typical elementary organic chemical analytical methods in that no specialized procedures were required. The aqueous solution was made basic (pH 12) by adding 10 M NaOH, and then extracted with three 40-mL portions of methylene chloride to remove non-acidic organic components. The aqueous solution was then made acidic (pH 1 to 2) and again extracted with three 40-mL portions of methylene chloride to recover acidic organic components. The methylene chloride extracts were dried by pouring them through a Drierite-filled drying tube. The Drierite was rinsed with three 10-mL portions of methylene chloride. Each extract was then concentrated to a volume of 5 to 10 mL on a rotary evaporator. These concentrated extracts were analyzed by GC-MS to identify the chemical components.

TABLE 12. Analysis of Solids from High-Moisture Biomass Gasification

Expt. No.	Mass	Percent Composition			
		C	H	N	H/C
129	1.57 g	71.3	3.4	2.5	0.56
113	27.43 g	4.3	0.9	<0.1	2.56
115	32.01 g	4.2	0.7	<0.1	1.87
134	4.88 g	76.0	3.9	1.0	0.61
90	31.14 g	3.7	0.5	<0.1	0.69
137	34.84 g	3.5	0.8	0.1	2.72
<hr/>					
Ni 1404	Ground Catalyst	3.05	0.43	0.14	1.68

Gas chromatography with a flame ionization detector (FID) was used to quantify the chemical components based on an added internal standard (decalin).

The basic extracts of the aqueous byproducts from the gasifier primarily contained a mixture of dozens of hydrocarbons, including light aromatics (benzene/toluene/xylenes) as well as straight-chain and branched aliphatics with carbon numbers from 9 to 16. The extracts from the acidified aqueous byproducts were more variable in composition. The noncatalyzed tests yielded primarily phenolic mixtures (phenol, cresols, and para-ethyl phenol), while the catalyzed experiments resulted in much lesser amounts of phenols dispersed in a mixture of hydrocarbons similar to that found in the extracts of the gasified solutions.

The data in Table 13 were derived from these analytical results in combination with the gas analyses for each of the respective experiments. The basis for determining carbon conversion included both the carbon in the biomass as well as the carbon in the sodium carbonate, since the carbonate cannot be directly recovered and may be distributed among the gas, liquid, and solid product streams. Since the nickel catalyst retained nearly all of its nickel and was not excessively coked, the carbon on the nickel catalyst as charged to the reactor was subtracted from the recovered solid residue to

TABLE 13. Product Distribution for High-Moisture Biomass Gasification

Expt. No.	Carbon Conversion, % of feed carbon				Mass Balance
	Gas	Dissolved	Solid	Total	
129	87	4	13	104	96
113	124	1	1	126	94
115	113	3	2	118	95
134	60	7	28	95	103
90	103	3	<1	106	100
137	133	2	1	136	--

determine the amount of residual solid carbon product (in the noncatalyzed cases, the solid carbon residue was determined directly). As seen in Table 13, the noncatalyzed experiments resulted in relatively high yields of solid carbon (129 and 134), while there was almost no solid carbon in the catalyzed tests. The level of dissolved carbon appeared to follow a similar trend. The gas yield data showed the strong effect of the catalyst on gas production. The mass balance for these experiments showed a relatively consistent 95% to 105% balance, with an elemental carbon balance typically in the range of 80% to 95%. The analysis of these byproducts and residues indicated that these materials cannot be ignored in determining the carbon balances around the experimental system.

Another important question related to the aqueous byproduct is the fate of the nitrogen found in some of the high-moisture biomass feedstocks. An analytical technique was developed to measure dissolved ammonia in the aqueous byproduct of the high-moisture biomass gasification system. The aqueous byproduct was analyzed after filtration of the nickel catalyst solids. An ammonia-specific electrode (ORION 95-12) was used to determine ammonium ion concentrations in the parts per million range. The electrode was calibrated with a series of ammonium chloride solutions. All samples were pH adjusted to pH > 11 by adding 10 M NaOH. Ammonia concentration data are presented in Table 14. Nitrogen determinations made with the P-E 240B elemental analyzer are also given for two experiments. The 240B produces inconsistent nitrogen results at levels of less than 1%; however, the results are indicative of the order of magnitude when compared with the ammonia-specific electrode results.

TABLE 14. Summary of Analyses Using Ammonia-Selective Probe

<u>Expt. No.</u>	<u>Biomass Type</u>	<u>Ammonia Concentration, ppm</u>	<u>Nitrogen by P-E 240B, %</u>
103	None	5.6	--
107	None	1.4	--
108	None	5.6	--
114	Sorghum	1260	--
126	Sorghum	126	--
159	Sunflower	1400	0.6
161	Anaerobic Sludge	2800	0.78

Nitrogen balances were determined for two experiments (159 and 161), in which total mass recoveries were attempted. The results of these balances are shown in Tables 15 and 16.

The data in Tables 15 and 16 indicate good balance for nitrogen. Apparently, the nitrogen in the biomass can be recovered as dissolved ammonia in the aqueous byproduct stream. By far, the largest nitrogen component in the batch experiments was the nitrogen cover gas. Little reaction of the cover gas to produce ammonia was apparent from these tests. Further analyses on products from the CRS experiments will provide more definitive information on the fate of the nitrogen in high-moisture biomass gasification.

LIQUEFACTION EXPERIMENTS

A number of experiments were performed to determine the yield and quality of oil obtainable from high-moisture biomass feedstocks when processed under typical direct liquefaction conditions. The experiments were performed batchwise in the same 1-L reactor. Approximately 300 g of high-moisture biomass were charged to the reactor in a stainless steel liner. Sodium carbonate was added to the feedstock (approximately 0.1 g/g dry biomass) except in the case of kelp, which already contained a high level of alkali as part of its chemical makeup.

TABLE 15. Nitrogen Balance Around Reactor System - Experiment 159

Nitrogen Inputs

29.65 g dry sunflower @ 0.95 wt% N = 0.28 g
4.75 L nitrogen cover gas = 5.54 g
Total Nitrogen Fed = 5.82 g

Nitrogen Outputs

Approx. 250 g aqueous @ 0.14 wt% N = 0.35 g
24.5 L vent gas @ 20.3 vol% N₂ = 5.80 g
Total Nitrogen Out = 6.15 g

Percent Recovered
 $\frac{\text{Output}}{\text{Input}} = 106\%$

TABLE 16. Nitrogen Balance Around Reactor System - Experiment 161

Nitrogen Inputs

304.09 g anaerobic sludge @ 0.16 wt% N = 0.49 g
4.67 L nitrogen cover gas = 5.45 g
Total Nitrogen Fed = 5.94 g

Nitrogen Outputs

Approx. 159 g aqueous @ 0.28 wt% N = 0.44 g
7.5 L vent gas @ 62.0 vol% N₂ = 5.43 g
Total Nitrogen Out = 5.87 g

Percent Recovered
 $\frac{\text{Output}}{\text{Input}} = 99\%$

The reactor was then sealed, purged with nitrogen, and pressurized with carbon monoxide to an initial pressure of 50 atm. The reactor was heated to 350°C (average heating rate of 5°C/min) and held at that temperature for 30 min. Even at the low temperatures and in the absence of the nickel catalyst, gas was evolved, as evidenced by an increase in reactor pressure. Typically, the reactor pressure would rise from 270 to approximately 340 atm over the period of the experiment. At the end of the allotted time, cooling water was flushed through the internal cooling coil, which permitted rapid (30°C/min) cooling of the reactor contents down to 200°C within 5 min. No samples were taken from the reactor during these experiments.

After the reactor had cooled to room temperature, the gas product was vented and a sample was analyzed. The typical gas composition included nearly equal parts of hydrogen and carbon dioxide with a 10% to 15% residual

amount of carbon monoxide and minor amounts of hydrocarbons. These results suggest a strong water-gas shift reaction as catalyzed by the sodium carbonate base (Elliott and Sealock 1983). The reactor was then opened and the two-phase liquid product was collected. The reactor was rinsed with acetone and the resulting wash solution filtered. The liquid product (approximately 250 g) was acidified to pH 2 with dilute HCl and then extracted with methylene chloride (3 x 40 mL).

The soluble and insoluble products were analyzed for elemental content of carbon, hydrogen, nitrogen, and oxygen with P-E 240 series instruments. The methylene chloride-soluble oil product was also analyzed as a methylene chloride solution on a GC equipped with a mass selective detector for qualitative analysis and a similar GC equipped with an FID for quantitative analysis. The compounds were identified by comparing mass spectra with library listings of known compounds in conjunction with a comparison of chromatograph column residence time with similar known compounds. Quantitative analysis was based on a known amount of internal standard (transdecahydronaphthalene) with detector response factors determined for various functional group types. Quantification was estimated at within $\pm 20\%$. DB-5 capillary columns were used in both chromatographs.

Results from the liquefaction experiments with five high-moisture biomass feedstocks are given in Table 17. The oil yield is based on the combined mass of acetone- and methylene chloride-soluble oils as a percent of the mass of dried feedstock calculated to an ash-free basis. The product oil elemental analysis is the calculated composite analysis for the combined acetone- and methylene chloride-soluble oils.

The detailed chemical analysis obtained by GC-MS of the five high-moisture-biomass-derived oils helped to define the differences in oil composition. Over 190 different compounds and isomers were identified in the five oils. The components were grouped by chemical functionality to give a clearer picture of this large amount of information. These groups are listed in Table 18.

TABLE 17. Experimental Results for Liquefaction Experiments

Feedstock	Oil Yield, %	Mass Percent Composition				Atomic H/C
		C	H	N	O	
		(combined oil analyses)				
Kelp	19.2	76.7	8.9	3.5	9.9	1.38
Water Hyacinth	26.0	76.3	9.9	3.3	10.5	1.54
Spent Grain	34.7	75.2	10.2	3.8	10.8	1.61
Napier Grass	34.4	74.5	8.5	0.4	16.7	1.36
Sorghum	26.6	75.9	8.7	1.7	13.7	1.36

TABLE 18. Chemical Functional Groups in High-Moisture Biomass Oil Products

Compound Group	Oil Components, mass %				
	Kelp	Water Hyacinth	Spent Grain	Napier Grass	Sorghum
Esters/Aldehydes/ Alcohols	0 (1) ^(a)	0 (0)	0 (1)	3 (4)	0 (0)
Cyclic Ketones	10 (17)	3 (12)	8 (13)	23 (31)	7 (15)
Furans	0 (0)	1 (1)	4 (3)	2 (3)	2 (3)
Phenols	32 (17)	35 (30)	30 (18)	45 (36)	34 (25)
Methoxyphenols	3 (3)	3 (2)	3 (1)	5 (5)	10 (5)
Benzenediols	10 (2)	6 (4)	0 (0)	6 (6)	24 (11)
Naphthols	9 (5)	2 (3)	0 (0)	5 (9)	9 (6)
Aromatic Oxygenates	1 (2)	3 (3)	6 (2)	4 (5)	2 (2)
Cyclic Hydrocarbons	2 (3)	1 (3)	3 (3)	3 (6)	4 (5)
Long-chain Hydrocarbons	6 (3)	15 (15)	5 (4)	3 (9)	4 (4)
Fatty Acids	10 (3)	8 (7)	8 (4)	1 (2)	5 (4)
Nitrogen Cyclics	16 (11)	16 (11)	19 (7)	0 (0)	0 (0)
Amines/Amides	3 (1)	6 (3)	15 (7)	0 (0)	0 (0)
Percent Identified	10.8	18.4	14.3	21.0	18.4

(a) Number of individual compounds and isomers in each compound group.

