SERI/TR-33-239 VOLUME I OF III UC CATEGORY: UC-61

A SURVEY OF BIOMASS GASIFICATION

VOLUME I - SYNOPSIS AND EXECUTIVE SUMMARY

JULY 1979

PREPARED UNDER TASK No. 3322

Solar Energy Research Institute

1536 Cole Boulevard Golden, Colorado 80401

A Division of Midwest Research Institute

Prepared for the U.S. Department of Energy Contract No. EG·77·C·01·4042

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FOREWORD

This survey was prepared by SERI staff and a number of consultants for the Department of Energy under Contract EG-77-C-01-4042, Task 3322. Compiled in three volumes, the survey covers the technical background of biomass gasification, the present status of research and development, and recommendations for future work. Volume I, Synopsis and Executive Summary, condenses the body of the report for the more casual reader. Volume II, Principles of Gasification, discusses the properties of biomass relevant to gasification and the specific kinetics and thermodynamics of biomass gasification reactions; it is intended for the researcher or engineer. Volume III, Current Technology and Research, details the present status of biomass technology and includes specific recommendations for the future.

This survey has been compiled by a number of SERI staff members and consultants under the direction of T. B. Reed. Although many authors contributed to the survey and are listed in the Table of Contents, many others had less formal input. We would like to thank them for their efforts.

> Clayton Smith, Branch Chief Bio/Chemical Conversion Branch

Approved for:

SOLAR ENERGY RESEARCH INSTITUTE

Acting Assistant Director for Research



TABLE OF CONTENTS

A SURVEY OF BIOMASS GASIFICATION

Volume I. Synopsis and Executive Summary

Volume II. Principles of Gasification

1. Introduction

T. B. Reed and D. Jantzen

SERI

2. The Potential Biomass Resource Base

R. Inman

SERI

3. Properties of Biomass Relevant to Gasification

M. Graboski and R. Bain

Colorado School of Mines

4. Beneficiation of Biomass for Gasification and Combustion

R. Bain

Colorado School of Mines

5. Pyrolysis - The Thermal Behavior of Biomass Below 600 C

T. Milne

SERI

6. Thermodynamics of Gas-Char Reactions

R. Desrosiers

SERI

7. Kinetics of Char Gasification Reactions

M. Graboski

Colorado School of Mines

Volume III. Current Technology and Research

8. Survey of Gasifier Types

T. B. Reed

SERI

9. Directory of Current Gasifier Research and Manufacturers

T. B. Reed and D. Jantzen

SERI

10. Survey of Current Gasification Research and Development

T. B. Reed, D. Jantzen, R. Desrosiers, T. Milne

SERI

11. Economics of Air Gasification for Retrofitting Oil/Gas Boilers

T. B. Reed, D. Jantzen, W. P. Corcoran, R. Witholder

SERI



TABLE OF CONTENTS (concluded)

- 12. Gas Conditioning
 R. Bennett
 Mittelhauser Corp.
- Production of Fuels and Chemicals from Synthesis Gas
 E. I. Wan, J. A. Simmins, T. D. Nguyen
 Science Applications, Inc.
- Institutional Role in Biomass Development C. Bendersky, C. Montano Pyros, Inc.
- 15. Recommendations for Future Gasification Research and Development
 T. B. Reed
 SERI

1



VOLUME I

TABLE OF CONTENTS

	Page
Synopsis	I-1
Purpose	I-1
Technical Background	I-1
Content of Report	I-2
Conclusions and Recommendations	I-3
Executive Summary	I-5
Introduction	I-5
The Potential Biomass Resource Base	I-6
Properties of Biomass Relevant to Gasification	I-9
Beneficiation of Biomass	I-10
Pyrolysis	
Thermodynamics of Gas-Char Reactions	I-12
Kinetics of Char Gasification Reactions	
A Survey of Gasifier Types	I-19
Directory of Gasifier Manufacturers	I-23
Survey of Gasifier Research	
Economics of Gasification for Existing Gas/Oil Systems	
Gas Conditioning Processes	
Production of Liquid Fuels and Chemicals from Biomass Gasification Institutional Support of Biomass Gasification and Related	I-30
Activities	
Recommendations for Future Gasification Research and Development	I-34



LIST OF FIGURES

		Page
S-1	Gasification Processes and Their Products	I-7
S-2	Biomass Adiabatic Reaction Temperatures	
S-3	Equilibrium Composition for Adiabatic Air/ Biomass Reaction	
S-4	Gas, and Char Energy Content for Oxygen and Air/	
	Biomass Equilibrium	I-16
S-5	Low Heating Value for Dry Equilibrium Gas for	
	Air/O ₂ - Biomass Reaction	I-17
S-6	Schematic Diagram of Updraft Gasifier	I-20
S-7	Schematic Diagram of Downdraft Gasifier	
S-8	Cost Comparisons Between Retrofitting Existing	
	Equipment and New Installation	I-28
	LIST OF TABLES	
		Page
S-1	Energy Content of Fuel Gases and Their Uses	I-8
S-2	Summary of the Annual Energy Potential of Existing	
	Sources of Biomass	I-9
S-3	Survey of Gasifier Research, Development, and Manufacture	I-24
S-4	Detailed Cost Breakdown for \$20/Ton Fuel	I-29
S-5	Selected Gas Conversion Syntheses	I-31
S-6	Summary Comparison of Current Methanol Production	
	Costs (\$1980)	I-32



SYNOPSIS

PURPOSE

This Survey of Biomass Gasification was written to aid the Department of Energy and the Solar Energy Research Institute Biological and Chemical Conversion Branch in determining the areas of gasification that are ready for commercialization now and those areas in which further research and development will be most productive. This summary gives a minimal amount of discussion of the technical background of gasification and focuses on conclusions and recommendations that affect policy.

The Executive Summary gives the highlights of each chapter of the survey for ready reference in condensed form. The survey itself, running to over 400 pages, presents relevant scientific background information, surveys the current status of gasification activities, and examines various questions relevant to the uses of the product gases.

TECHNICAL BACKGROUND

Solid fuels such as biomass (any material derived from growing organisms) and coal have a limited field of direct use because of problems of distribution, combustion, and emissions. Gaseous fuels, on the other hand, have been used for 150 years because they are clean burning and easy to distribute. In addition, the gases can be converted to liquid fuels or chemicals:

Thus gasification can continue to supply the "convenience" liquid and gaseous fuels that we have come to depend on during the age of low-cost fossil fuels. While there are dozens of gasifiers and routes to gas production, they all fall into the following categories:

<u>Pyrolysis</u> is the breakdown of matter, especially biomass or coal, by heat. By its nature it produces some gas, some oil, and some char (charcoal from biomass and coke from coal). In some pyrolytic processes the char and oil are valued products; in <u>pyrolytic gasification</u> they are a nuisance, and extensive subsequent processing, generally at higher temperatures, is needed to convert char and oil to gas. Pyrolysis and pyrolytic gasification produces a medium energy gas (MEG). The gas contains a wide variety of products including CO, H₂, methane, and other hydrocarbons.

Air gasification, while requiring a pyrolytic step, uses a minimal quantity of air and steam to convert the char to gas in a single unit. Air gasification of biomass is particularly simple, and about a million air gasifiers were built during World War II to operate cars and trucks or generate power. The gas produced is called "low energy gas" (LEG) because it is diluted by the nitrogen of the air. While not suitable for pipeline distribution, it can be used in retrofitting existing boilers now using oil or natural gas, as well as to drive engines for transportation or power generation.



Oxygen gasification is also a relatively simple process that produces a medium energy gas composed primarily of CO and H₂. While quite satisfactory for burning, it can also be used for chemical synthesis to make methanol, ammonia, H₂, CH₄, or gasoline and is called "synthesis gas" or "syngas."

Hydrogasification, in which H₂ gas is added under high pressure, is also being studied and has the potential for high, direct yields of methane.

Anaerobic digestion produces methane and carbon dioxide biologically from manure or sewage. While it is, by strict definition, a gasification method, it is not generally referred to as "gasification" and will not be considered in this survey.

Biomass gasifiers occur in a bewildering variety depending on the heat input form (air, oxygen, or pyrolytic); gas-solid contact method (updraft, downdraft, fluidized bed, or suspended flow); feedstock form (residues, pellets, powders); gasification temperature (dry ash or slagging); product (low or medium energy gas, char, or pyrolysis oil), heating rate and residence time (slow and fast pyrolysis).

CONTENT OF REPORT

The main report was structured to serve as an introductory handbook on topics relevant to gasification, as well as providing reviews of past and current activities of use to both the generalist and specialist.

CHAPTER 1 contains an introduction and history of biomass gasification.

CHAPTER 2 briefly summarizes the potential biomass resource base.

CHAPTER 3 discusses the properties of biomass relevant to gasification, including tables and compilations of useful data.

CHAPTER 4 reviews the <u>treatment processes</u> that may be needed to prepare biomass feedstocks for use in different gasification schemes.

CHAPTER 5 contains a literature review of <u>pyrolysis</u> of biomass, under both slow and fast heating conditions.

CHAPTER 6 presents new calculations of equilibrium compositions of biomass under conditions relevant to a wide variety of gasification schemes.

CHAPTER 7 details the kinetics and mechanism of gas-char reactions, leaning heavily on experience with coal chars.

CHAPTER 8 is a survey of gasifier types.

CHAPTER 9 consists of a $\frac{\text{directory}}{\text{development programs.}}$ of current manufacturers of gasifiers and $\frac{\text{gasifier}}{\text{development programs.}}$

CHAPTER 10 is a sampling of <u>current gasification R&D programs</u> and their unique features.



CHAPTER 11 compares <u>air gasification</u> for the conversion of existing gas/oil boiler systems to biomass feedstocks with the price of installing new biomass combustion equipment.

CHAPTER 12 treats gas conditioning as a necessary adjunct to all but close-coupled gasifiers, in which the product is promptly burned.

CHAPTER 13 evaluates, technically and economically, synthesis-gas processes for conversion to methanol, ammonia, gasoline, or methane.

CHAPTER 14 compiles a number of comments that have been assembled from various members of the gasifier community as to possible roles of the government in accelerating the development of gasifier technology and commercialization.

CHAPTER 15 includes recommendations for future gasification research and development.

CONCLUSIONS AND RECOMMENDATIONS

This survey has been written to outline the value of gasification, the technical base on which future work can proceed, and the activities now underway. Various people reading this information will draw different conclusions. We give here the conclusions on which we will base our work at SERI and toward which we recommend guiding the national program. None of these conclusions is immutable and we invite comment as to their validity.

