SERI/TR-33-239
Volume II

July 1979

A Survey of Biomass Gasification

Volume II - Principles of Gasification

Solar Energy Research Institute
A Division of Midwest Research Institute

1536 Cole Boulevard
Golden, Colorado 80401

Operated for the
U.S. Department of Energy
under Contract No. EG-77-C-01-4042

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price:
Microfiche $3.00
Printed Copy $9.50

NOTICE

SERI/TR-33-239
Volume II of III
UC Category: UC-61

A SURVEY OF BIOMASS GASIFICATION

VOLUME II - PRINCIPLES OF GASIFICATION

July 1979

Prepared Under Task No. 3322

MASTER

Solar Energy Research Institute
1536 Cole Boulevard
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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 reseacher 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.

CSS

Clayton Smith, Branch Chief
Bio/Chemical Conversion Branch

MASTER

Approved for:

SOLAR ENERGY RESEARCH INSTITUTE

K. J. Touryan
Acting Assistant Director for Research

SYNOPSIS

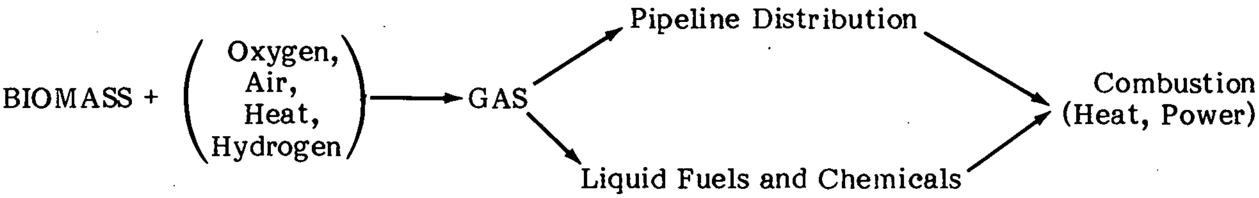
PURPOSE

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:

Pyrolysis 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 pyrolytic gasification 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, H_2, 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 H_2. While quite satisfactory for burning, it can also be used for chemical synthesis to make methanol, ammonia, H_2, CH_4, or gasoline and is called "synthesis gas" or "syngas."

Hydrogasification, in which H_2 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 treatment processes that may be needed to prepare biomass feedstocks for use in different gasification schemes.

CHAPTER 5 contains a literature review of pyrolysis 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 directory of current manufacturers of gasifiers and gasifier development programs.

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

CHAPTER 11 compares air gasification 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.

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CHAPTER 1

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CHAPTER 1

INTRODUCTION

1.1 HISTORY OF BIOMASS GASIFICATION

If fire is a cornerstone of civilization, the use of gaseous and liquid fuels has become the foundation of the modern age of technology. Many processes we now use would be impossible without these refined fuels, and all processes would be less efficient, less convenient, and more polluting. Although civilization might survive the exhaustion of fossil gas and liquid fuels, modern technology will be crippled unless we find a substitute. The gasification technology described here provides the basis for a continuing supply of both liquid and gaseous fuels.

It is difficult for modern man to conceive of a world without gaseous fuels, but gas was not discovered in the laboratory until the end of the 18th century and did not come into commercial and domestic use until 1830. By 1850 large parts of London had gas lights and there was a flourishing gas industry manufacturing gas from coal and biomass.

The early "gasworks" used iron retorts to heat the fuel, pyrolyzing it to gas, oils, and coke or charcoal. Later improvements were the use of fireclay and then silica retorts to achieve higher pyrolysis temperatures. The plants operated with a thermal efficiency which converted 70% to 80% of the energy in the fuel to salable products, producing a gas containing 500 Btu/SCF.

Another widely used process was the "blue water-gas process." The solid fuel was heated to very high temperatures with a blast of air (the "blow"), which formed a low energy gas (100 Btu/SCF) called "producer gas" for use as fuel for manufacturing processes. When sufficiently hot, the air was cut off and steam was blown in from the opposite end of the vessel (the "run"). This produced a higher energy gas (300 Btu/SCF). This "blue water-gas" (blue because it burned with a blue flame) could be converted to "carburetted water-gas" by using the high off-gas temperature to crack oils, yielding a gas with 500 Btu/SCF.

Using these processes, the gas industry grew rapidly and by the time of World War II there were 1,200 plants in the United States producing and selling gas. With the coming of the "big inch" and other pipelines in the 1930s natural gas gradually replaced manufactured gas, and these plants have almost all closed down. Now, with the increased cost of natural gas, gas producers are again being installed. A Wellman Incandescent gas plant operating on coal has recently been installed in York, Pa.

Gas has many advantages over solid fuels. Gas can be distributed easily; its combustion can be controlled to give high efficiency; it can be burned automatically; and it burns with low emissions, making "smokeless cities" possible. It burns with a higher temperature needed in many industrial processes and no local storage is necessary. It is ideal for cooking and heating in homes and is a necessity for many modern manufacturing processes. A given amount of energy is worth two to four times as much energy in the form of gas as it would be in the form of a solid fuel.

In addition, gas can be used to operate spark and diesel engines or turbines to generate power. The use of "producer gas" to run an engine was first tried around 1881. By the 1920s portable gas producers were being used to run trucks and tractors in Europe. These gas generators operated on either wood or charcoal and produced a gas with a rather high tar content. While it was possible to run engines on this gas, it was not convenient, and solid fuels for automotive use did not achieve wide acceptability. There was continued activity aimed at improving gas generators by individual inventors and a few companies until World War II. Commercial installations to run both stationary and mobile engines continued at a low level.

The beginning of World War II and the scarcity of liquid fuels in Europe intensified the search for domestically available fuels and resulted in a great surge of activity in designing and installing gas generators. In Sweden, approximately 75,000 vehicles (40% of the automotive fleet) were converted to generator gas operation within two years. Gas generators were also used on tractors, boats, motorcycles, and even on railway shunting engines. Techniques were developed for converting both diesel and spark ignition engines to generator gas operation. These engines operated reliably, although there was a derating of power output to approximately 75% of the gasoline rating, and considerable additional maintenance of filters, coolers, and the generator itself was required of the operator. It required 20 lb of wood to replace 1 gal. of gasoline (Generator Gas 1979).

The end of the war brought renewed supplies of liquid fossil fuels and a rapid reconversion of vehicles to diesel and gasoline. Since the war a few generators have been in operation, primarily in underdeveloped countries. The Swedish government has also maintained low level research and development programs for gasifiers, with the intention of maintaining military and economic preparedness in the event of a fossil fuel embargo. There has been limited experience with operation of a gas turbine on generator gas, but the indications are that no significant problems are expected. Commercial applications of gas turbines fueled with producer gas have not been attempted to date.

With the increase in oil prices following the formation of OPEC, there has been a renewed interest in all forms of gasification. A number of research projects are underway, aimed at producing fuel gas for pipeline use (see Volume III), and more than a score of manufacturers and research groups are developing air gasifiers for retrofitting existing boilers and power generation (Retrofit 1979).

1.2 TYPES OF GASIFICATION PROCESSES

Biomass can be converted to a number of useful products through the processes shown in Fig. 1-1. (Various terminologies are used, often loosely, to describe these processes. We will use the following terminology in this survey.)

Pyrolysis is the destructive decomposition of biomass using mainly heat to produce char, pyrolysis oil, and medium Btu gas. "Pyrolysis" is the name of an important stage in all gasification and combustion processes for both coal and biomass. However, it is also the name of a process which produces gas, char, and oil simultaneously. Therefore, its meaning must be inferred from context.

Pyrolysis Gasification. Pyrolysis processes historically have been operated primarily to yield char and oil products, with the gas burned to operate the process. However, some processes burn the oil and char to recover their heat in the form of higher yields of medium energy gas. The gas produced typically contains 300-500 Btu/SCF.

Air Gasification. If biomass is burned with a limited supply of air it produces a low energy gas containing primarily H_2 and CO, but diluted with nitrogen, typically containing 150-200 Btu/SCF. This gas is suitable for operation of boilers or engines but is too dilute to be transported in pipelines.

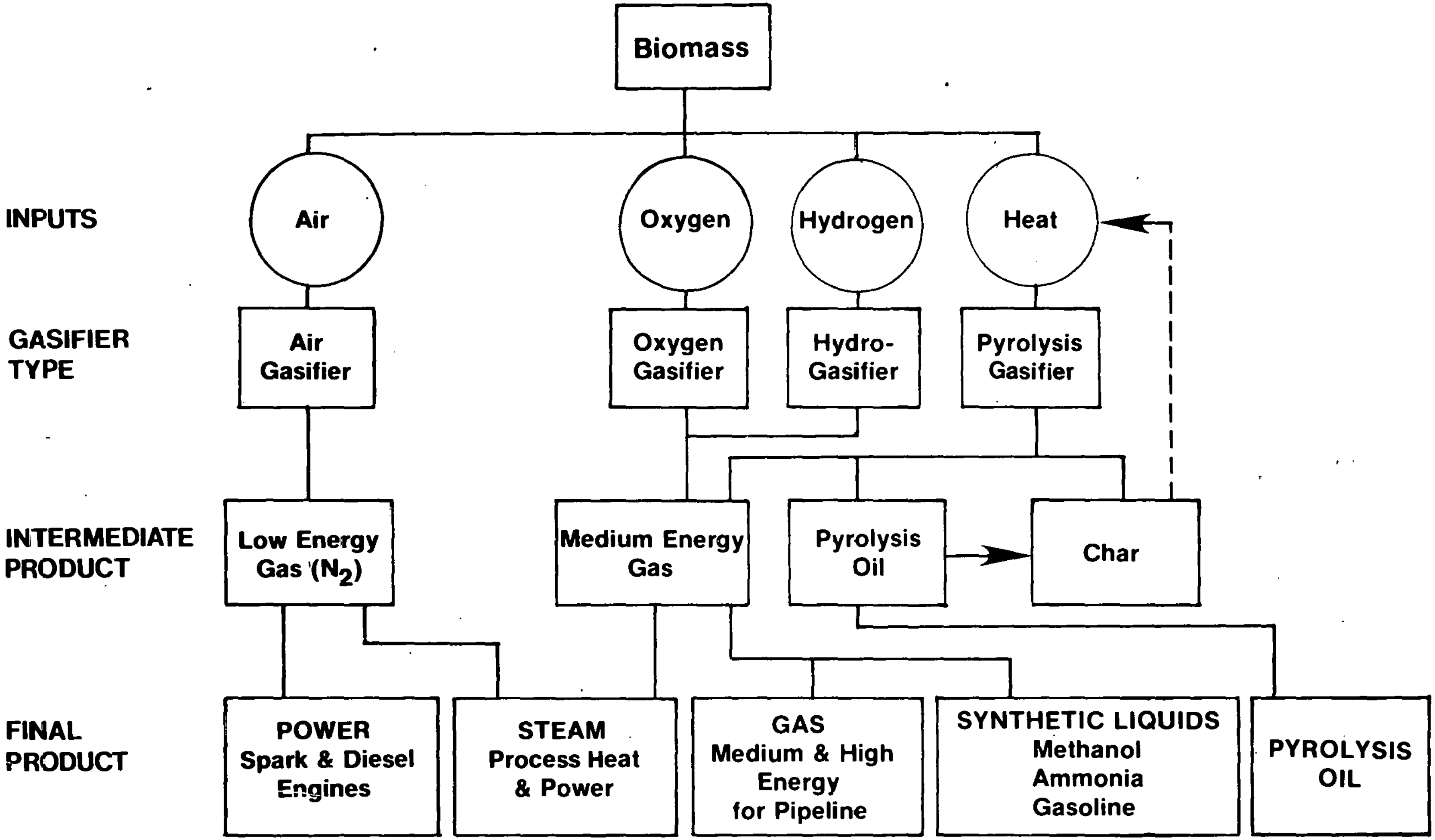

Figure 1-1. Gasification Processes and Their Products

Oxygen Gasification. If biomass is burned with a limited supply of oxygen it will yield a medium energy gas equivalent to the "town gas" of the 1930s, suitable for limited pipeline distribution, and containing 300 Btu/SCF. This gas can be used for industrial process heat or as synthesis-gas to make methanol, gasoline, ammonia, methane, or hydrogen.

Hydrogasification. Biomass has a low ratio of hydrogen to carbon compared to most liquid and gaseous fuels. In principle, biomass can be converted to gaseous or liquid fuels under pressure with hydrogen.

1.3 TYPES OF GASIFIERS

In addition to the general types of processes just defined, there are a number of types of gasifiers which are classified by different process variables. We briefly define them here and refer the reader to Volume III, Chapter 8, for a more complete discussion.

1.3.1 Method of Gas/Fuel Contact

Fixed Bed Gasifiers are used for bulky fuels such as wood chips, pellets, or corn cobs. They include updraft gasifiers (also called counterflow) in which air or oxygen is passed up through the reacting bed while the fuel passes down, producing a gas high in oil and tar; downdraft gasifiers (coflow), in which both fuel and air or oxygen pass downward through the hot bed, thus removing most of the tars from the product gas; and crossdraft, sloping grate, and other gasifier configurations.

Fluidized Bed Gasifiers typically use a wider range of fuel sizes, and the fuel is suspended in an upward flowing column of air. In addition to the biomass there is often a high percentage of an inert material, such as sand, which aids in the heat transfer to the fuel particles.

Suspended flow gasifiers use finely divided particles for very rapid gasification.

1.3.2 Ash Form

Dry ash gasifiers maintain grate temperatures below about 1100 C so that the ash can be removed as a fine powder. Slagging gasifiers maintain the grate temperatures above 1300 C so that the ash can be poured out as a liquid. Intermediate temperatures lead to ash with the consistency of molasses, which prevents further operation.

1.3.3 Gas Pressure

Atmospheric pressure gasifiers are the most easily constructed and operated. Suction gasifiers actually operate slightly below atmospheric pressure and are used mostly to power engines. Pressurized gasifiers typically operate at pressures of 10-100 atm, yielding a gas that can be put in pipelines or used immediately to operate turbines or as feedstocks for chemical synthesis.

1.4 ENERGY CONTENT OF FUEL GASES

The gases produced through gasification have a wide range of energy content and corresponding applications. These are summarized in Table 1-1. Note that natural gas has the highest energy content and can be used for any of the other applications. Its high energy content is important in long distance shipping but has little effect on process use. Use of gases with energy content below about 200 Btu/SCF may result in some loss of performance in engines or boilers.

1.5 THE RELATIVE MERITS OF BIOMASS AND COAL

Although coal was used in the larger producer gas installations described in Section 1.1, in many other cases wood or biomass were used because of ease of gasification and availability. We list here a number of factors which will influence the relative degree of development of coal and biomass for energy and fuels in the coming years.

1.5.1 Availability

- Coal is available in many places in high concentrations; other areas are located at great distances from the mines and involve higher costs for coal than for biomass.
- Biomass is widely available in smaller quantities and this favors dispersed use.
- Biomass may become available in larger quantities if energy plantations are developed (See Chapter 2).
- Biomass is renewable and will always be available in reasonable quantities (probably from 10 to 40 quads in the United States).

1.5.2 Technical Factors

- Biomass has a low energy density and occurs in a wide variety of forms, many unsuitable for combustion or gasification without pretreatment (drying or densification).
- Biomass is easier to burn or gasify because of its low pyrolysis temperatures and high concentration of volatiles.
- Biomass contains oxygen and water, which may be advantageous in gasification.

1.5.3 Environmental Factors

- Coal is high in sulfur content; biomass sulfur content is an order of magnitude lower.
- Coal has a high content of ash with no value; biomass ash content is lower and has value as fertilizer or for synthesizing chemicals. Coal conversion mobilizes toxic trace metals, and coal tars are highly carcinogenic.

Table 1-1. 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

- Coal mining is generally destructive of the land; proper biomass residue use or proper harvesting improves the land, but overcutting can also be very destructive.
- Coal combustion increases the CO_2 concentration in the atmosphere; steady-state biomass use does not increase CO_2 levels.

1.5.4 Economic Factors

- Coal, like gas and oil, has lower direct costs than biomass; however, consideration of environmental costs makes coal more comparable in cost to biomass; we do not now have methods for quantifying these costs.
- Biomass residues (such as solid municipal waste) can have negative or low cost, but collection and processing increases these costs.
- Small-scale use of biomass is favored by lower shipping costs and less difficult conversion.
- Large-scale use of coal is favored by the economies of scale required to offset the high cost of environmental control.

1.5.5 Conclusions

The combustion and gasification of both coal and biomass are feasible and necessary. Each energy resource will find its proper niche in the years to come, as dictated by the interplay of the considerations just discussed.

1.6 PURPOSE OF THIS SURVEY

The purpose of this survey is:

- to examine the properties and potential of the biomass resource relevant to gasification (Chapters 2 to 4);
- to summarize the basic science of biomass gasification (Chapters 5 to 7);
- to survey 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 governmental 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).

We believe that this survey accomplishes these tasks and will serve as a foundation for gasification research technology expansion over the next decades.

1.7 UNITS

In writing this survey we were faced with the following dilemma: If we use English units the survey will be understood in the United States, Canada, and England but will be less comprehensible in the rest of the world. If we use SI units it will be more understandable in the world at large and, possibly in several decades, worldwide. If we use both kinds of units the tables and figures will be greatly complicated. Therefore, in each chapter we have used the units now in common use for the subject matter. For conversion we refer the reader to any of dozens of sets of conversion tables but include here a few particularly applicable conversion factors.

Table 1-2. CONVERSION FACTORS

1 Btu/SCF[a]	=	34.54/N - m^3 [a]
1 Btu	=	1054 J
1 acre	=	4047 m^2
1 cal	=	4.184 J
1 hp	=	746 W
1 atm	=	1.013 X 10^5 Pa
1 ft^3	=	0.0283 m^3

[a] The volume of a gas in a standard cubic foot (SCF) is the volume that gas would occupy at atmospheric pressure and 60 F. The volume in normal cubic metres (N = m^3) is the volume it would occupy at 1 atm and 0 C.

1.8 REFERENCES

Generator Gas. 1979. Golden, CO: The Solar Energy Research Institute; SERI/SP-33-140; Jan.

Retrofit 79: Proceedings of a Workshop on Air Gasification. 1979. Golden, CO: The Solar Energy Research Institute; SERI/TP-49-183.

Chapter 2

The Potential Biomass Resource Base

R. Inman
SERI

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CHAPTER 2

THE POTENTIAL BIOMASS RESOURCE BASE

The ultimate applicability of all biomass conversion technologies, including biomass gasification, is restricted by the quantity of feedstocks that can be made available for conversion. A meaningful impact on the nation's energy supply could not be made, regardless of the number of potential applications or the developments achieved in conversion technologies, if the feedstock supply were inadequate. Hence the utility of biomass gasification is, ultimately, resource-limited.

The biomass resource base in the United States is immediately distinguished from other solar energy resources by its high degree of diversity. The corollary to this characteristic is that, while not all biomass or its components are equally suited to gasification, its diversity is translatable into versatility and hence affords the opportunity to produce diverse energy end-products and to develop diverse energy applications. A second distinguishing factor of this resource is its juxtaposition, and in some cases its supraposition, to the resource base used for food and fiber products. The special relationships between these feedstock sources, including in some cases direct competition for their use, weighs heavily upon the economics of energy applications.

The existing resource base is comprised of agricultural crop residues, manures from confined livestock and poultry operations, wood and bark mill residues from primary wood product manufacturing plants, bark residues from the wood pulp industry, logging residues from timber harvesting operations, noncommercial components of standing forests, and the organic fraction of municipal solid wastes. In addition to the existing base, it is believed that future biomass supplies could be supplemented by feedstock produced on energy farms. Overall, it would appear that there is a resource base of significant size and that this base will, in all probability, be expanded in future years as timber harvests increase and as energy farming needs and technologies develop. Each component of the resource base is characterized in this chapter.

2.1 AVAILABLE RESOURCES

2.1.1 Crop Residues

Crop residues consist of plant remains left in the field following harvest or harvested material discarded during the preparation of produce for packing and shipping. Approximately 320 million dry ton equivalents (DTE) of this potential energy feedstock are generated each year (Inman and Alich 1976), and it is estimated that about 278 million DTE are "available" (i.e., are already collected or could be collected with existing machinery [Table 2-1]). Almost half of this resource category consists of straw from the cultivation of small grain (wheat, rye, barley and rice) and grass seed crops, and more than one third of stover (the dried stalks and leaves) from corn and sorghum production. Only about 2.5% of the available resource is collected during the course of normal operations. Deterrents to the use of crop residues as an energy feedstock include: (1) their seasonality, (2) their high cost of collection and transport, and (3) their current ecological value in situ. Almost three fourths of the resource base is returned to the soil (plowed under) each year (Table 2-2). Some, largely corn stover, is pastured to livestock following harvest, and small portions are sold (straw, sugar beet pulp, and cotton gin

Table 2-1. ANNUAL AVAILABILITY OF CROP RESIDUES (1971-1973) [a]

Residue Category	Million Dry Tons
Corn and sorghum (field)	96.6
Small grains and grasses (field)	131.8
Other crops (field)	42.3
Collected residues	7.3
Total	278.0

[a] From Anderson 1972.

Table 2-2. DISPOSITION OF CROP RESIDUES (1971-1973) [a]

Disposition	Million Dry Tons
Sold for profit	11.3
Fed to livestock	52.3
Used as fuel	1.7
Disposed of at cost	6.8
Returned to soil	205.9
Total	278.0

[a] From Anderson 1972.

trash), used as a fuel (bagasse), or disposed of at cost (burned in the field). The great majority of the crop residue resource would be amenable to use as a gasification feedstock, should sustainable soil conservation practices permit.

2.1.2 Animal Manures

Animal manures are only marginally attractive as a gasification feedstock but could be used after drying. This resource, however, is relatively small (Table 2-3) and in all probability will eventually be used in its entirety as a substrate for methane production through anaerobic digestion, as a soil amendment, or as a recycled livestock feed.

2.1.3 Mill Residues

Wood and bark are preferred gasification feedstocks. One potential source of this feedstock is the residue from sawmills, plywood plants, and other primary wood manufacturing mills. These residues occur in a large variety of forms (slabs, edgings, sawdust, planer shavings, sander dust, ends, veneer trimmings, defective products, etc.). Over 86 million dry ton equivalents (DTE) per year are generated (Howlett and Gamache 1977), but less than one third of this resource is available for extended use as an energy feedstock (Table 2-4). Current uses for this material are dominated by the use of the coarse wood fraction for pulp manufacture (Howlett and Gamache 1977) and the direct

Table 2-3. **DISPOSITION OF ANIMAL MANURES FROM CONFINED ANIMAL OPERATIONS (1971-1973)** [a]

Disposition	Million Dry Tons
Sold for profit	3.9
Fed to livestock	0.2
Used as fuel	0.02
Disposed of at cost	4.5
Returned to soil	17.9
Total	26.5

[a] From Anderson 1972.

combustion of the remaining fractions for process steam and/or electric power generation is increasing rapidly. It is widely believed that the entire mill residue resource soon will be consumed by the forest products industry itself for pulp and fuel.

The figures presented in Table 2-4 do not include bark residues from pulp mills, which have been estimated to total about four million DTE per year (Inman and Alich 1976). Moreover, large piles of this material have been allowed to accumulate at certain pulp mills, forming veritable "biomass mines." The use of bark by the pulping industry to produce steam and electric power is also increasing because energy requirements of this segment of the wood industry dwarf those of primary wood manufacturing plants.

Table 2-4. **WOOD AND BARK MILL RESIDUES: GENERATION AND DISPOSITION ANNUALLY BY REGION (1970)** [a]

	Million Dry Tons		
Region	Total Generated	Residues Used	Residues Unused
Northeast	6.6	4.3	2.3
North Central	6.4	4.3	2.1
Southeast	11.4	6.9	4.5
South Central	16.7	12.1	4.6
Pacific Northwest	27.8	23.6	4.2
Pacific Southwest	8.8	5.5	3.3
Northern Rockies	6.6	4.5	2.1
Southern Rockies	1.8	0.8	1.0
Totals	86.1	62.0	24.1

[a] From Howlett and Gamache 1977.

2.1.4 Logging Residues

Portions of harvested or felled trees left in the woods following logging operations total over 83 million DTE annually (Howlett and Gamache 1977). The total resource is split almost evenly between hardwood and softwood residues (Table 2-5), but there are tremendous regional variations in this distribution. Virtually none of this resource is currently used as an energy feedstock due to the high cost of collection and the lack of appropriate collection machinery. It is widely expected, however, that changes in conventional energy economics will bring this resource into use within the mid-term.

Table 2-5. ANNUAL GENERATION OF LOGGING RESIDUES BY REGION AND TIMBER CATEGORY (1970)[a]

	Million Dry Tons		
Region	Softwood	Hardwood	Total
New England	1.94	2.03	3.97
Middle Atlantic	0.52	4.81	5.33
Lake States	0.55	3.12	3.67
Central States	0.07	4.47	4.54
Southern Atlantic	3.22	8.60	11.82
East Gulf	3.05	2.57	5.62
Central Gulf	4.13	6.45	10.58
West Gulf	5.02	4.68	9.70
Pacific Northwest	17.52	0.84	18.36
Pacific Southwest	4.31	0.63	4.94
Northern Rockies	3.60	Trace	3.60
Southern Rockies	0.98	0.10	1.08
Totals	44.91	38.29	83.21

[a] From Howlett and Gamache 1977.

2.1.5 Standing Forests

By far the largest existing resource is the surplus and noncommercial components of the standing forests. The total annual productivity of these components has been estimated to be almost 400 million DTE (Salo and Henry 1979) (Table 2-6). The harvest of this resource for energy production in all likelihood would be closely associated with both commercial timber harvest and timber stand improvement practices. Environmental concerns also will have to be served. Some of this resource could conceivably be managed as a renewable energy feedstock source.

2.1.6 Municipal Solid Wastes (MSW)

The organic component of MSW totals approximately 130 million DTE annually (Anderson 1972). This represents a generation rate of 3.5 lb per person per day, an amount which may even increase in the future. Most of this material is currently disposed of in landfills at a significant cost. Gasification of this refuse would appear to be an ideal "disposal" method.

Table 2-6. THE ANNUAL ENERGY RESOURCE REPRESENTED BY UNUSED STANDING FOREST PRODUCTIVITY (1976) [a]

Region	Million Dry Tons Surplus Growth	Mortality	Noncommercial[b] Timber	Total
Northeast	34.47	14.00	14.06	62.53
Northern Plains	0.94	0.76	1.00	2.70
Corn Belt	3.24	1.94	5.24	10.42
Southeast	37.06	9.65	11.18	57.89
Appalachian	40.29	9.35	13.41	63.05
Southern Plains	6.47	1.41	6.41	14.29
Delta States	23.18	6.18	8.71	38.07
Lake States	19.82	11.24	4.41	35.47
Pacific	0.00	20.29	20.18	40.47
Mountain	18.53	11.00	29.53	59.06
Totals	184.00	85.82	114.13	383.95

[a] From Inman and Alich et al. 1976.

[b] Includes noncommercial timber growth on commercial forest land and all timber growth on noncommercial forest land producing less than 20 ft^3 per acre-year of commercial timber.

2.1.7 Summary of Available Resources

As shown in Table 2-7, the existing resource base totals almost 15 fuel-quad equivalents. Only a portion of this resource base, however, could ever be expected to be applied to energy production. Economic and environmental concerns will influence the application of the two major resource components, standing forests and crop residues. Use of MSW probably will serve adequately only in large metropolitan areas where sufficient disposal credits can be realized. Wood and bark residues are largely captive resources of the forest products industry.

Table 2-7. 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	.33
Unused mill residues[a]	24.1	.41
Logging residues	83.2	1.41
Municipal solid wastes	130.0	1.63
Standing forests	384.0	6.51
Totals	925.8	14.44

[a] Does not include unused bark from wood pulp mills.

2.2 POTENTIAL BIOMASS RESOURCES

The presently available resources listed above provide sufficient incentive to develop biomass collection, combustion, and gasification systems. However, biomass production is the principal method of solar energy collection, and in the future we will need to expand our biomass base by more efficient utilization of present resources and development of new species and land for energy production. The following major categories, while more difficult to quantify than existing residues, are likely ways for enlarging the biomass energy base.

2.2.1 Biomass Mines

In addition to the continuing production of residues inventoried in this chapter, there are "biomass mines" composed of accumulations of residues from past years and including bark piles, the dumps of food processing industries, and the municipal landfills of cities. At present no estimate is available of the recoverable energy in these forms, but if it were assumed that 10% of the 6 quads/yr of municipal, crop, and mill residues dumped over the last 20 years could be recovered, we estimate that there might be 12 quads available in this form. In addition, removal of these wastes would be environmentally attractive. We recommend that a good assessment of this energy base be made.