The groups consisted of the following types of compounds:

Esters/Aldehydes/Alcohols	four- to six-carbon oxygenates
Cyclic Ketones	five- and six-carbon rings, many unsaturated, most alkylated
Furans	dihydrofuranones, hydroxymethyltetrahydrofuran
Phenols	phenol and alkylated (up to five carbons) phenols
Methoxyphenols	mono- and dimethoxyphenols and alkylated forms
Benzenediols	dihydroxybenzenes and alkylated (up to five carbons) forms
Naphthols	naphthols and methylated naphthols
Aromatic Oxygenates	bismethylguaiacol(?), phenylphenols, benzodioxin(?)
Cyclic Hydrocarbons	alkylindans, phenanthrene
Long-chain Hydrocarbons	C ₁₄ to C ₂₇ n-alkanes and olefins
Fatty Acids	C ₁₂ to C ₂₀ saturated and unsaturated acids
Nitrogen Cyclics	alkylpyrrolidinones, alkylaziridines(?), alkylpyrroles, alkylindoles
Amines/Amides	C ₈ to C ₂₂ amines/amides(?)

NOTE: Compounds followed by (?) are only tentatively identified.

These results verify that the carbohydrate structures found in biomass can be converted thermochemically to a mixture of primarily phenolic compounds. Hydrocarbons are not predominant; yet they may survive the processing in a significant yield given an appropriate feedstock.

Cyclic ketones are the other major component group that can be identified by GC-MS. Low molecular weight oxygenates and furans are minimized by the addition of base to the reaction medium, as has been demonstrated previously (Nelson et al. 1984).

A short series of tests were performed to determine the usefulness of iron oxide as an additive for liquefaction of high-moisture biomass. Iron

catalysts are commonly used for Fischer-Tropsch synthesis of liquids. Iron catalyst would be significantly less expensive than nickel and was studied to determine if it would have catalytic activity towards liquid production in the PNL system. Four batch experiments were carried out to investigate this approach both with and without sodium carbonate as a co-catalyst and both with and without carbon monoxide present as an added reducing gas. All of the experiments were performed in the 1-L batch reactor, which was held at 350°C for 20 min. Corn stover was used as the feedstock in all four experiments. Each experiment used approximately 350 g of biomass slurry containing a nominal 10 wt% solids in water. Where used, the sodium carbonate loading was 0.1 g Na equivalent/g dry biomass solids. The iron oxide (Fe_3O_4) was used at a loading of 1.0 g Fe equivalent/g biomass solids. The initial cold gas pressure was approximately 500 psig for each of the tests. Nitrogen was used as a cover gas in the carbon monoxide-free experiment. The results are listed in Table 19.

The oil yield data showed no obvious trends. Although the first three experiments with carbon monoxide appeared to show a 10% drop in oil yield with the elimination of the sodium carbonate, Test IV produced a higher oil yield than Tests I through III. These results are believed to reflect the poor mass recovery in Test I. If the data were normalized to 100 wt% mass recovery, Test I would have the highest oil yield at just under 34 wt%.

TABLE 19. Liquefaction Results with Corn Stover at 350°C for 20 Min

Test No.	Cover Gas	Additive	Oil Yield, wt%	Oxygen Content, wt%	Nitrogen Content, wt%	H/C Ratio, atom basis	Mass Balance, wt%
I	CO	Na_2CO_3	26.3	8.2	3.7	1.37	78
II	CO	$\text{Na}_2\text{CO}_3/\text{Fe}_3\text{O}_4$	25.8	8.9	2.5	1.39	95
III	CO	Fe_3O_4	23.9	8.1	2.0	1.28	92
IV	N_2	Fe_3O_4	31.3	8.5	2.6	1.26	96

The oil yield is based on the total organic material which was acetone- or methylene chloride-soluble. The oil qualities are based on the weight-averaged analyses for the two different fractions.

The quality of the oil produced, as measured by the oxygen content, nitrogen content, and H/C ratio, was quite similar for all experiments, with little difference in oxygen content. The nitrogen content of all four oils was relatively high. There was some indication that the iron oxide can help to reduce the nitrogen content of the oil. The H/C ratio was significantly higher for the products formed in the presence of sodium carbonate. Nonetheless, the relatively low H/C ratios measured for each experiment suggested that the material was highly aromatic.

These tests demonstrated once again the conversion of biomass into substantial yields of an oxygenated aromatic oil. Inorganic additives or reducing gas can have limited effects on the product quality and yield. In this case, with corn stover as a feedstock, the effect of alkali addition likely was masked by the alkali present in the biomass itself. The production of aromatic oil from agricultural wastes can be accomplished despite the relatively low amounts (compared with wood feedstocks) of lignin present. Apparently the alkali-catalyzed conversion of cellulose pyrolysis products to aromatics can be used to produce good yields of oil.

DISCUSSION OF RESULTS

The two principal goals of this project have been to 1) facilitate the direct thermochemical conversion of biomass to a methane-rich gas (or to high-valued liquid fuels at practical yields) and 2) widen the biomass resource base to include new feedstock materials that are readily available and cannot be used efficiently in other thermal or biological conversion processes. To meet these objectives, a wide range of high-moisture biomass feedstocks were analyzed and tested. Various processing parameters, including operating temperature, time at temperature, and the use of catalysts, were also evaluated relative to their importance to the conversion process. A major result of this work in the bench-scale, 1-L batch reactor has been to demonstrate the potential of aqueous catalyzed biomass gasification. This gasification system has been used to convert a wide variety of biomass and biomass-derived feedstocks. Gas yields have been obtained exceeding 6 scf of methane/dry, ash-free (DAF) pound of biomass. Gasification of over 90% of the biomass-derived carbon in the system has been achieved in approximately 15 min at a reaction temperature of 400°C. Further discussion of specific results is given below.

FEEDSTOCK EFFECTS

The results of this study show a wide range of reactivity/convertibility for the various high-moisture biomass feedstocks tested. Of the feedstocks tested, water slurries of cellulose were found to have the fastest rate of reaction. Little loss in rate was observed for cellulose when the reaction temperature was lowered from 400°C to 380°C. The cellulose was converted by the time the slurry had been heated to the planned operating temperature. Typically, about 45 min were required to raise the reactor temperature from ambient to 250°C, which was the temperature where reaction products were first observed. An additional 30 to 45 min were required to reach the final reactor temperature of 380°C to 400°C. Other feedstocks containing high levels of cellulose had similar high rates of reaction/conversion. Sunflower, sorghum, and napier grass were essentially gasified within 15 min after reaching 400°C. It appears that most terrestrial biomass will fall

into the same category with some reduction in reaction rate with the increase in noncellulosic (e.g., lignin) components. This relationship was well developed for wood and wood components in an earlier study (Sealock, Elliott, and Hallen 1982).

A second group of feedstocks can be defined that includes the aquatic biomass (kelp and water hyacinth) and the anaerobic digestion sludge derived from water hyacinth. These materials exhibited a similar fast rate of reaction yet produced a large residual, unconverted component. These feedstocks appeared to finish reacting within 15 min of reaching reaction temperature; yet 20% to 30% of the carbon in the feedstock remained dissolved in the aqueous phase and as residual solids. Neither the source of these unconverted materials nor the specific chemical form of the residual material has been determined.

A third family of feedstocks consisting of processed biomasses exhibited a somewhat different set of reaction properties. This group, represented by the grape pomace and spent grain, reacted at a slower rate than the other feedstocks and therefore required a longer residence time and/or a higher operating temperature. However, unlike the aquatic biomasses, these feedstocks can be completely converted given sufficient time to react. Wood, such as the Douglas fir tested in an earlier program (Sealock, Elliott, and Hallen 1982), probably also falls into this category, although no experiments with a wood flour slurry at high nickel catalyst loading have been conducted for a direct verification. It appears that the processed biomasses react more slowly because they contain less cellulose or other carbohydrates. For most of these materials, this lower cellulose content is a result of prior processing of the feedstock, which includes washing and crushing the feedstock and extracting the soluble sugars. These feedstocks probably consist of complex lignocellulosic materials and proteins, which are apparently less reactive.

The least reactive feedstocks tested were Kraft black liquor, peat, and lignite. Conversion of carbon in the feedstocks ranged from 23% for the black liquor after 45 min at 400°C to over 40% for the peat after only 15 min at 400°C. All three of these materials are deficient in cellulose and

contain more complex aromatic structures. Heteroatom contents, particularly sulfur, are also higher in these materials. Sulfur would likely have a detrimental effect of sulfiding and deactivating the nickel metal catalyst. Other trace elements could adversely affect the catalytic system as well. Only limited tests were performed with these feedstocks as a means of comparison since they do not fall into the category of biomass as defined by DOE. Additional studies regarding the conversion of these feedstocks at higher nickel loadings or with improved, more reactive nickel catalysts could provide better results.

Although the processed biomasses exhibited a lower rate of reaction, their relatively high carbon to oxygen ratio generally resulted in a greater yield of methane. Whereas the terrestrial herbaceous biomasses produced 5.3 to 5.5 scf methane/dry lb of feed, the processed biomasses produced nearly 7 scf of methane/dry lb. The larger yield of methane can be traced directly to the higher level of carbon content in the feedstock (approximately 50% for the processed biomasses compared with 40% to 45% for the herbaceous biomasses).

The effect of trace elements in the high-moisture biomass feedstocks has been a subject of limited investigation. Unlike earlier studies, which were performed with relatively clean feedstocks such as wood flour and cellulose (Sealock, Elliott, and Hallen 1982), these tests were made with whole crude biomass feedstocks. Many of the biomass materials tested in this project contained substantial amounts of ash-forming trace minerals. For example, kelp and sunflowers contained alkali metals and alkaline earths in sufficient concentration to be equivalent to the amount of sodium carbonate added as catalyst in many of the earlier experiments. Other feedstocks, such as the napier grass, sorghum, corn stover, hyacinth, and grape pomace, have alkali levels about 1 order of magnitude lower than the standard sodium carbonate catalyst concentration used. This lower level of alkali is still equivalent to 0.03 to 0.07 g carbonate equivalent/g biomass (3 to 7 mass%). Catalytic effects are expected to be important at this concentration range.

Other trace elements that could have adverse effects on the nickel catalyst have not yet been investigated. Sulfur is the primary candidate for

nickel deactivation. Sulfur is viewed as the main factor in the limited activity of the black liquor feedstock. On the other hand, spent grain appears to be a particularly appropriate feedstock because of its low sulfur content. The other high-moisture biomass feedstocks contained 0.1 to 0.2 mass% of sulfur, and the long-term effect of operation with these feedstocks on the nickel catalysts must be tested. Chlorine, iron, and phosphorus are other common elements that could lead to catalyst deactivation. Depending on future feedstock selection, these elements may require further study as to their long-term effects on the nickel catalyst.

PROCESS KINETICS AND THE ROLE OF CATALYST IN THE SYSTEM

The 1-L batch reactor used in these experiments proved to be a useful tool in obtaining relative reactivity data and in demonstrating the overall high yields of methane that could be obtained via low-temperature catalytic conversion of biomass. The system had serious shortcoming, however, with respect to collecting process rate data. The large thermal inertia of the reactor vessel itself resulted in experiments in which the collection of isothermal rate data was impossible. Feedstock transformation began at temperatures as low as 250°C, although gas formation did not begin at temperatures much below 300°C. Relatively reactive feedstocks such as cellulose were almost completely converted by the time the reactor contents reached 380°C.