- We recommend that both coal and biomass gasification be developed rapidly, because these two technologies will be required soon to supplement fuel supplies as oil and gas become increasingly costly or unavailable. Gasification can provide not only the gas needed for clean heat and power in our cities, but also the basis for synthesis of liquid fuels, SNG, ammonia, and olefins.
- Air gasifiers may find a place in domestic and commercial heating, but they
 certainly will be used in process heating and producing power for the biomass
 industries. Although research in progress may improve air gasification, we
 recommend immediate commercialization at the present level of development.
- Large-scale oxygen gasifiers may play a prominent role in the conversion of municipal waste. If small oxygen gasifiers and plants could be developed (50 tons/day), they could play a crucial role in energy self-sufficient farms, manufacturing ammonia and methanol or gasoline from residues at the farmers' cooperative level to eliminate the heavy dependence on fossil fuels that makes our farms vulnerable to inflating fuel costs and uncertain supply. We recommend development of a 50 ton/day to 100 ton/day pressurized oxygen gasifier to operate on farm or forest residues. From preliminary operation of a downdraft gasifier on oxygen, and from the thermodynamics presented in the survey, we believe that it will be possible to design an oxygen gasifier that produces clean synthesis gas in one step, eliminating the need for costly gas conditioning. In this regard we recommend that support be provided for research on energy efficient methods to separate oxygen from air.
- Pyrolytic gasifiers are not as well developed as oxygen gasifiers, but the majority
 of the research supported by EPA and DOE has been in this area. We recommend



continuing research and pilot work on many of these systems because they promise higher efficiencies and lower costs than oxygen gasification in production of medium energy gas. However, because it is not clear to what degree medium energy gas will be distributed in the United States, full-scale development of pyrolytic gasifiers must wait on decisions concerning the gas infrastructure in the United States. These decisions hinge on the costs of converting gas to methane for distribution versus distribution of lower energy and lower cost gas. One possible development would be the use of medium energy gas in captive installations and industrial parks but conversion of coal to methane for domestic distribution.

- We recommend top priority development of fast pyrolysis processes that give a high yield of olefins which can be converted directly to gasoline or alcohols. This seems to be the one truly new development in gasification since World War II. We recommend evaluating various feedstocks and particle size options at the bench level, combined with bench and engineering studies of process designs giving the very high heat transfer and short residence times necessary to produce these products. We also recommend evaluation of processes for reducing particle size at reasonable costs, since this appears to be a necessary adjunct to fast pyrolysis.
- Finally, we recommend a continuing effort to determine the molecular details of pyrolysis under carefully controlled but realistic laboratory conditions, to provide a firm foundation for understanding and thus improving all gasification processes.

A number of systems studies should be performed as adjuncts to the technical program.

- We recommend that the scale of gasification plants be studied immediately and, where appropriate, that programs be initiated to overcome scale limitations. In particular, coal is likely to supply gas heat for our cities, where large plants can clean the gas sufficiently and make methane for distribution. Because biomass is much cleaner it can be used on a smaller scale, a fact which is compatible with its wider distribution. If biomass residues must be processed at the 1,000 ton/day level or greater to be economically viable, very little biomass will be used as an energy source in this country. If it can be processed economically at the 100 ton/day level, it can be used more widely.
- We recommend a systems study of biomass energy refineries to be used in conjunction with farming and forestry operations, taking residues and converting them to the ammonia and fuel required to operate the farm and forestry operation, and shipping any surplus energy to the cities in the form of gaseous or liquid fuels.

For the longer term, and for biomass conversion plants of larger scale, economic analyses should be performed to identify suitable hybrid schemes. These include:

- production of methanol using a combination of biomass (low hydrogen/carbon ratio) and natural gas (high hydrogen/carbon ratio);
- joint electrolytic/gasification systems in which waste generates hydrogen and oxygen electrolytically, the oxygen is consumed in gasification, and the hydrogen increases the hydrogen/carbon ratio; and
- solar fast pyrolysis, in which the high intensity heat is supplied by solar collectors.



EXECUTIVE SUMMARY

The production of energy from biomass (any material derived from growing organisms) is now seen by many to be a leading near-term solar energy technology. Already, 1% to 2% of U.S. energy is generated by combustion of biomass, and this established technology is being commercialized wherever possible and with as much speed as possible. However, solid fuels have limited applications in modern industrial society and many environmental problems as well.

Fortunately, biomass can be gasified by a number of existing or developing processes. Air gasification (burning with a limited amount of air) is already being commercialized, but much engineering and scientific work remains before oxygen gasification (burning with limited oxygen) or pyrolytic processes (breaking down of matter, usually by heat) for gasification are ready for commercialization. We believe that gasification will be the leading edge of thermal biomass development for at least a decade. Therefore, before beginning specific projects we have made a survey of existing knowledge and present work in this area and in adjoining technologies (fuel synthesis, gas cleanup) whose development will enable gasification to have maximum impact.

The survey has a number of important goals:

- to examine the properties and potential of the biomass resource relevant to gasification (Chapters 1 to 4);
- to summarize the basic science of biomass gasification (Chapters 5 to 7);
- to look at the present state of research, development, and commercialization of gasifiers (Chapters 8 to 10);
- to examine processes associated with gasification for gas cleanup and synthesis
 of other fuels from biomass-gas (Chapters 11 to 13);
- to determine means by which gasification technology can be introduced more rapidly (Chapter 14); and
- to identify the areas where research and development will be needed in an intensified gasification development program (Chapter 15).

The survey fills over 400 pages and assembles in one place a wide range of technical and institutional information as an aid to engineers and decisionmakers in this field. The background and conclusions we believe will be of interest to policymakers and the larger nontechnical audience involved in energy policy are highlighted in this summary. Those interested in greater technical depth are referred to the main body of the survey.

INTRODUCTION (Chapter 1)

Gaseous fuels have many advantages over solid fuels. Gases can be burned more efficiently and with less emissions; the gas flame is more easily controlled for sensitive industrial processes such as glassmaking and drying; gases can be distributed easily for domestic and industrial use; gases can be used to operate engines for power generation and transport; modern gas/oil burners can be retrofitted easily to use gas generated from biomass residues or coal but not solid fuels; some gases can be used for chemical synthesis of liquid fuels and chemicals such as methanol, gasoline, or ammonia. Solid fuels can



be gasified efficiently in central plants, the cleaned gas can be distributed in pipelines, and the ashes and pollutants can be disposed of efficiently. This type of fuel distribution is necessary to the continued existence of our large cities, where local burning of solid fuels would entail enormous distribution and emission problems.

The gasification of coal and biomass began in about 1800 and the superior properties of gaseous fuels relative to solid fuels caused this technology to develop so fast that by about 1850 gas light for streets was commonplace. Before the construction of natural gas pipelines in the United States between 1935 and 1960, there were about 1,200 municipal "gasworks" serving larger towns and cities. During the petroleum shortages of World War II in Europe, almost a million small gasifiers were used to run cars, trucks and buses, using primarily wood as fuel. Although coal has been the preferred fuel for larger gasifiers in the past, technical and environmental changes are likely to give biomass a larger role in gasification in the future.

Gasification of solid fuels is accomplished in high-temperature processes similar to combustion that convert the fuel to a gas with minimal loss (typically 10% to 30%) of the energy of the solid fuel. The methods used for gasification can be divided into the four categories shown in Fig. S-1. Air gasification is the simplest process but gives a gas of low energy content that must be "close-coupled" to its immediate use for heat or power. Air gasification is already being commercialized. Oxygen gasification gives a gas of higher energy content that can be distributed in industrial pipelines or used for chemical synthesis of a variety of fuels and chemicals such as methanol, ammonia, methane, and gasoline. Commercial prototypes have been operated successfully. Pyrolysis also can yield gas of medium energy but in addition yields oils and chars that have a utility of their own. Pyrolytic processes are still in the development stage.* Fast pyrolysis can yield a gas especially rich in unsaturated hydrocarbons that can form the basis of The energy contents of various gases are listed in gasoline or alcohol synthesis. Table S-1 along with their uses. [We have used the terms "low energy gas" (LEG) etc., as more descriptive than "low Btu gas" (LBG) etc., and as compatible with international usage and the SI system.]

THE POTENTIAL BIOMASS RESOURCE BASE (Chapter 2)

The importance of biomass conversion technologies depends on the quantity of biomass that can be made available for conversion to gas. The existing resource base is comprised of agricultural residues, manures, wood and bark mill residues, logging residues, noncommercial (cull) trees in the forests, and the organic fraction of municipal solid wastes. The quantities potentially available are summarized in Table S-2, which shows an enormous total potential of about 15 quads. Not all of this resource can be collected, and the amount used will depend on energy costs, competition from other fuel and solar energy sources, environmental and ecological factors, etc.

^{*}Hydrogen can be used under pressure to give higher energy gases or liquids, but hydrogasification of biomass is still in its infancy.