2.2.2 Land Improvement Residues

Another category of biomass is that available through land improvement. Many millions of U.S. acres of land have been laid waste by man and presently support species of low value such as scrub, mesquite, and chapparal. Harvesting these plants for their biomass energy could pay the cost of improving this land.

2.2.3 Energy Farming

In the future, energy farming may supplement energy feedstock supplies. It has been estimated that from four to eight fuel-quad-equivalents of biomass could be produced should the need arise (Inman et al. 1977), presuming that research were directed to develop this agronomic technology to the point at which biomass yields were sufficient to make cash crop energy farming an economically competitive venture.

At present, the potential biomass resource base would not restrict the development of biomass gasification as an energy conversion technology. The extent to which this resource will actually be used as a gasification feedstock will depend upon a large number of factors whose interactions cannot be predicted accurately at this time.

2.3 REFERENCES

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Chapter 3

Properties of Biomass Relevant to Gasification

M. Graboski and R. Bain
Colorado School of Mines

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CHAPTER 3

PROPERTIES OF BIOMASS RELEVANT TO GASIFICATION

An understanding of the structure and properties of biomass materials is necessary in order to evaluate their utility as chemical feedstocks. This section summarizes available information on a variety of such properties including chemical analysis, heats of combustion and formation, physical structure, heat capacities, and transport properties of biomass feedstocks and chars. Much of the information reported is for wood materials; however, where data were available for other forms of biomass such as municipal solid waste and feedlot waste, they were included.

3.1 BULK CHEMICAL ANALYSIS OF BIOMASS

In evaluating gasification feedstocks, it is generally useful to have proximate and ultimate analyses, heats of combustion, and sometimes ash analyses. These provide information on volatility of the feedstock, elemental analysis, and heat content. The elemental analysis is particularly important in evaluating the feedstock in terms of potential pollution.

Table 3-1 lists the standard methods for evaluating carbonaceous feedstocks.

A number of instruments have been developed for determining elemental composition, most often, in biomass conversion, for carbon, hydrogen, nitrogen, sulfur, and oxygen. Chlorine normally is not determined by such analyzers. Most of these systems employ a catalytic combustion or pyrolysis step to decompose the sample to carbon dioxide, water, hydrogen sulfide, and nitrogen, which are then determined quantitatively by gas chromatography using flame ionization (FID) or thermal conductivity (TC) detectors. Oxygen is usually determined by catalytic conversion to carbon monoxide over a platinized carbon catalyst followed by GC analysis. A short list of some representative instruments is given in Table 3-2.

3.1.1 Proximate Analyses

The proximate analysis classifies the fuel in terms of its moisture (M), volatile matter (VM), ash, and (by difference) fixed carbon content. In the test procedure, the volatile material is driven off in an inert atmosphere at high temperatures (950 C) using a slow heating rate. The pyrolysis yield is representative of that for slow pyrolysis processes; fast pyrolysis techniques employing very rapid heating rates normally yield more volatile matter. The moisture determined by the proximate method represents physically bound water only; water released by chemical reactions during pyrolysis is classified with the volatiles. The ash content is determined by combustion of the volatile and fixed carbon fractions. The resulting ash fraction is not representative of the original ash, more appropriately termed mineral matter, due to the oxidation process employed in its determination. In the most exact analysis, small corrections to the ash weight are necessary to correct it to a mineral matter basis. The fixed-carbon content of an as-received sample is calculated by material balance. Thus:

$$FC = 1 - M - ASH - VM. \qquad (3\text{-}1)$$

Table 3-1. ASTM STANDARDS METHODS FOR GASIFICATION FEEDSTOCKS

Method	Test No.[a]	Repeatability (wt %)[b]	Reproducibility (wt %)[b]
Proximate Analysis			
Moisture	D-3175-73		
Less than 5%		0.2	0.3
More than 5%		0.3	0.5
Volatile Matter	D-3175-77		
High Temp. Coke		0.2	0.4
Bituminous Coal		0.5	1.0
Lignite		1.0	2.0
Ash	D-3174-73	0.5	1.0
Ultimate Analysis			
C	D-3178-73	0.3	—
H	D-3178-73	0.07	—
O	None		
N	D-3177-75	0.05	—
S	D-2361-66 [1978]		
less than 2%		0.05	0.10
more than 2%		0.10	0.20
Gross Heating Value	D-3286-77	50 Btu/lb	100 Btu/lb
Ash Analysis	D-295-69 [1974] D-3682-78 D-3683-78		
SiO_2		1.0	2.0
Fe_2O_3		0.3	0.7
CaO		0.2	0.4
K_2O		0.1	0.3
Na_2O		0.1	0.3
MgO		0.3	0.5
P_2O_5		0.05	0.15

[a] The two digit number following the second dash is the year the method was approved. The date in brackets is the year the test was reapproved without change.

[b] Taken fron Instit. of Gas Technology 1978.

The fixed carbon is considered to be a polynuclear aromatic hydrocarbon residue resulting from condensation reactions which occur in the pyrolysis step.

Table 3-2. ELEMENTAL ANALYZER EQUIPMENT

Instrument	Oxidant	Capability	Detection
Carlo Erba 1104	oxygen	C, H, N, O	FID & TC
Chemical Data Systems (CDS 1200)	oxygen	C, H, N, O, S and functional groups	FID & TC
Hewlett-Packard HP-185	MnO_2 added	C, H, N	FID & TC
Perkin Elmer 240	oxygen	C, H, N, O, S	TC

The most useful basis for reporting proximate analysis is the dry basis. In this instance the compositions are normalized to a moisture-free basis (denoted by *):

$$VM^* + FC^* + ASH^* = 1 \,, \tag{3-2}$$

and, for example,

$$VM^* = VM/(1 - M).$$

The moisture is reported as grams of moisture per gram of dry feedstock. Typical proximate analyses for solid fuels are given in Table 3-3, from which it is evident that common biomass materials are more readily devolatilized (pyrolyzed) than lignite and bituminous coals, yielding considerably less fixed-carbon residue. This is due to the much more aromatic structure of the coals which is produced by the geological coalification process. The higher volatile content of biomass materials makes them potentially useful feedstocks for pyrolysis processes. In general, the ash content of biomass materials is considerably lower than for coals. This is due to the fact that the bulk of the coal ash was deposited in coal beds by processes such as siltation and did not come from the parent carbonaceous material. An exception is municipal solid waste, which contains a high mineral content due to nonvolatile trash components such as metals and glass.

Table 3-3 also gives proximate analyses of wood chars derived from low-temperature carbonization. The volatile content, while reduced, is still a significant portion of the resulting chars.

3.1.2 Ultimate Analyses

Ultimate analyses generally report C, H, N, S and (by difference) O in the solid fuel. Table 3-1 lists the appropriate ASTM tests for these elements while Table 3-2 lists several manufacturers of modern elemental analyzers. Care must be exercised in using ultimate analyses for fuels containing high moisture content because moisture is indicated in the ultimate analysis as additional hydrogen and oxygen.

Table 3-3. PROXIMATE ANALYSIS DATA FOR SELECTED SOLID FUELS AND BIOMASS MATERIALS

(Dry Basis, Weight Percent)

	Volatile Matter (VM*)	Fixed Carbon (FC*)	Ash*	Reference
Coals				
Pittsburgh seam coal	33.9	55.8	10.3	Bituminous Coal Research 1974
Wyoming Elkol coal	44.4	51.4	4.2	Bituminous Coal Research 1974
Lignite	43.0	46.6	10.4	Bituminous Coal Research 1974
Oven Dry Woods				
Western hemlock	84.8	15.0	0.2	Howlett and Gamache 1977
Douglas fir	86.2	13.7	0.1	Howlett and Gamache 1977
White fir	84.4	15.1	0.5	Howlett and Gamache 1977
Ponderosa pine	87.0	12.8	0.2	Howlett and Gamache 1977
Redwood	83.5	16.1	0.4	Howlett and Gamache 1977
Cedar	77.0	21.0	2.0	Howlett and Gamache 1977
Oven Dry Barks				
Western hemlock	74.3	24.0	1.7	Howlett and Gamache 1977
Douglas fir	70.6	27.2	2.2	Howlett and Gamache 1977
White fir	73.4	24.0	2.6	Howlett and Gamache 1977
Ponderosa pine	73.4	25.9	0.7	Howlett and Gamache 1977
Redwood	71.3	27.9	0.8	Howlett and Gamache 1977
Cedar	86.7	13.1	0.2	Howlett and Gamache 1977
Mill Woodwaste Samples				
-4 Mesh redwood shavings	76.2	23.5	0.3	Boley and Landers 1969
-4 Mesh Alabama oakchips	74.7	21.9	3.3	Boley and Landers 1969
Municipal Refuse and Major Components				
National average waste	65.9	9.1	25.0	Klass and Ghosh 1973
Newspaper (9.4% of average waste)	86.3	12.2	1.5	Klass and Ghosh 1973
Paper boxes (23.4%)	81.7	12.9	5.4	Klass and Ghosh 1973
Magazine paper (6.8%)	69.2	7.3	23.4	Klass and Ghosh 1973
Brown paper (5.6%)	89.1	9.8	1.1	Klass and Ghosh 1973
Pyrolysis Chars				
Redwood (790 F to 1020 F)	30.0	67.7	2.3	Howlett and Gamache 1977
Redwood (800 F to 1725 F)	23.9	72.0	4.1	Howlett and Gamache 1977
Oak (820 F to 1185 F)	25.8	59.3	14.9	Howlett and Gamache 1977
Oak (1060 F)	27.1	55.6	17.3	Howlett and Gamache 1977

Table 3-4. ULTIMATE ANALYSIS DATA FOR SELECTED SOLID FUELS AND BIOMASS MATERIALS

(Dry Basis, Weight Percent)

Material	C	H	N	S	O	Ash	Higher Heating Value (Btu/lb)	Reference
Pittsburgh seam coal	75.5	5.0	1.2	3.1	4.9	10.3	13,650	Tillman 1978
West Kentucky No. 11 coal	74.4	5.1	1.5	3.8	7.9	7.3	13,460	Bituminous Coal Research 1974
Utah coal	77.9	6.0	1.5	0.6	9.9	4.1	14,170	Tillman 1978
Wyoming Elkol coal	71.5	5.3	1.2	0.9	16.9	4.2	12,710	Bituminous Coal Research 1974
Lignite	64.0	4.2	0.9	1.3	19.2	10.4	10,712	Bituminous Coal Research 1974
Charcoal	80.3	3.1	0.2	0.0	11.3	3.4	13,370	Tillman 1978
Douglas fir	52.3	6.3	0.1	0.0	40.5	0.8	9,050	Tillman 1978
Douglas fir bark	56.2	5.9	0.0	0.0	36.7	1.2	9,500	Tillman 1978
Pine bark	52.3	5.8	0.2	0.0	38.8	2.9	8,780	Tillman 1978
Western hemlock	50.4	5.8	0.1	0.1	41.4	2.2	8,620	Tillman 1978
Redwood	53.5	5.9	0.1	0.0	40.3	0.2	9,040	Tillman 1978
Beech	51.6	6.3	0.0	0.0	41.5	0.6	8,760	Tillman 1978
Hickory	49.7	6.5	0.0	0.0	43.1	0.7	8,670	Tillman 1978
Maple	50.6	6.0	0.3	0.00	41.7	1.4	8,580	Tillman 1978
Poplar	51.6	6.3	0.0	0.0	41.5	0.6	8,920	Tillman 1978
Rice hulls	38.5	5.7	0.5	0.0	39.8	15.5	6,610	Tillman 1978
Rice straw	39.2	5.1	0.6	0.1	35.8	19.2	6,540	Tillman 1978
Sawdust pellets	47.2	6.5	0.0	0.0	45.4	1.0	8,814	Wen et al. 1974
Paper	43.4	5.8	0.3	0.2	44.3	6.0	7,572	Bowerman 1969
Redwood wastewood	53.4	6.0	0.1	39.9	0.1	0.6	9,163	Boley and Landers 1969
Alabama oak woodwaste	49.5	5.7	0.2	0.0	41.3	3.3	8,266	Boley and Landers 1969
Animal waste	42.7	5.5	2.4	0.3	31.3	17.8	7,380	Tillman 1978
Municipal solid waste	47.6	6.0	1.2	0.3	32.9	12.0	8,546	Sanner et al. 1970

In order to avoid confusion and give a good representation of the fuel itself, ultimate analyses should be performed and reported on a dry basis; when this is done all hydrogen determined is truly a constituent of the fuel. For certain biomass materials like municipal solids and animal waste, the determination of chlorine is important because it represents a possible pollutant and corrosive agent in gasification and combustion systems.

Typical ultimate analyses for a variety of feedstocks are presented in Table 3-4.

All biomass materials have carbon contents considerably lower than coals; the atomic carbon to hydrogen ratio is much higher in coals than in biomass materials. For coal, the H/C ratio is unity, while for biomass the ratio is typically 1.5. The bound oxygen content of biomass materials is considerably higher, due to the ether, acid, and alcohol groups in the cellulose, hemicellulose, and lignin fractions of biomass, as will be discussed later in this section. The nitrogen and sulfur contents in coal are considerably higher than those in biomass. Thus, in direct biomass combustion, pollutants resulting from bound nitrogen and sulfur in the fuel generally are present in small enough quantities to meet EPA standards, although the high chlorine contents that are found in animal wastes can pose a severe pollution problem.

The relative "quality" of the volatile matter can be estimated using the ultimate analysis and simple stoichiometry. If it is assumed that the fixed carbon contains only carbon, then all hydrogen and oxygen plus a portion of the carbon are associated with the volatile material. Table 3-5 presents a typical calculation for the volatile fraction of lignite and Douglas fir bark.

Table 3-5. ELEMENTAL ANALYSIS OF VOLATILES LIBERATED BY PYROLYSIS FOR TWO SELECTED FUELS

	Wt % in Volatiles, Dry Basis			Molar Ratio Volatile		
Fuel	C	H	O	C	H	O
Lignite	17.4	4.22	19.17	1	2.91	0.83
Douglas fir bark	23.4	5.9	36.7	1	3.03	1.17

The C/H/O ratios of these volatile fractions are very similar despite the difference in feedstock. In the pyrolysis process, at relatively high temperatures,

$$\text{Volatiles} \rightarrow \begin{cases} CH_4 & (3\text{-}3) \\ CO + CO_2 & (3\text{-}4) \\ H_2O. & (3\text{-}5) \end{cases}$$

If we assume that CO is produced exclusively we can calculate the product analysis from pyrolysis.

Therefore, assuming:

$$C + 4H \rightarrow CH_4 \tag{3-6}$$

$$2H + O \rightarrow H_2O \tag{3-7}$$

$$C + O \rightarrow CO, \tag{3-8}$$

let X be the moles of carbon converted to methane, Y the oxygen converted to water, and Z the carbon to CO.

The material balance equations yield:

$$X = \frac{2 + (H/C) - 2\,(O/C)}{6} \tag{3-9}$$

$$Z = 1 - X \tag{3-10}$$

$$Y = \frac{O}{C} - Z. \tag{3-11}$$

In the calculation for methane it should be pointed out that as long as water-gas shift reaction equilibrium is attained, it makes no difference whether the nonhydrocarbon products are CO and H_2O or a mixture of CO, CO_2, H_2, and H_2O.

Table 3-6 presents such an analysis on a dry basis of 100 lb of fuel.

Table 3-6. EVALUATION OF FEEDSTOCKS FOR PYROLYSIS BY MATERIAL BALANCE CALCULATION

Feedstock	SCF Gas / 100 lb Dry Feed	Mole Fractions CH_4	CO	H_2O	lb C in CH_4 / 100 lb C in feed
Lignite	754	0.395	0.334	0.271	14.7
Douglas fir bark	1196	0.277	0.341	0.382	18.7

The gas derived from lignite is higher in quality than that from the fir bark due to the bark's greater potential to form water. The quantity of gas produced is greater for the fir bark due to the greater quantity of volatiles present. The most important factor is the fraction of carbon converted to methane. The woody material shows a greater potential to form methane on a carbon feed basis, indicating that it is a higher quality feedstock for pyrolysis. This may be attributed to the higher degree of aromaticity exhibited in coals.

Table 3-7 presents ultimate analysis for typical pyrolysis chars derived from biomass feedstocks. Except for the municipal solid waste char, all contain considerable quantities of voltatile constituents, including H and O, due to the low processing temperature.

Table. 3-7. ULTIMATE ANALYSIS DATA FOR SELECTED PYROLYSIS CHARS
(Dry Basis, Weight Percent)

Material	C	H	N	S	O	Ash	Higher Heating Value (Btu/lb)	Reference
Fir bark char	49.9	4.0	0.1	0.1	24.5	21.4	8,260	Pober and Bauer 1977
Rice hull char	36.0	2.6	0.4	0.1	11.7	49.2	6,100	Pober and Bauer 1977
Grass straw char	51.0	3.7	0.5	0.8	19.7	24.3	8,300	Pober and Bauer 1977
Animal waste char[a]	34.5	2.2	1.9	0.9	7.9	48.8	5,450	Pober and Bauer 1977
Municipal solid waste char (high temperature)	54.9	0.8	1.1	0.2	1.8	41.2	8,020	Sanner et al. 1970
Redwood charcoal (790 F to 1020 F)	75.6	3.3	0.2	0.2	18.4	2.3	12,400	Boley and Landers 1969
Redwood charcoal (860 F to 1725 F)	78.8	3.5	0.2	0.2	13.2	4.1	13,100	Boley and Landers 1969
Oak charcoal (820 F to 1185 F)	67.7	2.4	0.4	0.2	14.4	14.9	10,660	Boley and Landers 1969
Oak charcoal (1060 F)	64.6	2.1	0.4	0.1	15.5	17.3	9,910	Boley and Landers 1969

[a] Contains 3.7% Cl lumped with oxygen.

The C/H and C/O ratios are greater in all chars than in the fresh feed materials. The high-temperature municipal waste char has been almost completely devolatilized, as is evidenced by the low H and O contents.

3.1.3 Moisture Content of Fuels

Woody fuels and municipal solid waste samples are available with various moisture contents. The moisture is important in determining drying costs and as-received heat contents of the fuels.

Table 3-8 presents approximate ranges of moisture for typical biomass fuels. The effect of moisture on the recoverable heat is dramatic due to the heat requirements for vaporizing the moisture plus superheating the vapor.

Table 3-8. APPROXIMATE MOISTURE CONTENTS OF TYPICAL BIOMASS FUELS

Biomass Fuel	Moisture Content (wt %)
Bark	25-75
Coarse wood residue	30-60
Shavings	16-40
Sawdust	25-40
Sander dust	2-8
Municipal refuse	20
Air dry feedlot waste	12

3.1.4 Heating Values

The heating value of carbon feedstocks is determined by the ASTM method listed in Table 3-1. The experimental method employs an adiabatic bomb calorimeter which measures the enthalpy change between reactants and products at 25 C. The heating value obtained is termed the higher heating value because the water of combustion is present in the liquid state at the completion of the experimental determination.

The heating value may be reported on two bases. These are the gross or higher heating value and the net or lower heating value. The higher heating value (HHV) represents the heat of combustion relative to liquid water as the product. The lower heating value (LHV) is based on gaseous water. The difference in the heating value is the latent heat of the water of combustion. Heating values often are reported on both wet and dry fuel bases. The conversion between bases is simple in the case of the higher heating value, involving only normalizing out the moisture (M). This is true because the moisture present in the raw fuel is in the same state before and after combustion.

$$\mathrm{HHV}^* = \frac{\mathrm{HHV}}{(1 - M)} \quad . \tag{3-12}$$

Lower (net) heating values depend on the moisture content in a more complicated fashion. Since both the product water and moisture are present as vapor after combustion, a portion of the heat of combustion is used to evaporate the moisture. Therefore, using the latent heat of water, $\lambda = 980$ Btu/lb,

$$\mathrm{HHV}^* = \frac{\mathrm{LHV} + M\lambda}{(1 - M)} \quad . \tag{3-13}$$

To convert between higher (gross) and lower (net) heating values, the amount of water produced by combustion reactions, but not including moisture, must be known. If this is called W, lb water/lb fuel, then the heating values are related by:

$$\mathrm{HHV} = \mathrm{LHV} + W\lambda. \tag{3-14}$$

All heats reported in this chapter are higher (gross) heating values on a dry basis.

Table 3-4 reports higher heating values on a dry basis for a variety of biomass fuels. Typically, the heating values for coals are much greater than for biomass materials, ranging from 10 MBtu/lb to 14 MBtu/lb and 5 MBtu/lb to 9 MBtu/lb, respectively. This is principally due to the higher carbon content of the coals. Table 3-7 gives higher heating values for biomass chars. The values are low due to the high ash content of the chars; however, on a dry, ash-free basis, the heating values are similar to those of the coals.

A common method for estimating heating values of solid fuels is the Dulong-Bertholot equation (Spiers 1962) which permits the heating value to be estimated from the ultimate analysis. Table 3-9 presents a comparison of calculated and experimental gross heating values for biomass fuels and chars. For the fresh biomass feeds, the method consistently underpredicts the heating value. For the 14 feedstocks listed in Table 3-9, the average error in heating values is -6.8% or -500 Btu/lb. The method is least accurate for the samples with the highest oxygen content. In the case of the chars, the method is much more accurate, yielding an average error of 3.1% or 220 Btu/lb. The bias error for the five chars is only 1.2%, indicating that the equation is more applicable to the chars than to the fresh biomass.

A second method for estimating heating values is that of Tillman (1978). As shown in Table 3-9, the results for Tillman's equation, which uses only the carbon content, are much more accurate for the biomass materials than the Dulong-Berthelot equation. The average error is roughly 180 Btu/lb for the fresh feedstocks. Further, the predictions show no statistical bias. For the chars, however, the errors are roughly double those of the Dulong-Berthelot equation.

A third method of estimating gross heating values has been developed at IGT (Inst. of Gas Technology 1978) using the experimental heating values and ultimate analyses of more than 700 coal samples. When this heating value correlation is used to estimate the higher heating values of fresh biomass materials, the average error that results is approximately

Table 3-9. COMPARISON OF EXPERIMENTAL AND CALCULATED HIGHER (GROSS) VALUES USING PUBLISHED GHV CORRELATIONS

Material	Experimental HHV* (Btu/lb)	Dulong - Berthelot[a] Calc. (Btu/lb)	Dulong - Berthelot[a] Error (%)	Tillman[b] Calc. (Btu/lb)	Tillman[b] Error (%)	IGT[c] Calc. (Btu/lb)	IGT[c] Error (%)
Fresh biomass:							
Douglas fir	9052	8499	-6.1	9114	+0.7	9152	1.1
Douglas fir bark	9500	9124	-4.0	9848	-3.5	9694	2.1
Pine bark	8780	8312	-5.3	9114	+3.8	8947	1.9
Western hemlock	8620	7840	-10.7	8757	+1.6	8536	-1.0
Redwood	9040	8441	-6.6	9340	+3.3	9115	0.8
Beech	8906	8311	-5.1	8990	+2.6	8990	0.9
Hickory	8610	8036	-7.3	8620	-0.6	8746	1.6
Maple	8671	7974	-7.1	8802	+2.6	8684	0.2
Poplar	8920	8311	-6.8	8990	+0.8	8990	0.8
Rice hulls	6610	8128	-7.3	6520	-1.4	6707	1.5
Rice straw	6540	6160	-5.8	6652	+1.7	6648	1.7
Sawdust pellets	8814	7503	-14.9	8156	-7.8	8270	-6.2
Animal waste	7380	7131	-3.4	7310	-1.0	7542	2.2
Municipal solid waste (MSW)	8546	8128	-4.9	8231	-3.7	8642	-1.1
Paper	7572	6582	-13.1	7441	-1.7	7329	-3.2
Absolute Avg. Error			7.2		2.5		1.7
Bias Error			-7.2		-0.2		+0.4
Chars:							
Fir bark	8260	7961	-3.6	8663	+4.9	8184	-0.9
Rice hulls	6100	6026	-1.2	6050	-0.8	6058	-0.7
Grass straw	8300	8309	+0.1	8870	+6.7	8403	1.2
Animal waste	5450	5722	+5.9	5768	+5.8	5830	7.0
MSW	8020	8399	+4.7	9603	+19.7	8088	0.8
Absolute Avg. Error			3.1		7.6		2.1
Bias Error			+1.2		7.3		+1.5

[a] Dulong-Berthelot Equation: HHV, Btu/lb = $146.76\ C + 621\ H - \frac{N + O - 1}{8} + 39.96\ S$

[b] Tillman Equation: HHV, Btu/lb = $188\ C - 718$.

[c] IGT Equation: HHV, Btu/lb = $146.58\ C + 568.78\ H + 29.45 - 6.58\ A - 51.53\ (O + N)$.

Nomenclature: All values are weight percent, dry basis

A = Ash
C = Carbon
H = Hydrogen
N = Nitrogen
O = Oxygen
S = Sulfur

% Error = 100 [Calc. HHV - Exptl. HHV]/[Exptl. HHV]

Absolute Average Error = $\frac{|\%\ \text{Error}|}{n}$
N

Bias Error = $\frac{\%\ \text{Error}}{n}$
N

N = number of data points.

130 Btu/lb with a small positive statistical bias of approximately 26 Btu/lb. When used to predict biomass char heating values, the IGT correlation error is smaller than the errors for both the Dulong-Bertholot and Tillman correlations.

Of these three correlations, the IGT method seems to give the best estimates of biomass and biomass char heating values. The experimental error in the ASTM heating value is ± 100 Btu/lb while the IGT method yields an average error for chars and fresh biomass of about 150 Btu/lb. Experimental values should be used in cases where the elemental analysis is much different from materials previously tested.

3.1.5 Heats of Formation

In thermodynamic calculations, the heat of formation of the feedstocks is required. Heats of formation may be calculated rigorously from the heats of combustion, assuming that the only materials oxidized are C, H, N, and S, by posing the following reactions:

$$\text{Fuel} + O_2 \longrightarrow \left[\begin{array}{ll} CO_2,\ -94{,}052 \text{ cal/mole} & \qquad (3\text{-}15) \\ H_2O(L),\ -68{,}317 \text{ cal/mole} & \qquad (3\text{-}16) \\ NO_2,\ +7{,}960 \text{ cal/mole} & \qquad (3\text{-}17) \\ SO_2,\ -70{,}940 \text{ cal/mole} & \qquad (3\text{-}18) \end{array}\right.$$

The heat of formation of the fuel may be calculated as follows, assuming no chemical heat involving ash reactions:

$$H_f\ (25\ C) = (HHV^* + 0.018 \sum_{\text{products}} [H_{fi} n_{fi}])/(1 - ASH), \qquad (3\text{-}19)$$

in Btu/lb, dry, ash-free basis.