In the absence of useful rate data, several observations were made regarding the relative rates and supposed mechanisms for the low-temperature conversion process. Most of these observations are qualitative but do provide insight into the process.

Mechanism

The conversion of high-moisture biomass feedstocks (or any biomass feedstocks) is a complex, multi-step process. Because biomass is composed of a heterogeneous mixture of biopolymers and other less important constituents, a number of reaction pathways occur simultaneously. Many of these pathways eventually converge in the production of product gas. Figure 18 illustrates some of the reaction steps thought to occur in the high-moisture biomass

FIGURE 18. Role of Catalysts in the High-Moisture Gasification System

system. As in most reaction schemes proposed for biomass gasification, there is a pyrolysis/volatilization step, a gasification step, secondary gas reactions, and a char production step. Just as in conventional high-temperature gasification, the net result of these pathways is the production of methane and carbon dioxide gas, as well as hydrogen, ethane, carbon monoxide, and liquid and solid residual products. The major difference is simply the effect of the catalyst(s) and the high water to carbon ratio on the relative importance of individual steps (and hence, the final product composition).

Figure 18 indicates the supposed roles of the two co-catalysts (alkali and nickel) in the system. This model supports the observation that adding alkali to the system resulted in generally higher carbon conversion, albeit

at substantially reduced methane yields. The role of alkali in promoting gasification reactions and inhibiting coke formation has been well documented within the biomass and coal literature (Taylor and Neville 1921; Willson et al. 1974; Mudge, Sealock, and Weber 1979; Elliott, Hallen, and Sealock 1984). A less well-known role for solutions of alkali carbonates, but probably a more important one in this case, is the catalysis of the water-gas shift reaction by these salts (Elliott, Hallen, and Sealock 1983). As illustrated in Figure 18, this catalysis shifts the balance between competing reactions, resulting in a product gas distribution that is higher in hydrogen and carbon dioxide and substantially lower in methane.

The role of the nickel catalyst under conditions similar to those encountered in the high-moisture biomass reactor is somewhat less clear. However, the nickel catalyst has at least two possible mechanistic roles in the system, both involving the production of methane. The first is direct catalytic methanation of gas phase carbon monoxide and carbon dioxide, which is produced in the steam gasification of the biomass. These reactions:

have relatively well-understood kinetics and are reported extensively in the literature, although kinetic studies of these systems do not appear to have been extended to the process conditions present in the high-moisture biomass reactor. In general, these reactions are promoted by the same types of nickel catalysts used in the PNL system, and the rate of Reaction (1) is significantly greater than the rate of Reaction (2).

There is some qualitative evidence that these reactions do occur in the high-moisture system. In several experimental runs, gas samples taken over a period of 45 min to 1 h show a shift in gas composition at relatively constant levels of apparent carbon conversion to gas. These shifts in gas composition are almost invariably in the direction of methane, generally with a corresponding depletion of carbon dioxide and hydrogen. The absence of

significant quantities of carbon monoxide in the product gas (except in non-catalyzed experiments) could be an indication of the high rate of the carbon monoxide methanation reaction, relative to the rate of carbon monoxide production in the system.

The second proposed role of the nickel catalyst is not as clear cut, but seems to explain some aspects of the system's behavior. There is some qualitative experimental evidence that the catalytic mechanism is analogous to steam-reforming catalysts in the steam cracking and reforming of naphthas and other higher hydrocarbons. While steam reforming is commonly thought of as a means of producing synthesis gas from methane or higher hydrocarbons such as naphtha, steam reforming of hydrocarbons at low temperature (under 600°C) and high pressure favors the production of methane (Rostrup-Nielsen 1984). There is also evidence that, under proper conditions, methane production occurs by direct scission of the hydrocarbon chain on the surface of the steam-reforming catalyst, rather than by gasification to carbon oxides followed by subsequent methanation of carbon monoxide (Baker and Sealock 1988a,b). The hydrocarbons being cracked in the high-moisture biomass system are low-temperature pyrolytic tars and hydrolyzates formed during the heatup of the biomass. These materials are produced at temperatures between 250°C and 350°C. These tars are typically fragments of the storage and structural biopolymers such as cellulose and lignin and can exhibit a remarkable complexity in terms of numbers and types of components (Elliott 1985).

Assuming the model proposed here is valid (i.e., that the major gasification process for high-moisture biomass can be thought of as a two-step process consisting of low-temperature liquefaction of the biomass followed by catalyzed steam reforming of the pyrolysis tars), the following hypotheses regarding the system under study are suggested:

1. Addition of alkali in the two-catalyst system should promote gasification and lengthen nickel catalyst lifetime by inhibiting carbon formation, but may reduce methane yield by reducing the activity of the reforming catalyst. This latter effect may be masked by the documented role of alkali materials in increasing the rate of the competing water-gas shift reaction.

2. Highly aromatic compounds generally exhibit poorer reforming performance than saturated hydrocarbons. The implication for biomass gasification is that high-lignin feedstocks should exhibit slower reaction rates (at similar carbon/catalyst ratios) than noncyclic precursors such as cellulose, starches, and other carbohydrates.
3. The influence of alkali on reforming catalyst activity may be expected to exhibit complex behavior as a function of temperature. Reaction order with respect to steam (water) concentration may also be expected to exhibit complex behavior with respect to temperature and alkali concentration. These two factors have been identified as influencing the adsorption of water on the catalytic surface.
4. Potassium salts can be expected to have a greater inhibiting effect on methane production than sodium salts.

In light of experimental results, Hypothesis 1 is partially verified (the inability to perform long-duration experiments prevented meaningful studies of catalyst lifetime). Methane yield is reduced by the addition of alkali, and carbon conversion in the alkali-catalyzed experiments did tend to be somewhat higher than for comparable runs using just the nickel. However, as discussed earlier, the alternative explanations for these observations can be made. Hypothesis 2 appears to be substantiated both by the relative reactivities of various feedstocks (high-lignin feedstocks appeared to be slower to react) and by studies using organic model compounds (Baker and Sealock 1988a,b). Hypotheses 3 and 4 were not explicitly tested.

Catalyst Contacting

Another major factor affecting the process kinetics is the extent of catalyst contact with the biomass and biomass products. The dramatic catalyst concentration effect observed in this project highlighted the importance of good catalyst contacting. Even at the highest nickel concentrations, catalyst contacting may still be the limiting rate factor. Efficient engineering of the catalyst bed is required for process scaleup and was a major consideration in the development of the CRS.

The detailed study of the process kinetics is a major thrust for future research in the CRS. Construction of the system has just been completed. Design and operating objectives are discussed in the Future Work section of this report. Further testing of the steam-reforming model will be implicit in this testing. The application of this analogy could prove to be useful in directing future research efforts and in optimizing the process since there is a relative abundance of literature and substantial industry experience with the steam-reforming process.

GAS PRODUCT COMPOSITION

Although earlier reports suggested that good methane yields (25% to 30% by volume in the product gas composition) could be obtained by catalytic gasification of biomass water slurries (Sealock, Elliott, and Hallen 1982), the results shown here are the first to demonstrate efficient conversion of biomass solids to methane in a single step process. Gas compositions having methane concentrations of over 50 vol% have been achieved with spent grain, and results with model compounds have produced methane concentrations as high as 73 vol% (Baker and Sealock 1988a,b). Carbon monoxide is reduced to trace levels (<0.01 vol%) apparently through catalytic reaction with hydrogen to produce methane and via the water-gas shift reaction to produce hydrogen and carbon dioxide. The hydrogen content of the product gas is generally less than 5 vol%.

Ethane is present in nearly all of the product gases at a concentration of approximately 1 to 2 vol%, and minor amounts (<1 vol%) of higher hydrocarbons are also found in the product gas produced with some feedstocks. These products also contribute to the high calorific content of the gas. The balance of the product gas is carbon dioxide, which serves as the oxygen carrier after the oxygen is removed from the biomass structure. A number of commercial processes exist for the removal of carbon dioxide from the product gas, including some that permit operation at 1000 to 1500 psi. The carbon dioxide could be easily separated from the product gas if a high-Btu (pipeline quality) gas is desired. Otherwise, the carbon dioxide could be left in the product gas, which would result in a medium-Btu gas with a heating value of about 450 to 550 Btu/scf.

In contrast to the gas obtained from more conventional, high-temperature biomass and coal gasifiers, the high-moisture gasifier produces a very high Btu fuel gas (see Figure 19) with significant advantages for some applications. The high Btu content of the gas should permit its use in natural gas boilers without modification or significant derating of the burners. The high degree of methanation and ability to produce a product gas at pressures significantly above pipeline pressures is an advantage in the production of synthetic natural gas.

LIQUEFACTION TESTS

The liquefaction test results demonstrated oil product yields for high-moisture biomass feedstocks at levels comparable to those obtained from wood. Reported yields for wood liquefaction in aqueous slurries, such as those obtained in the Lawrence Berkeley Laboratory process (Figueroa, Schaleger, and Davis 1982), have typically been in the 25 to 30 wt% range. The quality of liquefaction products produced from high-moisture biomass is similar to those reported for wood liquefaction products. However, certain samples of high-moisture biomass product oils appear to have elemental compositions suggesting higher-quality products. Especially interesting are oils from spent grain and water hyacinth, which have high hydrogen to carbon ratios, and oil products from spent grain, water hyacinth, and kelp, which have relatively low oxygen contents. Oils from spent grain and aquatic biomasses (which contain a large amount of nitrogen) had significantly higher nitrogen contents than wood-derived oils.

The product compositions of the napier grass and sorghum-derived product oils have many similarities to wood-derived oils. When comparing these oils with high-pressure processed oils from Douglas fir, the same groups of cyclic ketones, phenols, naphthols, and dihydroxybenzenes dominate. The trace amounts of true hydrocarbon in the sorghum and napier grass oils are significantly different from the Douglas fir oils and are apparently feedstock-related. Nitrogen-containing compounds were not found in either the Douglas fir oils or the sorghum or napier grass oils produced in the PNL system.

FIGURE 19. Effect of Gasification Conditions on Product Quality

The large fraction of nitrogen-containing cyclic compounds is a distinguishing factor among the hyacinth, kelp, and grain oils when compared with earlier analyses of wood oil. Similar compounds were found in peat and sewage sludge oils (Russell, Molton, and Landsman 1980). Our results now extend this trend to high-protein feedstocks and green aquatic plants. It is obvious that a strong correlation exists between nitrogen content of the feedstock and the amount of nitrogen incorporated into the product oil. High-pressure liquefaction, even with a reducing gas environment and alkaline catalysis, cannot effect a preferential denitrogenation reaction. Substantial amounts of nitrogen are condensed into cyclic systems and remain in the oil product.

The oil products from these high-moisture biomasses have properties similar to the more widely studied wood-derived oils. The numerous applications of wood-derived oils have been discussed by others (Elliott 1981; Nelson et al. 1984). The high-moisture biomass oils should be amenable to the same types of applications. In addition, the nitrogen-containing components may be useful as high-value specialty chemicals if effective separation and recovery processes can be developed. Indoles in particular may be recoverable for use as fragrances or flavors. Furthermore, the hydrocarbon component may facilitate the direct use of these oils as fuels.