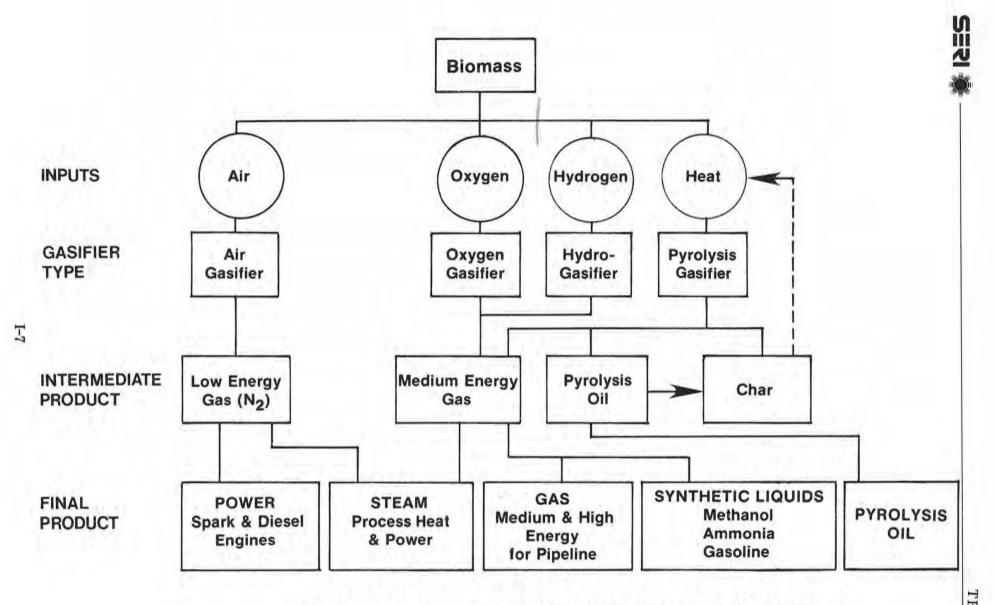


Figure S-1. Gasification Processes and Their Products

Table S-1. ENERGY CONTENT OF FUEL GASES AND THEIR USES

Name	Source	Energy Range (Btu/SCF)	Use
Low Energy Gas (LEG) [Producer Gas, Low Btu Gas]	Blast Furnace, Water Gas Process	80-100	On-site industrial heat and power, process heat
Low Energy Gas (LEG) [Generator Gas]	Air Gasification	150-200	Close-coupled to gas/oil boilers Operation of diesel and spark engines Crop drying
Medium Energy Gas (MEG) [Town Gas; Syngas]	Oxygen Gasification Pyrolysis Gasification	300-500	Regional industrial pipelines Synthesis of fuels and ammonia
Biogas	Anaerobic Digestion	600-700	Process heat, pipeline (with scrubbing)
High Energy Gas (HEG) [Natural Gas]	Oil/Gas Wells	1000	Long distance pipelines for general heat, power, and city use
Synthetic Natural Gas (SNG)	Further Processing of MEG and Biogas	1000	Long distance pipelines for general heat, power, and city use



Table S-2. SUMMARY OF THE ANNUAL ENERGY POTENTIAL OF EXISTING SOURCES OF BIOMASS

Resource	10 ⁶ Dry Tons/Year	Quads/Year
Crop Residues	278.0	4.15
Animal Manures	26.5	0.33
Unused Mill Residues ^a	24.1	0.41
Logging Residues	83.2	1.41
Municipal Solid Wastes	130.0	1.63
Standing Forests ^b	384.0	6.51
TOTALS:	925.8	14.44

^aDoes not include unused bark from wood pulp mills

In addition to these forms of existing biomass, there are several other large reservoirs of biomass energy that are even more difficult to quantify. A number of "biomass mines," consisting of past residues, have accumulated over the years. These include municipal wastes, sometimes even now digesting to give methane; food processing plant residues; and bark piles. Though only available on a one-time basis, the biomass mines are a potentially low-cost and environmentally attractive energy source.

A second unexploited category of biomass is that available through land improvement. Many acres of land have been laid waste by man and can support only the growth of such plant species as scrub, mesquite, and chapparal. Harvesting of these plants for their biomass energy and conversion of this energy to fuels could pay for the cost of improving the land.

Finally, there is the large potential of "energy plantations," in which land or even oceans and lakes could be used to raise biomass for energy purposes. Again, the economics of these processes, and energy needs, will determine the degree to which they are developed.

PROPERTIES OF BIOMASS RELEVANT TO GASIFICATION (Chapter 3)

Biomass is easier to gasify than coal because it has a much higher volatile content (typically 70% to 90%) and because it contains its own oxygen and water, two elements important in forming gaseous molecules from high-carbon feedstocks. With a few exceptions, biomass has less than 2% ash (while coal is typically 5% to 20%), and the typical biomass sulfur content is less than 0.1% as compared to 2% to 4% in coal. Biomass materials have carbon contents considerably lower than coals and the hydrogen/carbon ratio is typically 1.5; for coal it is close to 1.0.

These advantages of biomass for gasification are offset in part by a high moisture content, generally requiring drying before gasification, and by a lack of large concentrations of biomass, thus favoring small gasifiers with higher costs. However, very large quantities of biomass associated with many biomass processing plants (wood, lumber, food) are likely to be important in making these industries energy self-sufficient. Municipal solid waste also occurs in large quantities in the cities.

^bSurplus, noncommercial components



Biomass has three principal components—cellulose, hemicellulose, and lignin—and both the structure and the gasification of the infinite varieties of biomass can be understood in terms of the behavior of these components. In addition, minor amounts of extractables—hydrocarbons, tannins, oils, and resins—can add to the fuel and chemicals derived from biomass.

Because of the many forms in which biomass occurs, it is difficult to make general statements about the thermal properties of biomass relevant to gasification. The heat of combustion of pure cellulose is 7,250 Btu/lb and that of pure lignin is 11,500 Btu/lb, so that the heat of combustion of the various mixtures of cellulose and lignin in different forms of biomass ranges from about 7500 Btu/lb to 9500 Btu/lb, a much smaller range than for coals. Thermal conductivities are very low for biomass materials, ranging from 0.01 Btu/h-ft² (°F/ft) to 0.1 Btu/h ft² (°F/ft) depending on form, and this is important in the behavior of biomass during gasification. Other properties important in understanding the gasification process are the heat capacity and the diffusivities, particularly of transition charcoal forms. Though it is known that the porosity of charcoal greatly improves the kinetics of gasification, very few data are available on porosity, heat capacity, and diffusivity. Work is in progress at SERI to learn more about some of these properties.

BENEFICIATION OF BIOMASS (Chapter 4)

In many cases the energy content of biomass is unavailable because the biomass form is unsuitable for conversion. Often gasification processes require beneficiation of the biomass (improving its properties so that energy can be recovered more economically) before it can be used, and it is important to know the energy costs of each step.

Biomass often has a high moisture content, and some gasification processes require dry feedstock. Though in theory this water can be vaporized with an applied heat of 1000 Btu/lb water vaporized, in practice it requires 1500 to 2500 Btu/lb, depending on the efficiency of the drier. Fortunately, low-grade heat such as stack heat can be used for this purpose. Commercial equipment is widely available for both wood and agricultural biomass.

Often the physical form of available biomass is wrong for gasification because fixed-bed gasifiers require relatively large, solid pieces to allow room for gas passage, while fluid-ized and suspended gasification may require powders or dusts. Commercial equipment is available for reducing larger wood pieces to a size of half an inch; the energy needed to do this is less than 1% of the amount of energy contained in the wood. An interesting combination of size reduction and drying is accomplished in the "hot dog," a device used by forest industries to dry chips with waste stack heat.

Reducing particle size below half an inch becomes increasingly costly in energy. A new process, ECO-FUEL II, which uses a mild chemical attack on the biomass during milling, reduces required milling energy by an order of magnitude to make particles of about 200 μm . These very small particles, if available at a low cost, may make fast pyrolysis, with its high production of olefins, economically attractive.

Biomass has many properties that make it superior to coal as a fuel, but its bulk density is very low, thus increasing shipping and collection costs and reducing conversion rates in gasifiers and combustion units. Densification is a new technology that overcomes these disadvantages and makes essentially "instant coal" from biomass residues such as sawdust, bark, and straw. The biomass is dried to about 20% moisture content and then,



under high pressure, it is pressed or extruded to form pellets, briquettes, or logs. These have a specific gravity of 1 to 1.3 depending on the process, as compared to a specific gravity of 0.4 to 0.6 for wood and even less for other biomass forms. There is synergism between pelletizing and gasification: pellets are a superior feedstock for gasification, and gas fuel (from pellets) is an efficient way of drying pellets. The energy required for making pellets is 1% to 2% of the amount of energy in the dry biomass. Wet biomass must be dried, but this drying energy is largely recovered in the more efficient final gasification or combustion of the pellets.

PYROLYSIS (Chapter 5)

Pyrolysis is the breakdown of biomass by heat at temperatures of 200 C to 600 C to yield a medium energy gas, a complex pyrolysis oil, and char. All biomass gasification and combustion processes involve pyrolysis as a necessary first step: in combustion, subsequent oxidation of the products leads to total heat release; in gasification the products are used directly or are converted to other fuel forms.

There are two kinds of pyrolysis: slow and fast. At slow heating rates or with large pieces of biomass, pyrolysis leads to a high proportion of charcoal that must then be gasified. At the most rapid heating rates, cellulose is largely converted to a gas containing a high proportion of olefins that are valuable as a chemical feedstock; char production is minimal.

Although not yet proven quantitatively, it is commonly accepted that the pyrolysis of the many complex forms of biomass can be understood as the sum of the breakdown of its three components: cellulose, hemicellulose, and lignin. This is borne out qualitatively by comparison of laboratory analyses of the pyrolysis of components with those of whole biomass.

Pyrolysis is studied in the laboratory using several types of thermal analysis instruments. Thermogravimetric analysis (TGA) yields data on the weight loss of biomass as a function of either time (isothermal TGA) or temperature (dynamic TGA). These measurements yield the proximate analysis of the biomass sample, giving the percentages of moisture, volatiles, char, and ash. TGA data are useful in determining the rates of pyrolysis and are qualitatively relevant to pyrolysis in gasifiers though fixed bed gasifiers probably pyrolyze at slower rates than are convenient in the laboratory while fast pyrolysis is beyond the range of ordinary laboratory instruments. The decomposition rate of cellulose is usually fitted by a classical kinetic equation of the form:

dV/dt = V A exp (-E/RT)

where V is the remaining volatile component at temperature T, A is an adjustable constant, R is the gas constant, and E is the activation energy. This equation can also predict the decomposition of hemicellulose and lignin but with less accuracy.

Another very useful technique in understanding pyrolysis is the semiquantitative technique of differential thermal analysis (DTA) that has been supplanted recently by the quantitative differential scanning calorimetry (DSC). Both techniques measure the heat input to the sample at a constant heating rate and determine whether various stages of the pyrolysis are endothermic (requiring heat) or exothermic (producing heat).



At fast heating rates leading primarily to gas, pyrolysis seems to be endothermic across the entire temperature range. Thus, the faster pyrolysis techniques require a moderate heat input at pyrolysis temperatures. That slower pyrolysis leads to more char formation and is exothermic at higher temperatures is consistent with the observation that pyrolysis can be "autothermic," and a pyrolytic gasifier, if properly arranged and insulated, requires no net heat input for partial gasification.

The gases and liquids evolved during pyrolysis are commonly measured with mass spectrometry, infrared spectrophotometry, or gas and liquid chromatography. Analysis suggests that at the temperature of pyrolysis the primary products are not affected by the presence of air, steam, or hydrogen, and that pressure is not an important variable except as it influences the escape of primary products. A great deal of work has been done on the chemical mechanisms involved in the breakdown of cellulose, with less known about lignin, wood, and hemicelluloses. More work is required on the effect of particle size and heating rates on both primary and secondary pyrolysis of the products.