In this equation, n_{fi} is the moles of species i formed per 100 lb of dry biomass on combustion (i can be CO_2, $H_2O(l)$, NO_2, SO_2) while H_{fi} is the heat of formation of i at 25 C in cal/mole. The factor 0.018 puts the formation enthalpy on a Btu per pound of biomass basis. The HHV is treated as a positive number. The heat of formation is normalized to a dry, ash-free basis for purposes of comparison. Table 3-10 presents heat of formation for a variety of feedstocks. The data show a definite trend in terms of the rank (degree of aromatization) of the materials involved. Biomass is very low in rank since its structure consists of only single aromatic rings (benzene derivatives). Fuels of higher rank—peat, lignite, bituminous, and anthracite coals — have structures containing progressively larger aromatic clusters. Typical bituminous coal structures contain from four to six condensed aromatic rings. The fuel of highest rank is graphite. The coals tend to have low heats of formation which increase in the exothermic sense as the rank decreases. Most woody materials exhibit a constant heat of formation in the range of -2200 Btu/lb. Materials such as straw and rice hulls have higher heats of formation, on the order of -2700 Btu/lb. The biomass chars generally exhibit heats of formation intermediate between coals and fresh biomass materials. Figure 3-1 shows how the heats of formation depend on the H/C ratio of the feedstock. It is evident that the biomass chars, although

Table 3-10. HEATS OF FORMATION FOR TYPICAL FUELS AND BIOMASS MATERIALS

(Basis: Dry, Ash-Free Solid)

Material	H_f(77 F) (Btu/lb)	H/C, Mole Ratio
Charcoal	+ 142	
Pittsburgh seam coal	- 209	
Western Kentucky No. 11 coal	- 323	
Utah coal	- 540	
Wyoming Elkol	- 648	
Lignite	-1062	
Douglas fir	-2219	1.45
Douglas fir bark	-2081	1.26
Pine bark	-2227	1.33
Western hemlock	-2106	1.38
Redwood	-2139	1.33
Beech	-2480	1.45
Hickory	-2344	1.57
Maple	-2203	1.43
Poplar	-2229	1.45
Rice hulls	-2747	1.78
Rice straw	-2628	1.56
Sawdust pellets	-1860	1.65
Animal waste	-2449	1.55
Municipal solid waste	-2112	1.51
Fir bark char	-1580	0.96
Rice hull char	-1136	0.87
Grass straw char	-1581	0.87
Animal waste char	-1536	0.76
Municipal solid waste char	-213.8	0.18

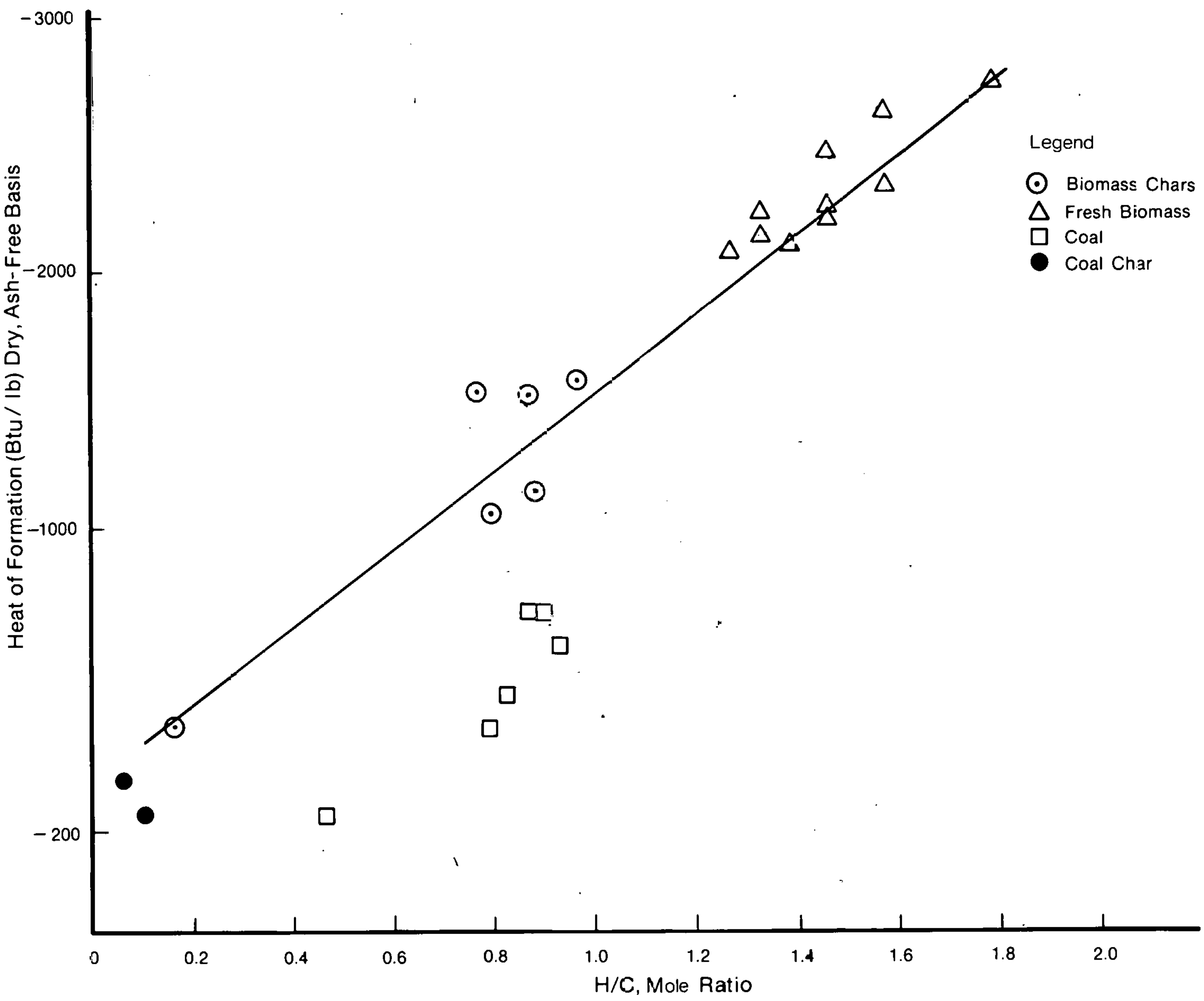


Figure 3-1. Heats of Formation of Carbonaceous Fuels

similar in ultimate analysis to coals, do not correlate with the coals in terms of H/C ratio. This is probably due to the coal's greater degree of aromatization, which is a result of the coalification process.

Heats of combustion for biomass materials can be calculated using the heat of formation data based on the following empirical correlation for biomass materials:

$$H_f\ (77\ F) = -1437\ H/C - 149 \qquad (3\text{-}20)$$

with H/C as mole ratio, Btu/lb, dry ash-free basis.

For natural biomass materials and their chars, the following equation results, based on the ultimate analysis and the pertinent combustion reactions:

$$\begin{aligned} HHV^* &= (141C + 615H - 10.2N + 39.95S) \\ &- (1 - ASH)\left(\frac{17{,}244H}{C}\right) + 149. \end{aligned} \qquad (3\text{-}21)$$

The HHV* is the gross heating value on a dry basis, Btu/lb, and the analytical data are expressed in weight percent. This equation cannot be expected to function for manmade materials such as plastics or for noncellulose-derived materials like leather. Table 3-11 shows that this equation predicts heating values more accurately than the previously tested methods, yielding errors of only $\pm$ 100 Btu/lb of material, which is within experimental error. The equation is similar in form to the IGT equation.

3.1.6 Ash

Table 3-12 shows that the ash content of most woods is on the order of 1%. The ash is composed principally of CaO, K_2O, Na_2O, MgO, SiO_2, Fe_2O_3, P_2O_5, SO_3 and Cl (Wise 1946). The first five oxides generally comprise the bulk of the ash although P_2O_5 is present in some ashes in concentrations as high as 20%. Calcium oxide generally represents half of the total ash, and the potassium oxide content is on the average 20%. Trace metal analysis also indicates the presence of aluminum, lead, zinc, copper, titanium, tin, nickel, and thallium.

3.2 CHEMICAL COMPOSITION OF WOODS

In characterizing and correlating reactivity data for pyrolysis and gasification, it is necessary to have some idea of the chemical structure of the reactant material. Woods can be analyzed in terms of fractions of differing reactivity by solvent extraction techniques. This section provides some of the relevant information on the structure and composition of these reactive fractions which will be useful in later discussions of gasification kinetics (Chapter 7) and pyrolysis (Chapter 5).

Woods can be separated into three fractions: extractables, cell wall components, and ash. The extractables, generally present in amounts of 4% to 20%, consist of materials derived from the living cell. The cell wall components, representing the bulk of wood, are principally the lignin fraction and the total carbohydrate fraction (cellulose and

Table 3-11. COMPARISON OF CALCULATED AND EXPERIMENTAL HEATS OF COMBUSTION USING HEAT OF FORMATION EQUATION

	Experimental HHV* (Btu/lb)	Calculated HHV* (Btu/lb)	% Error	
Douglas fir	9052	9039	-0.12	
Douglas fir bark	9500	9617	1.23	
Pine bark	8780	8938	1.80	
Western hemlock	8620	8590	-0.35	
Redwood	9040	9124	+0.93	
Beech	8096	8906	1.67	
Hickory	8610	8610	-0.69	
Maple	8671	8671	+1.06	
Poplar	8920	8906	-0.15	
Rice hulls	6610	6646	+0.54	
Rice straw	6540	6728	2.88	
Sawdust pellets	8814	8154	-7.49	
Animal waste	7380	7442	0.85	1.63%
Municipal solid waste	8546	8357	-2.21	120 Btu/lb
Paper	7572	7385	-2.47	
Fir bark char	8260	8295	+0.43	
Rice hull char	6100	5967	-2.19	1.44%
Grass straw char	8300	8434	1.61	102 Btu/lb
Animal waste char	5450	5595	+2.66	
Municipal solid waste char	8020	7994	-0.32	

hemicellulose) termed holocellulose. Lignin, the cementing agent for the cellulose fibers, is a complex polymer of phenylpropane. Cellulose is a polymer formed from d (+)-glucose while the hemicellulose polymer is based on other hexose and pentose sugars. In woods, the cell wall fraction generally consists of lignin/cellulose in the ratio 43/57. Residues of the total wood, such as bark and sawdust, have differing compositions.

Table 3-12 presents some analyses of woods on a dry basis while Table 3-13 presents data for typical wood barks.

Table 3-12. CHEMICAL ANALYSES OF REPRESENTATIVE WOODS[a]
(wt %)

Sample	Ash	Extractables	Lignin	Holocellulose
Softwoods[b]				
Western white pine	0.20	13.65	26.44	59.71
Western yellow pine	0.46	15.48	26.65	57.41
Yellow cedar	0.43	14.39	31.32	53.86
Incense cedar	0.34	20.37	37.68	41.60
Redwood	0.21	17.13	34.21	48.45
Hardwoods[c]				
Tanbark oak	0.83	16.29	24.85	58.03
Mesquite	0.54	23.51	30.47	45.48
Hickory	0.69	19.65	23.44	56.22

[a] Encyclopedia of Chem. Tech. 1963, p. 358.
[b] Softwood refers to conifer woods.
[c] Hardwood refers to deciduous woods.

Table 3-13. CHEMICAL ANALYSES OF REPRESENTATIVE WOOD BARKS[a]
(% Dry Basis)

Species	Lignin	Extractables	Ash	Holocellulose[b]
Black spruce	45.84	24.78	2.1	27.28
Fir	39.16	30.37	3.1	27.37
White birch	37.8	21.6	1.5	39.1
Yellow birch	36.5	19.9	2.9	40.7
Beech	37.0	18.3	8.3	36.4

[a] From Wise 1946.
[b] By difference.

In comparing the ultimate analysis data for barks and whole woods in Table 3-4, there is no indication that the chemical makeup of the feedstocks is different. However, from the extractable and cell wall analyses it is evident that the lignin and extractable contents of barks are much greater than those of whole woods. It should be expected that these materials would exhibit different overall reactivities due to their chemical differences.

3.2.1 Cellulose

The carbohydrate fraction of plant tissues is composed of cellulose and hemicelluloses, which are moderate to high molecular weight polymers based on simple sugars. Cellulose itself is derived from d-glucose while the hemicelluloses are principally polymers of d-xylose and d-mannose. The hemicellulose composed of pectin generally is present in only very small quantities in woody material but can be a substantially abundant constituent of the inner bark of trees.

The cellulose polymer is shown in Fig. 3-2.

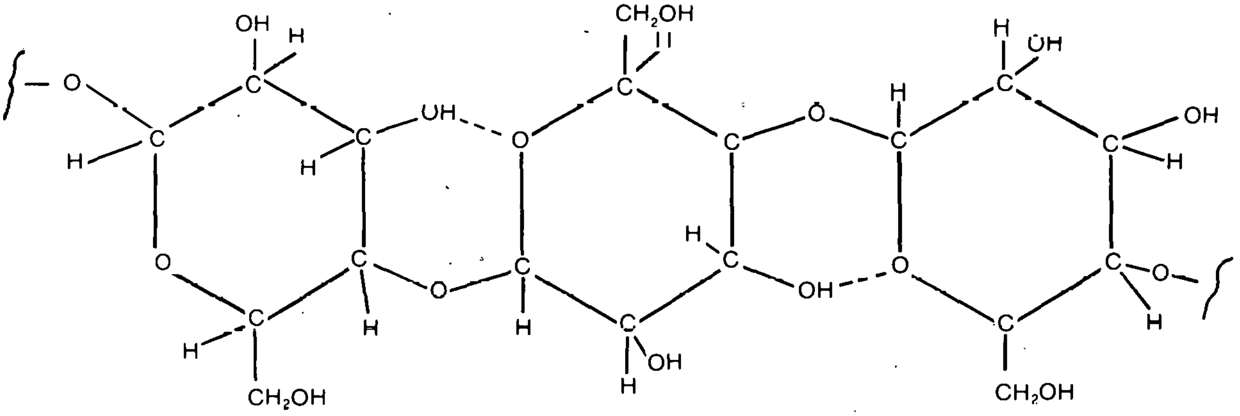


Figure 3-2. The Cellulose Molecule

Cellulose is composed of d-glucose units ($C_6H_{10}O_5$) bound together by ether-type linkages called glycosidic bonds. Glucose is a hexose, or six carbon sugar. In wood the polymers form thread-like chains of molecular weight greater than 100,000. In cotton, 3000 or more units with a combined molecular weight of 500,000 may be present in chains, yielding an extended length of 15,700 Å and cross section of 4 by 8 Å. These very long, thin molecules can be coiled and twisted but, because of the arrangement of the ether linkage, the chain is stiff and extended. An additional contribution to rigidity results from the hydrogen bonding between a hydroxyl hydrogen and the ring oxygen in the adjacent monomer. The threads are woven amongst each other in a random fashion, termed amorphous cellulose, and also fitted together in a crystalline arrangement. Strong van der Waals forces and hydrogen bonds between threads (termed secondary bonding) give rise to a lamellae structure. The weakest bond in the chain direction is the C-O glycosidic bond with an energy of 50 kcal. Cellulose fibers are thus very strong.

The dominant physical characteristic of cellulose is its extreme insolubility, which retards not only acid and enzymic hydrolysis but also the removal of lignins and hemicelluloses interspersed through the cellulose structures. The strong secondary bonding is responsible for the insolubility. Cellulose can be dissolved by strong acids such as hydrochloric, sulfuric, and phosphoric.

Pyrolysis of cell wall materials provides a mixture of volatile materials, tars, and char. The proportion of each fraction and its composition depends on the reaction conditions including temperature, pressure, heating rate, and atmospheric composition. Char results from the condensation of aromatic compounds formed from the primary decomposition products. Since aromatics are not present initially, the amount of char formed by condensation reactions is relatively small. Recent reviews of cellulose chemistry may be found in Shafizadeh and McGinnis (1971), Jones (1969), and references in Chapter 5.

3.2.2 Principal Hemicelluloses

Interlaced with cellulose in the cell walls are a number of other polymeric sugars termed hemicelluloses. These are generally differentiated from true cellulose by their solubility in weak alkaline solutions. Figure 3-3 shows a sequence employed by Timell (1967) for isolating softwood polysaccarides. Hemicelluloses are not precursors of cellulose; they are distinctly different compounds that contain acidic and neutral molecules of low and high molecular weight. In contrast to cellulose, which appears to be universal and invariant as the structural polysaccharide of higher land plants, the hemicellulose polysaccharides show a significant variation in composition and structure among species. Several reviews of hemicellulose chemistry have been presented by Polglase (1955), Aspinall (1959), and Whistler and Richards (1970).

Most hemicelluloses contain two to four (and occasionally five to six) simpler sugar residues. D-xylose, d-glucose, d-mannose, d-galactose, l-arabinose, d-glucuronic acid, and 4-O-methyl-d-glucuronic acid residues constitute the majority of hemicellulose monomers as shown in Fig. 3-4. The structure is similar to that of cellulose except that the hemicellulose polymers generally contain 50 units to 200 units and exhibit a branched rather than a linear structure.

These structural characteristics, as well as the number and proportion of different sugar residues present (degree of heteropolymerization), largely determine the observed physical properties of hemicelluloses. The heteropolymerization decreases the ability to form regular, tight-fitting crystalline regions and thus makes hemicellulose more soluble than cellulose. Solubility is also increased due to the branching, which decreases the number of intermolecular hydrogen bonds, and the decreased degree of polymerization compared to cellulose.

3.2.2.1 Xylans

Xylans, the most abundant of the hemicelluloses, are polymers of d-xylose ($C_5H_{10}O$). Xylose is a pentose sugar. The xylan fraction of cellulose is often termed pentosan. They are most abundant in agricultural residues such as grain hulls and corn stalks. Hardwoods (deciduous) and softwoods contain appreciable amounts of xylans. Xylan chains are short, exhibiting molecular weights on the order of 30,000 or less. In addition, some xylans contain carboxylic acid and methyl-ether groups. Typical xylans are shown in Fig. 3-5. The acidic xylans contain d-glucuronic acid or the methylate acid as terminal branch units.

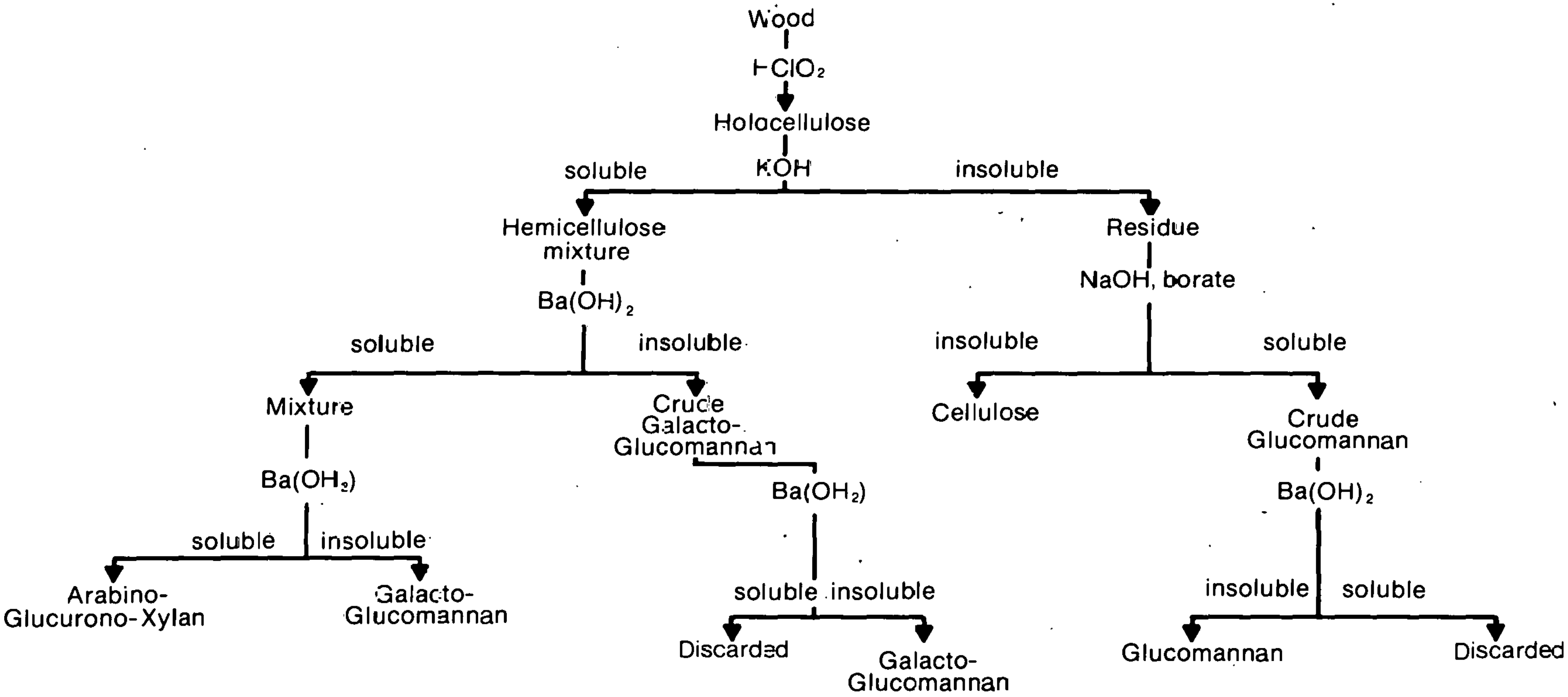
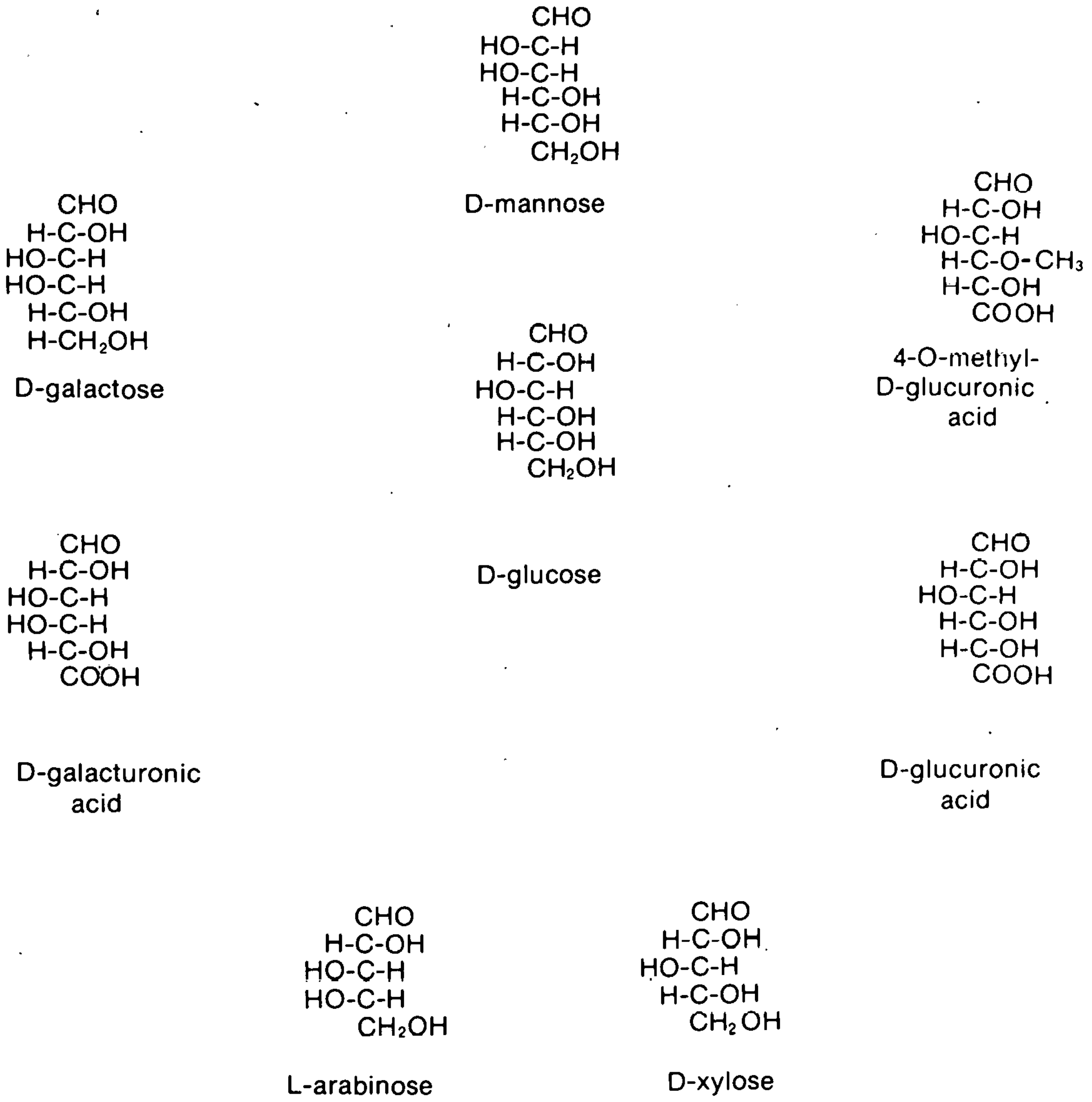


Figure 3-3. Extraction Sequence for Isolation of Softwood Polysaccharides



$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{CH_2OH}\end{array}$$

D-mannose

$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{H{-}CH_2OH}\end{array}$$

D-galactose

$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{CH_2OH}\end{array}$$

D-glucose

$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}O{-}CH_3}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{COOH}\end{array}$$

4-O-methyl-D-glucuronic acid

$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{COOH}\end{array}$$

D-galacturonic acid

$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{COOH}\end{array}$$

D-glucuronic acid

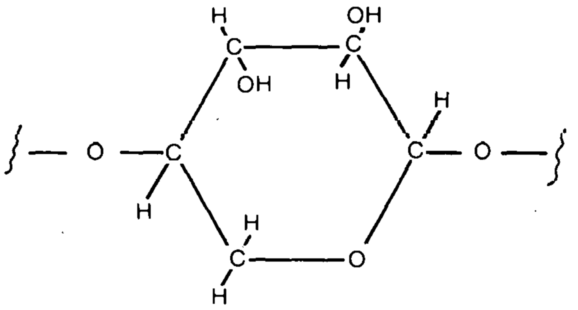
$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{CH_2OH}\end{array}$$

L-arabinose

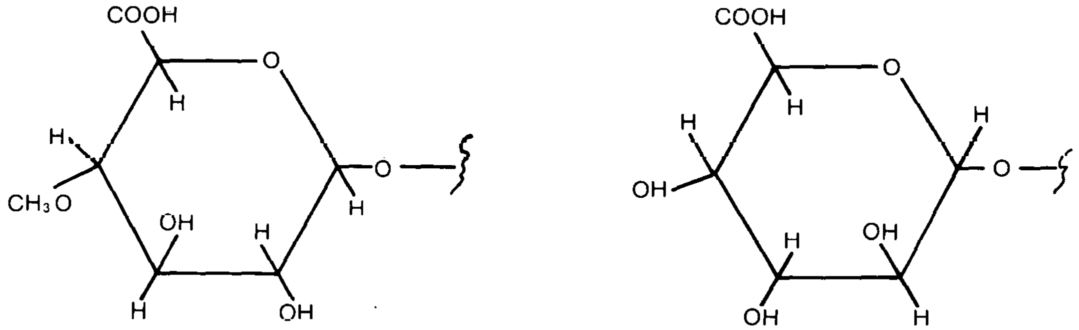
$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{HO{-}C{-}H}\\ \mathrm{H{-}C{-}OH}\\ \mathrm{CH_2OH}\end{array}$$

D-xylose

Figure 3-4. Structural Interrelationship of Commonly Occurring Hemicellulose Component Sugars



Xylan



Acid Xylans-Terminal Groups

Figure 3-5. Xylan Hemicellulose Structures

Some of the acid xylans are of low molecular weight. They are known as hemicellulose-B and are differentiated from the normal xylans and other neutral hemicelluloses in that they are not precipitated from the alkaline extract by neutralization.

3.2.2.2 Mannans

Mannan-based hemicelluloses include glucomannans, which are built up from linked d-glucose and d-mannose residues in about a 30:70 ratio, and galactoglucomannans, made up of linked d-galactose, d-glucose, and d-mannose in 2:10:30 ratios. In softwoods, mannans are present in substantial amounts while in hardwoods there is generally very little mannan hemicellulose.

3.2.3 Cellulose Data for Woods

Table 3-14 presents some data on the cellulose content of woods. The holocellulose fraction of hardwoods is composed principally of cellulose and xylans. The total content of mannans and other hemicelluloses averages only 4.8% for the four samples. In softwoods, the cellulose fraction is about the same as in hardwoods. However, mannans are present to a much greater extent; the mannans equal or exceed the total xylans in the conifers. Other hemicelluloses are present at 5.4% on the average for the four samples.

Table 3-14. BREAKDOWN OF HOLOCELLULOSE FRACTION OF WOODS[a]

	Wt % in Holocellulose				
	Cellulose	Xylans	Acidxylans	Mannans	Others
Hardwoods					
Trembling aspen	71.5	20.0	4.1	2.9	1.5
Beech	64.5	23.8	6.5	2.9	2.3
Sugar maple	69.8	20.0	5.9	3.1	1.2
Southern red oak	59.8	28.3	6.6	2.9	2.4
Softwoods					
Eastern hemlock	69.0	6.1	5.0	17.1	2.8
Douglas fir	64.6	4.2	4.2	16.0	11.0
White spruce	65.2	9.5	5.0	16.3	3.9
Jack pine	65.1	10.1	5.6	15.1	4.0

[a] From Encyclopedia of Chem. Tech, 1963. p. 358.

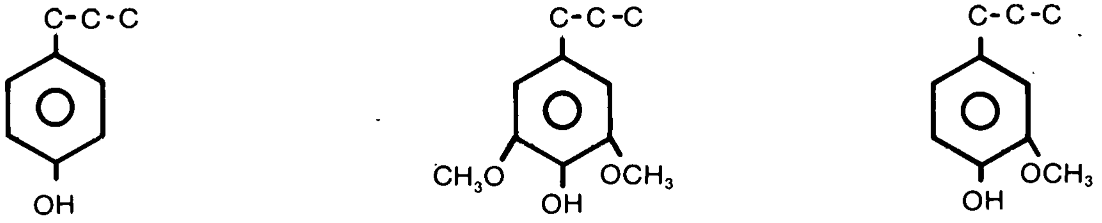
3.2.4 Lignin

The noncarbohydrate component of the cell wall, termed lignin, is a three-dimensional polymer based primarily on the phenylpropane unit. Lignin is deposited in an amorphous state surrounding the cellulose fibers and is bound to the cellulose directly by ether bonds. Its exact structure is not known, although considerable information is available based on its chemical reactivity. In solubility analyses, lignin is defined as the cell wall portion not soluble in 72% sulfuric acid. Table 3-15 gives typical elemental analyses of wood lignins.