The nitrogen-containing components in some of the high-moisture biomass oils is a concern when considering their use as fuels. Direct utilization of these oils would certainly lead to higher levels of NO_x emission. The nitrogen-containing components have also been indicated as a source of fuel instability during storage and as cancer-causing agents. Hydrotreating these oil products to remove the nitrogen is a possible means of upgrading the products. However, hydrodenitrogenation of the heterocyclic compounds is a difficult and costly procedure compared with hydrodeoxygenation of the phenolics (which would also be accomplished in a hydrotreating type of oil upgrading).

SYSTEM MODELING

As might be expected from thermodynamic considerations, methane yields from the low-temperature gasification of biomass are considerably higher than those obtained from conventional thermochemical gasification processes operating at much higher temperatures. Although prediction of reaction equilibrium in the system is complicated by the nature of the feedstocks and the extreme conditions of pressure, a comparison of the results from the gasification of brewer's spent grain at 400°C with the results of an ASPEN-PLUSTM(a) simulation of o-cresol gasification at the same conditions shows surprising similarities (Table 20).

The results of this simulation, while only approximate, indicate the relatively close approach to equilibrium achieved in the reactor. The effect of temperature, pressure, and choice of model compound are all areas of interest for future simulations. The close approach to equilibrium (and the relative lack of liquid products observed during this experiment) indicates that the catalysis of the reactions is quite effective.

COMPARISON WITH ANAEROBIC DIGESTION

The high-moisture gasification system being developed in this project invites comparison with anaerobic digestion as a means of producing methane from biomass. Furthermore, the high-moisture gasification system can serve as an add-on to anaerobic digestion processes to convert the unreacted materials remaining after biochemical conversion of lignin-containing feedstocks. The systems are similar in that both the feedstocks employed and the products produced are analogous. While the actual mechanism for producing the methane is very different for each process, the processes may be thought of as filling the same technological niche with regard to potential application. This section presents a brief comparison of the two approaches.

The methane yields from some high-moisture feedstocks were derived from published data and compared with yields obtained using comparable feedstocks

(a) Aspen Technology, Inc., Cambridge, Massachusetts.

TABLE 20. Comparison of Estimated Equilibrium Gas Composition with Experimental Data^(a)

Gas	Experimental, mol %	Estimated, mol %
CO	<0.1	0.02
CO ₂	40.1	39.1
CH ₄	52.5	59.7
H ₂	4.7	1.2
C ₂ 's	0.8	trace

(a) Normalized to dry gas basis.

in the high-moisture gasification system. These comparisons are shown in Table 21. As shown in the table, this system was able to produce yields of methane that are comparable or superior to the reported methane yields from anaerobic digestion. Furthermore, the cold gas efficiency^(a) of the process is higher than anaerobic digestion, since there is an additional energy contribution to the product gas from the hydrogen, ethane, and carbon monoxide that are present in the high-moisture product gas. These gases are present in quantities sufficient to raise the energy content of the product gas by 30 to 50 Btu/scf, or about 6% to 14% above the energy yield obtained from methane only. Thus, assuming a comparable methane yield from kelp of 2.1 scf/dry lb, high-moisture gasification would yield approximately 10% more energy in the product gas, the difference being accounted for by the production of hydrogen and ethane. The comparison for water hyacinth is even more dramatic; the high-moisture gasification system has a cold gas efficiency of approximately 71%, while the anaerobic digestion process has a cold gas efficiency of just 45.4%.

From an engineering standpoint, the major differences between high-moisture biomass gasification and anaerobic digestion are gas production rate, gas yield, and process stability. Table 22 lists some qualitative comparisons.

(a) Cold gas efficiency = (energy value of product)/(energy value of feedstock).

TABLE 21. Methane Yield Comparisons

<u>Feedstock</u>	<u>Anaerobic Digestion Methane Yield</u>	<u>High-Moisture Gasification Methane Yield</u>
Water Hyacinth	1.6-2.9 scf/lb TS	4.1 scf/lb TS
Macrocystis Kelp	1.8-2.9 scf/lb TS	2.1 scf/lb TS
Sorghum	≈4.5 scf/lb TS	5.2 scf/lb TS

TS = total solids.

The parameters compared in Table 22 are particularly important in determining the process economics and flexibility and the degree of technical and economic risk involved in commercialization. Gas production rate, for example, is primarily an engineering concern, as it affects the sizing, design, and capital cost of reactors and related equipment in the process. In general, the higher the production rate, the smaller the reactor. In this case, cost comparisons between reactors are complicated by the relatively high degree of complexity required of the high-moisture biomass reactor to operate at required pressure and temperature in comparison to the near-ambient conditions found in the anaerobic digester. Process yield is directly related to the operating economics of the process and can have a significant impact on the capital costs of the plant, as well. Poor process stability can dramatically and adversely impact the flow of operating costs/revenues from an energy-producing facility and can also determine the degree of technical and financial risk involved in the process.

The two processes have often been presented as competing technologies; however, a collaborative paper (Butner et al. 1988) prepared by PNL and Dr. D. P. Chynoweth (University of Florida) showed that the technologies can also be complementary. The paper discussed the use of the PNL high-moisture gasifier concept to gasify the unconverted effluent from an anaerobic digester. The integration of thermochemical and biochemical conversion concepts is the subject of an earlier patent (not incorporating the PNL high-moisture gasification concept) issued to the Institute for Gas Technology (IGT), who used the term "BIOTHERMGAS" to describe the concept. Dr. Chynoweth is a co-inventor listed on the patent.

TABLE 22. Comparison of Engineering Aspects of High-Moisture Gasification and Anaerobic Digestion

<u>Feature</u>	<u>High-Moisture Gasification</u>	<u>Anaerobic Digestion</u>
Typical Gas Production Rate (average)	8 vol CH ₄ vol reactor · h	0.03 vol CH ₄ vol reactor · h
Process Flexibility	Process can convert high-lignin, noncellulosic feedstocks.	Process cannot efficiently convert lignin-rich feedstocks.
Gas Yield	Varies somewhat with feedstock; somewhat affected by cellulose and lignin content of feed.	Varies with feedstock; directly related to cellulose and lignin content of feedstock.
Reactor Requirements	Relatively small reactors high cost per volume.	Large reactors with low cost per volume.
Process Stability	Process appears to be relatively insensitive to feedstock variations and is insensitive to biological contamination of the feedstock.	Process may be sensitive to feedstock variations and can be poisoned by introduction of chemical and/or biological contaminants.
Process Dynamics	Process can respond rapidly to changes in load requirements.	Process is slow to respond to load changes.

As an experimental basis for the joint paper, several samples of digester effluent were collected by Dr. Chynoweth and his students from a large digester being used to convert a mixture of water hyacinth and sewage sludge to methane. The samples were withdrawn after residence times of 7 to 14 days, and contained between 1 and 7 wt% solids. These samples were processed in the high-moisture batch reactor, and yields were extracted from the data. The yields were then used to establish a material and energy balance around a conceptual hybrid process operating at an arbitrary mass throughput of feedstock. The model was used to study the effect of selected process parameters (reactor yields, etc.) on the overall process yield and process thermodynamic efficiency.

A major conclusion of the paper (which was based on ASPEN simulation of the conceptual hybrid process, using experimental yield data) was that the high-moisture gasification system appeared to achieve net energy production at relatively low solids content (typically about 2 wt% solids); a second conclusion was that the overall efficiency of the bio/thermal process was greater than the efficiency of either process individually. The high methane selectivity of anaerobic digestion and the high gas yields of high-moisture gasification appear to be complementary. Further explorations in this direction are anticipated.

A major conclusion of the paper, which was based on ASLV results of the combined kinetic process, using experimental data, was that the thermodynamic gasification system appeared to achieve net energy production at relatively low solids content (typically about 2 wt. solids) a second conclusion was that the overall efficiency of the bio-chemical process was greater than the efficiency of either process individually. The high methane selectivity of anaerobic digestion and the high gas yield of high temperature gasification appear to be complementary. Further exploration in this direction are anticipated.

TECHNOLOGY TRANSFER AND RELATIONSHIP TO OTHER PROJECTS

Pacific Northwest Laboratory manages a technology transfer program to help U.S. industry implement the results of government and privately funded studies. As part of this program, the results of high-moisture biomass gasification research and other spinoff applications of the technology are being transferred to industry to assist in solving technical problems and to help meet future energy needs.

PATENT STATUS AND TECHNOLOGY TRANSFER

A patent is pending on the high-moisture gasification process that was developed under a basic research project sponsored by the Gas Research Institute (GRI). Battelle Development Corporation (BDC) has purchased from GRI all of GRI's right, title, and interest in the invention and patents. Royalties will be shared between GRI and BDC if the process is commercialized.

Through PNL, BDC has subsequently entered a licensing agreement with Onsite*Offsite, Inc., located in Pasadena, California. Onsite*Offsite, a turnkey engineering and construction management firm, has been granted the rights to license the process for the gasification of biomass and several types of waste materials, including food processing wastes. Onsite*Offsite is aiding PNL in transferring this and related technology to industry. Several additional patent applications were filed during the first half of 1988 to establish ownership of the technology in the biomass, food processing, water cleanup, and hazardous waste destruction fields. Onsite*Offsite will be actively marketing the technology in these fields, and industrial support for the development of various applications of the technology is likely. This notable industrial interest increases the potential for cost sharing of larger-scale systems. Several major companies have expressed interest in the technology (mainly as an energy production/waste disposal technology).

As part of their effort, Onsite*Offsite has (at their own expense) prepared preliminary designs and models for a 5-wet-ton/day transportable unit and for a 1.25-wet-ton/day skid-mounted process development unit for

potential location at the PNL Chemical Engineering Laboratory. A model of the mobile unit designed for gasification of food processing and other waste materials is shown in Figure 20.

RELATIONSHIP TO OTHER PROJECTS

The process chemistry, developed from ongoing biomass gasification research in this study, serves as a basis for current and future projects. Three main research areas of interest are biomass gasification, gasification of industrial and food processing wastes, and catalytic destruction of hazardous organics in aqueous streams. Projects in each of these fields will be carried out in FY 1988 under DOE and industrial sponsorship.

The PNL Northwest Hazardous Waste Research, Development, and Demonstration Center (sponsored by DOE and EPA) is providing funds for continuing the batch reactor tests and for initial tests with hazardous organics in the high-moisture biomass CRS in FY 1988. These tests are based on the positive results of the proof-of-principle tests conducted in the batch reactor in FY 1987 (Baker and Sealock 1988a,b), which have led to a continuation-in-part patent application. The Center will also provide cost sharing for constructing and operating a larger-scale system.

Additional funding in the food processing area is expected in FY 1988. The DOE Waste Energy Reduction Division of the Office of Industrial Programs will sponsor initial tests in the CRS with food processing waste (feedstock outside the high-moisture biomass scope as defined by DOE). Industry-funded research in this area is also anticipated. Continued effort will be expended in obtaining joint government and private funds to build a scaleup unit that can be used to provide the technical and economic information required to build a commercial system.

EVALUATION OF PROCESS ECONOMICS

This part of the project did not include a detailed analysis of the process economics. Since the analysis would be based only on the batch experiments, it would be subject to changes as the process develops. A preliminary analysis was undertaken previously by Mittelhauser for GRI

FIGURE 20. Model of Mobile Pilot Facility

(Pack, Desrosiers, and Kamali 1985). Large contingencies were required because of uncertainties related to process kinetics, reactor design, catalyst lifetime, and biomass feeding systems. We plan a detailed economic analysis following operation of the CRS that will incorporate more definitive information on feeding systems, catalyst lifetime, and process kinetics.