An emerging field that is relevant to gasification is "fast pyrolysis," the very rapid heating of finely divided biomass resulting in maximal gas yields. A number of investigations, some aimed at converting solid municipal waste to energy forms, have determined the composition of the products resulting from various heating techniques. In addition, some investigators are examining the subsequent "gas phase pyrolysis" of the oils produced from the solid, a process which is likely to become very important if gas is the only product desired. Furthermore, this vapor cracking can yield other products, primarily olefins, of much greater value than the products obtained in conventional solid pyrolysis. These products are valuable precursors to gasoline or alcohol.

THERMODYNAMICS OF GAS-CHAR REACTIONS (Chapter 6)

Pyrolysis at temperatures of 200 C to 600 C is a nonequilibrium process. However, in gasification pyrolysis is generally followed by an oxygen, air, or steam conversion of the resulting oils, tar, and char to CO, H₂, or methane, and under some conditions the combined reactions closely approach equilibrium. Thermodynamic calculations, while not necessarily enabling accurate predictions of gas compositions in gasification, are at least restrictive in that they set the boundaries to what is possible in gasification.

As a part of the survey of the current state of knowledge of gasification, we used a computer program to predict the equilibrium gas compositions to be expected under a wide variety of conditions encountered in gasification. This allows rapid comparison with experimental results and often suggests useful modifications to processes.

A useful parameter in understanding the various gasification and combustion processes is the adiabatic flame (reaction) temperature (AFT), the temperature that would be reached by the products of the reaction if equilibrium were achieved. This temperature is shown in Fig. S-2 as a function of the equivalence ratio (ER), the ratio of the actual oxygen content of the air supplied to the oxygen required for complete combustion. Thus, for an equivalence ratio of 1.0, the flame temperature of biomass when burned in pure oxygen is about 2800 C, while for combustion in air it is 2050 C, close to that observed in wood combustion.

Gasification with air or oxygen occurs at an equivalence ratio of 0.25 to 0.3. In this region the reaction temperature is only 700 C to 1100 C in air and about 100 C higher in oxygen.

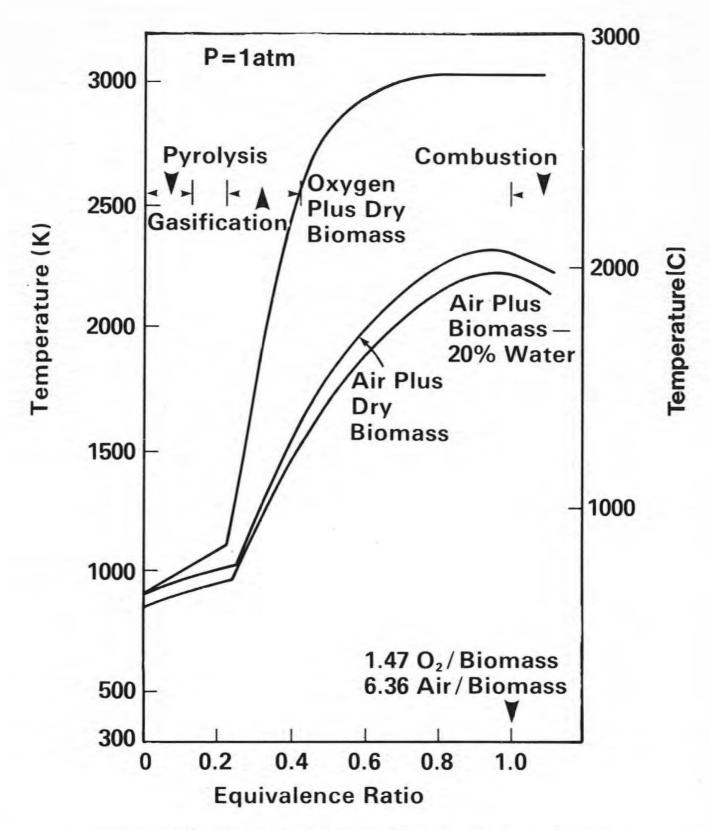


Figure S-2. Biomass Adiabatic Reaction Temperatures



The equilibrium gases produced during these processes are shown in Fig. S-3 where it is also shown that at the lowest equivalence ratios some methane is formed while CO and H₂ are the predominant fuel gases. At increasing equivalence ratios, char is converted to gas up to an equivalence ratio of 0.25. As the equivalence ratio approaches 1.0 for complete combustion, fuel gases are converted to the combustion products. This can also be seen in Fig. S-4, which shows the energy content of char and gas as the ER increases. The heating values (heat of combustion per unit volume) of the gases produced in oxygen and air gasification are shown as a function of ER in Fig. S-5.

A phenomenon occurring in the gasification region called "flame temperature stabilization" is an important factor in comprehending the operation of gasifiers. A series of reactions involving carbon, hydrogen, and oxygen are highly endothermic above about 500 C; in these reactions the initial combustion products $\rm H_2O$ and $\rm CO_2$ are reduced to form the fuel gases $\rm H_2$ and $\rm CO$. Though kinetically slow at temperatures below 800 C (see section on kinetics), these reactions become very fast above 1200 C. Thus as long as any $\rm H_2O$ or $\rm CO_2$ is present in the gas-char mixture, temperature increases will be suppressed and fuel gas will be produced. For this reason gasification equipment is relatively simple and does not have to be made of the highly temperature resistant materials used in combustion equipment. Furthermore, this buffering of the flame temperature also gives relatively stable gas compositions.

Finally, an equivalence ratio of zero corresponds to no oxidation and pure pyrolysis. Figure S-2 shows the surprising result that even without any oxygen or energy addition, biomass could reach a temperature of about 900 K (627 C) if a kinetic route to equilibrium could be found. Biomass pyrolysis can be regarded as a means of bringing biomass to equilibrium with a minimum of energy loss, time, and equipment. Unfortunately, this equilibrium includes formation of about 30% char; so, a second task in gasification is conversion of any unwanted char to gas. This is accomplished most easily by using the char to reduce $\rm H_2O$ to $\rm H_2$, but this, in turn, complicates the process. (Biomass often contains as much as 50% excess water that can thus be put to good use here.) The effect of water addition on the conversion of char has been examined at various temperatures and pressures.

In updraft gasifiers the initial reaction is in the hot zone (where equilibrium may be approached) but subsequent reactions occur at successively lower temperatures so that it is not expected that these equilibrium calculations will have much relevance to the final gas composition, though they are important in understanding the reactions at the grate. In downdraft gasifiers combustion occurs first and then the gases are drawn through the hot charcoal, thus having a good chance to reach a quasi-equilibrium. Finally, in fluidized bed gasifiers a number of variations of temperature can be used to produce specific intermediate equilibrium states, thus giving better control over gas composition.

KINETICS OF CHAR GASIFICATION REACTIONS (Chapter 7)

Although equilibrium favors the formation of fuel gases in any system where there is an excess of char, the rate of conversion of char to gas depends in a rather complex fashion on the kinetics of the reactions. Without catalysts, very little reaction occurs below about 800 C, but at higher temperatures the reactions become very rapid and equilibrium considerations dominate. The degree of reaction is influenced by the particle size; the physical properties of the char, especially its porosity and lifetime; and the methods of contacting gas with char in fixed-bed, fluidized-bed, or suspended flow gasification.