Table 3-15. ELEMENTAL ANALYSIS OF WOOD LIGNIN

Type	C (%)	H (%)	O (%)	OCH_3 (%)	Molecular Weight
Softwood	63.8	6.3	29.9	15.8	10,000
Hardwood	59.8	6.4	33.7	21.4	5,000

It is assumed, based on much evidence, that the lignins are composed of several monomer groups as shown in Fig. 3-6. These are combined to form the polymer by a variety of linkages involving the aromatic rings and functional groups. The polymer formed contains only single aromatic rings as shown in Fig. 3-7 (structural formula).



p-hydroxylphenylpropane

syringylpropane

guaiacylpropane

Figure 3-6. Several Monomer Units in Lignin

The representative structure contains the phenylpropane substituted as sinapyl, coniferyl, and p-coumaryl alcohols as shown in Fig. 3-8. Lignification, as discussed by Freudenberg (1965), is thought to occur by dehydration-polymerization of these alcohol units. Thermal pyrolysis of lignin generally yields a considerable amount of char. It is likely that thermal pyrolysis and lignification follow the same route to yield a condensed polynuclear aromatic structure.

The amount of lignin present varies among materials. Typical amounts for woods and barks are given in Tables 3-12 and 3-13. Table 3-16 gives data for a variety of other biomass materials.

3.2.5 Extractables

The nature and quantity of extractables vary widely among woods. Table 3-17 lists the types of extractables found in a variety of woody materials. The resin and volatile oils are fragrant and found most abundantly in softwoods. Waxes, fatty acids, pigments, and carbohydrates are commonly found in all woods. Starches account for about 3% of the total wood. Since the quality and nature of extractables vary, the products after pyrolysis and gasification vary.

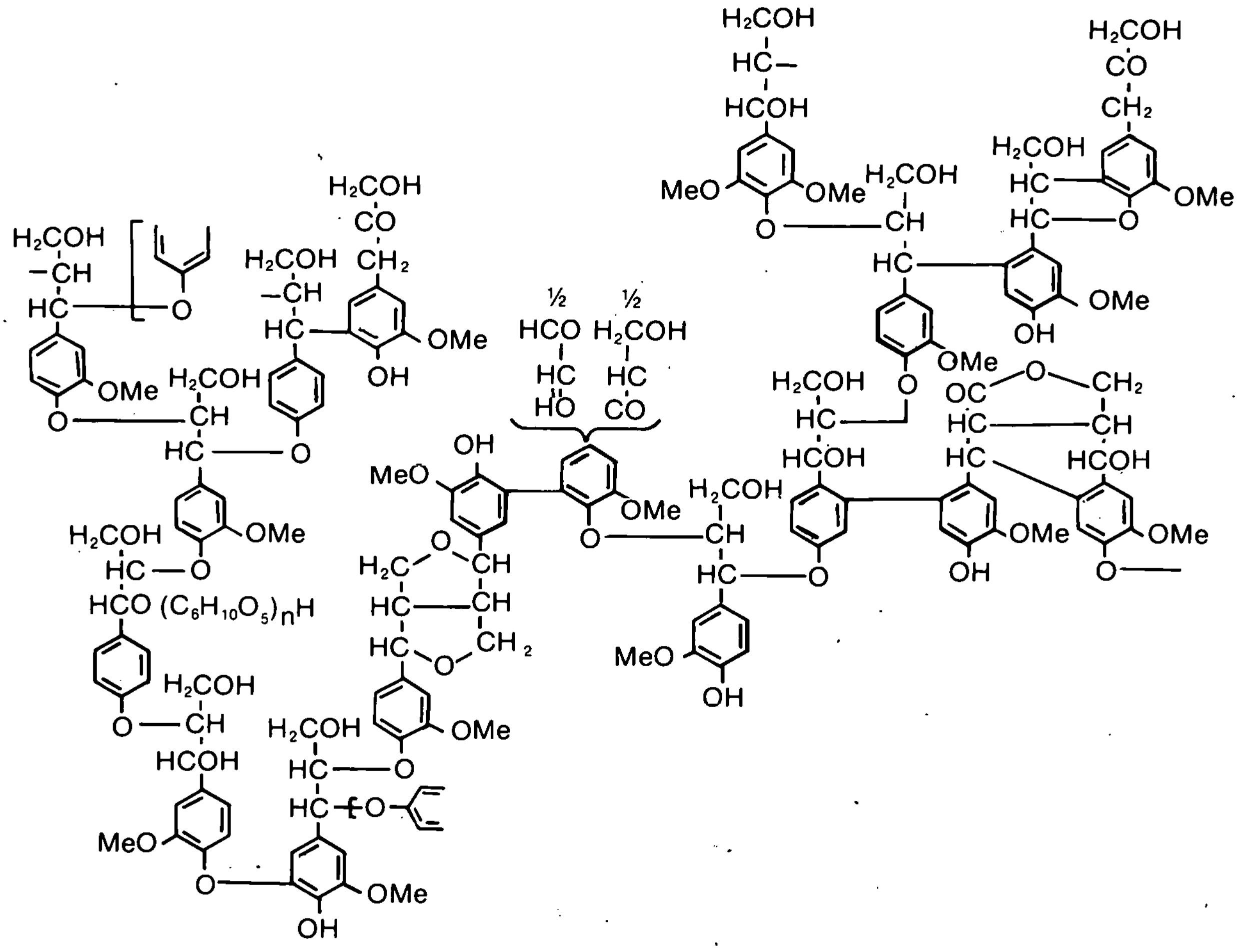
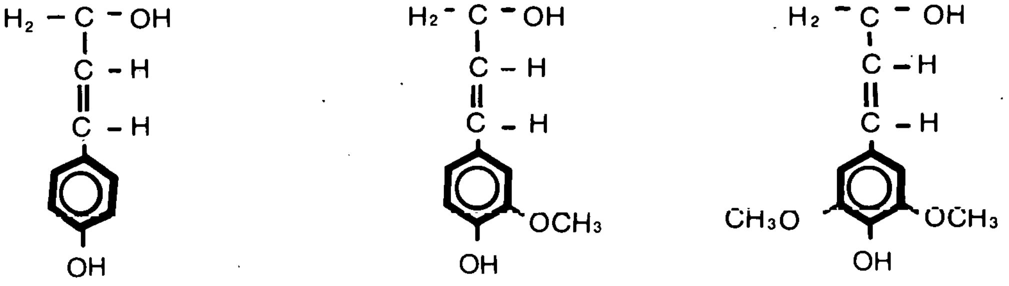


Figure 3-7. Representative Structure of Coniferous Lignin



p-coumaryl alcohol

coniferyl alcohol

sinapyl alcohol

Figure 3-8. p-Hydroxycinnamyl Alcohols

Table 3-16. LIGNIN IN MISCELLANEOUS PLANT MATERIAL[a]

Material	Wt %, Dry Unextracted Material
Rice hulls	40.0
Bagasse	20.3
Peanut shells	28.0
Pine needles	23.9
Wheat straw	13.9
Corncobs	13.4

[a] From Encyclopedia of Chem. Tech. 1963, p. 361.

Table 3-17. EXTRACTABLE COMPONENTS OF WOOD

Volatile Oils (removed by steam or ether soluble)

- Terpenes ($C_{12}H_{16}$)
- Sesquiterpene ($C_{15}H_{24}$)
  and their oxygenated derivatives

Resins and Fatty Acids (soluble in ether)

- Resin acids ($C_{20}H_{30}O_2$)
- Fatty acids (oleic, linoleic, palmitic)
- Glyceryl esters of fatty acids
- Waxes (esters of monohydroxy alcohols and fatty acids)
- Phytosterols (high molecular weight cyclic alcohols)

Pigments (soluble in alcohol)

- Flavonols
- Pyrones
- Anthranols
  (multi-ring naphthenic and aromatic alcohols, chlorides, ketones acids)
- Tannins (amorphous polyhydroxylic phenols)

Carbohydrate Components (water soluble)

- Starch
- Simple sugars
- Organic acids

Table 3-18 presents some typical extraction data on woods. The bulk of the extractables may be removed by hot water and ether. The ether-soluble portion is usually much greater for the softwoods, showing the higher content of volatile oils and resins. Thc hot water extraction, which leaches some tannins as well as the carbohyrates, gives yields approximately the same for the soft- and hardwoods.

3.3 WOOD STRUCTURE

Wood is composed of cells of various sizes and shapes. Long pointed cells are known as fibers; hardwood fibers are about 1 mm in length, while softwood fibers vary in length from about 3 mm to 8 mm. The mechanical properties of wood depend largely on its density which, in turn, is largely determined by the thickness of the cell walls.

3.3.1 Physical Structure of Softwoods

Figure 3-9 shows a typical softwood structure taken from Siau (1971). In softwoods, the fluid conducting elements are the longitudinal tracheids and ray tracheids. Longitudinal and horizontal resin canals are also present in many species.

Table. 3-18. EXTRACTION DATA FOR WOODS[a]

	Wt % of Solubles	
Sample	Hot Water	Ether
Softwoods		
Western yellow pine	5.05	8.52
Yellow cedar	3.11	2.55
Incense cedar	5.38	4.31
Redwood	9.86	1.07
Western white pine	4.49	4.26
Longleaf pine	7.15	6.32
Douglas fir	6.50	1.02
Western larch	12.59	0.81
White spruce	2.14	1.36
Hardwoods		
Tanbark oak	5.60	0.80
Mesquite	15.09	2.30
Hickory	5.57	0.63
Basswood	4.07	1.96
Yellow birch	3.97	0.60
Sugar maple	4.36	0.25
Average—Softwoods	6.25	3.36
Average—Hardwoods	6.44	1.09

[a] From Encyclopedia of Chem. Tech. 1963, p. 358.

Longitudinal tracheids, shown in Fig. 3-10, make up the bulk of the structure of softwoods. These are long, hollow, narrow cells having no openings that are tapered along the radial surfaces for a considerable portion of the lengths where they are in contact with other tracheids. The surfaces of the tracheids are dotted with pits, minute depressions in the plant tissue wall which permit the movement of water and dissolved materials between tracheids. The pit is covered with a semipermeable membrane. Pits

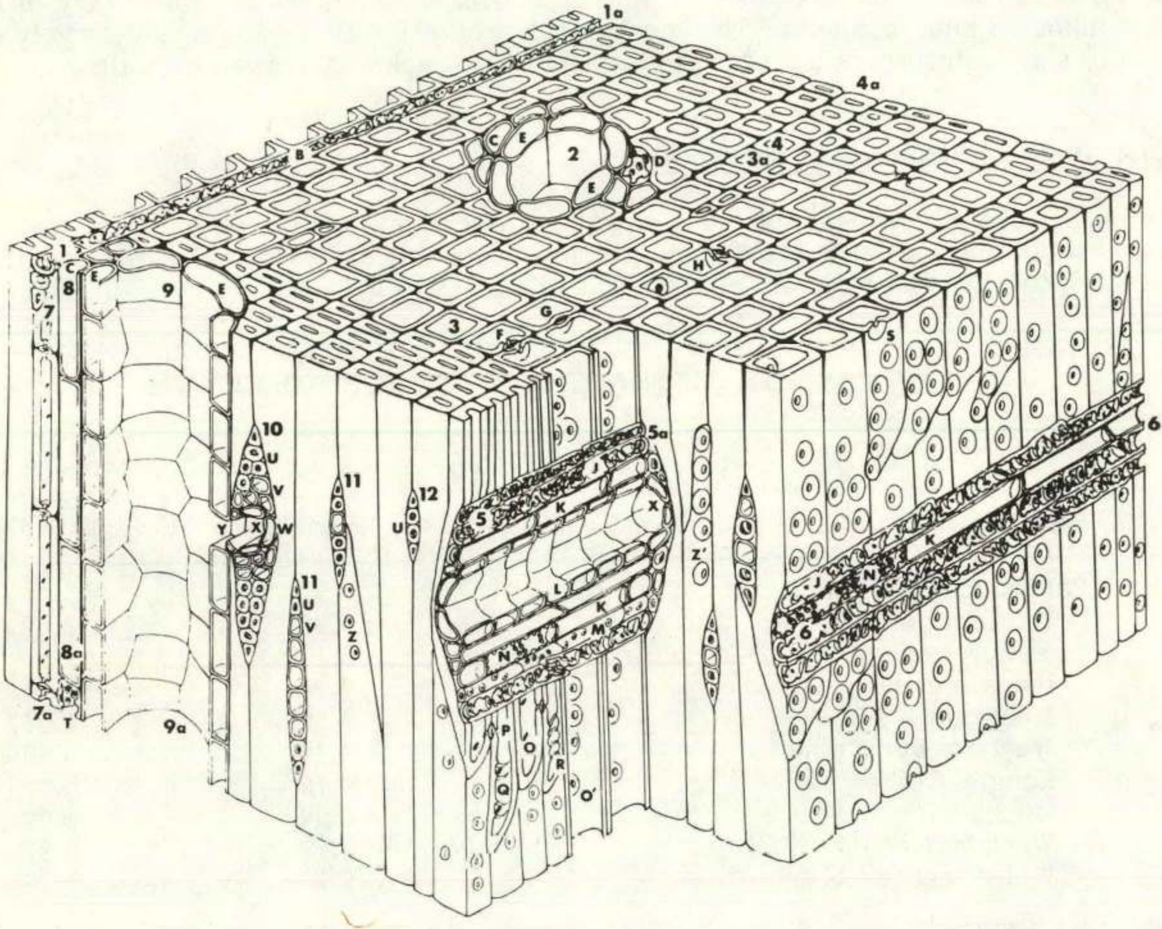


Figure 3-9. Gross Structure of a Typical Southern Pine Softwood

Transverse view. 1-1a, ray; B, dentate ray tracheid; 2, resin canal; C, thin-walled longitudinal parenchyma; D, thick-walled longitudinal parenchyma; E, epithelial cells; 3-3a, earlywood tracheids; F, radial bordered pit pair cut through torus and pit apertures; G, pit pair cut below pit apertures; H, tangential pit pair; 4-4a, latewood.

Radial view. 5-5a, sectioned fusiform ray; J, dentate ray tracheid; K, thin-walled parenchyma; L, epithelial cells; M, unsectioned ray tracheid; N, thick-walled parenchyma; O, latewood radial pit (inner aperture); O', earlywood radial pit (inner aperture); P, tangential bordered pit; Q, callitroid-like thickenings; R, spiral thickening; S, radial bordered pits (the compound middle lamella has been stripped away removing crassulae and tori); 6-6a, sectioned uniseriate heterogeneous ray.

Tangential view: 7-7a, strand tracheids; 8-8a, longitudinal parenchyma (thin-walled); T, thick-walled parenchyma; 9-9a, longitudinal resin canal; 10, fusiform ray; U, ray tracheids; V, ray parenchyma; W, horizontal epithelial cells; X, horizontal resin canal; Y, opening between horizontal and vertical resin canals; 11, uniseriate heterogeneous rays; 12, uniseriate homogeneous ray; Z, small tangential pits in latewood; Z', large tangential pits in earlywood.

are oriented in softwoods as adjacent pairs (pit pairs); fluid flow occurs between tracheids in the direction normal to the principal direction of flow.

The tracheid diameter varies from 15 to 80 μm according to species, with a length ranging from 1200 to 7500 μm. Average values of diameter and length, respectively, are 33 μm and 3500 μm. The inner diameter which is available for flow is typically 20-30 μm. The effective radius of the pit openings is 0.01 to 4 μm due to the restriction created by the membrane. Typically, a tracheid contains 50 pits. In addition to pit pairs allowing longitudinal flow, there are also pit pairs leading from longitudinal tracheids to ray tracheids, permitting radial flow.

The volumetric composition of a typical softwood is as follows:

Longitudinal tracheids	93%
Longitudinal resin canals	1%
Ray tracheids	6%

Since the principal voidage is oriented longitudinally, the magnitude of the permeability in the longitudinal direction is much greater than the radial permeability. Figure 3-11 shows a schematic model for flow through a softwood.

3.3.2 Physical Structure of Hardwoods

The structure of a typical hardwood is shown in Fig. 3-12. The dominant feature of the hardwood structure is the large open vessels or pores. Tracheids and pits are present but contribute significantly more resistance to flow. In a typical hardwood, the following structural composition is present:

Vessels	55%
Tracheids	26%
Woods rays	18%
Others	1%

Vessels are large, with diameters of 20 to 30 μm. The vessels are short, connected by "perforation plates" which offer very low flow resistance. Thus the vessels behave as long capillaries. Figure 3-13 shows the nature of flow through hardwoods.

3.3.3 Permeability

Permeability is important in pyrolysis. During heating, pyrolysis gases and liquids are generated within the particle and must pass through the porous stucture to the surroundings. Low permeability may significantly affect the product distribution by increasing the residence time of the primary pyrolysis products in the hot zone, thereby increasing the probability that they will enter into secondary reactions. Pelletized, densified biomass will have a low permeability compared with natural woods. Table 3-19 shows the range of permeability for various natural woods.

In natural soft- and hardwood structures, it is evident that the porosity is directed principally in the vertical direction in the livewood. Physical properties such as thermal

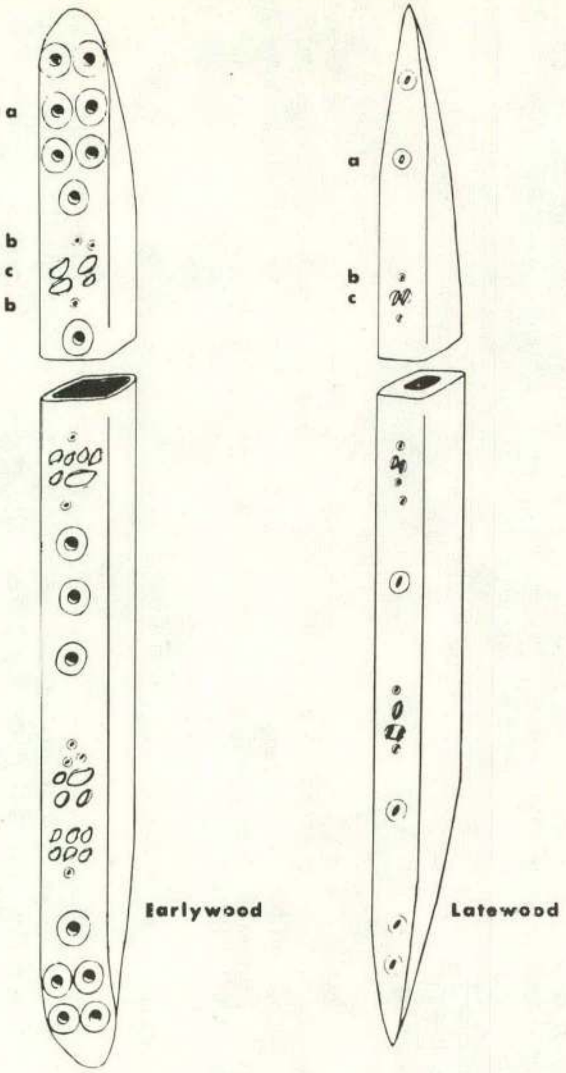


Figure 3-10. Radial Surfaces of Earlywood and Latewood Tracheids

(a,) intertracheid bordered pits: (b,) bordered pits to ray tracheids; (c,) 13 pinoid pits to ray parenchyma.

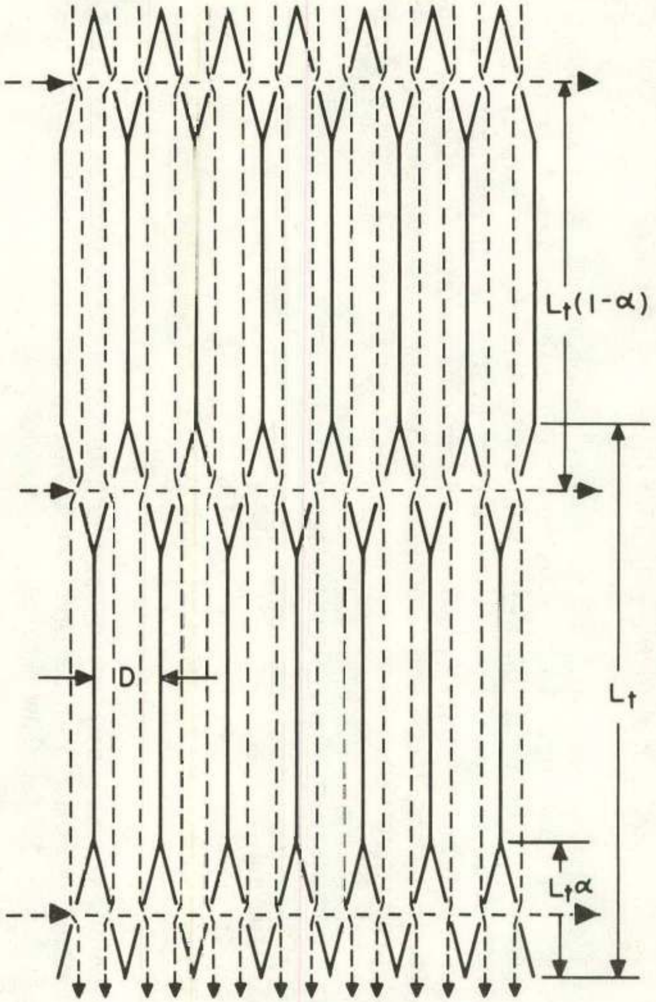


Figure 3-11. Softwood Flow Model

Tangential section showing pits on the radial surfaces of the tapered ends of the tracheids.

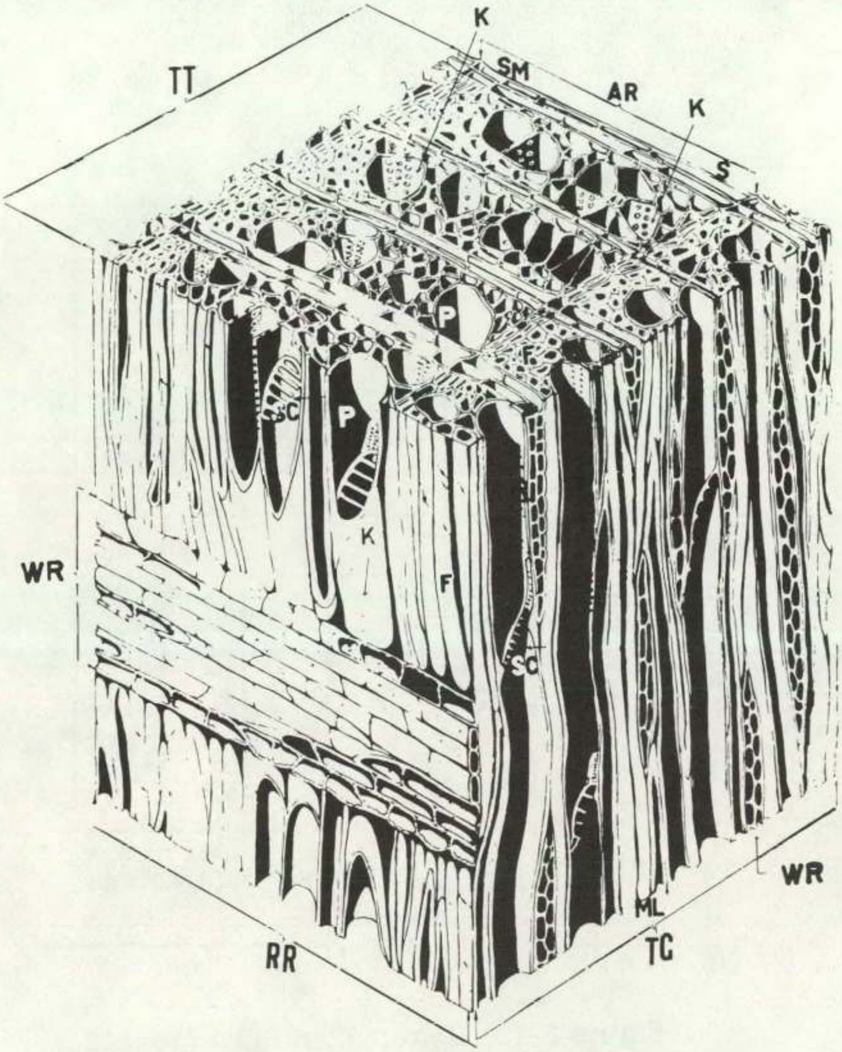


Figure 3-12. Gross Structure of a Typical Hardwood

Plane TT is the cross section. RR is the radial surface, and TG is the tangential surface. The vessels or pores are indicated by P, and the elements are separated by scalariform perforation plates, SC. The fibers, F, have small cavities and thick walls. Pits in the walls of the fibers and vessels, K, provide for the flow of liquid between the cells. The wood rays are indicated at WR. AR indicates one annual ring. The earlywood (springwood) is designated S, while the latewood (summerwood) is SM. The true middle lamella is located at ML.

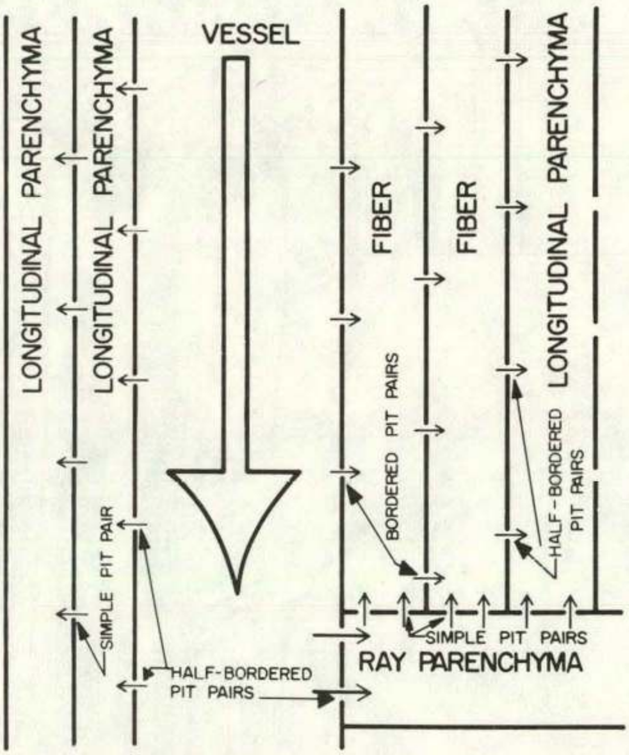


Figure 3-13. Generalized Flow Model for Hardwoods

The relative magnitude of the flow is indicated by the size of the arrow.

conductivity and diffusivity therefore depend on direction within fresh wood. Such a behavior is termed anistropic.

During densification, the voidage of the wood is greatly reduced and these physical properties become more uniform or isotropic. Other forms of compacted biomass, such as sawdust pellets or compacted municipal solid waste, can also be expected to be more or less isotropic.

3.4 PHYSICAL PROPERTIES

In addition to heating value, the other major physical data necessary for predicting the thermal response of biomass materials under pyrolysis, gasification, and combustion processes are thermal conductivity, heat capacity, true density, and diffusion coefficients.

Table 3-19. TYPICAL PERMEABILITY VALUES

Permeability $\left[\frac{cm^3\ (air)}{cm\ atm}\right]$	Longitudinal Permeabilities	
10^4	Red Oak	R≈150 μm
10^3	Basswood	R≈20 μm
10^2	Maple, pine sapwood, Douglas fir sapwood (Pacific coast)	
10^1	Spruces (sapwood) Cedars (sapwood)	
10^0	Douglas fir heartwood (Pacific coast)	
	White oak heartwood Beech heartwood	
10^{-1}	Cedar heartwood Douglas fir heartwood (intermountain)	
10^{-2} 10^{-3} 10^{-4}		Transverse permeabilities. (The species are in approximately the same order as those for longitudinal permeabilities.)

3.4.1 Thermal Conductivity

Thermal conductivity is defined in general terms as a proportionality factor which relates heat flow through a material to a temperature difference across a specified distance in that material. Mathematically, thermal conductivity is defined by Fourier's Law of Heat Conduction, given here for unidimensional heat flux in the x-direction in rectangular coordinates:

$$q_x = - k_x \frac{dT}{dx} \tag{3-21}$$

Most homogeneous materials are isotropic, and the thermal conductivity varies only with temperature

$$q = - k\nabla T \tag{3-22}$$

However, most naturally occurring biomass materials are anistropic. For wood, the thermal conductivity is a function of temperature and spatial direction. Modified biomass materials, such as densified wood, probably do not exhibit the same type of anisotropic behavior as the naturally occurring biomass materials. Thermal conductivity should be related to the various materials present in a substance. Thus in biomass thermal conductivity should be a function of the major constitutents, including moisture, cellulose, hemicellulose, and lignin.