FIGURE 30. Money on mobile bill of exchange

FUTURE RESEARCH IN HIGH-MOISTURE BIOMASS GASIFICATION

Future efforts in this project will center on the operation of the CRS. The specific objective will be to obtain the information required to further develop the concept and to provide the continuous processing data required to scale up the system. Development of additional governmental and industrial support to assist in the scaleup of the system and in transferring the technology to the private sector will also be an important aspect of future work.

HIGH-MOISTURE BIOMASS CONTINUOUS REACTOR SYSTEM

The design and construction of the CRS has been completed. The operation of the CRS is seen as an important step in demonstrating the technical viability of the high-moisture biomass gasification concept. While the batch system has proven its utility as a cost-effective means of screening potential feedstocks and demonstrating the basic concept of high-moisture biomass gasification, the closed-system nature of the equipment places serious constraints on its flexibility. The CRS was designed to overcome these constraints and to supplement the data already collected from the batch reactor system. The continuous system will permit valuable engineering information to be collected, including isothermal rate data and catalyst effectiveness over extended periods of time. Parametric studies will also be conducted to determine the effect of temperature, pressure, and water to biomass ratio on the conversion of biomass and the yield of methane. A list of future activities considered important is presented below.

- Obtain accurate rate data and determine residence time effects. These data are important for determining reactor size requirements and reactor optimization, and for understanding the basic chemistry of the reactor system.
- Determine catalyst lifetime and deactivation rates. In a catalytic reactor, catalyst lifetime can exert a major force on process economics. One of the perceived advantages of the aqueous system is the long catalyst lifetime expected to result from a reactor

environment unfavorable to coking. The continuous system is the only practical means of testing this assumption.

- Collect data to model the effect of pressure on reaction rate and product distribution. In the batch system, reactor pressure was not easily changed during an experiment. Since it is believed that the system could operate under a broader pressure range than has been investigated to date, it is important to conduct these experiments. Of particular importance is the ability to operate under lower than usual pressures, since the successful operation at lower pressure would have favorable impact on process economics.
- Demonstrate the viability of using thermal pretreatment of the biomass to facilitate pumping of the slurry. Preliminary experiments indicate that thermal pretreatment (several minutes at 200°C to 300°C) of the biomass could effectively change the physical and chemical structure of the biomass to facilitate pumping of coarsely chopped slurry. This concept needs to be investigated because it could greatly facilitate the eventual scaleup of a process built on the high-moisture gasification concept.
- Study the effect of biomass solids concentration. This effort has not been practical in the batch system, but is appropriate for study in the continuous system. The range of solids used will depend primarily on whether or not the feed particle can be reduced and/or on the effectiveness of the thermal pretreatment.

DESIGN OF THE CONTINUOUS REACTOR SYSTEM

The design of the CRS was planned to take each of the experimental needs into account and to provide maximum experimental flexibility. The system was sized to fit existing equipment and to match existing and/or available equipment with expected flow and residence time parameters. The design parameters are listed in Table 23. The system configuration was also designed to make optimum use of available technology for computerized data acquisition and process control, thereby allowing more and higher-quality data to be collected.

TABLE 23. Design Parameters for the Continuous Reactor System

Temperature	300°C to 420°C
Pressure	1200 to 6500 psia
Reactor Type	Carberry-type back-mixed reactor
Residence Time	<5 to 60 min
Throughput	0.25 to 5 L/h slurry

The CRS has been fully fabricated and is undergoing preliminary testing. A schematic diagram of the finished system is shown in Figure 21. The implementation of key system functions is discussed below.

CONTINUOUS REACTOR SUB-SYSTEMS

The following sections provide a detailed description of the CRS to be used as the experimental system for future research.

Feed Preparation and Handling

The primary concern with the feed preparation system is the size reduction of the feedstock slurry to a point where it can be pumped in the positive displacement pump selected for the system. Thus, to a large degree, the selection of size reduction equipment is driven by the requirements of the pumping system. For this system, fairly stringent size reduction requirements exist due to the high precision and small scale of the equipment employed. Requirements for larger systems are expected to be somewhat less demanding since the larger equipment will have higher tolerances and larger orifices on key components such as check valves.

To simplify the feed preparation process, it is being carried out in a batch mode, using a 2-gal batch, stirred ball mill manufactured by Union-Process Company. This device uses specially cut stainless steel grinding pellets to produce fine pulps from fibrous materials. A 2-hp electric motor is used to drive a stirrer.

1. Feed Tank
2. Milton-Roy Pump
3. 400 W Preheater Loop
4. 1 Liter Carberry Autoclave
5. Primary Condenser
6. Badger Pressure Letdown Valve
7. Condensation Pot
8. Differential Pressure Transmitter
9. Badger Level Control Valve
10. Liquid Collection Tank on Lead Cell
11. Secondary Condenser
12. Omega Gas Flow Meter
13. Foxboro 931C Process Gas Chromatograph

FIGURE 21. Schematic of Continuous Reactor System

Following this initial size reduction step, a second size reduction step is likely to be required for some feedstocks. Initial tests have indicated that the autohydrolysis of biomass slurries at 250°C for short periods of time (less than 5 min) is adequate to produce a pumpable slurry from sorghum, a fibrous material.

Pumping and Flow Control

Feedstock pumping is being carried out by a Milton-Roy packed plunger style pump, with a design rating of 4 L/h at 7500 psig. As with all reciprocating positive displacement pumps, this equipment employs check valves on the pump inlet and outlet. These valves are prone to plugging and leaking in slurry applications, which places severe demands on the feed preparation operations. The pump has been successfully tested with water, microcrystalline cellulose slurries, and hydrolyzed sorghum slurries. The signal from a flow sensor will be used to control the pumping rate by adjusting the stroke length of the Milton-Roy pump. The type of flow sensor to be used has not yet been determined.

Reactor

The primary requirement of the reactor vessel (besides the mechanical integrity to withstand the reaction conditions) is to provide adequate mixing to approximate a CSTR. The use of the CSTR model is important for simplifying the collection of meaningful rate data from this complex system. The reactor selected is a 1-L Carberry-type reactor, manufactured by Autoclave Engineers. This reactor is similar in design to the better-known Berty reactor. Both reactors employ a basket containing the catalyst, which is located in the center of a well-mixed cylindrical vessel. In the Carberry reactor, the basket itself provides most of the agitation by spinning on an axially aligned shaft. Propeller-type impellers both above and below the basket provide additional agitation. The feed to the reactor is introduced in the bottom of the vessel, with the outlet located at the reactor top.

The selection of the Carberry-type reactor was based on a number of factors. The primary consideration was the relative simplicity of data analysis from stirred-tank reactors. Almost as important was the virtual elimination of temperature and concentration gradients in this type of

reactor (Mahoney, Robinson, and Myers 1978). The elimination of these gradients is a critical requirement in obtaining rate data that can be reliably scaled to commercial-scale equipment, since transfer effects are decoupled from intrinsic surface rate data. The rate data can then be corrected for transfer effects on the basis of well-documented correlations derived for the specific flow regimes expected in the commercial-scale reactor.

Reaction Product Recovery

Immediately upon leaving the reactor vessel, the hot product gases pass through a water-jacketed section of tubing which acts as a quench (see Figure 21). The gases are then let down in pressure to the condenser pressure. The condenser is designed to operate over a range of pressures from 5 to 250 psig. The pressure is let down in a single stage across the orifice of a Badger Meter research control valve, which is driven by a pressure controller that monitors the reactor pressure.

The cooled, low-pressure gas stream enters the condenser, where the water vapor condenses out and collects in a receiver located below the condenser. A vapor trap located between the condenser and the collection pot prevents the collection pot from contributing substantial amounts of "dead volume" to the gas sampling system. A tap located at the bottom of this vapor trap also allows small samples (~4 mL) of condensate to be collected, again with relatively little dead volume in the sample line.

The product gas leaves the condenser at room temperature, passes through a filter to trap any entrained liquid water, and through an Omega thermal mass flow meter, which determines the total mass flow of gas through the system. A slipstream of the product gas is then sent to the Foxboro process GC for analysis. The remainder of the gas is vented.

The liquid effluent from the system is collected in an 8-L tank located on an electronic scale. The liquid is collected for later analysis and is critical in the closure of the material balance around the system.

Instrumentation and Control

Instrumentation and control of the CRS is considerably more complex than is required by the batch system because of additional variables to be controlled and the increased amount of data to be collected. Computerized data acquisition systems are used to compensate for this greater complexity. Nearly all of the process data (including pressure, flow rate, temperature, and gas analysis) can be monitored and logged with a personal computer-based system.

The pitfalls of a completely computerized process are avoided by a "distributed control" built into the system. Each process control loop (preheater temperature, reactor temperature and pressure, and condenser liquid level) is controlled by its own dedicated process loop controller. Each of these controllers communicates with the computer. The computer logs the process data from the controllers along with the rest of the process data.

Product Analysis

Product analysis is used to determine material balances and conversion rates around the reactor system. Two types of streams are expected to be produced in the reactor: a liquid stream (which may contain some entrained solids) and a gaseous stream. The gaseous stream principally will be composed of CO₂, CH₄, H₂, and C₂ compounds, as well as water vapor. The gas composition is determined using a Foxboro 931C process GC, which can measure these gas concentrations with reasonable accuracy and precision in a short time (<5 min). This rapid turnaround is important to establishing steady-state operation during relatively limited duration experiments (most experiments will not last longer than 5 to 6 h).

Liquid analysis will be made by the same methods employed during batch experiments, which include wet lab and chromatographic methods. This analysis will be made on a batch basis, since the amount of carbon-containing material leaving in the liquid stream is relatively small. Small samples (≈4 mL) will be collected during steady-state operations for determining the COD and TOC of the reactor effluent.

The design of the CRS was established by the type of data it is expected to produce. Consequently, it is expected that high-quality rate data will be obtained. The results of the initial tests will be presented at technical meetings and in the literature.

RELATED PUBLICATIONS

This document is the first formal report for the DOE-funded project, "Low-Temperature Thermochemical Conversion of High-Moisture Biomass Feedstocks to High-Valued Fuels." An ongoing record of monthly and quarterly technical progress reports has been submitted to the Technical Field Office for Biomass Thermochemical Conversion and to the Program Manager for Thermochemical Conversion in the Biofuels and Municipal Waste Technology Division at DOE Headquarters in Washington, D.C. In addition, papers have been submitted to the periodic Proceedings of the Biomass Thermochemical Conversion Contractors' Meeting. Numerous other journal articles, symposium proceedings, papers, and presentations have been prepared as part of this project. These documents are listed below in order of publication.

Sealock, L. J., Jr., and D. C. Elliott. 1984. "Thermochemical Gasification of High-Moisture Biomass Feedstocks." In Proceedings of the 16th Biomass Thermochemical Conversion Contractors' Meeting, pp. 161-176. CONF-8405157, National Technical Information Service, Springfield, Virginia.

Elliott, D. C., R. T. Hallen, and L. J. Sealock, Jr. 1984. "Alkali Catalysis in Biomass Gasification." Jour. Anal. Appl. Pyrol. 6(3):299-316.

Elliott, D. C., and L. J. Sealock, Jr. 1984. "Low-Temperature Gasification of High-Moisture Biomass." Presented at the Amer. Chem. Soc. Natl. Meeting, Carbohydrate Division, August 25-31, 1984, Philadelphia. CARB-0064, abstract only.