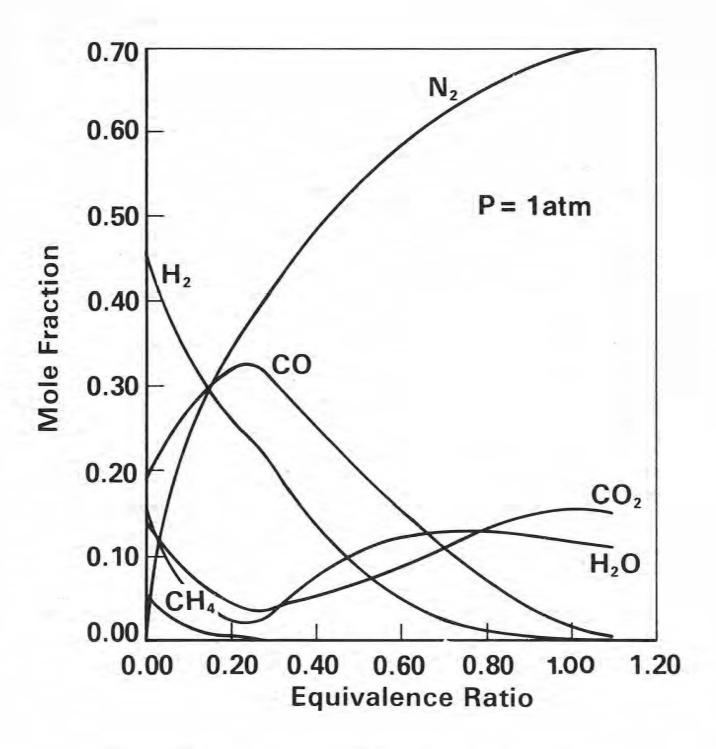


Figure S-3. Equilibrium Composition for Adiabatic Air/Biomass Reaction

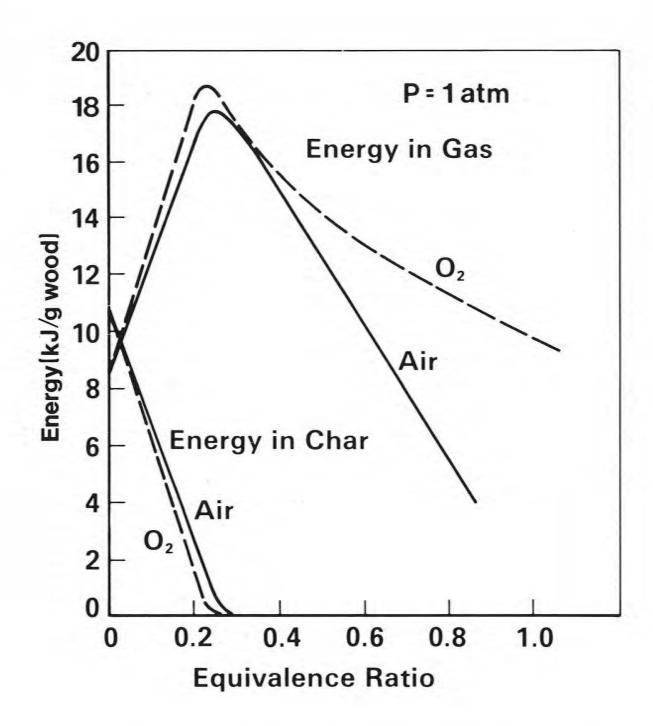


Figure S-4. Gas and Char Energy Content for Oxygen and Air/Biomass Equilibrium

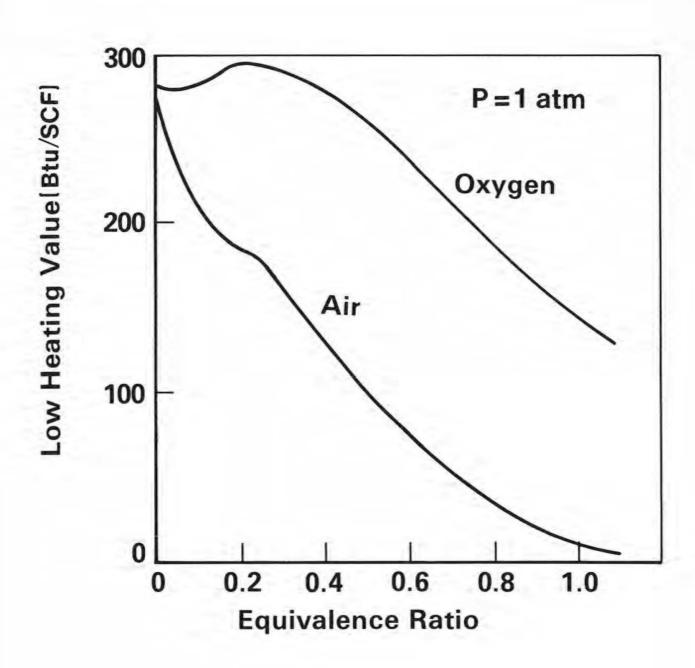


Figure S-5. Low Heating Value for Dry Equilibrium Gas for Air/O₂ - Biomass Reaction



Fortunately, a great deal of work done in the gasification of coal is also applicable to biomass. However, very little of this work has been applied to biomass, a task for the coming years.

In the reaction of char to form gas, the following steps occur in series and each can, under certain conditions, limit the reaction rate:

- diffusion of reactants across the boundary layer at the external char surface;
- · diffusion of gas through the pores of the solid;
- adsorption, surface reaction, and desorption of gas on the pore wall;
- diffusion of products out of the pore; and
- diffusion of products across the boundary layer.

The overall reaction rate (i.e., the effective reaction rate in a practical situation) is composed of two factors: the rate of heat and mass transfer between the bulk gas surrounding the char particle and the particle, and the true kinetics of reaction at the char surface or in the pores. A very useful parameter in evaluating the relative importance of these two factors is the "effectiveness factor," a measure of the effect of pore volume and surface on reaction rate.

The external heat and mass transfer are described by well-known equations in terms of the heat and mass transfer coefficients which, in turn, depend on diffusion coefficients, thermal conductivities, reactant concentrations, and other gas properties. At sufficiently high temperatures, these coefficients do not change rapidly with temperature.

The mass transfer coefficient behaves like a diffusion coefficient. If an Arrhenius behavior is assigned to the mass transfer coefficient, at sufficiently high temperatures the effective activation energy is very low, only about 4 kcal/mole. There is also an activation energy required for heat transfer, and as a practical consequence at high temperatures the particle temperature can be significantly lower (endothermic reaction) or higher (exothermic reaction) than the surrounding gas temperature.

At lower temperatures, the gasification reactions occur principally within the char particle, requiring the reactants to diffuse into the pores to the reacting surface. The average rate of diffusion within the pores relative to the rate of diffusion to the particle surface is given by the effectiveness factor. Effectiveness factors are estimated for biomass chars and, at low temperatures with small particles, external heat and mass transfer are not limiting. At temperatures over 1100 C for gasification reactions and at lower temperatures for combustion reactions, the effectiveness factor approaches zero and external heat and mass transfer are limiting. The porosities of chars produced from biomass materials are such that comparable gasification rates are obtained at temperatures 100 C to 200 C lower than those required for coal.

Particle size also determines the degree to which mass and heat transfer are limiting. For the small particles encountered in suspended or fluidized-bed gasification, external transfer is never important below about 1100 C. However, for fixed-bed operation and large particles, transfer becomes limiting at lower temperatures. Adaptation to biomass of the heat and mass transfer equations developed in coal gasification is an important task in gasification research.



Much theoretical and experimental work has been done to determine the mechanism of the reaction of ${\rm CO}_2$ and steam with chars. Such mechanistic studies are necessary to elucidate these gasification reactions for biomass. These studies should be coupled with experimental work on the reactivities of the various forms of char that arise during pyrolysis and that change as the char is consumed. Data show that chars from biomass are much more reactive than those from coal. Several investigators have determined the effect of catalysis on char gasification and found mixed results, ranging from the anticatalytic effects of many minerals to a tripled reaction rate catalyzed by ${\rm K}_2{\rm CO}_3$.

An interesting field now being explored is hydrogasification of coal. The rapid heating of char in a hydrogen atmosphere enhances hydrocarbon yields. Few studies of the kinetics of biomass hydrogasification have been done, but this should be a fruitful field of research.

A SURVEY OF GASIFIER TYPES (Chapter 8)

The central problem in gasification is to convert all of the elements comprising solid biomass into gases containing the highest possible energy. Yet no combination of the constituent elements of dry biomass leads directly to gas only. For instance, an equilibration of dry biomass at 1000 C would give:

$$CH_{1.4}O_{0.6} \rightleftharpoons 0.7 H_2 + 0.6 CO + 0.4 C \text{ (solid)}$$

in which $\mathrm{CH}_{1.4}\mathrm{O}_{0.6}$ is a representative formula for biomass and the solid char formed contains a significant part of the biomass energy. Gasification at lower temperatures avoids equilibrium and produces a high proportion of oil in addition to char. Conversion of these chars and oils to gases can be done by four basic types of gasification: air gasification, oxygen gasification, hydrogasification, and pyrolytic processes comprising generally more complex cycles.

Air Gasification

The simplest form of gasification is air gasification, in which the excess char formed by purelysis is burned with a limited amount of air at an equivalence ratio of about 0.25, requiring 1.6 g air per gram of biomass.

The simplest air gasifier is the updraft gasifier shown in Fig. S-6. Air is drawn up through a fixed bed of biomass on a grate. At the lowest and hottest level on the grate, combustion and char gasification occur; as the gases rise they reach the successively lower temperature pyrolysis and drying zones and exit the gasifier at low temperatures, saturated with pyrolysis oils and water. Ideally, this gas is burned immediately in a boiler, the so-called "close-coupled" operation. The temperature of the output gas must be kept high enough to prevent condensation of oils before combustion, yet low enough to prevent the oils from coking. A number of these units are now in operation in the United States.

Oil production is largely eliminated in downdraft gasifiers (Fig. S-7), where air is introduced between the char zone and the pyrolysis zone. Heat from the char zone pyrolyzes the biomass above; the tars and oils pass down through a bed of hot charcoal where they are cracked and reduced, mostly to $\rm H_2$ and $\rm CO$ fuel gas. Several million of these gasifiers were used in Europe during World War II to operate cars and trucks.

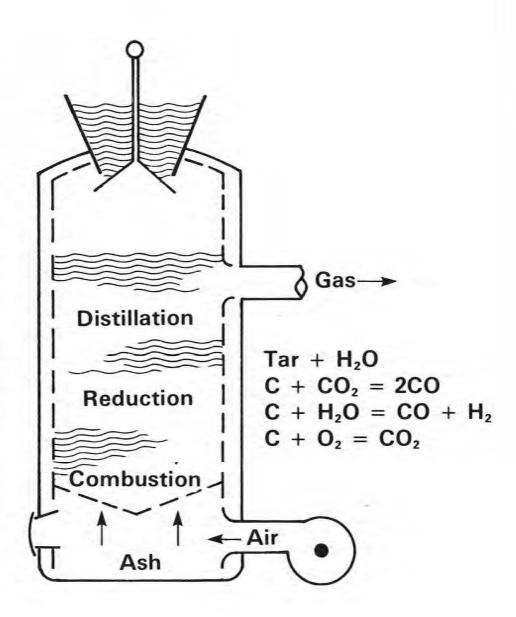


Figure S-6. Schematic Diagram of Updraft Gasifier



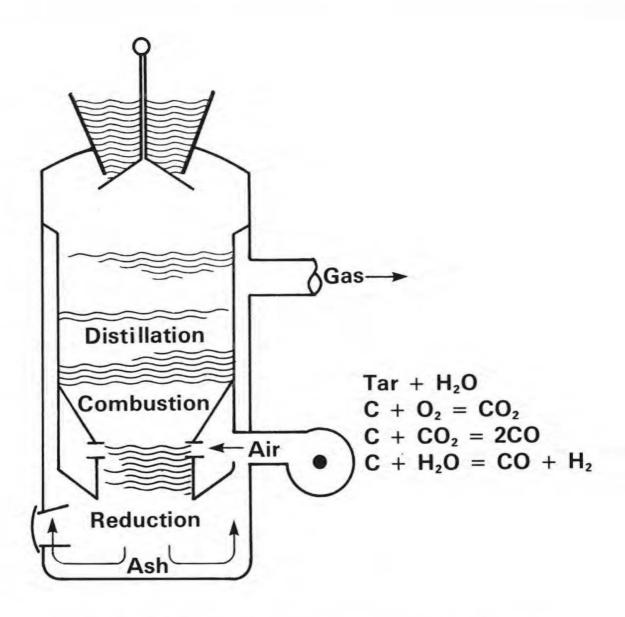


Figure S-7. Schematic Diagram of Downdraft Gasifier



Fixed-bed gasifiers require biomass of a relatively uniform size larger than several centimetres in the smallest dimension, so that gas passages are provided in and around the particles. A wider range of particle size and higher throughput can be achieved with fluidized-bed gasifiers, in which a sufficiently large flow of gas is maintained to provide a fluidized bed. Fluidized-bed gasifiers often contain a solid heat transfer agent such as a catalyst or sand and generally require a recycling of the product gas to maintain fluidization. It is claimed that these gasifiers minimize oil production and maximize char consumption, but they are in the early stages of development.

Air gasifiers are simple, cheap, and reliable and have operated almost continuously for decades at a time. Their chief drawback is that the gas produced is low in energy and would be uneconomical to distribute; it must be used on-site for process heat to operate engines and for power generation.