Table 3-20 compiles available thermal conductivity data for biomass materials. No data are available for compacted biomass feedstocks. In general, no chemical analyses are presented with the data. The bulk of the data are probably effective thermal conductivities of powders rather than of the solids. The conductivities for solid woods, for example, are two to ten times greater than for many of the other biomass materials listed in Table 3-20 (e.g., sawdust and redwood shavings). Most data sources do not specify the state of the materials.

Steinhagen (1977) has summarized thermal conductivity data for several woods over the range -40 C to +100 C as a function of moisture content and has shown that moisture is an important parameter in wood conductivity. Since the moisture content is not known for the bulk of the entries in Table 3-20, the data presented are at best only semi-quantitative.

Completely lacking in the available data are thermal conductivities at higher temperatures. If thermal conductivity values are to be used in modeling pyrolysis or gasification processes, then new data over the actual range of processing conditions must be developed, including data for densified materials.

3.4.2 Heat Capacity

Heat capacity as normally reported is defined in terms of the enthalpy content of a material and represents the relative ability of a material to store energy. Enthalpy is a function of temperature and pressure.

$$H = H(T,P) \tag{3-24}$$

Table 3-20. THERMAL CONDUCTIVITY OF SELECTED BIOMASS MATERIALS

Material	Bulk Density (lb/ft^3)	Temperature (F)	Thermal Conductivity (Btu/ft-h-F)	Reference
Ashes, wood	—	32-212	0.040	Kern 1950
Cardboard	—	—	0.037	Kern 1950
Carbon, porous, with grain				
Grade 60 48% porosity	65.5[a]	Room Temp.	0.083	Perry and Chilton 1973
Grade 45 47% porosity	64.9[a]	Room Temp.	0.083	Perry and Chilton 1973
Grade 25 47% porosity	64.3[a]	Room Temp.	0.083	Perry and Chilton 1973
Carbon refractory brick 17% porosity	102.9[a]	Room Temp.	1.33	Perry and Chilton 1973
Celotex, sheet fiber from sugar cane	13.2	—	0.028	Handbook Chem. Phys. 1966
	14.8		0.028	Handbook Chem. Phys. 1966
	14.4	32	0.0253	McAdams 1954
	14.4	0	0.0242	McAdams 1954
	14.4	-100	0.0208	McAdams 1954
	14.4	-200	0.0175	McAdams 1954
	14.4	-300	0.0133	McAdams 1954
Charcoal - from maple, beech, and birch				
Coarse	13.2	—	0.030	Handbook Chem. Phys. 1966
6 mesh	15.2	—	0.031	Handbook Chem. Phys. 1966
20 mesh	19.2	—	0.032	Handbook Chem. Phys. 1966
Charcoal flakes	11.9	176	0.043	McAdams 1954
	15	176	0.051	McAdams 1954
		0 to 100	0.11	Perry and Chilton 1973
Coke powder				
Cork, regranulated				
Fine particles	9.4	—	0.025	Handbook Chem. Phys. 1966
3/16-in. particles	8.1	—	0.026	Handbook Chem. Phys. 1966
Corkboard	5.4	—	0.021	Handbook Chem. Phys. 1966
	7.0	—	0.022	Handbook Chem. Phys. 1966
	10.6	—	0.025	Handbook Chem. Phys. 1966
	14.0	—	0.028	Handbook Chem. Phys. 1966
	6.9	32	0.0205	McAdams 1954
	6.9	0	0.0200	McAdams 1954
	6.9	-100	0.0183	McAdams 1954
	6.9	-200	0.0142	McAdams 1954
	6.9	-300	0.0100	McAdams 1954
Cork, pulverized	10.0	32	0.035	McAdams 1954
	10.0	100	0.039	McAdams 1954
	10.0	200	0.032	McAdams 1954
Cotton	5.0	200	0.037	McAdams 1954
	5.0	100	0.035	McAdams 1954
	5.0	32	0.0325	McAdams 1954
	5.0	-100	0.0276	McAdams 1954

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[a] Apparent density, defined in Section 3.4.3.

Table 3-20. THERMAL CONDUCTIVITY (continued)

Material	Bulk Density (lb/ft^3)	Temperature (F)	Thermal Conductivity (Btu/ft-h-F)	Reference
Cotton	5.0	-200	0.0235	McAdams 1954
	5.0	-300	0.0198	McAdams 1954
Graphite				
2 3/4 in. diam., 3/4 in. thick				
30% porosity	98.6[a]	—	7.30	Handbook Chem. Phys. 1966
Porous, Grade 60 52% porosity	65.5[a]	—	4.17	Handbook Chem. Phys. 1966
Porous, Grade 45 53% porosity	64.9[a]	—	3.75	Handbook Chem. Phys. 1966
Porous, Grade 25 53% porosity	64.3[a]	—	3.33	Handbook Chem. Phys. 1966
Paper	—	—	0.075	McAdams 1954
Paper or pulp, macerated	2.5-3.5	—	0.021	Lewis 1968
Sawdust, various	12.0	—	0.034	Handbook Chem. Phys. 1966
Redwood	10.9	—	0.035	Handbook Chem. Phys. 1966
(and shavings)	8-15	—	0.0375	Lewis 1968
Sawdust (soft pine and oak)				
10-40 mesh	—	-295	0.016	Chow 1948
	—	-180	0.0195	Chow 1948
	—	-105	0.0235	Chow 1948
	—	-55	0.0265	Chow 1948
	—	-20	0.0295	Chow 1948
	—	+5	0.0325	Chow 1948
	—	+30	0.0335	Chow 1948
	—	+35	0.0385	Chow 1948
	—	+63	0.040	Chow 1948
Shredded redwood bark	4.0	32	0.0290	McAdams 1954
	4.0	-100	0.0235	McAdams 1954
	4.0	-200	0.0196	McAdams 1954
	4.0	-300	0.0155	McAdams 1954
	—	-50	0.0168	Rowley et al. 1945
	—	-25	0.0180	Rowley et al. 1945
	—	+25	0.0203	Rowley et al. 1945
	—	+75	0.0226	Rowley et al. 1945
Sheet Insulite, from wood pulp	16.2	—	0.028	Handbook Chem. Phys. 1966
	16.9	—	0.028	Handbook Chem. Phys. 1966
Wood fiber. mat	1.7	60	0.016	Rowley et al. 1945
	1.7	0	0.018	Rowley et al. 1945
	1.7	+50	0.020	Rowley et al. 1945
	1.7	+100	0.023	Rowley et al. 1945
Blanket	3.5	-50	0.016	Rowley et al. 1945
	3.5	0	0.018	Rowley et al. 1945
	3.5	50	0.020	Rowley et al. 1945
	3.5	100	0.022	Rowley et al. 1945
Excelsier	1.64	-50	0.019	Rowley et al. 1945
	1.64	0	0.022	Rowley et al. 1945

[a] Apparent density, defined in Section 3.4.3.

Table 3-20. THERMAL CONDUCTIVITY (concluded)

Material	Bulk Density (lb/ft^3)	Temperature (F)	Thermal Conductivity (Btu/ft-h-F)	References
Excelsior	1.64	50	0.025	Rowley et al. 1945
	1.64	100	0.024	Rowley et al. 1945
Solid woods				
Balsa	8-12	-300	0.0151	Gray et al. 1960
	8-12	-285	0.0150	Gray et al. 1960
	8-12	-260	0.0167	Gray et al. 1960
	8-12	-207	0.0183	Gray et al. 1960
	8-12	-190	0.0192	Gray et al. 1960
	8-12	-160	0.0208	Gray et al. 1960
	8-12	-130	0.0233	Gray et al. 1960
	8-12	-95	0.0232	Gray et al. 1960
Balsa, across grain	7.3	—	0.028	Handbook Chem. Phys. 1966
	8.8	—	0.032	Handbook Chem. Phys. 1966
	20		0.048	Handbook Chem. Phys. 1966
Cypress, across grain	29	—	0.056	Handbook Chem. Phys. 1966
Mahogany, across grain	34	—	0.075	Handbook Chem. Phys. 1966
Maple, across grain	44.7	122	0.11	McAdams 1954
Fir	26	75	0.063	Chapman 1974
Oak	30-38	86	0.096	Chapman 1974
Yellow pine	40	75	0.085	Chapman 1974
White pine	27	86	0.065	Chapman 1974
Pine, white, across grain	34	59	0.087	McAdams 1954
	32	—	0.032	Handbook Chem. Phys. 1966
Pine, Virginia, across grain	34	—	0.082	Handbook Chem. Phys. 1966
Pine board, 1 1/4-in. thick	—	-50	0.0515	Gray et al. 1960
	—	0	0.054	Gray et al. 1960
	—	+50	0.0575	Gray et al. 1960
	—	+100	0.059	Gray et al. 1960
Pine, with grain	34.4	70	0.20	McAdams 1954
Oak, across grain	51.5	59	0.12	McAdams 1954

and

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial p}\right)_T dp. \tag{3-25}$$

For solids and liquids $\partial H/\partial P$ is very small and

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT. \tag{3-26}$$

By definition the temperature dependency term $(\partial H/\partial T)_p$ called heat capacity at constant pressure, C_p, and is reported on a per unit weight basis. The resulting equation for the enthalpy change is as follows:

$$\Delta H = \int_{T_o}^{T} C_p \, dT. \tag{3-27}$$

This equation is normally used for materials of constant mass and no phase transitions. For example, if water is driven out of wood the apparent heat capacity may change very rapidly with temperature; the same is true for other phase transitions. Generally, if phase transitions are incorporated the enthalpy change will be:

$$\Delta H = \int_{T_o}^{T_p} C_p^{\alpha} dT + \Delta H_{\text{phase transition}} + \int_{T_p}^{T} C_p^{\beta} \, dT, \tag{3-28}$$

where

C_p^{α}, C_p^{β} = heat capacities of phases 1 and 2, and

T_p = temperature at which phase change occurs.

The heat capacity is a function of the composition and temperature but not the density of the material as long as compacting does not alter the chemical structure.

The data on heat capacity are limited. Some typical values are given in Table 3-21. No characterization data are reported for the samples.

Several C_p equations have been developed to predict the heat capacities of wood at temperatures to 100 C. As an example of specific heat equations for woods, Beall (1968) shows the equation in which moisture is an important parameter in estimating the heat capacity:

$$C_p = 0.259 + (9.75 \times 10^{-4})M + 6.05 \times 10^{-4}\, T_1 + 1.3 \times 10^{-5} M\, T_1, \tag{3-29}$$

where

M = % moisture, up to 27%.

Table 3-21. HEAT CAPACITY

Material	F (F)	Btu/lb-F	Reference
Carbon	78-168	0.168	Perry 1973
	103-1640	0.314	Perry 1973
	132-2640	0.387	Perry 1973
Charcoal	50	0.16	Perry 1973
Cellulose	—	0.32	Perry 1973
Oak	—	0.57	Perry 1973
Fir	75	0.65	Chapman 1974
Yellow pine	75	0.67	Chapman 1974
Cork	68	0.45	Chapman 1974

Other methods are available and generally are for the same temperature range.

As with thermal conductivity, no references were readily available for heat capacity of biomass materials for the temperature range of thermal processing conditions needed for pyrolysis or gasification; new data are needed for applicable temperature ranges.

3.4.3 Density

The density of the material is important in considering energy contents of fuels on a volumetric basis, such as for transporting, solids handling, and sizing reaction vessels. There are three ways of reporting solid material density: bulk density, apparent particle density, and skeletal density. These density values differ in the way in which the material volume is calculated. The bulk density volume basis includes the actual volume of the solid, the pore volume, and the void volume between solid particles. Apparent particle density includes solid volume and pore volume. Skeletal density, or true density, includes only solid volume. The three values are related as follows:

$$\rho_a = \rho_s (1 \; \epsilon_p) \qquad (3\text{-}30)$$

$$\rho_b = \rho_a (1 - \epsilon_b), \qquad (3\text{-}31)$$

where

ρ_s = skeletal density, weight/volume
ρ_a = apparent density, weight/volume
ρ_b = bulk density, weight/volume

$$\epsilon_p = \text{particle porosity} = \frac{\text{volume of pores}}{\text{volume of pores and volume of solid}}$$

$$\epsilon_b = \text{bed porosity} = \frac{\text{volume of external voids}}{\text{volume of external voids and volume of particles}}$$

Densification of biomass is accomplished by reducing the particle porosity ϵ_p.

The density of biomass depends on the nature of the material, its moisture content, and degree of densification. Raw, oven-dry biomass (with 7% to 8% moisture) has an apparent density of about 40 lb/ft^3 (hardwoods) and 28 lb/ft^3 (softwoods). The density of woods with high moisture contents can be as high as 60 lb/ft^3. Densification produces particles with apparent bone dry densities of 55 lb/ft^3 to 75 lb/ft^3. The skeletal density of oven dry biomass has been reported to be 91 lb/ft^3 (Siau 1971).

3.4.3.1 Effect of Moisture Content on Density

The apparent density of wood and biomass depends on the moisture content. The dry and wet biomass apparent densities are related as follows from the moisture content obtained from the proximate analysis of the raw feedstock:

$$\rho_a(D) = (1 - M)\ \rho_a(R), \tag{3-32}$$

where

$\rho_a(D)$ = apparent density of dry biomass,
$\rho_a(R)$ = apparent density of raw biomass, and
M = proximate moisture.

For a typical raw biomass with 50% moisture and apparent dry density of 30 lb/ft^3, the raw biomass sample has a density of 60 lb/ft^3.

3.4.3.2 Densification

Densification by compaction reduces the internal voidage of the biomass material and reshapes the particles so that the bulk density is increased. The bulk density of green wood chips is typically 20 lb/ft^3, while the apparent density is on the order of 60 lb/ft^3. The typical external void fraction ϵ_b for chips is therefore about 0.67. The high voidage is due to the shape of the particles. Reshaping the particles to cylinders typically reduces the void fraction ϵ_b to about 0.5 and thus raises the bulk density to about 30 lb/ft^3. Thus the weight per unit volume is increased 50% by reshaping, and more material can be transported in the same carrier volume.

Densification of biomass by decreasing the particle porosity further improves handling. For raw, dry biomass of apparent density of 30 lb/ft^3, the particle porosity, ϵ_p, is typically 0.67 assuming 91 lb/ft^3 for the skeletal density. For densified samples, with reported apparent bone dry densities of 55 lb/ft^3 to 75 lb/ft^3, the particle porosity has decreased to 0.4 to 0.18. Thus in densification a large fraction of the internal voidage is removed.

Representative values of density are shown in Table 3-20 for uncompacted materials. As with thermal conductivity, the state of the material (and thus the type of density reported) is not specified for many solids.

3.4.4 Diffusion Coefficients in Biomass Materials

No data are readily available in the literature on gas diffusion coefficients in either natural or pelleted biomass materials or in their pyrolysis chars.

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SERI

Chapter 4

Beneficiation of Biomass for Gasification and Combustion

R. Bain
Colorado School of Mines

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CHAPTER 4

BENEFICIATION OF BIOMASS FOR GASIFICATION AND COMBUSTION

This section presents a relatively brief discussion of various methods of biomass beneficiation, with emphasis on methods that improve the properties of biomass materials with respect to suitability as gasification or combustion feedstocks. Beneficiation is very broad in scope, and this discussion is not meant as a comprehensive survey of the status of all beneficiation processing methods. (The use of a particular process as an example of a type of beneficiation process does not constitute an endorsement of that process.) Before discussing types of processes for biomass beneficiation, a brief discussion of basic definitions pertinent to beneficiation is required.

Beneficiation is defined as the treatment of some parent material, in this case biomass, so as to improve the physical and/or chemical properties of that material. Emphasis here is on improvement of gasification and combustion properties.

The major types of beneficiation processes to be discussed are drying, comminution, densification, physical separation, and chemical modification. In drying, physically bound water is driven off (the removal of chemically bound water is not included). By comminution, the particle size of a parent material is reduced to a desired range by shredding, cutting, grinding, or pulverization. In densification, the apparent particle density and the bulk density of a material are increased so as to lower transportation costs or processing equipment size by reducing the volume of material to be handled.

Physical separation involves the segregation of various components of a parent material into discrete subfractions. The purpose of this separation is varied; in some cases the separation may improve gasification or combustion properties, while in other cases the separation may be justified on economic grounds.

Chemical modification involves changing the chemical structure of the parent material to make the material more amenable to further processing. In many cases, the waste material or byproducts from a conversion process may also be considered to be a chemically modified biomass; for example, the furfural waste materials from a process producing furfural from corn silage could be considered an indirect beneficiation processing product (Lipinsky et al. 1977).

This section is divided into two subsections based upon two major types of biomass materials: wood and wood products (forestry biomass); and municipal solid wastes (MSW). In each section the advantages and disadvantages of various processes are discussed and available economic data are included. Agricultural biomass beneficiation has not been included due to lack of readily available data.

4.1 WOOD AND WOOD PRODUCTS

In this section various methods for beneficiation of wood and associated wood products are discussed. Emphasis is placed on processes such as comminution, drying, and densification of forestry biomass materials. Beneficiation processes for wood products aim to produce from the parent biomass a material that is a better quality feedstock for gasification or combustion, that has a higher volume energy density or higher specific surface area, and that has a higher gross heating value; if comminution adds heat and concurrently dries, all these goals have the same purpose—to make the use of wood and wood products economically viable.

4.1.1 Comminution

Size reduction processes are traditionally divided into four major classifications:

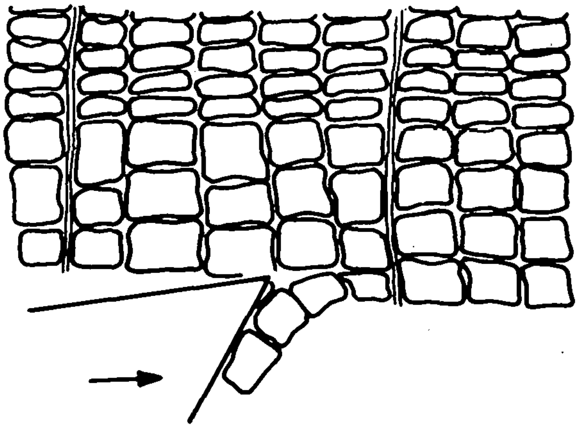
- compression—used for coarse reduction of solids;
- impaction—used for reduction to a broad range of particle sizes;
- cutting—used to produce solids of a definite size and shape, with few or no fines; and
- attrition—used to produce fine solids from nonabrasive materials.

The basic laws of comminution are given in many textbooks (McCabe and Smith 1967) and are used to estimate the energy requirements for crushing and the energy efficiency of size reduction. These laws are Kick's Law, which reflects the energy absorbed by a solid to the energy produced by crushing, and Rittinger's Law, which predicts that the work required for crushing is proportional to the change in surface area of the solid. These crushing laws were developed for the crushing or grinding of hard, friable solids such as coal, bauxite, and shale. The comminution of wood and wood products involves a process that Dornfield et al. (1978) call fiberization. There are basic differences between the grinding of wood and other biomass materials, and the grinding of hard materials that are caused by the fibrous, anisotropic, and compressive properties of wood. Also affecting comminution are the moisture content, the freshness (how long since harvesting has occurred), and type of wood (springwood, summerwood, etc.).

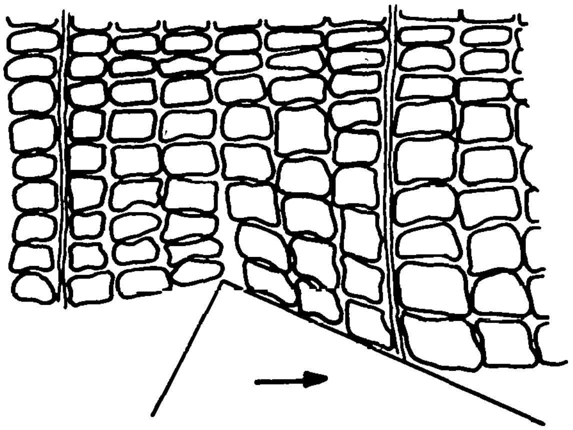
The comminution processes of interest for woods are mainly compression and cutting, although impaction and attrition are undoubtedly important in high-speed cutting operations. A representation of the two processes of interest was given by Dornfield (1978) and is shown as Fig. 4-1. It illustrates qualitatively the physical mechanisms taking place during wood size reduction.

Because little theoretical information has been published to predict energy requirements and power efficiencies in wood size reduction, the remaining discussion concerns specific types of equipment. The comminution equipment used is mainly cutting grinders. Systems used for reducing wood wastes are generally designed for field operation. The advantage of performing the size reduction in the field is in lowering transportation costs by increasing the wood bulk density and thereby the volume energy density. Cost data were compiled for ERDA by the MITRE Corporation (Bliss and Black 1977) for selected commercial comminution equipment; these data are shown in Table 4-1. The reported costs, fixed plus operating, ranged from $4.40 to $6.60 per dry ton equivalent. Qualitative discussions of various commercial systems are given below to indicate the types of equipment used in wood and wood waste size reduction.

The first system is the Morbark "Total Chipharvester" (Morbark Industries Product Bulletin), a portable, trailer-mounted harvesting machine designed to produce 5/8-in. to 1-in. chips from cut hardwood trees up to 22-in. diameter. The system also incorporates a separator to remove 90% of the dirt or sand and 50% of bark and foliage from the



Fiber Cutting by Sharp Abrasive Grits



Compression-Relaxation of Fiber by Conditioned Grits

Figure 4-1. Comminution Mechanisms

Table 4-1. EQUIPMENT ADAPTABLE TO COLLECTING AND/OR REDUCING FOREST RESIDUES[a]

Equipment	Slope Limitation[b] (%)	Size Diameter (in.)	Limitation Length (ft)	Cost per DTE[c] ($)	Support Equipment Needed[d]	Manufacturer
Morbark Chipharvester	limit of skidder	22	none	6.60	skidders and chain saws	Morbark Ind., Inc. Winn, Mich.
Precision Tree Harvester	limit of skidder	22	none	6.60	skidders and chain saws	Precision Chipper Corporation Birmingham, Ala.
Nicholson Ecolo Chipper	limit of skidder	24	none		skidders and chain saws	Nicholson Mfg. Co. Seattle, Wash.
Tree Eater	20	10	none	5.50 (11 DTE/h)	none	Tree Eater Corp. Gurdon, Ark.
Wagner-Bartlett Stump Splitter-Remover	limit of loader	96	none	3.50/stump	mounted on loader	Wagner Mfg. Co. Portland, Ore.
National Hydro-Ax	30	6	none	4.40 (11 DTE/h)	none	National Hydro-Ax Incorporated Owatoma, Minn.
Kershaw Klear Way	25	6	none	4.40 (11 DTE/h)	none	Kershaw Mfg. Co., Incorporated Montgomery, Ala.

[a] From Bliss and Black 1977.
[b] Based on working performance on firm soils.
[c] Includes all known costs; fixed and maintenance, move in and out, and necessary personnel.
[d] Does not include equipment needed for accumulation of reduced residues.

product chips. The chipped bark and foliage can also be recovered for fuel. The maximum throughput of the system is one ton per minute. The system uses knives mounted on a 75-in. diameter high speed disc for performing the actual chipping. No power consumption data per ton processed have been published.

The Mobile Harvestor, manufactured by Nicholson Manufacturing Company (Nicholson Mfg. Co. Product Bulletin) both fells trees up to 12 in. diameter and chips trees up to 19 in. diameter. The chipper is a three-knife, 48-in. diameter by 48-in., 550 rpm disc, and the nominal system capacity is 25 green tons/h. Again, no power consumption data were available.

Williams Patent Crusher and Pulverizer Company (Williams Product Bulletin) manufactures the "Hot Dog" shredder system that combines drying and shredding operations into one unit. The system can process 30 tons/h of wood or wood products. The shredding mill uses rotating hammers at high temperature. No information was given concerning power consumption.

Montgomery Hogs (Montgomery 1974) use a punch-and-die cutting action with fixed teeth rotating through fixed anvil slots. The units are designed to give minus 3/4-in. particles. Unit capacities vary from 7.5 tons/h to 100 tons/h. Reported horsepower requirements range from 100 to 500 hp. The units can be mounted as fixed or portable installations.

4.1.2 Drying

The general advantages of drying wood are well known. Removal of water reduces the weight of material that must be transported or handled in a processing plant, thereby lowering operating costs. In addition, the removal of water generally produces a feedstock of better quality for combustion and gasification processes. Table 4-2 shows the combustion efficiency for burning wood as a function of moisture content. Since most fresh woods contain considerable water (40 to 60 wt %) appreciable energy can be saved in later processing. This savings can be significant in processing energy requirements if waste heat from another processing step, such as the combustion step, is used to supply the thermal energy for drying. (An exception may be steam gasification in which water is one of the process feed materials.) The disadvantages of drying are also well known: in any processing step, equipment and operating costs must be considered in evaluating the usefulness of the process.

In general, drying of a biomass material means removing water from the solid to reduce the moisture content to an acceptably low value. In wood and wood products this moisture content reduction is usually accomplished by thermal drying, as opposed to mechanical drying done in centrifuges or presses. The major types of drying equipment used for particulate solids drying are screen conveyor dryers, screw-conveyor dryers, rotary dryers, and flash dryers, all of which are standard processing equipment. Detailed discussions of these dryers can be found in Perry's (1963) and McCabe and Smith (1967). Although the theoretical analysis of drying processes can become complicated, it can be divided into two parts to simplify the analysis: a steady-state drying process and a transient drying process. An example of rate drying curves is given in Fig. 4-2. The constant rate line is the steady-state portion of the drying process.

Both steady-state and transient drying operations can be modeled by the appropriate heat and mass transfer equations. Detailed derivations of drying models can be found in references such as Perry's (1963), McCabe and Smith (1967), and Treybal (1968).

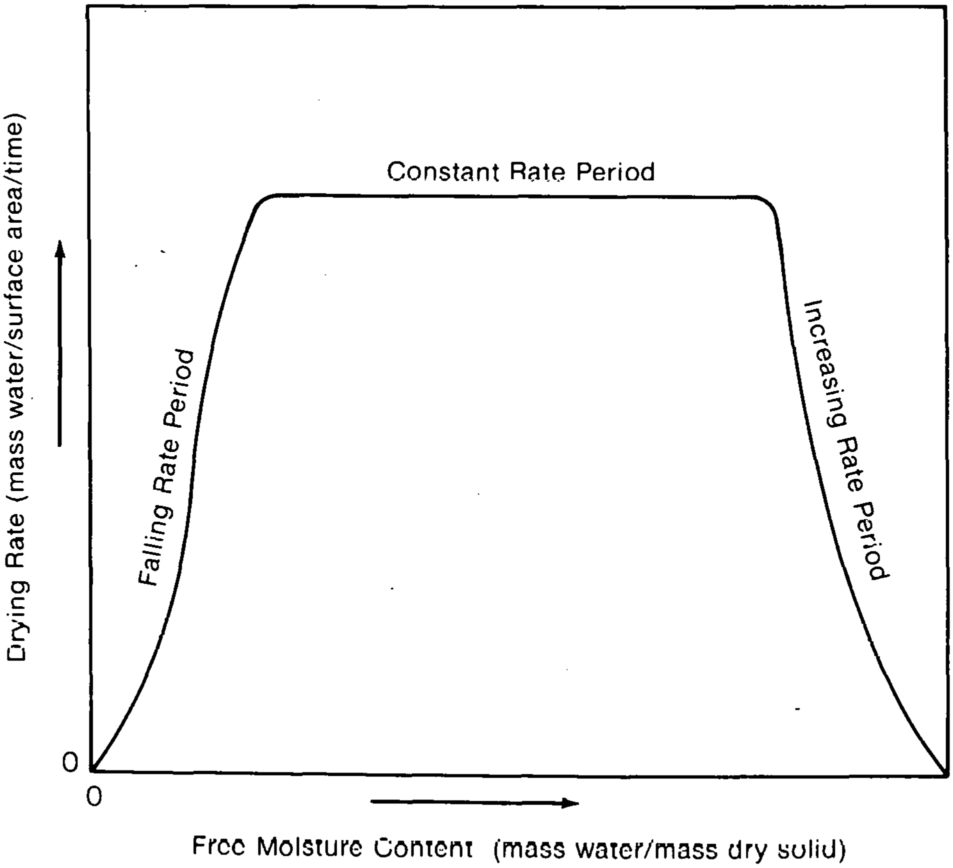


Figure 4-2. Typical Drying Rate Curve

Reed and Bryant (1978) reported that although it theoretically requires about 1000 Btu to evaporate 1 lb of water, in drying wood it actually requires 1500 Btu to 2500 Btu to evaporate 1 lb of water, the precise value being dependent upon dryer efficiency.