Butner, R. S., L. J. Sealock, Jr., and D. C. Elliott. 1984. "Expanding the Biomass Resource Base Through the Thermochemical Gasification of High-Moisture Biomass Feedstocks." Presented at the National Meeting on Biomass R&D for Energy Applications, October 1-3, 1984, Arlington, Virginia.

Butner, R. S., L. J. Sealock, Jr., and D. C. Elliott. 1985. "Development of Water-Slurry Gasification System for High-Moisture Biomass." In Energy from Biomass and Wastes IX, ed. D. L. Klass, pp. 523-540. Institute for Gas Technology, Chicago.

Butner, R. S., L. J. Sealock, Jr., and D. C. Elliott. 1985. "Development of Water-Slurry Gasification System for High-Moisture Biomass." Biotech. and Bioeng., Symp. No. 15, ed. C. D. Scott, pp. 3-16. John Wiley and Sons, New York.

Butner, R. S., L. J. Sealock, Jr., and D. C. Elliott. 1985. "Thermochemical Gasification of High-Moisture Biomass Feedstocks." In Alternative Energy in the Midwest Research and Applications: Conference Proceedings, Volume II, pp. 9.33-9.40. Illinois Dept. Energy and Nat. Resources, Springfield, Illinois.

Butner, R. S., D. C. Elliott, and L. J. Sealock, Jr. 1986. "Advanced Thermochemical Biomass Gasification." Paper No. 101(c), presented at the Annual Meeting Amer. Inst. Chem. Eng., November 7, 1986, Miami.

Butner, R. S., D. C. Elliott, and L. J. Sealock, Jr. 1986. "Effect of Catalyst Type and Concentration on Thermal Gasification of High-Moisture Biomass Feedstocks." Biotech. and Bioeng. Symp. No. 17, ed. C. D. Scott, pp. 169-177. John Wiley and Sons, New York.

Butner, R. S., Elliott, D. C., and Sealock, L. J., Jr. 1986. "Low-Temperature Thermochemical Conversion of High-Moisture Biomass Feedstocks." In Proceedings of the 1985 Biomass Thermochemical Conversion Contractors' Meeting, pp. 193-209. CONF-8510167, National Technical Information Service, Springfield, Virginia.

Butner, R. S., L. J. Sealock, Jr., and D. C. Elliott. 1986. "Thermochemical Conversion of High-Moisture Biomass Feedstocks to Methane-Rich Gas Products." In Energy from Biomass and Wastes X, ed. D. L. Klass, pp. 1645-1646. Institute for Gas Technology, Chicago.

Butner, R. S., D. C. Elliott, and L. J. Sealock, Jr. 1987. "Energy Recovery from Aquatic Biomass in a Thermochemical Reactor." In Aquatic Plants for Water Treatment and Resource Recovery, eds. K. R. Reddy and W. H. Smith, pp. 739-745. Magnolia Publishing Inc., Orlando, Florida.

Elliott, D. C., L. J. Sealock, Jr. and R. S. Butner. 1987. "Product Analysis from Direct Liquefaction of Several High-Moisture Biomass Feedstocks." Amer. Chem. Soc., Div. Fuel Chem. Prepts. 32(2):186-194.

Butner, R. S., D. C. Elliott, and L. J. Sealock, Jr. 1988. "Low-Temperature Thermochemical Conversion of High-Moisture Biomass Feedstocks." In Proceedings of the 1987 Biomass Thermochemical Conversion Contractors' Review Meeting, pp. 99-113. CONF-8705212, National Technical Information Service, Springfield, Virginia.

Butner, R. S., D. C. Elliott, and L. J. Sealock, Jr. 1988. "Thermochemical Gasification of Wet Biomass and Wastes." Presented at the Spring Meeting, Amer. Inst. Chem. Eng., March 9, 1988, New Orleans.

Butner, R. S., D. C. Elliott, L. J. Sealock, Jr., and D. P. Chynoweth. 1988. "A Process Study of the Biothermal Conversion of Water Hyacinths to Methane." In Applied Biochemistry and Bioengineering, ed. C. D. Scott. Humana Publishers, Boca Raton, Florida.

Elliott, D. C., R. S. Butner, and L. J. Sealock, Jr. 1988. "Low-Temperature Gasification of High-Moisture Biomass." In Research in Thermochemical Biomass Conversion, eds. J. Kuuster and A. Bridgwater. Elsevier Applied Science, Ltd., Barking, England.

REFERENCES

- American Public Health Association. 1980. Standard Methods for Examination of Water and Wastewater, 15th edition, eds. A. E. Greenberg, J. J. Connors, D. Jenkins, and M.A.H. Franson. Washington, D.C.
- Amin, S., R. C. Reid, and M. Modell. 1975. "Reforming and Decomposition of Glucose in an Aqueous Phase." Presented at the Aerospace Division of American Society of Mechanical Engineers Intersociety Conference on Environmental Systems, April 10, 1975, San Francisco.
- Antal, Jr., A. Brittain, C. DeAlmeida, W. Mok, and S. Ramayya. 1987. "Catalyzed and Uncatalyzed Conversion of Cellulose Biopolymer Model Compounds to Chemical Feedstocks in Supercritical Solvents." In Energy from Biomass and Wastes X, ed. D. L. Klass, pp. 865-878. Institute for Gas Technology, Chicago.
- Baker, E. G., and L. J. Sealock, Jr. 1988a. Catalytic Destruction of Hazardous Organics in Aqueous Solutions. PNL-6491-2, Pacific Northwest Laboratory, Richland, Washington.
- Baker, E. G., and L. J. Sealock, Jr. 1988b. "Catalytic Destruction of Hazardous Organics in Aqueous Wastes." In Proceedings of the 5th National Conference on HWHM '88 Hazardous Wastes and Hazardous Materials, pp. 459-462. The Hazardous Materials Research Institute, April 19-21, 1988, Las Vegas, Nevada.
- Butler, J. L. 1982. "Biomass Research Program of the USDA Southern Agricultural Energy Center." In Proceedings of the Intersoc. Energy Convers. Eng. Conf. 17, Vol. 1. CONF-820814, National Technical Information Service, Springfield, Virginia.
- Butner, R. S., D. C. Elliott, and L. J. Sealock, Jr. 1986. "Effect of Catalyst Type and Concentration on Thermal Gasification of High-Moisture Biomass Feedstock." Biotech. and Bioeng. Symp. No. 17, ed. C. D. Scott, pp. 169-177. John Wiley and Sons, New York.
- Butner, R. S., D. C. Elliott, L. J. Sealock, Jr., and D. P. Chynoweth. 1988. "A Process Study of the Biothermal Conversion of Water Hyacinths to Methane." In Applied Biochemistry and Bioengineering, ed. C. D. Scott. Humana Publishers, Boca Raton, Florida.
- Cushman, J. H., A. F. Turhollow, and J. L. Elmore. 1987. Herbaceous Energy Crops Program, Annual Report for FY 1986. ORNL-6369, National Technical Information Service, Springfield, Virginia.
- Elliott, D. C. 1981. "Description and Utilization of Product from Direct Liquefaction of Biomass." In Biotech. & Bioeng., Symp. No. 11, pp. 187-198. John Wiley and Sons, New York.

Elliott, D. C. 1985. Analysis and Comparison of Biomass Pyrolysis/Gasification Condensates--An Interim Report. PNL-5555, Pacific Northwest Laboratory, Richland, Washington.

Elliott, D. C., and L. J. Sealock, Jr. 1983. "Aqueous Catalyst Systems for the Water-Gas Shift Reaction. 1. Comparative Catalyst Studies." Ind. & Eng. Chem., Prod. Res. & Dev. 22:426-431.

Elliott, D. C., and L. J. Sealock, Jr. 1985. "Low Temperature Gasification of Biomass Under Pressure." In Fundamentals of Thermochemical Biomass Conversion, eds. R. P. Overend, T. A. Milne, and L. K. Mudge, pp. 937-950. Elsevier Applied Science Publishers, Ltd., London.

Elliott, D. C., R. T. Hallen, and L. J. Sealock, Jr. 1983. "Aqueous Catalysis Systems for the Water-Gas Shift Reaction. 2. Mechanism of Basic Catalysis." Ind. & Eng. Chem., Prod. Res. & Dev. 23:471-475.

Elliott, D. C., R. T. Hallen, and L. J. Sealock, Jr. 1984. "Alkali Catalysis in Biomass Conversion." Jour. Anal. Appl. Pyrol. 6:299-316.

Figueroa, C., L. L. Schaleger, and H. G. Davis. 1982. "LBL Continuous Bench-Scale Liquefaction Unit, Operation and Results." In Energy from Biomass & Waste VI, pp. 1097-1112. Institute of Gas Technology, Chicago.

Mahoney, J. A., K. K. Robinson, and E. C. Myers. 1978. "Catalysts Evaluation with Gradientless Reactor." CHEMTECH. 8:758-763.

Milne, T. A. 1986. Biofuels Glossary. SERI/SP-271-2828, Solar Research Energy Institute, Golden, Colorado.

Modell, M. 1985. "Gasification and Liquefaction of Forest Products in Supercritical Water." In Fundamentals of Thermochemical Biomass, eds. R. P. Overend, T. A. Milne, and L. K. Mudge, pp. 95-119. Elsevier Applied Science Publishers, Ltd., London.

Modell, M., R. C. Reid, and S. Amin. September 1978. "Gasification Process." U.S. Patent 4,113,446.

Mudge, L. K., L. J. Sealock, Jr., and S. L. Weber. 1979. "Catalyzed Steam Gasification of Biomass." Jour. Anal. Appl. Pyrol. 1:165-175.

Nelson, D. A., P. M. Molton, J. A. Russell, and R. T. Hallen. 1984. "Application of Direct Thermal Liquefaction for the Conversion of Cellulosic Biomass." Ind. & Eng. Chem., Prod. Res. & Dev. 23:471-475.

Pack, G. E., R. E. Desrosiers, and K. Kamali. 1985. Preliminary Technical and Economic Evaluation of a Low Temperature Thermochemical Gasification Process. GRI-85/0058, Gas Research Institute, Chicago.

Ranney, J. W., and D. H. Dawson. 1987. Biomass Research Directions in Forestry. CONF-8706194-1, National Technical Information Service, Springfield, Virginia.

Rostrup-Nielsen, J. R. 1984. Catalytic Steam Reforming. Springer-Verlag, Berlin.

Russell, J. A., P. M. Molton, and S. D. Landsman. 1980. "Chemical Comparisons of Liquid Fuel Produced by Thermochemical Liquefaction of Various Biomass Materials." Presented at the 3rd Miami International Conference of Alternative Energy Sources, December 17, 1980, Miami.

Sanders, R. W., K. B. Olsen, W. C. Weimer, and K. K. Nielsen. 1983. "Multi-Element Analysis of Unweighed Oil Samples by X-Ray Fluorescence Spectrometry with Two Excitation Sources." Anal. Chem. 55:1911.

Sealock, L. J., Jr., D. C. Elliott, R. T. Hallen, R. D. Barrows, and S. L. Weber. 1981. "Kinetics and Catalysis of Producing Synthetic Gases from Biomass." Annual Report. GRI-80/0116, PB82-214347, National Technical Information Service, Springfield, Virginia.