Oxygen Gasification

The production of low energy gas is not a problem in oxygen gasifiers, in which the product is undiluted by nitrogen from air and could be distributed in an industrial pipeline network, as town gas was distributed in the United States until 1940. In addition, the medium energy gas is a necessary precursor to the manufacture of methanol, ammonia, methane, or gasoline.

Updraft oxygen gasification has been demonstrated with municipal solid waste (MSW - Purox process). A small downdraft oxygen gasifier has been operated on a SERI contract. The chief disadvantage of oxygen gasification is that it requires an oxygen plant or nearby source of oxygen and thus increases the cost of gasification.

Hydrogasification

Research is just beginning on the effects of added H₂ (or CO) on gasification, with emphasis on enhanced direct methane production.

Pyrolysis Gasification

Oxygen and air gasifiers consume char directly by increasing the oxygen content of the biomass to permit gas formation. In pyrolytic processes gas, oil, and char all are formed simultaneously in a reactor. Subsequently the char and oil are converted in a separate reactor to heat and additional gas. The subsequent process recirculates hot solids or hot gases as a heat exchange medium for additional conversion of the char and oil to gas. A high moisture content in the biomass, a liability in air and oxygen gasification, contributes hydrogen in pyrolytic processes.

The four types of gasifiers mentioned in Fig. S-1 can be grouped into a large number of subdivisions according to various characteristics:

- Fuel type: including biomass, solid municipal waste, peat, coal;
- Fuel size: chunks, shreds, pellets, powder;
- Fuel gas contact: updraft (counterflow), downdraft (co-flow), fluidized bed, suspended particle;



- Ash form: dry ash for grate temperature below about 1100 C; slagging for temperatures above 1300 C, depending on feed;
- Pressure: Although no pressurized biomass gasifiers now exist, there are a number of advantages to building gasifiers operating at 10 to 100 atm; and
- · Catalyst use.

Of the many types of gasifiers, those for which examples are given in the main body of the report are listed in Table S-3.

DIRECTORY OF GASIFIER MANUFACTURERS (Chapter 9)

Questionnaires were sent to the manufacturers and researchers listed in Table S-3, who are currently working on gasifiers; the results are given as a directory listing the various characteristics of existing gasifiers by manufacturer.

SURVEY OF GASIFIER RESEARCH (Chapter 10)

Where scientific and engineering studies are in progress for gasification processes, the processes are summarized. Gas compositions, salient features, and the present status of many of the projects listed in Table S-3, among others, are given in more detail. Some of the projects are primarily research, developing information useful to the gasification community; others are in the development stage, characterizing a particular gasifier in engineering terms and determining and solving operational problems. Others have been built on a commercial scale and are being use-tested. References in the literature are provided where available. The listing is not complete, relying heavily on current studies supported by DOE. Additions and corrections are welcome.

ECONOMICS OF GASIFICATION FOR EXISTING GAS/OIL SYSTEMS (Chapter 11)

A particularly attractive feature of gasification is that it permits continued use of existing gas/oil equipment. This retrofit capability has caused a great deal of interest in air gasification and a number of companies have been formed to manufacture and sell air gasifiers.

In comparing the cost of retrofitting existing equipment to new installations, it is estimated that the purchase of an air gasifier in the size range from 5 MBtu/h to 100 MBtu/h, for attachment to existing boilers, will cost about two-thirds of the cost of a new solid fuel installation, as shown in Fig. S-8. Furthermore, the simplicity of gasburning boilers suggests that a gasifier combined with a new gas boiler will be comparable in price to installing a new, solid-fueled boiler. The gasifier combination offers lower emissions and higher turndown ratios than the solid-fueled boiler, and the option to burn gas or oil.

In order to compare gas costs of various technologies, SERI has adapted the cost analysis method developed at the Electric Power Research Institute (EPRI). This method was used to estimate the costs of gas produced in two gasifiers. The resulting costs are shown in Table S-4 for biomass costing \$20/dry ton. Since gasifiers are low in capital costs, the conversion and operating costs (first year) are \$0.17/MBtu to \$0.26/MBtu. At



Table S-3. SURVEY OF GASIFIER RESEARCH, DEVELOPMENT, AND MANUFACTURE a,b

	Gasi	fier Type			Size
Organization	Input	Contact Mode	Fuel Products	Operating Units	Btu/h
Air Gasification of Biomass					
Alberta Industrial Dev. Edmonton, Alb., Can.	A	F1	LEG	1.1	30M
Applied Engineering Co., Orangeburge, SC 29115	A	U	LEG	1	5M
Battelle-Northwest Richland, WA 99352	A	U	LEG	1-D	-
Century Research, Inc. Gardena, CA 90247	A	Ü	LEG	1	80M
Davy Powergas, Inc. Houston, TX 77036	A	U	LEG-Syngas	20	
Deere & Co. Moline, IL 61265	A.	D	LEG	1	100kW
Eco-Research Ltd. Willodale, Ont. N2N 558	. A	Fl	LEG	1	16M
Forest Fuels, Inc. Keene, NH 03431	A	U	LEG	4	1.5-30M
Foster Wheeler Energy Corp. Livingston, NH 07309	A	U	LEG	1	
Fuel Conversion Project Yuba City, CA 95991	A	D	LEG	-1	2M
Haleyon Assoc. Inc. East Andover, NY 03231	A	U	LEG	4	6-50M
Industrial Development & Procurement, Inc. Carle Place, NY 11514	A	D	LEG	Many	100-750kW
Pulp & Paper Research Inst., ^c Pointe Claire, Quebec H9R 3J9	A	D	LEG	-	-
Agricultural Engr. Dept. Purdue University W. Lafayette, IN 47907	A	D	LEG	1	0.25M
Dept. of Chem. Engr. Texas Tech University Lubbock, TX 79409	A	FI	LEG	I	0.4M
Dept. of Chem. Engr. Texas Tech University Lubbock, TX 79409	A	Ü	LEG	1	-
Vermont Wood Energy Corp. Stowe, VT 05672	A	D	LEG	1	0.08M

^aTable notation defined at end of table.

^bUnless noted otherwise, the gasifiers listed here produce dry ash (T < 1100 C) and operate at 1 atm pressure.

(Coal gasifiers and future biomass gasifiers may operate at much higher pressures.)

^cOperates at 1-3 atm pressure.



Table S-3. SURVEY OF GASIFIER RESEARCH, DEVELOPMENT, AND MANUFACTURE (continued)

	Gasi	fier Type			Size
Organization	Input	Contact Mode	Fuel Products	Operating Units	Btu/h
Dept. of Ag. Engr. Univ. of Calif. Davis, CA 95616	A	D	LEG	Ī	64,000
Dept. of Ag. Engr. Univ. of Calif. Davis, CA 95616	A	D	LEG	1	6M
Westwood Polygas (Moore)	A	U	LEG	1	
Bio-Solar Research & Development Corp. Eugene, OR 97401	A	U	LEG	1	
Oxygen Gasification of Biomass					
Environmental En. Eng. Morgantown, WV	0	D	MEG	1P	0.5
IGT-Renugas	0,5	P1	MEG		
Pyrolysis Gasification of Biomass					
Wright-Malta Ballston Spa, NY ^a	PG	0	MEG (C)	1R, 1P	4
Coors/U. of MO	P	Fl		12	
U. of Arkansas	P	0	MEG (C)	IR	
A & G Coop Jonesboro, AR	P	0	MEG (C)	IC	
ERCO Cambridge, MA	P	F1	PO, C	1P, (1C)	16, (20)
ENERCO Langham, PA	P		MEG, PO, C	1P, 1C	
Garrett Energy Research	MH		MEG	1P	
Tech Air Corporation Atlanta, GA 30341	P	U	MEG, PO, C	4P, 1C	33

^aOperates at 10 atm pressure.



Table S-3. SURVEY OF GASIFIER RESEARCH, DEVELOPMENT, AND MANUFACTURE (continued)

	Gasifi	er Type			Size
Organization	Input	Contact Mode	Fuel Products	Operating Units	Btu/h
M. Antal Princeton Univ. NS	PG	0	MEG, C	1 R	
M. Rensfelt Sweden	PG	0	MEG, C	1 R	
Texas Tech Lubbock, TX	PG	F1	MEG	1 P	
Battelle-Columbus Columbus, OH					
Air Gasification Solid Municipal Waste (CSMW)					
Andeo-Torrax ^a Buffalo, NY	A	U	LEG	4C	100M
Battelle NW Richmond, VA 99352					
Oxygen Gasification of SMW					
Union Carbide (Linde) Tonowanda, NY ^a	0	ū	MEG	* : 1 , *	100M
Catorican Murray Hills, NS	0	U			9M
Pyrolysis Gasification of SMW					
Monsanto, Landgard, Enviro-chem.	P, C	K	LEG, O, C	1 D	20 (375)
Envirotech, Concord, CA	P	MH	LEG	1 P	
Occidental Res. Corp El Cajon, CA	P	F1	PO, C, MEG	1 C	
Garrett En. Res. & Eng. Hanford, CA	P	МН	MEG	1P	
Michiga Tech, Houghton, MI	P	ML	MEG		
U. of W. Va-Wheelebrator Morgantown, WV	P, G, C	Fl	MEG	1P	
Pyrox Japan	P, G, C	Fl	MEG	IC	
Nichols Engineering	P		MEG, C		

^aThese gasifiers produce slagging (T > 1300 C) instead of dry ash.



Table S-3. SURVEY OF GASIFIER RESEARCH, DEVELOPMENT, AND MANUFACTURE (concluded)

	Gasifier Type				Size
Organization	Input	Contact Mode	Fuel Products	Operating Units	Btu/h
ERCO Cambridge, MA	P	F1	MEG	1P	16
Rockwell International Canoga Park, CA	P	MS	MEG, C	1P	16
M. J. Antal Princeton, NS	P	0	MEG, C	2R	

TABLE NOTATION: (by columns)

Input: A = air gasifier; O = oxygen gasifier; P = pyrolysis process; PG = pyrolysis gasifier; S = steam; C = char combustion

Contact Mode: U = updraft; D = downdraft; O = other (sloping bed, moving grate); Fl = fluidized bed; S = suspended flow; MS = molten salt; MH = multiple hearth

Fuel Products: LEG = low energy gas (~150-200 Btu/SCF) produced in air gasification; MEG = medium energy gas produced in oxygen and pyrolysis gasification (350-500 Btu/SCF); PO = pyrolysis oil, typically 12,000 Btu/lb; C = char, typically 12,000 Btu/lb

Operating Units: R = research; P = pilot; C = commercial size; CI = commercial installation; D = demonstration

Size: Gasifiers are rated in a variety of units. Listed here are Btu/h derived from feedstock throughput on the basis of biomass containing 16 MBtu/ton or 8000 Btu/lb, SMW with 9 MBtu/ton. () indicate planned or under construction.