Table 4-2. THE EFFECT OF MOISTURE CONTENT ON HEAT RECOVERY AND COMBUSTION EFFICIENCY[a]

Moisture Content (%)	Recoverable Heat[b] (Btu/lb)	Combustion Efficiency (%)
0.00	7,097	82.5
4.76	7,036	81.8
9.09	6,975	81.1
13.04	6,912	80.4
16.67	6,853	79.7
20.00	6,791	78.9
23.08	6,730	78.3
28.57	6,604	76.8
33.33	6,482	75.4
42.86	6,178	71.8
50.00	5,868	68.2
60.00	5,252	61.1
66.67	4,639	53.9
71.43	4,019	46.7

[a] From Bliss and Black 1977.

[b] Theoretical values based on a maximum heating value of 8,600 Btu/lb, an initial wood temperature of 62 F, a flue gas temperature of 450 F, an initial air temperature of 62 F and 50% excess air.

Bliss and Black (1977) have presented information concerning the residual fuel value of hogged fuel as a function of moisture content (see Fig. 4-3). Miller (1977) has presented figures for energy requirements for conventional kiln drying in which he reports that it takes 96.2 MBtu to dry 25.4 thousand board feet of 2 in. southern pine from 50% moisture to 10% moisture. This reduces to 2.67 MBtu/ton of dry wood processed, or approximately 1500 Btu/lb of water evaporated.

Gulf (1978) reports that a barrel of distillate fuel oil contains 5.82 MBtu of energy. This gives an estimated drying cost of $5.50/ton of wood if oil is sold at $12/barrel. The residual fuel value would increase by $12/ton of dried wood. These costs indicate possible economic feasibility for the drying process, although transportation, labor, and capital cost also would be needed to determine realistic feasibility estimates.

4.1.3 Densification

Reed and Bryant (1978) recently presented a comprehensive state-of-the-art evaluation of processes that produce densified biomass fuels (DBF). A review of their findings is presented here.

Five methods of densification for biomass materials are in commercial operation at the

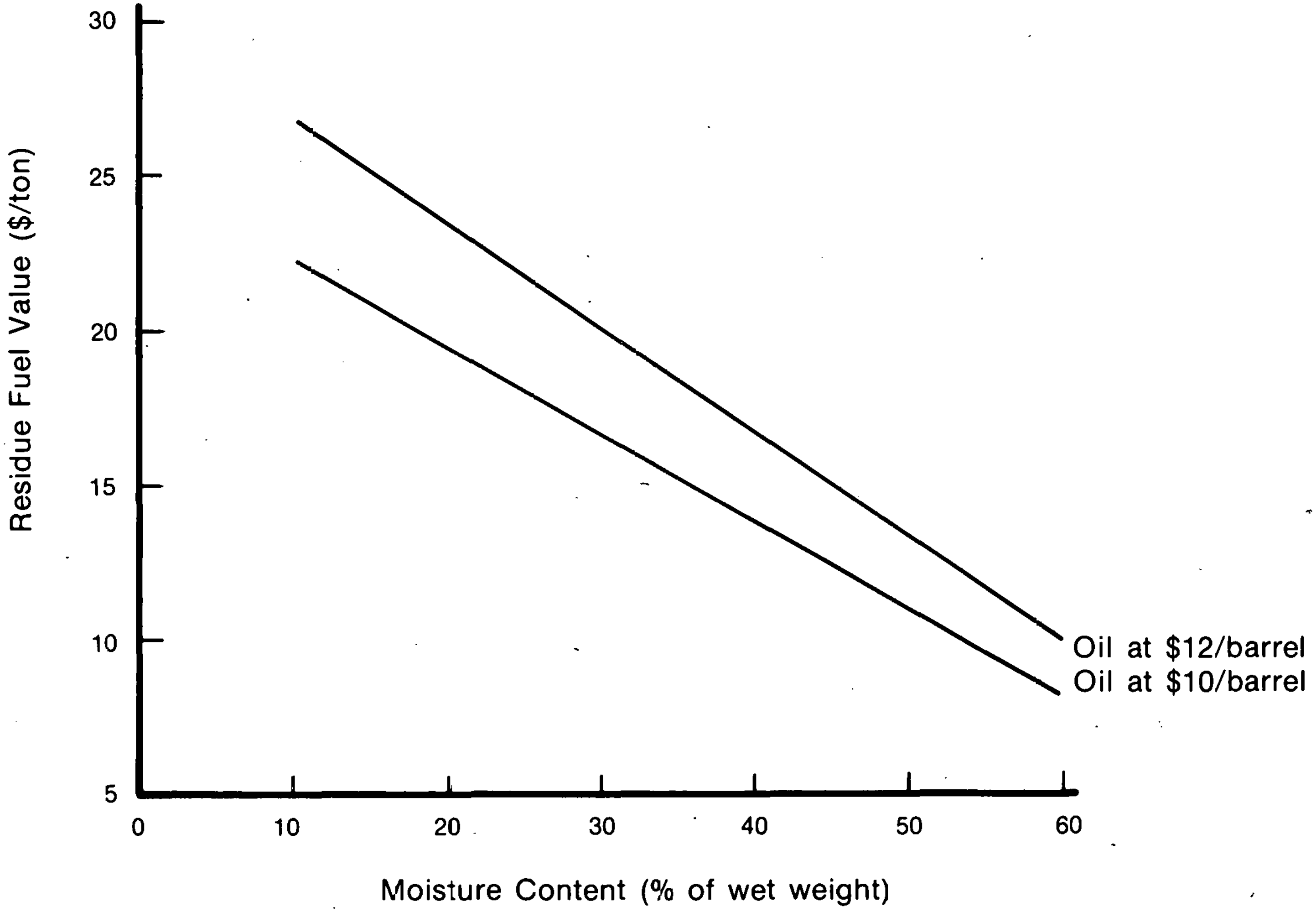


Figure 4-3. Relationship of Hog Fuel Value to Moisture Content Under Two Oil Price Assumptions

present time, with other processes in the development stage. The five processes are:

- pelleting—a die perforated with 1/4-in. to 1/2-in. holes rotates against pressure rollers, forcing feedstock through the holes at high pressure and densifying the feedstock;
- cubing—a modified form of pelleting producing a large size product (1-in. to 2-in.);
- briquetting—feed is compacted between rollers containing cavities; product looks like charcoal briquettes;
- extrusion—a screw forces a feedstock under high pressure into a die, forming 1-in. to 4-in. diameter cylinders; and
- rolling-compressing—employs a rotating shaft to wrap fibrous material and produce high density rolls of 5-in. to 7-in. diameter.

The densification process takes advantage of the physical properties of two of the major components of biomass materials, cellulose and lignin. Cellulose is stable to 250 C, while lignin begins to soften at temperatures as low as 100 C. Densification is carried out at temperatures that ensure that the cellulosic material remains stable but that soften the lignin fraction, making it act as a "self-bonding" agent that gives the final DBF its mechanical strength. Water content must be controlled in the range from 10% to 25% to minimize pressure requirements for densification.

Densification proceeds by heating a biomass material (of the proper moisture content) to 50 C to 100 C to soften the lignin, followed by mechanical densification that increases the biomass density to a maximum of 1.5 g/cm^3 and heats the material another 20 C to 50 C. The additional temperature increase liquefies waxes that act as additional binders when the product is cooled.

A list of manufacturers of densification equipment is given in Table 4-3. A detailed discussion of existing biomass densification plants was given by Reed and Bryant (1978) and is reproduced here, except for the ECO-FUEL II process, which is discussed in Section 4.2.4. Table 4-4 presents a list of DBF process developers.

A typical biomass compaction plant is shown in Fig. 4-4. The first step in the process is separation—stones and sand must be removed from forest or agricultural wastes and inorganics from municipal waste. The remaining biomass portion is then pulverized with hammer mills or ball mills to a size somewhat smaller than the minimum dimension of the pellets to be formed. This fraction is then dried in a rotary kiln or convection dryer. Finally, dried biomass is fed into the compactor which delivers pellets for storage or use.

Table 4-3. **MANUFACTURERS OF DENSIFICATION EQUIPMENT FOR FEED AND FUEL**[a]

Company	Type of Equipment
Agnew Environmental Products, Grants Pass, Ore.	Extruder
Agropack, Medina, Wash.	Roller-Compressor
Bonnet Co., Kent, Ohio	Wood and Wax Extruder
Briquettor Systems, Inc., Reedsport, Ore.	Extruder
California Pellet Mill Co., San Francisco, Calif.	Extruder and Pellet Mills, Cuber
Gear Cube Co., Moses Lake, Wash.	Cuber
Hawker Siddeley Canada Ltd., Vancouver, B.C.	Extruder
John Deere, Moline, Ill.	Cuber
Papakube Corp., San Diego, Calif.	Extruder Cuber
Reydco Machinery Co., Redding, Calif.	Extruder
Sprout Waldron, Muney, Pa.	Pellet Mills
Taiga Industries, Inc., San Diego, Calif.	Extruder

[a] From Currier 1977; Cohen and Parrish 1976. There may be other manufacturers unknown to the authors; this list in no way constitutes an endorsement by SERI or the authors.

One of the more completely developed processes to date is R. Gunnerman's Woodex process (Gunnerman 1977), employing a hammer mill, dryer, and pellet mill. A 120-ton/day plant has been operating since 1976 in Brownsville, Ore. Gunnerman's company, Bio-Solar, recently installed a second, 300-ton/day plant in Brownsville; its dryer operates completely on pellets. Bio-Solar sells its products to customers in Oregon and Washington, where a major purchaser is the Western State Hospital near Tacoma. Two other Woodex plants are operating at the Sierra Power Corporation in Fresno, Calif., and the E. Hines Company in Burns, Ore. Three plants are under construction, and several business groups have acquired Woodex licenses.

A continuous flow extrusion technique is used by Taiga Industries* (Bremer 1975). Pulverized biomass with a moisture content of 10% is compressed by a screw, then fed into a prepressure chamber, where it is forced against a rotating spiral die-head with a cutting edge as shown in Figure 4-5. The frictional heat of the die face converts the biomass into a semifluid; the die-heat shears off a spiral slice of compressed biomass, forcing it into the die chamber. The densified product is expelled and cut to a specified length by a rotating flail. Taiga produces either a 10-cm by 30-cm log or 2.5-cm briquettes with a specific gravity of 1.2 to 1.45. The process expends 50 hph to 90 hph to produce 1 ton/h of DBF.

Another process, originally developed by Edward Koppelman to upgrade lignite, has been modified for biomass feedstocks and is now pending patent issuance (Koppelman 1977). SRI International, in cooperation with Koppelman, has constructed a pilot plant and tested various feedstocks. Details of the process are considered proprietary information but general features are: a water slurry feed system; a pyrolysis reactor; a water

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*Taiga publishes a Mod-Log sales brochure that describes the modified Bremer process, plant operations, cost, etc.

Table 4-4. DBF PRODUCERS AND DEVELOPERS: PROCESS STATUS[a]

	Process Status	
Company	Commercial	Under Development
Bio-Solar Corp., Eugene, Ore. (Woodex)	X	
Combustion Engineering Corp.	X	
Guaranty Performance, Independence, Kans.	X	
Lehigh Forming Co., Easton, Pa.	X	
National Center for Resource Recovery (NCRR), Washington, D.C.		X
Papakube Corp., San Diego, Calif.	X	
SRI International		X
Taiga Industries, San Diego, Calif.	X	
Teledyne National, Cockeysville, Md.	X	
University of California Richmond Field Station		X
Vista Chemical and Fiber, Los Gatos, Calif.		X

[a] This list does not constitute an endorsement of particular processes by SERI or the authors. Furthermore, it is not exhaustive listing of processes.

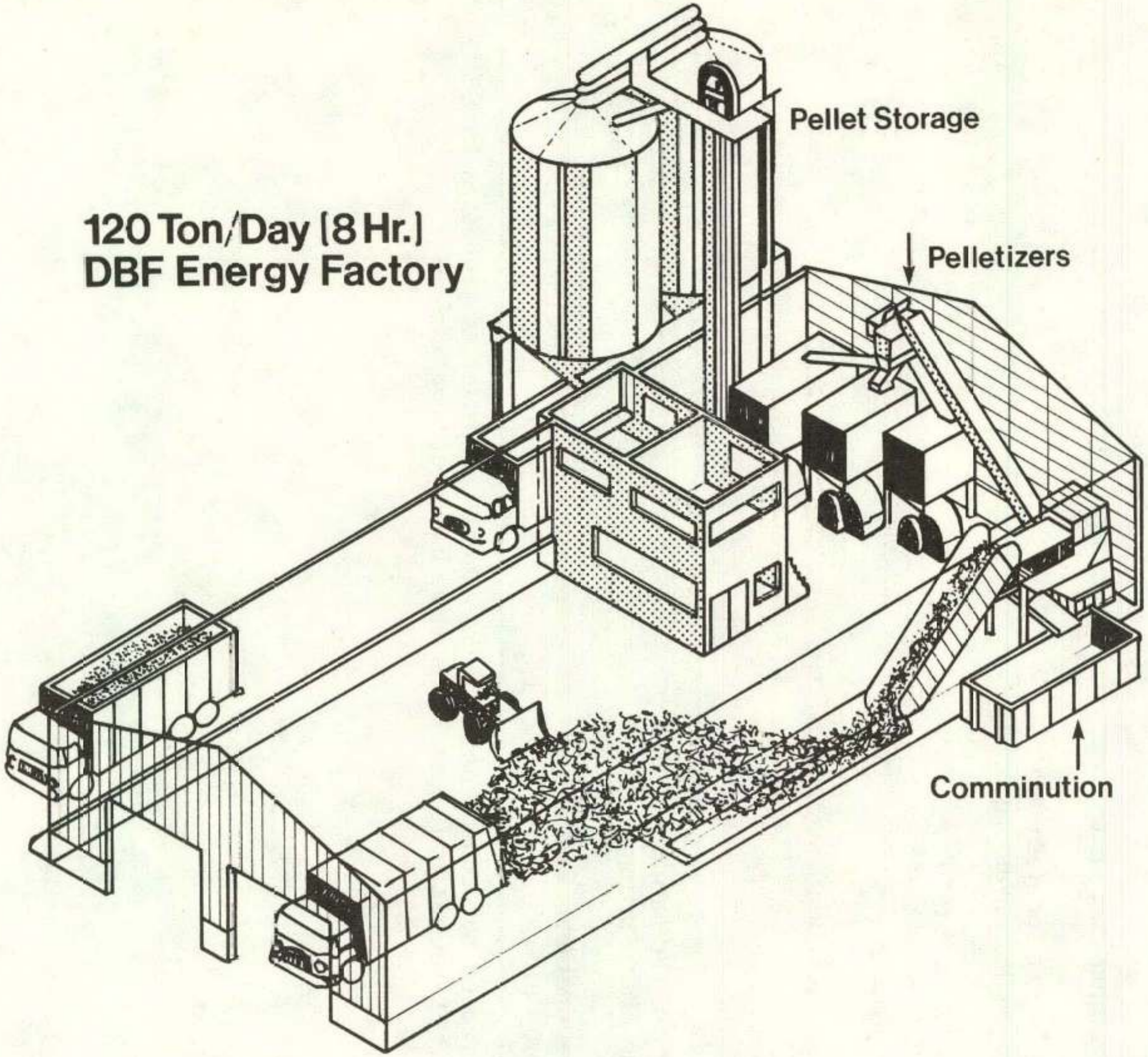

Figure 4-4. Typical Biomass Compaction Plant (PapaKube Corp.)

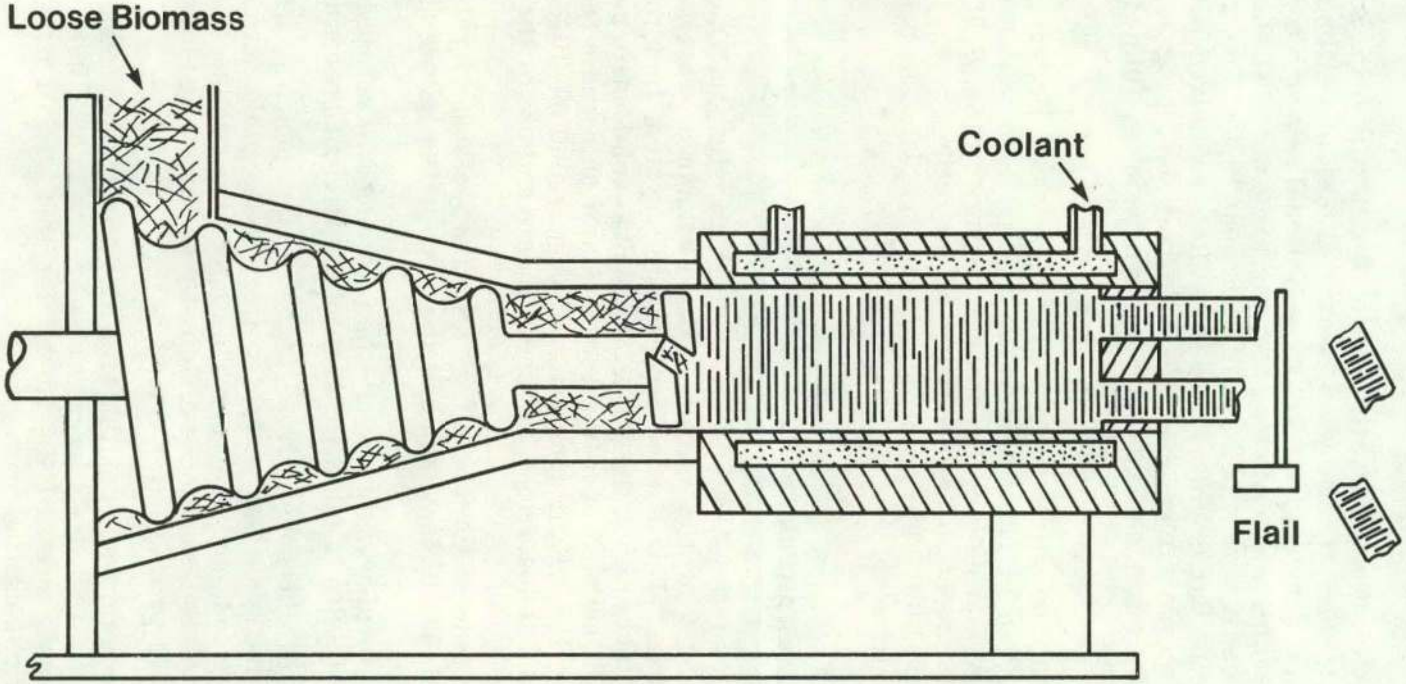

Figure 4-5. Taiga Extrusion Process

recovery system; and an output stream of a carbonaceous solid, a combustible gas, and a small amount of aromatic liquid. Product yields and composition depend on the feedstock and process variables (temperature, pressure, water content, and reaction time). SRI claims a process energy efficiency of 85% to 90%. The projected cost for an 1,800-ton/day plant is $10 to $15 million.

Solid waste densification is an attractive option because it helps solve two urban problems simultaneously: energy supply and waste disposal. Baltimore County and the Maryland Environmental Service, with Teledyne National as prime contractor, are operating a plant that separates combustibles from the solid waste stream, shreds that fraction, and then compacts it with a pellet mill (Herrman 1978). Ten tons per day are sold to a paper mill in Spring Grove, Pa., where the pellets are mixed with bark, ground in a hog mill and blown into a boiler. A full-scale burn test program is now underway. Contracts with a utility and cement company are pending, following confirmation of performance.

Typical energy consumption values for pelleting of sawdust, fir bark, aspen, and municipal solid waste are given in Table 4-5, which shows 1% to 3% consumption of energy based upon the energy content of the product. Overall process efficiency for a 300-ton/day bark pelleting operation incorporating pulverization, drying, and pelleting steps has been estimated at 92.8%. The reported cost of this plant has been estimated to add $0.80/MBtu to the feedstock cost.

4.2 MUNICIPAL SOLID WASTES

The major purpose of beneficiation of municipal solid wastes (MSW) has been to solve the disposal problems created by the extremely large volume of wastes generated by large metropolitan populations. This is done by creating a system that recycles the valuable materials and energy contained in the waste. Municipal solid waste processing operations can be divided into two major areas: the separation of an organic feedstock suitable for further processing and the actual conversion of this organic feedstock. This discussion focuses on the preparation operations, not the ultimate end use of the organic product.

Figure 4-6 presents a general flowsheet for various processing operations. In general, all MSW preparation plants use at least some of the steps in the following general outline.

- Preliminary (primary) shredding—the incoming raw refuse is reduced in size to 1 or 2-in. particles to allow further, more efficient processing.
- Separation of inorganics from organics—inorganic materials such as iron, aluminum, and glass are separated from the organic materials such as paper, cardboard, wood, and leaves. This operation produces an organic fraction which can be processed more efficiently and an inorganic fraction that is more amenable to byproduct recovery.
- Drying of organic fraction—this step also produces a product more amenable to processing and that has a larger gross heating value. In an integrated resource recovery plant, much of the energy for this operation is waste heat from a pyrolysis or combustion process.
- Secondary shredding—the particle size of the organic fraction is further reduced. This step is necessary for downstream processing in systems incorporating entrained flow pyrolysis or gasification operations.

Table 4-5. ENERGY REQUIRED FOR PELLETING (300-HP PELLET MILL)[a]

Feedstock	Fraction Electrical Production Rate metric tonnes/h (tons/h)	of Product Energy Used kWh/metric tonne (kWh/ton)	Energy Consumed (%)
Sawdust	6.1	36.8	
	(6.7)	(33.5)	2.3
Aspen wood	8.2	27.2	
	(9.0)	(24.8)	1.7
Douglas fir bark	4.5	49.2	
	(5.0)	(44.7)	3.1
Municipal solid waste	9.1	16.4	
(MSW)	(10.0)	(14.9)	1.0

[a] From Reed and Bryant 1978.

NOTES:

(1) 11.6 kJ (11,000 Btu) thermal/kWh.

(2) The pelleting of MSW is volume limited in a 300-hp mill due to low density of feedstock—actual horsepower usage is 200 hp.

(3) The figures in this table are only representative; values are highly dependent on feed size, moisture content, etc.

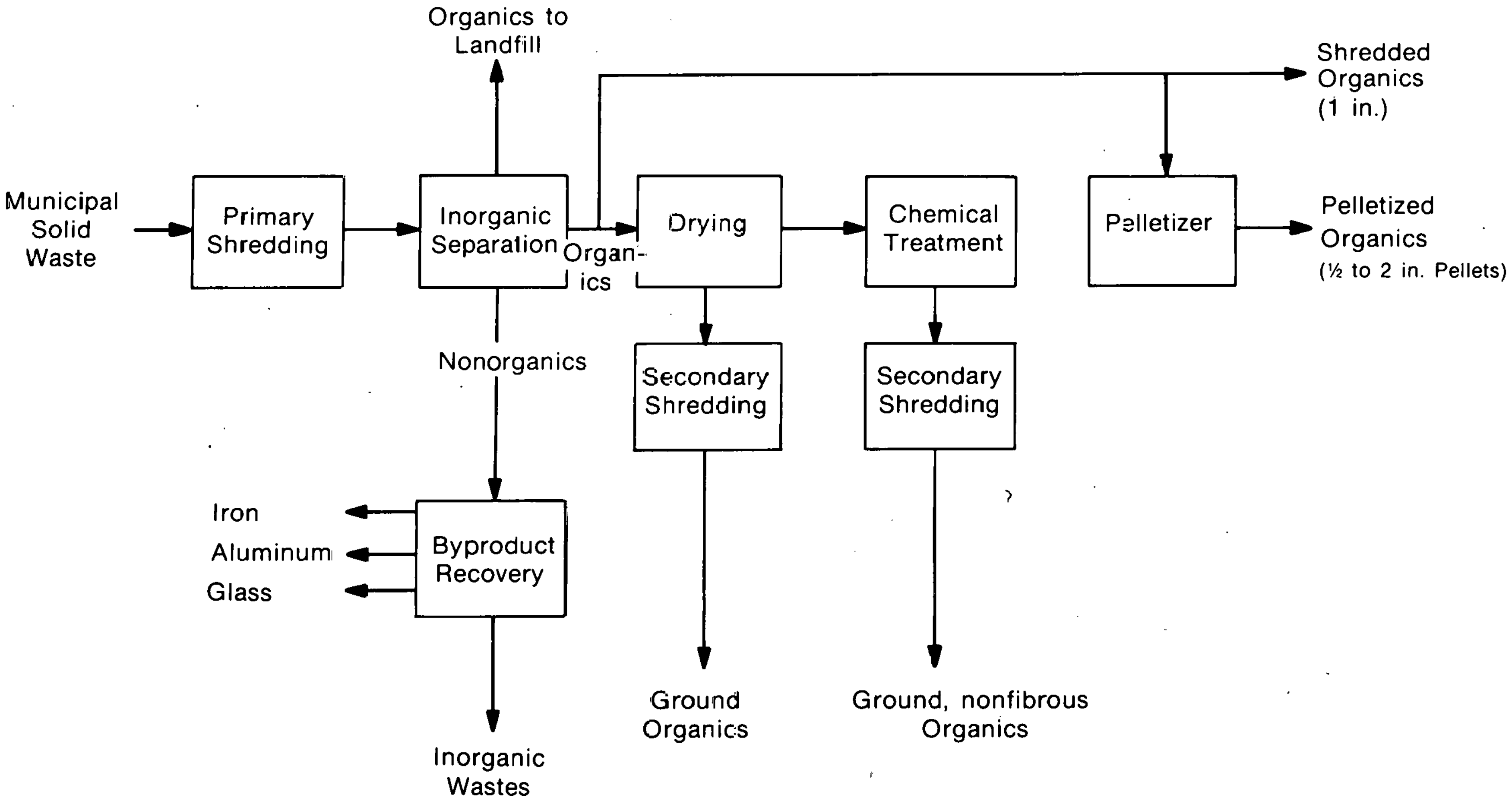

Figure 4-6. Processing of Municipal Solid Waste

- Densification—in some processes the organic fraction is densified by pelletization. This step makes a fuel with a higher volume energy density to both reduce the volume of material to be handled and to make the fuel compatible with existing materials handling facilities in power plants using coal as fuel.
- Chemical treatment—this process normally involves a chemical treatment to break down fibers chemically and therefore change shredding costs and the nature of the final product.

4.2.1 Primary Shredding

The general criteria for primary refuse grinders or shredders are that (1) the shredding should involve little or no addition of water to the feed, to minimize energy required for later drying operations; (2) material of the desired size should be removed as quickly as possible from the shredder to minimize production of fine inorganic material that would increase the difficulty of metals and glass recovery and would increase the ash content of the organic fraction by increasing the difficulty of ash-organic separation; and (3) the shredding process should be performed with little or no pretreatment of the feed refuse.

There are many types of size reduction equipment. Table 4-6 lists types of equipment (McCabe and Smith 1967) and their possible application in MSW processing.

Three general types of shredding equipment meet the criteria for raw refuse: hammer mills, vertical ring grinders, and flail mills. A hammer mill uses a high speed rotor on which are carried hammers of many different configurations (e.g., stirrups, bars, or fixed rings). The rotor runs in a housing containing grinding plates and the particle size of the product solid is governed by the clearance between the hammers and grinding plates. If a hammer mill is used for primary shredding, two or three stages may be required to obtain the necessary particle size range.

A vertical ring grinder consists of a large vertical rotor with peripheral grinding rings, usually gear-like, enclosed in a heavy casing. The feed material is ground mainly by attrition between the grinding rings and the protrusions on the casing. Each ring is mounted independently from the other rings, thus allowing shocks caused by particularly hard objects to be distributed over the entire machine. A flail mill operates on the same principle as a vertical ring grinder but instead of rings uses articulated arms which self relieve. Because of the strain-relieving properties of the latter two mills, the maintenance costs are normally lower than those of hammer mills.

Many companies have presented power consumption curves for primary grinding. Garrett Research and Development Company, Inc. (Garrett and Finney 1973) performed tests, the results of which are compared to data from Combustion Equipment Associates (Benningson and Rogers 1975) in Fig. 4-7. The differences in power requirements of the two systems result from the use of a chemical treatment step in the CEA process to produce "ECO-FUEL II." Therefore, the Garrett data are more applicable when only the energy consumption of shredding is to be estimated. To compare realistically the different power consumption curves, the overall cost (both economics and energy) of the two process schemes would need to be known. There is undoubtedly some tradeoff between shredding power consumption and chemical costs. A more detailed discussion of the chemical treatment step is given in Section 4.2.5.