Sealock, L. J., Jr., D. C. Elliott, and R. T. Hallen. 1982. "Kinetics and Catalysis of Producing Synthetic Gases from Biomass." Final Report. GRI-82/0038, PB83-188644, National Technical Information Service, Springfield, Virginia.

Simkovic, I., T. Leesonboon, W. Mok, and M. J. Antal, Jr. 1987. "Dehydration of Carbohydrates in Supercritical Water." Amer. Chem. Soc., Div. Fuel Chem. Prepts. 32(2):129-132.

Stafford, D. A., D. L. Hawkes, and R. Horton. 1980. Methane Production from Waste Organic Matter. CRC Press, Boca Raton, Florida.

Taylor, H. S., and H. H. Neville. 1921. "Catalysis in the Interaction of Carbon with Steam and with Carbon Dioxide." J. Am. Chem. Soc. 43:2055-2071.

Willson, W. G., L. J. Sealock, Jr., F. C. Hoodmaker, R. W. Hoffman, D. L. Stinson, and J. L. Cox. 1974. "Alkali Carbonate and Nickel Catalysis of Coal-Steam Gasification." In Advances in Chemistry Series: Coal Gasification, Vol. 131, pp. 203-216. American Chemical Society, Washington, D.C.

APPENDIX

SUMMARY OF BIOMASS CONVERSION EXPERIMENTS

TABLE A.1. Summary of Biomass Gasification Experiments

Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
Cellulose											
166	380	1.18	0.00	97.6	5.5	3.9	47.8	0.0	43.2	3.7	513
165	400	1.21	0.00	87.5	5.2	5.4	45.4	0.0	44.7	3.6	532
164	400	1.17	0.00	103.8	4.7	6.5	55.0	0.0	33.6	3.9	428
162	400	1.17	0.00	101.0	4.9	7.4	52.0	0.0	35.9	3.7	451
195	380	1.16 (OC)	0.00	88.2	3.1	21.2	49.3	0.9	23.0	3.0	356
109	400	0.15	0.27 (Mg)	72.5	3.1	11.3	52.5	0.0	35.1	1.2	412
100	400	0.15	0.27 (Mg)	71.9	3.0	10.6	52.7	0.0	35.6	1.1	414
97	400	0.15	0.97 (Cs)	79.4	2.9	18.5	53.6	0.0	25.9	1.9	356
98	400	0.15	0.29 (Ca)	69.8	2.4	13.6	53.2	0.0	31.1	2.0	394
101	400	0.15	0.31 (Na)	65.5	2.4	16.2	54.3	0.0	27.5	1.9	364
111	400	0.15	0.31 (Na)	64.3	2.3	17.1	54.4	0.0	26.4	2.1	358
96	400	0.15	0.40 (K)	72.1	2.3	18.4	53.9	0.1	25.6	2.0	354
95	400	0.15	0.97 (Cs)	58.4	2.1	17.8	54.2	0.0	26.0	2.0	356
94	400	0.15	0.40 (K)	68.7	2.0	19.2	54.8	0.0	24.1	2.0	340
Corn, stover											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
135	450	0.27	0.37	89.6	2.8	33.5	46.5	0.0	16.3	2.2	311
136	400	0.20	0.40	72.9	1.5	34.3	50.7	0.0	11.1	1.3	246
139	450	0.00	0.00	55.1	1.5	19.3	56.5	0.0	12.1	2.8	233
138	400	0.00	0.00	80.9	0.9	18.7	63.6	0.0	7.1	2.2	170
Douglas Fir, wood flour											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
45	400	0.15	0.31	49.8	2.6	21.6	47.6	0.0	29.0	1.8	395
15	400	0.15	0.31	49.1	1.5	20.1	62.0	0.1	16.3	1.5	255
43	400	0.15	0.31	40.3	1.0	32.7	54.4	0.1	11.0	1.8	248
Anaerobic Digestion Residue											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
167	380	1.61	0.00	85.3	4.7	6.4	49.5	0.0	41.0	1.2	457
163	400	1.62	0.00	69.0	4.7	9.5	39.4	0.0	47.3	1.4	534
74	450	0.61	0.83	50.2	1.7	43.5	40.5	0.0	13.5	2.6	322
72	400	0.41	0.84	23.6	0.5	40.6	48.7	0.4	9.0	1.4	248
73	400	0.00	0.00	13.1	0.1	22.9	68.8	0.0	5.8	2.5	176
161	400	(dil slu)	0.00	141.0	N D	13.5	68.4	0.0	17.3	0.4	226

TABLE A.1. (contd)

Grape Pomace											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	(volume % @ 15 min)					HHV (BTU/scf)
						[H2]	[CO2]	[CO]	[CH4]	[C2's]	
171	395	1.17	0.00	44.5	3.1	9.6	47.7	0.0	40.2	1.0	455
177	400	0.97	0.00	38.6	2.2	11.3	54.1	0.0	31.9	1.3	382
182	396	1.42 (OC)	0.00	43.7	2.6	9.7	52.5	0.6	34.1	1.2	399
183	395	1.09 (OC)	0.00	32.5	2.0	15.6	48.3	0.6	32.4	1.4	405
173	390	0.98	0.00	20.8	1.1	11.2	55.8	0.7	30.2	1.1	363
172	380	0.93	0.00	11.0	0.4	8.8	65.2	0.9	22.9	0.9	279
Kelp, macrocystis											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	(volume % @ 15 min)					HHV (BTU/scf)
						[H2]	[CO2]	[CO]	[CH4]	[C2's]	
176	400	1.23	0.00	78.8	2.9	7.1	48.4	0.0	41.9	1.5	473
56	450	0.20	0.27	89.0	1.4	35.2	49.8	0.0	13.0	2.0	280
11	400	0.15	0.31	68.7	1.2	30.1	53.8	0.1	13.5	3.0	285
46	400	0.15	0.31	57.1	1.1	37.7	47.5	0.0	13.1	1.8	285
12	400	0.15	0.31	73.2	0.9	29.7	56.2	0.2	10.5	3.5	262
10	400	0.15	0.31	56.9	0.8	32.9	54.5	0.1	10.7	1.8	246
9	400	0.15	0.30	33.2	0.4	38.1	53.5	0.0	6.6	1.9	222
32	400	0.00	0.00	16.5	0.1	20.5	73.4	4.0	2.1		101
176	400	1.23	0.00	63.3	2.1	6.7	46.0	0.0	44.3	1.6	498
Napier Grass											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	(volume % @ 15 min)					HHV (BTU/scf)
						[H2]	[CO2]	[CO]	[CH4]	[C2's]	
150	400	1.41	0.00	123.8	7.6	4.6	47.3	0.0	43.8	2.6	503
90	400	0.96	0.26	100.8	5.2	6.9	51.1	0.0	40.6	1.4	458
53	450	0.26	0.35	109.8	5.0	28.8	40.2	0.0	27.9	3.2	430
89	450	1.10	0.30	90.9	4.4	19.3	49.0	0.2	30.2	1.3	392
86	400	0.92	0.25	78.1	4.3	8.8	51.2	0.0	38.7	1.3	443
91	450	0.54	0.29	78.5	4.0	20.8	47.2	0.2	30.4	1.4	400
84	450	0.43	0.23	75.8	3.7	20.0	46.9	0.3	31.3	1.6	409
85	400	0.48	0.26	66.8	3.7	9.1	51.2	0.0	37.8	1.8	444
39	400	0.15	0.31	71.4	3.3	22.5	50.0	0.0	25.0	2.4	367
93	450	0.21	0.29	69.1	2.6	26.3	50.0	0.2	21.5	1.9	337
44	400	0.15	0.31	66.9	2.0	24.5	55.1	0.0	18.0	2.5	304
134	450	0.00	0.00	44.5	1.2	15.5	60.7	1.1	13.9	3.5	254
25	400	0.00	0.00	21.8	0.3	7.8	69.0	10.3	10.3	2.6	207
133	450	0.00	0.00	51.3	0.9	14.9	62.4	0.0	3.3	3.3	138
150	400	0.00	1.41	74.3	2.9	16.2	52.9	0.1	26.3	0.0	320

TABLE A.1. (contd)

Potato Peeling Waste											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
49	450	0.23	0.31	70.9	3.2	34.0	39.4	0.0	21.7	5.0	414
38	400	0.15	0.31	46.4	2.0	27.6	50.2	0.0	20.4	1.8	327
5	400	0.16	0.31	40.1	0.9	30.8	56.6	0.0	10.9	1.7	239
24	400	0.00	0.00	17.4	0.1	12.2	79.0	0.3	5.6	3.0	148
Sunflower, stover											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
148	400	1.02	0.00	148.3	6.4	3.6	48.5	0.0	44.9	1.7	495
159	400	1.18	0.00	87.8	5.1	5.0	45.5	0.0	45.7	2.4	520
50	450	0.24	0.33	108.4	4.2	34.5	39.4	0.0	22.7	4.4	417
57	450	0.32	0.43	107.9	3.4	37.3	43.5	0.0	17.7	1.6	327
62	450	0.36	0.53	98.9	3.2	34.7	45.3	0.2	18.3	1.6	325
60	450	0.35	0.47	82.9	3.0	21.5	50.8	0.0	25.3	2.3	366
61	450	0.32	0.41	69.0	1.9	37.3	42.8	0.0	18.1	1.8	335
130	450	0.00	0.00	85.4	1.8	27.9	50.8	0.2	14.9	2.5	285
37	400	0.15	0.31	42.3	1.4	31.9	53.5	0.1	12.7	1.8	263
58	450	0.13	0.18	48.9	1.3	28.0	55.2	0.0	14.4	2.5	279
29	400	0.00	0.00	28.0	0.3	17.7	72.7	0.0	7.5	2.1	169
Brewer's Spent Grain											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
174	398	1.07	0.00	55.7	3.9	9.6	44.2	0.0	43.1	1.4	492
137	400	1.46	0.00	107.0	8.8	4.9	41.3	0.0	51.3	0.8	549
140	400	1.24	0.00	143.2	10.3	5.8	40.1	0.0	49.0	1.0	532
54	450	0.25	0.33	53.4	2.9	35.5	40.8	0.0	21.4	2.9	382
185	395	1.31 (OC)	0.00	36.3	1.8	12.3	51.5	0.0	31.1	1.7	384
186	395	0.89 (OC)	0.00	31.4	1.6	18.1	45.6	0.0	30.9	1.9	404
132	450	0.00	0.00	33.1	0.7	13.8	56.7	8.6	13.4	7.6	337
6	400	0.15	0.31	25.2	0.6	32.2	57.1	0.0	8.6	2.1	228
40	400	0.15	0.31	22.0	0.4	37.7	53.0	0.0	7.9	1.4	227
20	400	0.00	0.00	15.9	0.2	10.6	79.9	0.6	5.6	3.3	149

TABLE A.1. (contd)