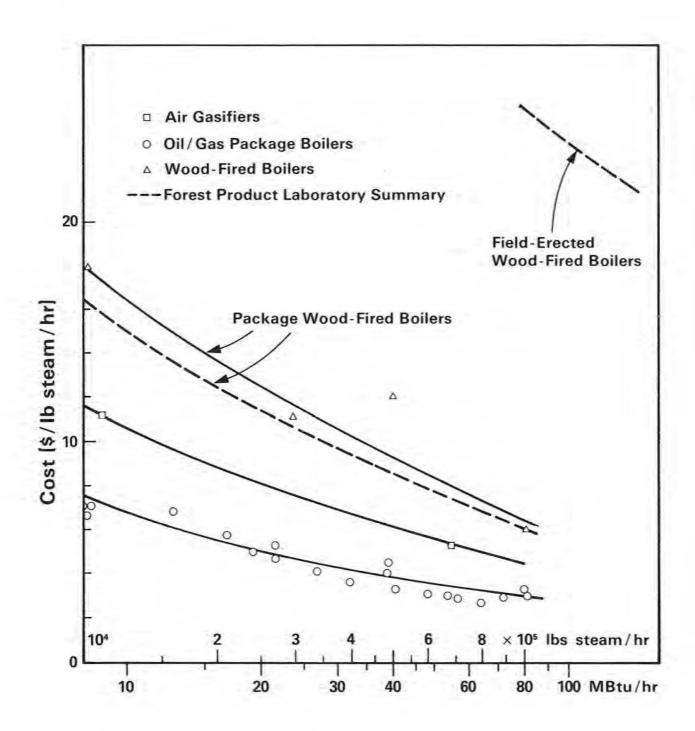


Figure S-8. Cost Comparisons Between Retrofitting Existing Equipment and New Installations



\$20/dry ton, total costs for gas are to \$2.58/MBtu to \$4/MBtu. However, many manufacturers have biomass residues available at a cost considerably lower than \$20/ton.

Table S-4. DETAILED COST BREAKDOWN FOR \$20/TON FUEL (\$/MBtu)

		er "A" Btu/h)	Gasific (85 MI	
	1978 Cost	Levelized Cost	1978 Cost	Levelized Cost
Operating Costs	\$0.11	\$0.15	\$0.13	\$0.19
Capital Costs	0.06	0.09	0.13	0.19
Fuel Cost	2.55	3.75	2.32	3.40
TOTAL COSTS	\$2.72	\$3.99	\$2.58	\$3.78

GAS CONDITIONING PROCESSES (Chapter 12)

Any working gasifier is only a part of a system involving solid feed delivery, gas conditioning, and final use. Conditioning the gas can be as costly and difficult as gasification itself. The Mittelhauser Corporation has made a thorough study of the existing methods and the costs of gas scrubbing, one form of gas conditioning.

If the gas from a gasifier is to be used directly for heat (close-coupled operation) there is probably no need for conditioning. In all other cases, however, oils, tars, and hydrocarbons contained in the gas may prohibit its distribution in a pipeline or its use as a chemical feedstock. To condition the gas for its final use, it is necessary to employ a range of available commercial equipment.

The raw gas typically contains as much as 5% (by weight) of oxygenated oils and tar vapor. These can be removed by scrubbing with a spray of the oil itself or with water in a variety of scrubber designs, followed by a mist eliminator or an electrostatic precipitator, depending on the final application. If the gas is to be used primarily for heat, this treatment is generally sufficient.

If the gas is to be used for chemical synthesis of methanol, ammonia, gasoline, or natural gas, further conditioning is required because of the presence of hydrocarbons that can affect the catalyst and possibly of sulfur (though biomass is relatively low in sulfur). Also, the carbon/hydrogen ratio of the gas must be adjusted to the proper value for chemical synthesis. The processes of hydrogenation, re-forming, and cryogenic separation to accomplish these ends are discussed.

The design of gas conditioning plants is studied and commercial practice is illustrated. Examples of costs for hydrogenation, re-forming, and cryogenic separation plants are developed. For instance, the capital cost of gas cleanup for methanol manufacture is



\$127/daily ton. Although it is probable that improvements can be made in both gasification itself and in cleanup, this is a very sizable fraction of processing cost and must not be overlooked.

PRODUCTION OF LIQUID FUELS AND CHEMICALS FROM BIOMASS GASIFICATION (Chapter 13)

Gasification is already becoming important for the production of manufactured gases to replace natural gas and oil. Ultimately of equal importance may be the production of liquid fuels and chemicals, from what is known as "synthesis gas," often called "syngas," a mixture of CO and H₂. Commercial processes for using this gas already exist and are summarized in Table S-5. Here it is evident that a wide variety of useful products can be made, provided that syngas can be produced from biomass. This chapter, prepared by Science Applications Inc., provides an understanding of syngas technology and some examples of the costs of making synthetic fuels and chemicals.

Also shown in Table S-5 are the percentages of the heating value of syngas lost in conversion to the products shown and the "equilibrium" temperature for the conversion reaction. Conversion must normally be made at temperatures below this value and therefore will require catalysts and often high pressure. There also is an energy loss involved in conversion, though the penalty is justified by the higher value of the product.

The most important of the syngas reactions in the United States today is the production of methanol. Currently about a billion gallons per year are made from natural gas, primarily for the plastics industry. The reaction utilizes a CuO-ZnO catalyst at a pressure of 100 atm at about 300 C. All of the syngas conversions are exothermic, and reactors must be specially designed to carry this heat away; on the other hand, this heat is available at a relatively high temperature and can be used for compression and power generation.

Several other methanol catalysts are also available, and a new, liquid phase methanol synthesis process is being developed that removes the reaction heat more efficiently. Projections show a cost advantage of about 15% over present processes. Present processes based on natural gas have efficiencies of 50% to 70%. Biomass processes are projected to have overall efficiencies in the 30% to 50% range.

A number of studies have been made of the cost of methanol production from wood, refuse, gas, and coal in the past five years. The results of these studies, brought to a common basis for comparison, are presented in Table S-6. Here production costs from wood are projected to be \$0.50 to \$1.35/gal based on feedstock costs from \$20 to \$48/dry ton. Methanol costs from refuse are projected to be \$0.72 to \$0.42/gal based on a \$6 to \$14/ton credit for waste disposal.

An interesting new concept in the manufacture of methanol is that of the hybrid biomass-methane plant. Syngas produced from biomass is hydrogen-poor, and increasing the hydrogen content requires additional processing. Syngas from re-forming natural gas is hydrogen-rich. Therefore there would be considerable advantage in using a biomassmethane feedstock anywhere that isolated gas wells can be used. Depending on the gasification process, it is expected that the yield would be increased two to five times over that achievable with the biomass alone, and processing costs would be reduced.

Table S-5. SELECTED GAS CONVERSION SYNTHESES

Reaction	Approximate T ^o C at Which ΔF = 0 ^a	ΔH ^a (keal/mol product)	Percent of Heating Value of Syngas Lost ^C
Methanol: CO + 2H ₂ = CH ₃ OH	140	-10.3 ^b	15.2 ^b
Ethanol: $2 \text{ CO} + 4\text{H}_2 = \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$	300	-11.8 ^b	17.4 ^b
Methane: $CO + 3H_2 = CH_4 + H_2O$	690	-12.3	18.2
Nonane: $9CO + 19H_2 = C_9H_2O + 9H_2O$	410	-12.0	17.8
Decane: $10CO + 19H_2 = C_{10}H_{22} + 10H_2O$	410	-12.0	17.8
Alkane + CH_2 : R-R' + CO + $2H_2$ = RCH_2R' + H_2O	380	-12.0	17.8
Ethylene: $2CO + 4H_2 = C_2H_4 + 2H_2O$	380	-8.4	12.4

^aAll species in standard gas states unless otherwise noted.

^bAlcohol in liquid state.

^cSyngas heating value is approximately 67.8 kcal/mol.

Source	Plant Size (Ton MeOH /day)	Feedstock		Reforming Oxidation or	Methanol	Capital	Annual Operation & Maintenance			Unit Production Cost	
		Туре	Throughout per/day	Gasification Process	Synthesis Process	Cost ^a (Million \$)	Cost (Million \$)	Feedstock Cost	(\$/gal) MeOH)	(\$/ Ton MeOH)	(\$/ MBtu)
Badger Plants, Inc.	58,300	Coal	63,000	Slagging Gasifier	Lurgi low pressure	3,800	593	\$31/ton	0.23	69	3.7
Ralph M. Parsons	245	Refuse 25.8% moisture	1,500 tons	Purox (Union Carbide)	Low pressure	126	16	\$-14/ton ^b	0.72	217	10
Mathematical Sciences Northwest	275	Refuse 25% moisture	1,500 tons	Purox (UC)	ICI low pressure	31	3,1	\$-6.4/tonb	0.42	127	6.5
Reed, T.	300	Wood (dried)	900	not reported	Available commercial process	45	5.0	30.3	0.58	173	8.9
Intergroup Consulting Economists (Canada)	1,000	Wood 35% moisture	2,380	Purox	Available commercial process	223	16	37	0.76	229	11.8
Mackay and R. Sutherland (Canada)	1,000	Wood (dried)	3,160	not reported	ICI medium pressure	223	13,8	46	0,96	290	15
MITRE	1,340	Wood 50% moisture	3,400	Purox	ICI low pressure	130	21	45	0.66	199	10
MITRE	335	Wood 50% moisture	850	Purox	ICI low pressure	46	8.9	45	0.84	253	13
Raphael Katzen Associates	500	Wood waste 50% moisture	1,500	Moore- Canada	Vulcan Cincinnati intermediate pressure	90	7	48	1.35	404	20.7
Raphael Katzen Associates	2,000	Wood waste 50% moisture	6,000	Moore- Canada	Vulcan Cin. I. P.	237	N/A	48	1.02	304.0	15.6
SRI	666	Wood 50% moisture	1,000	Oxygen blow gasification	not specified	100.8	9.0	19.1	0.51	154	7.96
SRI	1990	Wood 50% moisture	3,000	Oxygen blow gasification	not specified	268.7	29.4	19.1, 38.2	0.50, 0.62	150, 185	7.77, 9.53

a Costs were extrapolated to 1980 dollars by using the Chemical Engineering Cost Index with appropriate extrapolation, b Negative numbers mean that the methanol producer receives money by taking the feedstock (refuse in this case). This money comes from the refuse and drop charges.