Table 4-6. CURRENT SIZE-REDUCTION EQUIPMENT AND POTENTIAL APPLICATIONS TO MUNICIPAL SOLID WASTE[a]

Basic Types	Variations	Potential Applications to Municipal Solid Waste
Crushers	Impact	Direct application as a form of hammer mill
	Jaw, roll, and gyrating	As a primary or parallel operation on brittle or friable material
Cage disintegrators	Multicage or single cage	As a parallel operation on brittle or friable matorial
Shears	Multiblade or single blade	As a primary operation on wood or ductile materials
Shredders, cutters, and chippers	Pierce-and-tear type	Direct as hammer mill with meshing and shredding members, or parallel operation on paper and boxboard
	Cutting type	Parallel on yard waste, paper, boxboard, wood, or board plastics
Rasp mills and drum pulverizers		Direct on moistened municipal solid wastes, also as bulky item sorter for parallel line operations
Disk mills	Single or multiple disk	Parallel operation on certain municipal solid waste fractions for special recovery treatment
Wet pulpers	Single or multiple disk	Second operation on pulpable material
Hammer mills		Direct application or in tandem with other types

[a] From Weinstein and Toro 1976.

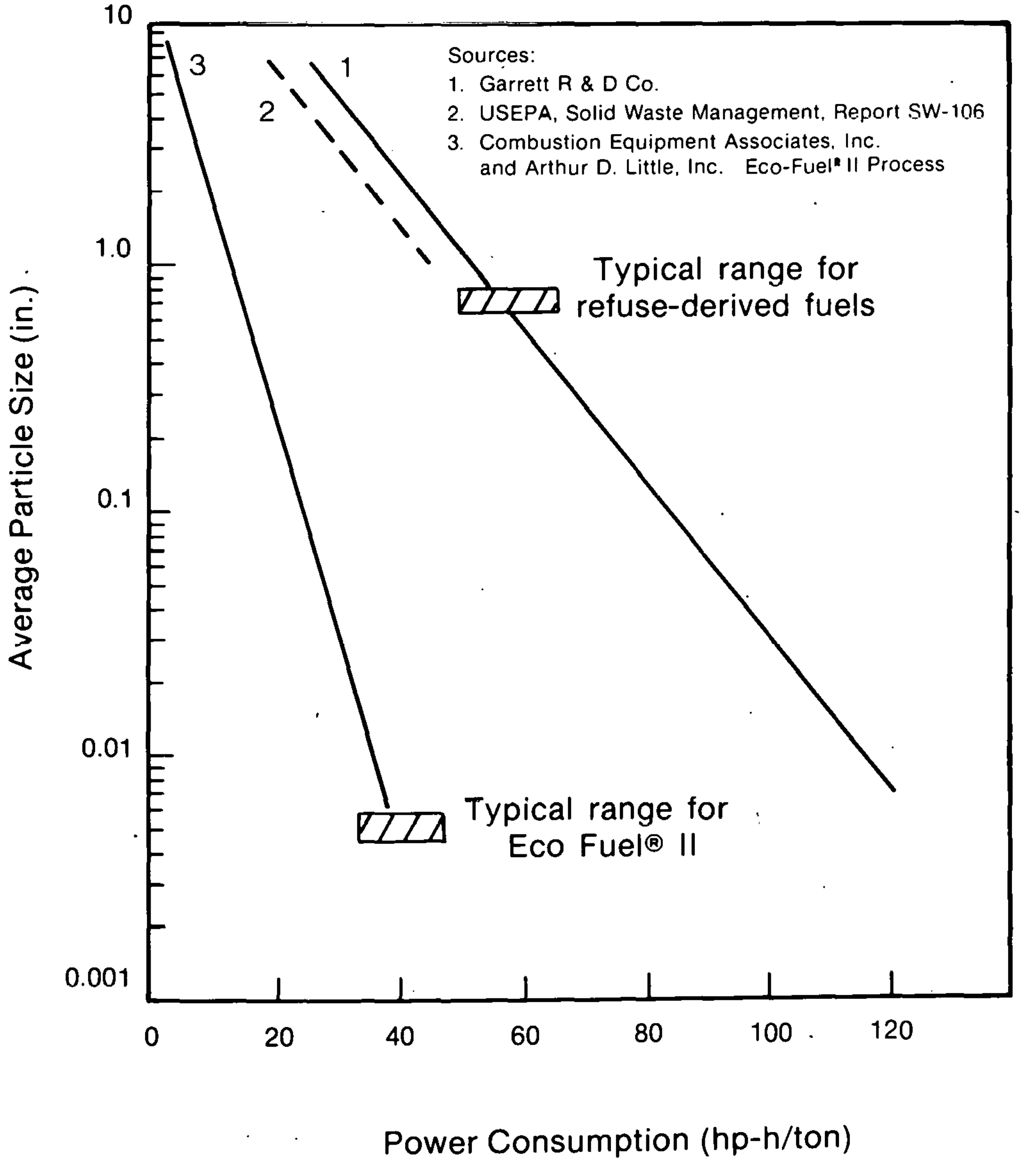

Figure 4-7. Average Particle Size Vs. Power Consumption for Size Reduction of MSW

4.2.2 Separating Inorganic Material From Organics

Depending upon the moisture content of the feed, a drying step may be required before the separation of inorganic from organic material. Among the more common methods of separation is the use of an air classifier. A large amount of research (Garrett and Finney 1973) has been performed in this area, and the concept has been incorporated into various resource recovery systems (Weinstein and Toro 1976, Section 4.0). Air classifiers may be zig-zag, straight-vertical, straight-horizontal, etc. All operate on the principle that the organics are low-density materials with large surface areas and that the inorganic materials are high-density with small surface areas. Classifiers are operated with the air flow rate maintained such that the superficial air velocity is larger than the terminal settling velocities of the organic particles but lower than the terminal settling velocities of the inorganic particles. Since there is overlap in settling velocities, the separation in an air classifier is not complete, and more than one classifier may be used, or the classification step may be followed by a screening step to give the desired degree of separation.

After the organic-inorganic separation has been accomplished the inorganic fraction may be further classified to recover iron, aluminum, and glass. Since this fraction does not contain a high proportion of the total biomass materials, no discussion is presented here. Detailed information on this topic can be found in many references (e.g., Garrett and Finney 1973; Weinstein and Toro 1976). A consideration that justifies the separation of these important byproducts is the fact that they can be sold to at least partially offset the cost of the beneficiation and conversion processes. Cheremisinoff and Morresi (1976) reported that these byproducts had a potential selling price of $3.70/ton of MSW in 1971. Garrett Research and Development (Chemical Week, 11 Dec. 1974) reported in 1971 that their resource recovery system cost $5.40/ton. By 1974 the processing cost had risen to $12.90/ton, but the revenues from byproducts and pyrolytic oil had risen to $10.36/ton. Therefore, the separation and recovery of byproducts is economically justified in a MSW plant.

4.2.3 Drying of Organic Fraction

The various types of drying processes were discussed in Section 4.1.2. The organic fraction of MSW normally has been ground and separated from the inorganic material, and its resulting density is such that the drying step is conducted in a rotary drier or an entrained flow-flash drier with direct solid-gas contact. The advantages of drying discussed for wood and wood products also apply to MSW. An example of downstream boiler efficiency (Kohlkepp 1974) with the organic fraction as a combustion boiler fuel (see Fig. 4-8) further reinforces the need for drying. No information is available showing the drying step costs versus downstream processing efficiency in resource recovery systems. These costs are normally lumped into total beneficiation (prep plant) costs.

4.2.4 Densification

Alter and Arnold (1978) reported on a pilot plant operation to produce a densified refuse-derived fuel. The organic material leaving the secondary shredding process was fed to a small pellet mill manufactured by California Pellet Mill Company. In the pellet mill a die rotated past stationary rollers which formed a nip, forcing the feed material into the die. The product from the pelletizer in the pilot plant run had the following average properties:

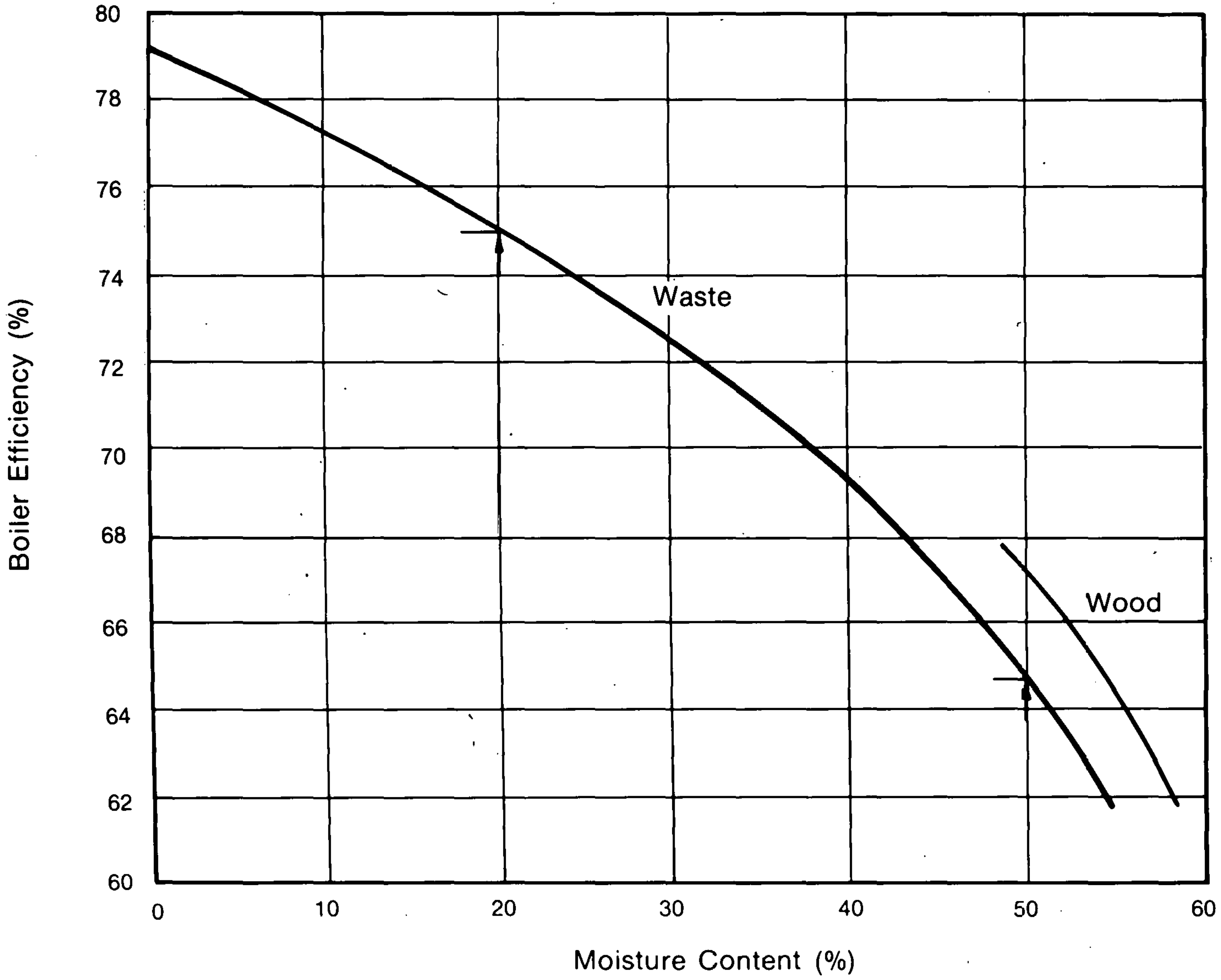

Figure 4-8. Boiler Efficiency Vs. Moisture Content

Diameter - 0.5 in.
Length - 0.71 in.
Pellet Density - 73 lb/ft^3
Bulk Density - 39 lb/ft^3
Moisture Content - 19 wt %
Ash Content - 26.5 wt %

Alter and Arnold (1978) also presented data for pelletizer power consumption as a function of pelletizing rate, for rates as high as 9 tons/h (see Fig. 4-9). Energy consumption ranged from 16 kWh/ton at rates of 2 tons/h to 4 kWh/ton at rates of 7 tons/h.

4.2.5 Chemical Modification

One chemical modification technique is discussed here, the "ECO-FUEL-II" process (Benningson and Rogers 1975) developed by Arthur D. Little, Inc. A production facility has been constructed to accomplish the primary shredding step, a ferrous metals separation step, a screening step, and a chemical treatment step.

In the chemical treatment step, a small amount of an inorganic acid, such as sulfuric acid (Combustion Equipment 1975) is added to the remaining refuse, mainly organics; the acid embrittles the cellulosic materials present, probably by rupturing the ether linkage structure of the cellulose molecules. The chemically treated material is then mixed with hot steel balls in a ball mill. This process both grinds and drys the organic materials at temperatures up to 400 F. The high temperature is said to enhance the embrittling action of the acid and therefore to lower the power requirements in the ball mill operation. The product of this process after residual inorganic separation is a nonfibrous dry solid with an average particle size of 0.006 in. The reported power requirements for grinding (see Figure 4-2) are much lower than for conventional shredding processes. The product has a high bulk density (30 lb/ft^3 to 35 lb/ft^3) in comparison to dried shredded fuels (3 lb/ft^3 to 5 lb/ft^3).

As a final comment on the discussion of beneficiation of municipal solid wastes, economic comparison among beneficiation processes are not presented here because capital and operating cost data for MSW plants generally have not been reported in the detail necessary to calculate the cost of the process steps. Schulz et al. (1976) compared all of the major resource recovery systems and compiled general costs for front-end plants (see Table 4-7). They show the cost of three of the beneficiation processing steps discussed here. Primary shredding costs $2.66/ton of MSW, air classification $1.73/ton of MSW, and secondary shredding $1.20/ton. Schulz et al. claim a $4.18 credit/ton of MSW for byproducts when sold. This means that the actual end usage of the organic fraction will determine process economics.

Physical/chemical modification, while generally not required for gasification, is the goal of several new processes for disruption of the lignocellulosic complex structure. The processes provide an altered form of biomass in which the lignin, hemicellulose, and cellulose fractions are more readily separated by chemical and enzymatic means.

The Iotech process (Iotech 1979) uses high pressure (200-600 psi) steam to soften the biomass and then decompresses the biomass supersonically through a nozzle. The combination of shear and heat modifies the biomass matrix in a controllable, reproducible manner that can be designed for a specific process, i.e., ethanol fermentation, fast pyrolysis, etc. A similar process is used for explosive decompression (at approximately 250-psi steam) of municipal waste (Burke 1979). This process is said to require 60 Btu/lb trash.

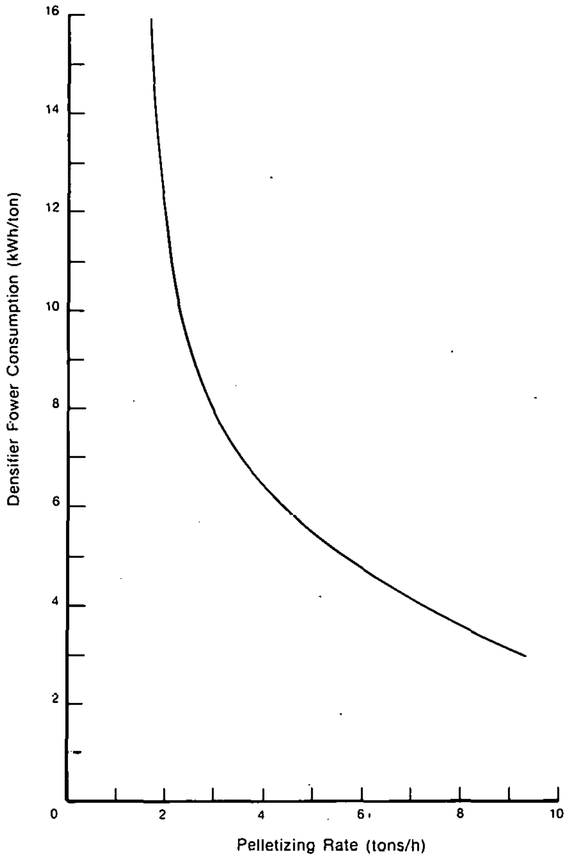

Figure 4-9. Densifier Power Consumption for NCPR Pelletizing Tests (Smoothed Data)

Table 4-7. MATERIALS RECOVERY: UNIT OPERATIONS COSTS[a]
(Basis: 1,000 ton/day Plant)

Unit Operations	Capital Cost ($/ton MSW)	Operating Cost ($/ton MSW)	Amortized Operating Cost ($/ton MSW)
Primary shredding (to -4 in.)	0.49	2.17	2.66
Air classification	0.31	1.42	1.73
Secondary shredding (to -1 in.)	0.16	1.04	1.20
Magnetic metals recovery	0.08	0.44	0.52
Rising current and heavy media separation	0.10	0.66	0.76
Roll crushing and electronic separation	180	0.06	0.53
Color sorting	425	0.14	0.56
Froth flotation	295	0.10	0.43
		Total	$8.39/ton MSW

[a]From Shulz et al. 1976.

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Chapter 5

Pyrolysis - The Thermal Behavior of Biomass Below 600 C

T. Milne
SERI

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CHAPTER 5

PYROLYSIS - THE THERMAL BEHAVIOR OF BIOMASS BELOW 600 C

5.1 INTRODUCTION

This chapter focuses on pyrolysis as a precursor to gasification under both anaerobic conditions (steam, H_2, self-generated gas) and aerobic conditions (air, O_2). Pyrolysis of carbonaceous materials has been defined as incomplete thermal degradation, resulting in char, condensable liquids or tars and gaseous products, generally in the absence of air (Soltes and Elder 1979). Gasification generally refers to the combination of pyrolysis followed by higher temperature reactions of the char, tars, and primary gases to yield mainly low molecular weight gaseous products. In fast pyrolysis the distinction between pyrolysis and gasification becomes blurred.

Extensive literature exists pertaining to low temperature, slow pyrolysis where the emphasis is on char (carbonization), liquids (wood distillation), and both char and liquid (destructive distillation). For example, Soltes and Elder (1979) have reviewed pyrolysis with the emphasis on obtaining organic chemicals from biomass. Much information also exists on the mild thermal degradation of wood, papers, etc., in the context of structural integrity, aging, and other factors (Stamm 1956).

Two broad approaches to gasification can be distinguished: (1) gasifiers in which relatively large particles are subjected to inherently slow heating rates and long residence times, yielding gaseous products that approach equilibrium, and (2) gasifiers in which rather finely divided material is heated rapidly (fast pyrolysis), and the products are quenched after short residence times, to preserve high concentrations of nonequilibrium pyrolysis products. The following review of past work is divided into these two broad categories, treating biomass and its major components according to the kinds of study most often used.

5.2 SLOW PYROLYSIS

With macroscopic pieces of carbonaceous solids, the heating rate is controlled by heat transfer throughout the usually poorly conducting material. Heating rates of the order 0.01 C/s to 2 C/s are likely. This range of heating rates corresponds to the capability of commercially available thermal analytical instrumentation such as DSC, TGA, and DTA measuring devices. Much work has been done with very small samples under such slow heating rates, yielding data that may or may not be relevant to pyrolysis conditions in real gasifiers. Past work is summarized here for the three major components of biomass and for wood. For each type of material, the behavior is discussed under five headings: (1) thermogravimetric analysis (TGA), in which the sample weight loss is followed under both isothermal and dynamic heating; (2) kinetic analysis of pyrolytic data; (3) differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in which latent and reaction heat effects are either inferred or measured directly; (4) gas and other product analyses, in which various techniques are used to determine primary and secondary decomposition products; (5) morphological and related studies, in which structural information is obtained as pyrolysis proceeds; and (6) molecular mechanisms, in which all of the above information is used to deduce the molecular course of the pyrolysis.

5.2.1 Thermogravimetric Analysis (TGA)

The thermal behavior of biomass is studied most often by measuring the rate of weight loss of the sample as a function of time and temperature. The rates observed are functions not only of time and temperature, but also of the size and the density of the sample. This complexity reflects the range of behavior in different kinds of gasifiers, but there is not necessarily an exact relationship between laboratory experiments and pyrolysis during gasification; nevertheless, TGA offers a semiquantitative understanding of the pyrolysis process under well-controlled laboratory conditions. A number of commercially available instruments of high sensitivity can measure weight loss versus time or temperature under such conditions.

Two types of results are found in the literature: isothermal TGA data showing the rate of pyrolysis at a fixed temperature (e.g., Fairbridge and Ross 1978) and dynamic TGA data showing weight loss at a fixed heating rate (e.g., Shafizadeh and McGinnis 1971, Fig. 5-1). Each type of result has a useful function (see kinetics discussion below).

In addition to yielding kinetic data, the dynamic TGA measurements can yield data equivalent to a proximate analysis; namely moisture content, volatile content, char, and ash, as shown for a sample of flax shives in Fig. 5-2.

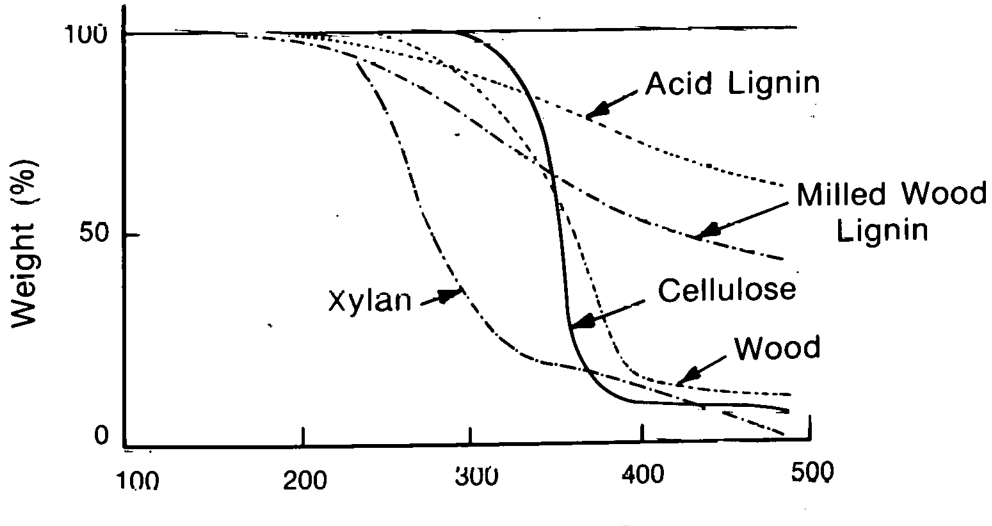

Figure 5-1. Examples of TGA Cottonwood and Its Components, Taken from Shafizadeh and McGinnis (1971)

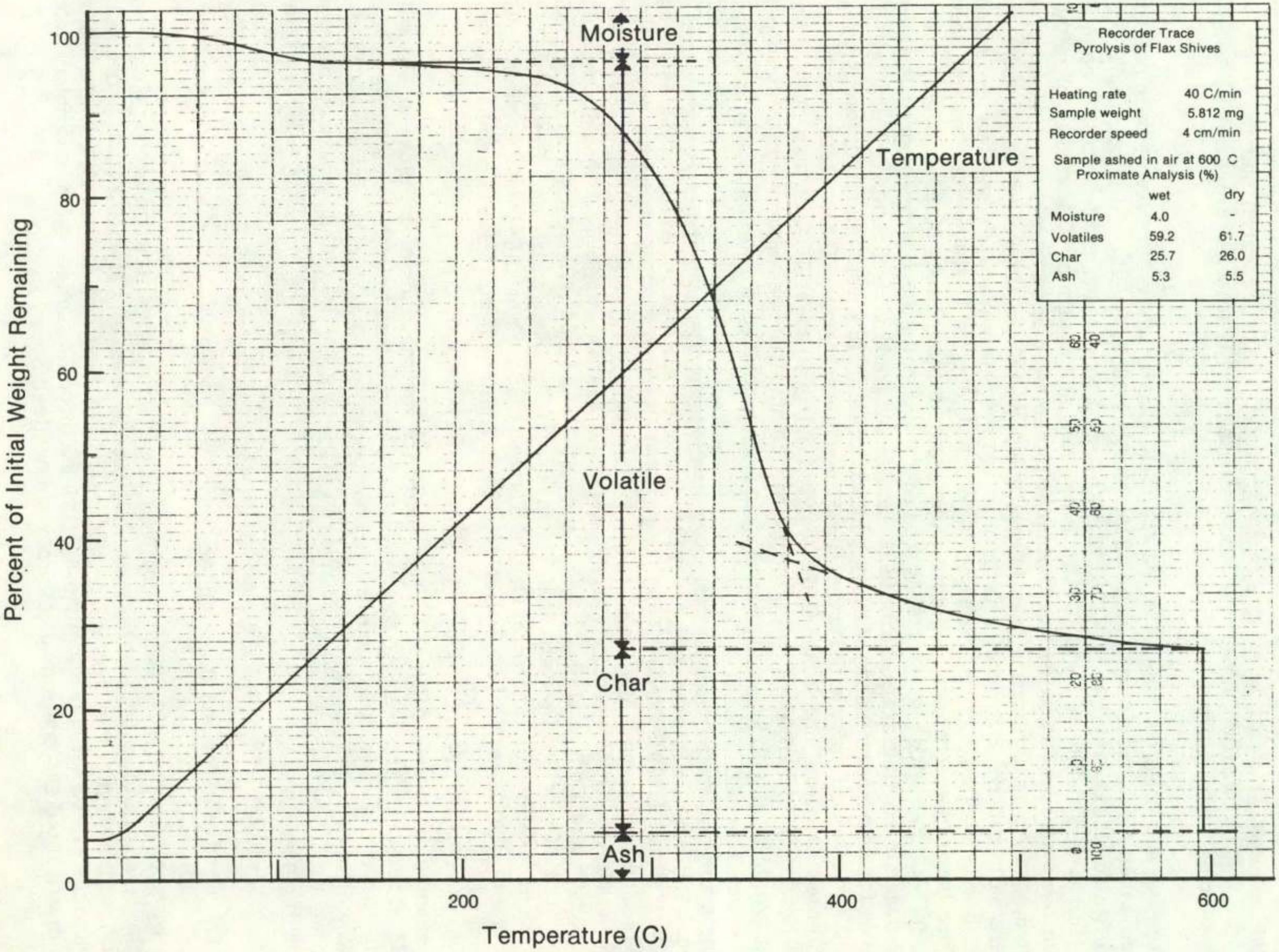

Figure 5-2. A Typical Dynamic TGA Result Obtained with Flax Shives and Showing Moisture, Volatile Matter, Char, and Ash Content

5.2.1.1 Cellulose

In its many forms cellulose has received more extensive study than biomass or any of its other components. This stems from the fact that cellulose is the major component of most biomass, from its relevance in the context of fire research and municipal solid waste (MSW) utilization, and surely also because it is the least complicated, best-defined major component of biomass.

Extensive and detailed reviews of the thermal behavior of cellulose have been published, (Shafizadeh 1975 and 1968; Welker 1970; MacKay 1967; Broido and Kilzer 1963; Kilzer and Broido (1965); Antal et al. 1979) with the most recent and most extensive being that of Molton and Demmitt (1977). Both isothermal and dynamic TGA studies of cellulose have been made, often with small samples in commercial instruments. Vacuum, inert, steam, and air environments have been studied as well as the effect of impurities and added salts and the degree of crystallinity and polymerization. Only a few examples of the diverse studies can be discussed here. Aldrich (1974) studied the weight loss of rather large cylinders of α-cellulose under radiant heat fluxes of 0.4 cal/cm^2-s to 1.1 cal/cm^2-s. Fairbridge et al. (1978) studied fibrous cellulose powder in both isothermal and dynamic heating experiments in N_2 and air. Broido (1966) compared dynamic TGA curves for ash-free cellulose (0.01%), pure cellulose (0.15% ash), and cellulose with 1.5% $KHCO_3$ added. Lipska and Parker (1966) made isothermal TGA measurements on α-cellulose. Cardwell and Luner (1976) carried out isothermal TGA on two pulps. Basch and Lewin (1973) looked at the influence of fine structure on vacuum pyrolysis of cellulose. Antal et al. (1979) pyrolyzed cellulose from a number of sources at varying rates.