Sorghum											
Run	Temp	Ni conc	Alkali conc	Carb Conv	CH ₄ Yield	(volume % @ 15 min)					HHV
No.	(C)	(g/g)	(g/g)	(%@15min)	(scf/dry lb)	[H ₂]	[CO ₂]	[CO]	[CH ₄]	[C ₂ 's]	(BTU/scf)
112	400	1.26	0.00	195.7	10.9	5.7	49.5	1.0	42.9	0.9	472
118	400	1.21	0.09	151.5	8.3	9.4	48.7	0.0	40.7	1.3	465
116	400	1.12	0.25	156.7	7.7	11.8	50.3	0.0	36.5	1.4	432
113	400	1.38	0.00	130.7	7.7	7.5	48.3	0.0	43.4	0.7	476
124	450	1.52	0.10	153.2	7.3	24.3	45.9	0.2	29.6	1.0	396
114	400	1.17	0.08	125.3	7.0	8.5	49.8	0.0	40.3	1.4	460
115	400	1.23	0.18	131.3	7.0	0.9	53.4	0.0	36.0	1.6	395
127	450	1.25	0.34	159.6	6.8	28.0	46.2	0.2	23.5	1.2	350
120	400	1.32	0.29	136.1	6.2	13.8	52.3	0.0	32.6	1.3	397
81	450	0.27	0.94	113.4	6.1	25.7	41.5	0.2	31.2	1.5	425
122	400	1.25	0.36	127.6	5.7	13.7	51.9	0.0	33.0	1.5	404
119	400	1.11	0.16	94.6	5.5	9.5	50.5	0.0	38.4	1.6	447
125	450	1.28	0.17	123.9	5.4	24.2	47.5	0.2	25.7	1.4	363
126	450	1.11	0.23	122.4	5.4	25.2	45.9	0.2	26.4	1.2	370
160	400	1.17	0.00	92.6	5.2	5.6	50.3	0.0	40.2	2.6	
123	450	1.25	0.00	109.9	5.1	18.5	47.6	0.1	30.1	1.9	398
117	400	1.14	0.33	81.2	4.2	12.0	52.8	0.0	33.7	1.5	406
77	450	0.30	0.00	86.1	4.2	24.4	46.0	0.2	28.3	1.1	386
47	450	0.25	0.33	88.7	4.0	33.0	40.2	0.0	22.5	4.3	408
87	450	0.23	0.00	98.2	4.0	26.8	45.4	0.2	26.6	1.1	375
83	450	0.22	recycle	78.2	3.3	25.7	49.4	0.2	23.0	1.8	347
78	450	0.28	0.19	74.4	3.1	27.9	46.7	0.2	23.2	2.1	361
82	450	recycle	0.35	142.3	2.6	34.1	54.2	0.2	9.2	2.4	246
88	450	0.26	0.19	66.8	2.5	26.6	49.2	0.2	22.2	1.8	342
129	450	0.00	0.00	75.8	2.3	24.5	54.9	0.2	16.8	3.2	305
42	400	0.15	0.31	48.2	1.9	21.0	53.2	0.0	23.5	2.3	345
35	400	0.15	0.31	46.7	1.2	33.1	52.8	0.1	12.2	1.9	263
33	400	0.15	0.31	37.1	1.1	30.3	54.0	0.1	13.8	1.9	270
36	400	0.15	0.31	29.1	1.1	32.0	48.3	0.0	17.8	2.0	317
34	400	0.15	0.31	40.8	1.1	35.7	50.9	0.1	11.6	1.7	262
27	400	0.00	0.00	26.0	0.4	14.1	74.4	0.2	8.5	2.7	179
187	250	0.00	0.00	phys chng	0.0	---	---	---	---	---	---
189	200	0.00	0.00	very little	0.0	---	---	---	---	---	---
188	150	0.00	0.00	very little	0.0	---	---	---	---	---	---

TABLE A.1. (contd)

Water Hyacinth											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	(volume % @ 15 min)					HHV (BTU/scf)
						[H2]	[CO2]	[CO]	[CH4]	[C2's]	
175	400	2.14	0.00	73.1	4.0	9.4	51.2	0.0	37.4	1.1	428
55	450	0.52	0.71	61.3	1.6	48.0	39.3	0.0	11.4	1.3	294
41	400	0.30	0.62	29.6	0.6	41.9	48.7	0.0	8.1	1.3	240
8	400	0.30	0.61	17.7	0.5	39.9	52.5	0.0	6.4	1.2	214
31	400	0.00	0.00	14.8	0.1	21.7	70.1	0.0	5.4	2.8	172
175	400	2.14	0.00	70.3	4.1	9.6	41.6	0.0	46.1	1.3	520
Peat											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	(volume % @ 15 min)					HHV (BTU/scf)
						[H2]	[CO2]	[CO]	[CH4]	[C2's]	
190	405	1.70 (OC)	0.00	44.8	3.2	11.3	49.6	0.8	35.9	0.9	418
69	450	0.23	0.31	45.5	2.1	25.6	52.0	0.2	20.1	2.1	323
68	450	0.23	0.31	41.4	1.7	26.2	54.4	0.2	17.4	1.9	294
Coal, lignite											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	(volume % @ 15 min)					HHV (BTU/scf)
						[H2]	[CO2]	[CO]	[CH4]	[C2's]	
141	400	1.08	0.00	122.5	6.6	13.3	56.9	0.0	27.5	0.4	329
48	450	0.18	0.24	24.5	0.8	32.1	53.4	0.0	11.6	2.9	271
66	450	0.18	0.24	23.3	0.8	22.4	60.1	0.0	15.6	2.0	264
Kraft Pulp Black Liquor											
151	400	1.29	0.00	6.2	0.2	10.4	70.9	0.0	16.6	1.4	226
Deionized Water (control)											
Run No.	Temp (C)	Ni conc (g/g)	Alkali conc (g/g)	Carb Conv (%@15min)	CH4 Yield (scf/dry lb)	[H2]	[CO2]	[CO]	[CH4]	[C2's]	HHV (BTU/scf)
							(volume % @ 0 min)				
102	445	5 g	6.75 g	N A	N A	33.8	58.8	0.0	3.9	0.6	159
104	450	5 g	6.75 g	N A	N A	54.1	44.6	0.0	1.3	0.0	189
105	400	5 g	10.13 g	N A	N A	76.8	23.2	0.0	0.0	0.0	250
107	450	5 g	6.75 g	N A	N A	52.0	48.0	0.0	0.0	0.0	169
108	445	5 g	6.75 g	N A	N A	N D	N D	N D	N D	N D	N D
145	400	35 g	0.00	N A	N A	52.8	42.6	0.0	4.6	0.0	218
146	400	35 g	10.13 g	N A	N A	41.4	58.6	0.0	0.0	0.0	135
O C = offspec catalyst											
dil slu = dilute anaerobic digestion sludge											
N A = not applicable to the experiment											
N D = not determined											

TABLE A.2. Summary of Biomass Liquefaction Experiments

Biomass Type	Run No.	Temp (C)	Alkali conc (g/g daf)	Iron Conc (g oxide/g)	Oil Yield (g/100g daf)	C (%elemental composition)	H	O	N	H/C atom ratio
Kelp	63	360	0.53	0.00	15.0	74.8	8.9	12.3	4.0	1.41
	65	354	0.00	0.00	19.2	76.7	8.9	9.9	3.5	1.38
Napier Grass	70	351	0.19	0.00	34.4	74.5	8.5	16.7	0.4	1.36
Water Hyacinth	71	351	0.03	0.00	10.5	not determined - - - - -				
	143	345	0.15	0.00	26.0	76.3	9.9	10.5	3.3	1.54
Spent Grain	142	350	0.07	0.00	34.7	75.2	10.2	10.8	3.8	1.61
Sorghum, stover	144	345	0.08	0.00	26.6	75.9	8.7	13.7	1.7	1.36
Corn, stover	178	352	0.10	0.00	26.3	75.5	8.7	8.2	3.7	1.37
	179	352	0.11	1.05	25.8	76.3	8.9	8.9	2.5	1.39
	180	352	0.00	1.14	23.9	77.3	8.3	8.1	2.0	1.28
	181	352	0.00	1.07	31.2	75.5	8.1	8.5	2.6	1.26

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

	S. Friedrich Biofuels and Municipal Waste Technology Division U.S. Department of Energy Forrestal Building (CE-341) 1000 Independence Avenue Washington, D.C. 20585	R. Beale Vice President, Operations Lamb-Weston P.O. Box C 1900 Tri Cities, WA 99302
	S. L. Natof Division of Improved Energy Productivity U.S. Department of Energy Forrestal Building (CE-141) 1000 Independence Avenue Washington, D.C. 20585	C. G. Coble Texas A&M University College Station, TX 77840
10	DOE/Office of Scientific and Technical Information	D. P. Chynoweth Agricultural Engineering Department Frazier Rogers Hall University of Florida Gainesville, FL 32611
	M. J. Antal Department of Mechanical Engineering University of Hawaii 2540 Dole Street Honolulu, HI 96822	H. W. Ewart Tree Top, Inc. Technical Center 111 S. Railroad Ave. P.O. Box 248 Selah, WA 98942
	R. E. Bailey Kraft Food 2211 Sanders Rd. Northbrook, IL 60062	B. Goodman Solar Energy Institute 1617 Cole Blvd. Golden, CO 80401
5	N. G. Banns Onsite*Offsite, Inc. 2500 E. Foothills Blvd Suite 201 Pasadena, CA 91107	H. Haines Energy Division DNRC 32 South Ewing Helena, MT 59601
	S. P. Barone Gas Research Institute 8600 West Bryn Mawr Avenue Chicago, IL 60631	B. Haley Miller Brewing Company 651 N. 39th Street Milwaukee, WI 53233
		W. M. McKinney United Catalysts, Inc. P.O. Box 32370 Louisville, KY 40302

No. of
Copies

H. Meyer
Gas Research Institute
8600 W. Bryn Mawr Avenue
Chicago, IL 60631

C. R. Nelson
Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, IL 60631

M. A. Paisley
Battelle-Columbus Division
505 King Avenue
Columbus, OH 43201

O. H. Pattison, P.E.
Southwest Bio-Energy, Inc.
Star Route, Box 58
Clovis, NM 88101

J. Pereira
Process Development and
Optimization Center
Corporate Research and
Development
Anheuser-Busch Companies, Inc.
Executive Offices
One Busch Place
St. Louis, MO 63118

R. Radford
Ocean Spray Cranberries, Inc.
Box 195
Markham Star Route
Aberdeen, WA 98520

G. Simons
California Energy Commission
1516 - 9th Street, MS-43
Sacramento, CA 95801

No. of
Copies

W. H. Smith
Center for Biomass Energy Systems
University of Florida
3038 McCarty Hall
Gainesville, FL 32611

F. Sparber
Independent Solar Research
Route 1, Box 192-A
Belin, NM 87002

D. J. Stevens
Solar Energy Research Institute
1617 Cole Blvd.
Golden, CO 80401

R. J. Weisskirchen
The Blitz-Weinhard Brewing Company
1133 West Burnside Street
Portland, OR 97209

FOREIGN

R. D. Hayes
Bioenergy Division
Energy, Mines and Resources Canada
580 Booth Street
Ottawa, Ontario K1A 0E4
Canada

Christian Roy
Université Laval
Chemical Engineering Department
Faculté des sciences et génie
Pavillion Pouliot
Sainte-Foy, Québec G1K 7P4
Canada

Domenico San Filippo
Research Division
Shamprogetti
20097 S. Donato Milanese
Milan, Italy

No. of
Copies

No. of
Copies

ONSITE

3 DOE Richland Operations Office

E. C. Norman
D. R. Segna
J. J. Sutey

71 Pacific Northwest Laboratory

E. G. Baker
R. S. Butner (3)

D. C. Elliott (3)
E. A. Eschbach
S. R. Gano
M. A. Gerber
R. S. Kemper
G. G. Neuenschwander
G. F. Schiefelbein
L. J. Sealock, Jr. (50)
J. L. Straalsund
L. D. Williams
Publishing Coordination
Technical Report Files (5)