The hybrid system has advantages for retrofitting existing natural gas methanol plants, with biomass replacing as much as 30% of the natural gas feedstock, possibly reducing methanol cost. For long-term development, methane could be derived from anaerobic digestion of biomass, municipal solid waste, sewage sludges, or peat. Another variation envisions augmenting methanol production with hydrogen from electrolysis of water or thermochemical closed cycles driven by solar energy. The oxygen from electrolysis could be used in the gasifier.

Although methanol synthesis is the most highly developed alcohol production process at present, catalysts containing alkali or alkaline earth oxides with acid metals (chromates, manganates, molybdates) have been used to produce a mixture of alcohols with 42% methanol, 38% higher alcohols, and 15% aldehydes and acetals. Higher alcohols have a higher energy content than methanol and high octane properties, and investigations of these catalysts should be a part of any alcohol fuel program.

Hydrocarbon fuels have been made from synthesis gas since the 1920s by the Fischer Tropsch process and were an important route to synthetic fuels used by Germany during World War II. They have been produced in South Africa since the early 1950s, and capacity there is now being increased fivefold. The Fischer Tropsch process suffers from having a very wide variety of products, including olefins, alcohols, and waxes. The principal components of the catalyst are cobalt and iron. Nitrided and carburized iron catalysts improve yields of middle distillates and reduce yields of waxes and olefins. Synthesis occurs at about 250 C at 20 atm. Recent work at Exxon is directed toward sulfur resistant catalysts. Since biomass contains little sulfur, use of biomass for Fischer Tropsch processing could offer considerable savings.

Recently, the Mobil Corporation has announced a new process for converting methanol to gasoline using molecular sieves. If the C_3 and C_4 olefins are alkylated with the isobutane produced in the reaction, the process gives over 90% yields of high octane gasoline from methanol. Conversion is projected to cost \$0.06/gal of gasoline and requires 2.4 gallons of methanol per gallon of gasoline produced. Gasoline from methanol requires 23% more energy than is contained in the methanol feedstock. Since methanol can be burned in spark engines with 26% to 45% higher efficiency than gasoline, this is a severe energy penalty. The cost of producing gasoline from wood by the Mobil process has been estimated to range from \$1.89 to \$2.51/gal.

Ammonia has been called a "fuel for biomass," because modern farming achieves efficient production of biomass with ammonia fertilization. Furthermore, ammonia is produced in a series of reactions from synthesis gas in plants basically similar to those used for methanol production. Thus it is natural to include the possibility of product ammonia in any biomass gasification scheme, and a methanol/ammonia plant small enough for operation on farm residues at a farmer's cooperative would go a long way toward making the American farmer independent of fossil fuel inputs.

Typically, ammonia is made at pressures to 200 atm using FeO-Fe₂O₃ catalysts and small additions of other metallic oxides. Recent studies of the synthesis of ammonia from wood show a mass conversion efficiency of 1.7 to 2.0 tons of biomass required per ton of ammonia produced. For wood costing \$20 to \$45/dry ton, ammonia would cost \$120 to \$300/ton.

Since these costs are competitive with ammonia produced by current industrial processes, production of ammonia may well be the first chemical use of biomass derived synthesis gas. With current technology, methanol is the best liquid fuel that can be



produced thermally from biomass feedstocks. In the long term, new technologies may play a significant role in improving the economics of all the gasification processes for producing alcohols, gasoline, methane, H₂, and chemicals.

INSTITUTIONAL SUPPORT OF BIOMASS GASIFICATION AND RELATED ACTIVITIES (Chapter 14)

A questionnaire asking for opinions on possible roles for government assistance was sent by Pyros, Inc., to a number of manufacturers, researchers, and members of government and private institutional groups interested in biomass utilization and gasification in particular. Twenty responses were received and are summarized.

RECOMMENDATIONS FOR FUTURE GASIFICATION RESEARCH AND DEVELOPMENT (Chapter 15)

This survey has been written to outline the value of gasification, the technical base on which future work can proceed, and the activities now underway. Various people reading this information will draw different conclusions. We give here the conclusions on which we will base our work at SERI and toward which we recommend guiding the national program. None of these conclusions is immutable and we invite comment as to their validity.

- We recommend that both coal and biomass gasification be developed rapidly, because these two technologies will be required soon to supplement fuel supplies as oil and gas become increasingly costly or unavailable. Gasification can provide not only the gas needed for clean heat and power in our cities, but also the basis for synthesis of liquid fuels, SNG, ammonia, and olefins.
- Air gasifiers may find a place in domestic and commercial heating, but they
 certainly will be used in process heating and producing power for the biomass
 industries. Although research in progress may improve air gasification, we
 recommend immediate commercialization at the present level of development.
- Large-scale oxygen gasifiers may play a prominent role in the conversion of municipal waste. If small oxygen gasifiers and plants could be developed (50 tons/day), they could play a crucial role in energy self-sufficient farms, manufacturing ammonia and methanol or gasoline from residues at the farmers' cooperative level to eliminate the heavy dependence on fossil fuels that makes our farms vulnerable to inflating fuel costs and uncertain supply. We recommend development of a 50 ton/day to 100 ton/day pressurized oxygen gasifier to operate on farm or forest residues. From preliminary operation of a downdraft gasifier on oxygen, and from the thermodynamics presented in the survey, we believe that it will be possible to design an oxygen gasifier that produces clean synthesis gas in one step, eliminating the need for costly gas conditioning. In this regard we recommend that support be provided for research on energy efficient methods to separate oxygen from air.
- Pyrolytic gasifiers are not as well developed as oxygen gasifiers, but the majority
 of the research supported by EPA and DOE has been in this area. We recommend
 continuing research and pilot work on many of these systems because they promise higher efficiencies and lower costs than oxygen gasification in production of
 medium energy gas. However, because it is not clear to what degree medium



energy gas will be distributed in the United States, full-scale development of pyrolytic gasifiers must wait on decisions concerning the gas infrastructure in the United States. These decisions hinge on the costs of converting gas to methane for distribution versus distribution of lower energy and lower cost gas. One possible development would be the use of medium energy gas in captive installations and industrial parks but conversion of coal to methane for domestic distribution.

- We recommend top priority development of fast pyrolysis processes that give a high yield of olefins which can be converted directly to gasoline or alcohols. This seems to be the one truly new development in gasification since World War II. We recommend evaluating various feedstocks and particle size options at the bench level, combined with bench and engineering studies of process designs giving the very high heat transfer and short residence times necessary to produce these products. We also recommend evaluation of processes for reducing particle size at reasonable costs, since this appears to be a necessary adjunct to fast pyrolysis.
- Finally, we recommend a continuing effort to determine the molecular details of pyrolysis under carefully controlled but realistic laboratory conditions, to provide a firm foundation for understanding and thus improving all gasification processes.

A number of systems studies also should be performed as adjuncts to the technical program.

- We recommend that the scale of gasification plants be studied immediately and, where appropriate, that programs be initiated to overcome scale limitations. In particular, coal is likely to supply gas heat for our cities, where large plants can clean the gas sufficiently and make methane for distribution. Because biomass is much cleaner it can be used on a smaller scale, a fact which is compatible with its wider distribution. If biomass residues must be processed at the 1,000 ton/day level or greater to be economically viable, very little biomass will be used as an energy source in this country. If it can be processed economically at the 100 ton/day level, it can be used more widely.
- We recommend a systems study of biomass energy refineries to be used in conjunction with farming and forestry operations, taking residues and converting them to the ammonia and fuel required to operate the farm and forestry operation, and shipping any surplus energy to the cities in the form of gaseous or liquid fuels.

For the longer term, and for biomass conversion plants of larger scale, economic analyses should be performed to identify suitable hybrid schemes. These include:

- production of methanol using a combination of biomass (low hydrogen/carbon ratio) and natural gas (high hydrogen/carbon ratio);
- joint electrolytic/gasification systems in which waste generates hydrogen and oxygen electrolytically, the oxygen is consumed in gasification and the hydrogen increases the hydrogen/carbon ratio; and
- solar fast pyrolysis, in which the high intensity heat is supplied by solar collectors.

1. SERI Report No. TR-33-239	2. NTIS Accession No.	Recipient's Accession No.		
s Gasification	5. Publication Date July 1979			
	6.			
	8. Performing Organization Rept. No.			
Name and Address	10. Project/Task/Work Unit No. Task #3322			
earch Institute/DO ard 80401	11. Contract (C) or Grant (G) No. (C) (G)			
on Name and Address	13. Type of Report & Period Covered Technical Report 14.			
	TR-33-239 s Gasification sis and Executive Name and Address earch Institute/D0 ard 80401	s Gasification sis and Executive Summary Name and Address earch Institute/DOE ard 80401		

15. Supplementary Notes

Volume I of 3 volumes

16. Abstract (Limit: 200 words)

Biomass can be converted by gasification into a clean-burning gaseous fuel that can be used to retrofit existing gas/oil boilers, to power engines, to generate electricity, and as a base for synthesis of methanol, gasoline, ammonia, or methane. This survey describes biomass gasification, associated technologies, and issues in three volumes. Volume I contains the synopsis and executive summary, giving highlights of the findings of the other volumes. In Volume II, the technical background necessary for understanding the science, engineering, and commercialization of biomass is presented. In Volume III, the present status of gasification processes is described in detail, followed by chapters on economics, gas conditioning, fuel synthesis, the institutional role to be played by the federal government, and recommendations for future research and development.

17. Document Analysis

a.Descriptors Biomass; Gasification; Gases; Methanol; Gasoline; Ammonia; Methane; Synthesis; Reviews; Pyrolysis; Anaerobic Digestion; Bioconversion; Data; Waste Processing; Equilibrium; Reaction Kinetics; Synthetic Fuels Industry; Recommendations; Purification; Gasifiers; Commercialization; Economics b.Identifiers/Open-Ended Terms

c. UC Categories

61

18. Availability Statement NTIS, US Dept. of Commerce 5285 Port Royal Road Springfield, VA 22161

Supt. of Government Documents
U.S. Government Printing Office
Washington, DC 20402
Stock Number 061-000-00338-0

19. No. of Pages 43 20. Price \$4.50