Weight loss experiments have also been carried out by: Van Krevelen et al. (1951); Stamm (1956); Corlateanu et al. (1974); Kosik et al. (1972); Akita and Kase (1967); Duvvuri et al. (1975); Barooah and Long (1976); Ramiah (1970); Madorsky et al. (1956, 1958); Shafizadeh and McGinnis (1971); Muhlenkamp and Welker (1977); Patel et al. (1970); McKay (1968); Parks (1971); Arseneau (1971); Mack and Donaldson (1967); Chatterjee and Conrad (1966, 1968); Tang and Neill (1964); Davidson and Losty (1965); Nunomura et al. (1975); Kato and Takahashi (1967); Shafizadeh and Bradbury (1979); Broido and Weinstein (1970, 1971); Chatterjee (1968); Cabradilla and Zeronian (1976); Murty and Blackshear (1966); McCarter (1972); Ainscough et al. (1972); and Ramiah and Goring (1967).

An example of a typical dynamic TGA curve for several kinds of cellulose, measured at SERI, is shown in Fig. 5-3. At the moderate heating rates shown here cellulose is stable to temperatures over 300 C and then decomposes over a rather narrow range of about 50 C leaving a char residue of 5% to 15%, depending on the cellulose source, size, and heating rate. Isothermal weight loss curves have been reported by Stamm (1956) for lower temperatures.

5.2.1.2 Hemicellulose and Holocellulose

The hemicelluloses, partly because of their lesser abundance in wood and partly because of their variety of constituents, poorly defined degree of polymerization and crystallinity, and ambiguous extraction procedures, have received less study than cellulose. Work includes extracted hemicelluloses, pure components such as xylan, and holocellulose (lignin extracted and containing cellulose and hemicellulose).

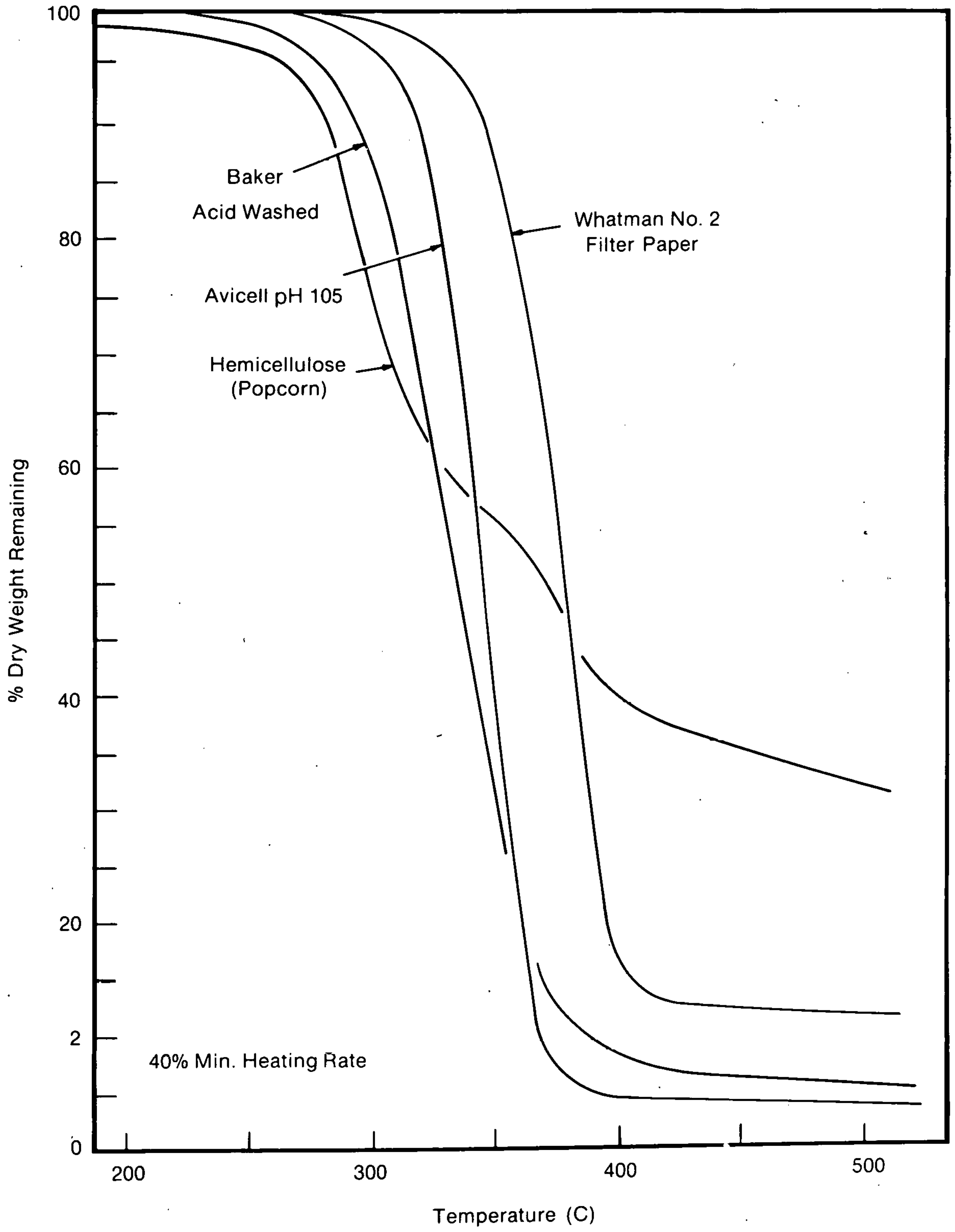

Figure 5-3. Pyrolysis of Cellulose and Hemicellulose

TGA of holocellulose has been done by Duvvuri et al. (1975); Fang et al. (1975); and Domburg et al. (1969). Hemicellulose and xylan have been studied by Ramiah (1970); Browne (1958); Stamm (1956); Tang (1964); Domburg et al. (1969); Shafizadeh et al. (1972); and Shafizadeh and McGinnis (1971). Ramiah and Goring (1967) used dilatometry to follow pyrolysis. All studies indicate that the hemicelluloses are the least stable major component of wood, perhaps due to their lack of crystallinity. A typical TGA curve was shown in Fig. 5-1 (Shafizadeh and McGinnis 1971).

5.2.1.3 Lignin, Bark, and Black Liquor

Lignin is the most complicated, least understood, hardest to extract without change, and most refractory component of wood. Consequently, the interpretation of experiments with lignin is the most empirical and shows the most variable behavior of the wood constituents. Its behavior has been reviewed by Roberts (1970); Beall and Eickner (1970); Soltes and Elder (1979); Allan and Mattila (1971); and Tang (1964).

Weight loss experiments have been carried out on various lignin preparations by Van Krevelen et al. (1951); Duvvuri et al. (1975); Ramiah (1970); Shafizadeh and McGinnis (1971); Stamm (1956); Goos (1952); and Fang et al. (1975). Fairbridge and Ross (1978); Tran and Rai (1978) and Rensfelt et al. (1978) have done TGA on bark. A typical thermogram for two lignins is shown in Fig. 5-1. Minor decomposition appears to start at lower temperature than for cellulose, but most lignin pyrolysis occurs at higher temperatures. Large differences are seen in lignins prepared by different procedures. Acid lignin appears to be more stable than other derived lignins.

5.2.1.4 Wood and Other Biomass

It is reasonable to assume, at least qualitatively, that the pyrolysis of wood is closely related to the three major components of biomass, and several of the studies cited above reach this conclusion, though not with a quantitative demonstration (Antal et al. 1979). Reviews relevant to wood pyrolysis include Roberts (1970, 1971a,b); Beall and Eickner (1970); Tang (1964); Tran (1978); and Soltes and Elder (1979).

The pyrolysis of wood and related substances, measured through weight loss behavior, has been reported by Rensfelt et al. (1978); Babu (1979); Browne and Brenden (1964); Browne and Tang (1963); Corlateanu et al. (1974); Tang and Eickner (1968); Heinrich and Kaesche-Krischer (1962); Stamm (1956); Fairbridge and Ross (1978); Hileman et al. (1976); Shafizadeh and McGinnis (1971); Leu (1975); Muhlenkamp and Welker (1977); Duvvuri et al. (1975); Havens et al. (1971); Barooah and Long (1976); and Maa and Bailie (1978). The general features are what would be expected from the composition though quantitative comparisons are questionable. A typical TGA curve for hardwood is shown in Fig. 5-1.

TGA data on a few other forms of biomass such as manure, papers, and straw have been reported in many of the references listed above.

5.2.2 Kinetic Analysis of Pyrolysis

The sharp, well-defined TGA curves, especially for cellulose, suggest that a relatively simple reaction controls the decomposition kinetics prevalent at relatively slow heating rates, and a great deal of effort has gone into fitting classical kinetic theory to TGA data in general (Wendlandt 1974) and for biomass components in particular (Antal et al. 1979). Unfortunately, there is no generally accepted method for extracting kinetic data from dynamic TGA data, and the data can be fit quite well with a range of the adjustable constants. Whatever the theoretical merits of the resulting kinetic data, they serve to predict pyrolysis data over a range of conditions and thus should have engineering utility in designing and understanding gasifiers having slow heating rates. We will sketch here only enough of the kinetic background to make the results comprehensible.

The thermal decomposition curves can be fit using a general equation of the form:

$$dV/dt = k\,V^n , \tag{5-1}$$

where

$$k = A \exp(-E/RT) , \tag{5-2}$$

and V is the fraction of total volatiles remaining at temperature T. If the sample is heated at a constant rate, R = dT/dt, then Eq. 5-1 becomes

$$dV/dT = k\,V^n/R . \qquad (5\text{-}3)^*$$

Unfortunately, a wide variation of the activation energy E, the pre-exponential factor A, and the order n can give satisfactory fits to the data. Many investigators arbitrarily choose n = 1. Furthermore, it is not easy to measure sample temperature accurately in a free balance pan, particularly in vacuum. Table 5-1 (Antal et al. 1979) shows the variation of activation energy measured on cellulose and wood by a number of investigators. Antal et al. postulated that researchers who achieved the best temperature measurement found that E lay in the range 26-33. One of the most convincing aspects of these measurements is that they can predict the decomposition rate of cellulose quite well over a range of slow heating rates varying by a factor of 30 (Antal et al. 1979). However, present analyses do not predict the variation of char formation with pyrolysis conditions, and this would be especially useful for gasification.

The TGA curves for cellulose are relatively simple and can be fit using Eqs. 5-1 to 5-3. However, the TGA data for lignin, hemicellulose, and compound biomass are complex and will require a more complex theory for accurate description. Nevertheless, equations of this form can still be used for engineering prediction.

5.2.3 Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

TGA records mass change during pyrolysis but not energy changes. In differential thermal analysis a thermocouple junction placed in the sample records the difference in temperature between the sample and another inert material. If an endothermic reaction occurs the sample temperature lags that of the reference, while an exothermic reaction causes sample temperature to lead the reference temperature. This gives a qualitative measure of the sign and degree of energy absorption or evolution during pyrolysis.

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*This equation cannot be solved analytically and various approximations and computer integrations are required to determine the constants.

Table 5-1. PYROLYSIS KINETICS DERIVED FROM EXPERIMENTS UTILIZING SMALL (~1 g) SAMPLES

Sample	Reference	Experiment	E(kcal/g-mole)
Cellulose	Akita and Kase (1967)	TGA, TC in Vacuum	53.5
Cotton	Madorsky, Hart and Straus (1956)	TGA, TC in Vacuum	50.
Cellulose	Ramiah (1970)	TGA, TC in Vacuum	36.-60.
Cellulose	Tang (1964)	TGA, TC in Vacuum	56.
Cellulose	Tang and Neil (1964)	TGA, TC in Vacuum	53.-56.
Cellulose	Arseneau (1971)	TGA, Flowing N_2	45.4
Wood	Browne and Tang (1963)	TGA, Flowing N_2	35.8
Cotton	Chatterjee and Conrad (1966)	TGA, Flowing N_2	33.
Cotton	Mack and Donaldson (1967)	TGA, Flowing N_2	48.8
Cellulose	Lipska and Parker (1966)	Fluidized Bed	50.
Cellulose	Chatterjee (data of Lipska and Parker) (1965)	Fluidized Bed	42.
Cellulose	Lipska and Woodley (1969)	Fluidized Bed	42.
Cellulose	McCarter (1972)	Evolved Gas	40.5
Cellulose	Murphy (1962)	Evolved Gas	39.4
Cellulose	Martin (1965)	Radiation	30.
Cellulose	Shivadev and Emmons (1974)	Radiation	26.
Cellulose	Lewellen, Peters and Howard (1976)	Electrically heated screen	33.4

Recently this type of data has been made quantitative in the technique of differential scanning calorimetry. In this case, an electrical circuit adds heat to or subtracts heat from the sample to keep its temperature identical with that of the reference and records the amount of heat added or held back.

5.2.3.1 Cellulose

Many workers have used DTA to observe, semiquantitatively, the heat effects on pyrolysis of small samples (Patel et al. 1970; Parks 1971; Mack and Donaldson 1967; Tang and Neill 1964; Herbert et al. 1969; Akita and Kase 1967; Broido 1966; Shafizadeh and McGinnis 1971; Arseneau 1961, 1963; Ramiah 1970; Berkowitz 1957; Tang and Eickner 1968; Breger and Whitehead 1951; Sandermann and Augustin 1963; Domansky and Rendos 1962; and Domberg et al. 1969). In a few cases the more quantitatively interpretable DSC has been used (Arseneau 1971; Mack and Donaldson 1967; Basch and Lewin 1973; Muhlenberg and Welker 1977). Finally, transient heat balances in pyrolyzing material have been used to estimate heat effects (Browne and Brenden 1964).

Typical curves obtained in DTA and DSC are shown in Figs. 5-4 (from Shafizadeh and McGinnis 1971) and 5-5. Qualitative agreement exists that the pyrolysis of cellulose, at least in the absence of very extensive secondary charring reactions in large samples, is entirely endothermic. The exact nature of the heat effects is quite sensitive to the extent of secondary reactions and to added impurities, as shown by the DSC curves for thin and thick specimens in Fig. 5-5.

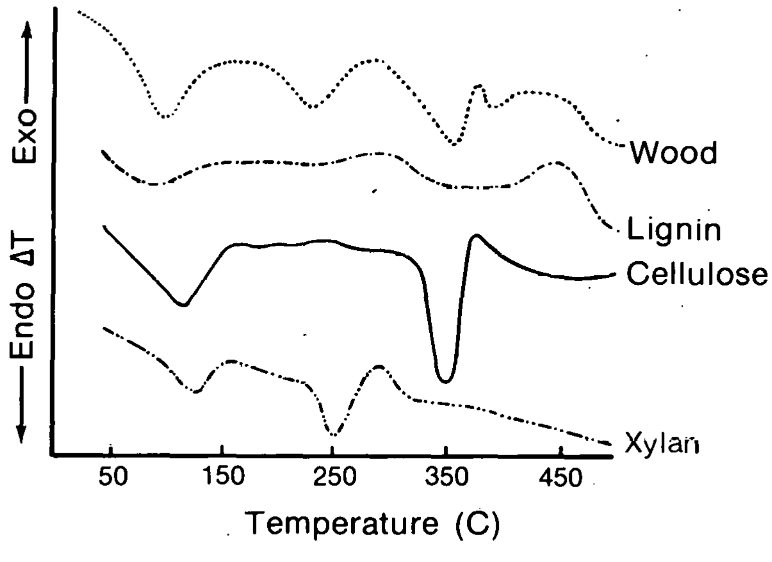


Figure 5-4. Differential Thermal Analysis of Cottonwood and Its Components

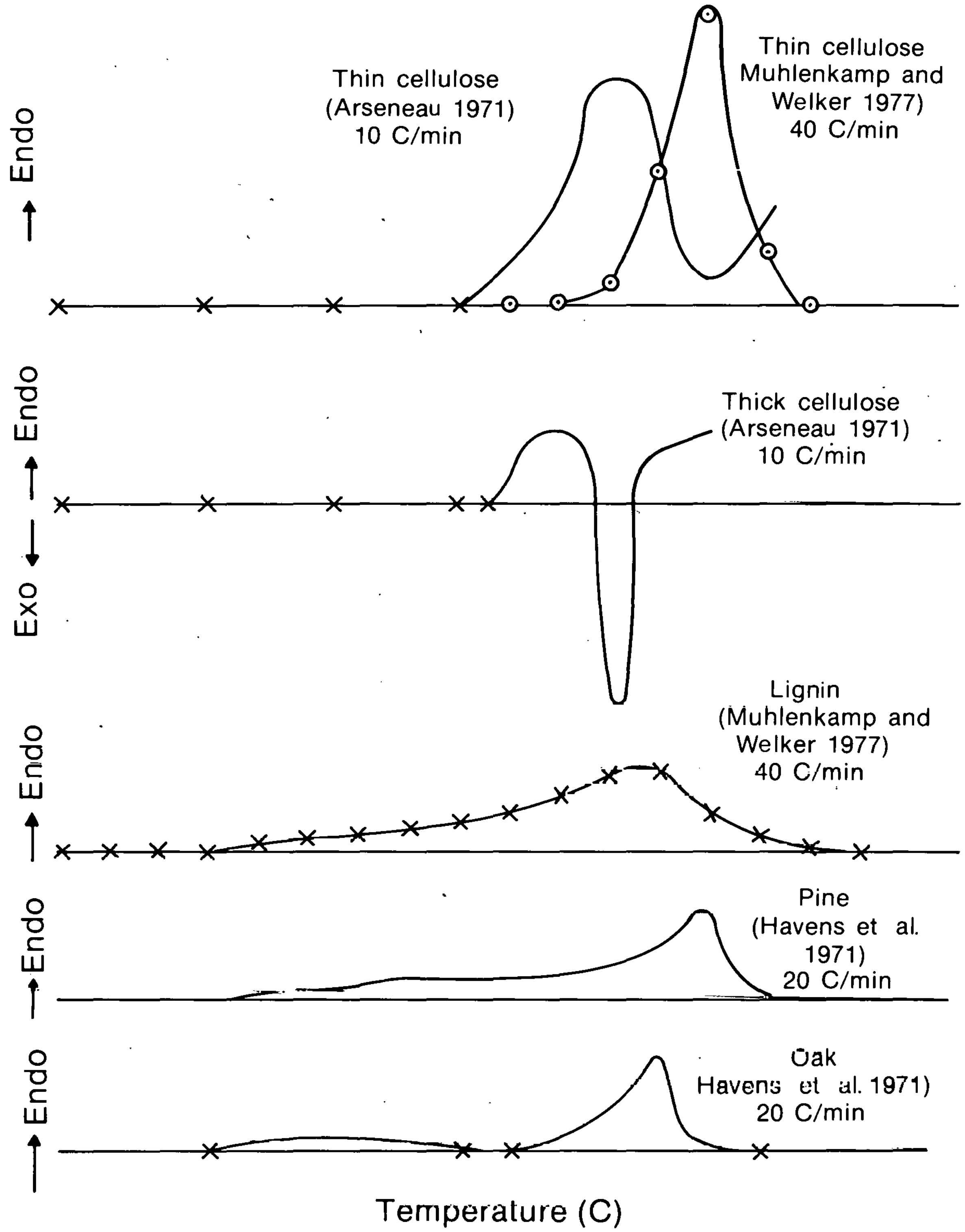


Figure 5-5. Selected Results of Differential Scanning Calorimetry of Wood and Its Components

5.2.3.2 Hemicellulose and Holocellulose

DTA data have been obtained by Ramiah (1970); Fang et al. (1975); Arseneau (1961); Sandermann and Augustin (1963); Domansky and Rendos (1962); Domburg et al. (1969); and Shafizadeh and McGinnis (1971) for hemicelluloses and holocelluloses. No DSC measurements have come to our attention. As in cellulose, the decomposition of hemicelluloses appears to be endothermic, at least for the small samples usually employed. A representative DTA curve is shown in Fig. 5-4.

5.2.3.3 Lignin, Bark, and Black Liquor

DTA curves have been generated for lignins and bark by Fang et al. (1975); Arseneau (1961); Berkowitz (1957); Sandermann and Augustin (1963); Domansky and Rendos (1962); Domburg et al. (1969); Ramiah (1970); Shafizadeh and McGinnis (1971); Tang and Eickner (1968); and Breger and Whitehead (1951). The only DSC study discovered is that of Muhlenkamp and Welker (1977) on punky douglas fir. DTA and DSC curves are shown in Figs. 5-4 and 5-5.

5.2.3.4 Wood and Other Biomass

DTA analysis has been popular in spite of the ambiguities in its quantitative interpretation (Arseneau 1961; Shafizadeh and McGinnis 1971; Tang and Eickner 1968; Heinrich and Kaesche-Krischer 1962). In general, researchers have seen the features of component DTA curves in the whole wood thermogram (Fig. 5-4) (Breger and Whitehead 1951; Sandermann and Augustin 1963; Domansky and Rendos 1962; Domburg et al. 1969). The more interpretable DSC has been applied by Leu (1975); Muhlenkamp and Welker (1977); and Havens et al. (1971). Heats of wood pyrolysis have been deduced indirectly from measurements of temperature distributions in larger, pyrolyzing wood specimens (Roberts and Clough 1963; Bamford et al. 1946). The DSC results, and a reinterpretation of the data of Roberts and Clough by Kung and Kalelkar (1973), support the heat of pyrolysis of wood as endothermic, at least where secondary, char forming reactions are not extensive. DSC curves for pine and oak wood are shown in Fig. 5-5.

5.2.4 Gases and Other Products Evolved During Pyrolysis

5.2.4.1 Cellulose

A great deal of effort has been spent on analysis of the gaseous and condensable products of pyrolysis of cellulose, more often from the standpoint of deducing pathways of decomposition than from the relevance to subsequent gasification (McKay 1968; Byrne et al. 1966; McCarter 1972; Bolton et al. 1942; Min 1977; Madorsky et al. 1956, 1958; Davidson and Losty 1965; Robb et al., 1966; Halpern and Patai 1969; Tsuchiya and Sumi 1970; Glassner and Pierce 1965; Lipska and Wodley 1969; Smith and Howard 1937; Schwenker and Pacsu 1957; Greenwood et al. 1961; Venn 1924; Fairbridge et al. 1978; Schwenker and Beck 1963; Murphy 1962, Antal et al. 1979; and Goos 1952). Gas chromatography and mass spectrometry are widely employed. Occasionally, special techniques are used on the condensed phase, such as x-ray, density, measurements of degree of polymerization, ESR, IR, and vapor-phase thermal analysis.

Table 5-2. PYROLYSIS PRODUCTS OF CELLULOSE REPORTED IN TWO DIFFERENT STUDIES

	Wt % of Sample		
	(Antal et al. 1979) 500 C	(Tsuchiya and Sumi 1970) 320 C	 520 C
Total Accounted For	64%	89.5%	68.0%
Char	12	67.8	12.8
Tar[a]	35	10.3	28.4
Water	—	9.3	20.7
H_2 [b]	0.4		
CO [b]	18	0.5	2.6
CO_2 [b]	30	1.5	2.9
CH_4 [b]	0.5		
C_2H_4 [b]	0.5		
C_3H_6 [b]	0.5		
C_2H_6	0.5		
Other	1.3		
Hydrocarbons		—	0.3
Furan	0.03		0.04
2-Methylfuran		0.02	0.05
Furfural		0.06	0.08
5-Methylfural			
5-Hydroxymethyl Furfural		0.01	0.08
Levoglucosan[c]		3.8	18.2
1, 6-Anhydro-D-Glucofuranose		0.2	2.2
-D Glucose[c]		0.03	0.2
-D Glucose[c]		0.04	0.3
Dimers of Anhydroglucose		0.2	0.4
Unknown[c]		0.12	0.08
Unanalyzed Tar[c]		5.9	7.0

[a] Includes all tar fractions below.
[b] Upper limits - mass balance only 64%.
[c] Tar fraction.

Some examples of yields of char, tar, and gases are given in Table 5-2 for several pyrolysis experiments. The nature of the products depends on the rate of heating, the temperature, the degree to which primary pyrolysis products are confined in the char, and the presence of additives (catalysts), so that the results shown are not necessarily representative. For moderately fast pyrolysis the nature of the surrounding atmosphere (air, steam, H_2, inert) has little effect. Pressure is not a major variable either, except as it influences the escape of primary products.

5.2.4.2 Hemicellulose and Holocellulose

A few studies have been made on the gaseous and other products of holocellulose and hemicellulose pyrolysis (Fang and McGinnis 1975, 1976; Goos 1952; Shafizadeh et al. 1972; and Stamm 1956). Holocellulose and hemicellulose tend to yield more gases and less tar than cellulose. Table 5-3 gives examples of product compositions for pyrolysis of a holocellulose and a hemicellulose.

Table 5-3. PYROLYSIS PRODUCTS FROM A HOLOCELLULOSE (FANG AND MCGINNIS [1976]) AND A HEMICELLULOSE (XYLAN) (SHAFIZADEH [1977])

	Wt % Product	
	Holocellulose (400 C)	Xylan (500 C)
Char	20.2	10
Tar	—	64
Water	37.3	7
CO_2	11.0	8
CO	5.3	—
Low Molecular Weight Hydrocarbons	0.4	
Methanol	1.1	1.3
Acetaldehyde	0.2	2.4
Acetic Acid	1.4	1.5
Furan	0.5	Trace
Acrylaldehyde	0.07	
Diacetyl	0.2	
1-Hydroxy-2-Propanone	0.06	0.4
2-Furaldehyde	0.5	4.5
Acetone-Propionaldehyde		0.3
2-3-Butanedione		Trace
3-Hydroxy-2-Butanone		0.6

5.2.4.3 Lignin, Bark, and Black Liquor

Much of the work yielding gas from lignin originates in gasification studies of black liquors (Liu et al. 1977; Brink 1976; Goheen et al. 1976; Prahacs et al. 1967a,b; 1971; Barclay et al. 1964; Rai and Tran 1975; and Schlesinger et al. 1973). In these studies pyrolysis and gasification were not always separated clearly so that probably only the lower temperature composition (500 C to 600 C) reflects lignin pyrolysis behavior. Vroom (1952); Fairbridge and Ross (1978); Schlesinger et al., (1973); and Rensfelt (1978) measured gas or product compositions from pyrolyzing bark. Goos (1952); Stamm (1956); Fletcher and Harris (1947, 1952); and Hileman et al. (1976) looked at products from lignin, Hileman et al. by subtracting the pyrolysis mass spectrum of cellulose from that of wood for comparison with the spectrum of extracted lignin.

Some of the products obtained in lignin pyrolysis are given in Table 5-4.

Table 5-4. EXAMPLES OF VOLATILE PRODUCTS FROM LIGNIN PYROLYSIS

	Douglas Fir Lignin[a] Pyrolyzed at 400-445 C for 7.5h	Kraft Black Liquor[b] Pyrolyzed at 490 C
Char	53-64.6%	Methyl mercaptan
Aqueous distilled	15-25%	Dimethyl sulfide
Tar	~9%	Benzene
Gases	—	Toluene
Organic acids	formic, acetic propionic plus traces of others	m and/or p-Xylene Anisol Phenol
Phenols	phenol, o-cresol p-cresol, guaiacol 2, 4-xylenol, 4-methyl and ethyl guaiacol, 4-n-propylguaiacol	o-cresol m and/or p-cresol 2, 5 and/or 2, 4 dimethyl 3, 5 dimethyl phenol
Catechols	catechol, 4-methyl and ethyl catechol, 4-n-propyl catechol	2, 3 dimethyl phenol 3, 4 dimethyl phenol

[a] Fletcher and Harris 1952.
[b] Brink et al. 1971.

5.2.4.4 Wood and Other Biomass

As expected, the products from wood pyrolysis are more complex than those from the wood components listed above. No study is known which demonstrates that the gaseous products of wood are the sum of its components under comparable pyrolysis conditions. Product analyses for wood, under conditions where pyrolysis may predominate, have been reported by Knight (1976); Babu (1979); Appell and Pantages (1976); Appell and Miller (1973); Stern et al. (1965); Schlesinger et al. (1973); Stamm (1956); Goos (1952); Rensfelt et al. (1978); Brink (1976); and Min (1977). Support studies for gasifier research tabulated in a later section also contain pyrolysis gas behavior. Catalysts have a large effect on the pyrolysis of cellulose and wood, but only a small effect on the pyrolysis of lignin. Table 5-5 gives some examples of product yields from the literature.

In general, pyrolysis of other forms of biomass gives similar products, except that manure contains a high proportion of volatile fatty acids and lignin products.

5.2.5 Morphology of Biomass During Pyrolysis

Surprisingly few investigations have involved time-dependent studies of the morphology of cellulose during pyrolysis (McCarter 1972). A recent exception is the study by Fairbridge et al. (1978) in which SEM and krypton absorption were used to characterize the developing chars.

No morphological studies have been found for the hemicelluloses and holocelluloses or lignin during pyrolysis.

Knudson and Williamson (1971) observed morphological changes in wood heated in air. Though much work has probably been done on the characteristics of chars produced in carbonization, we are not aware of systematic, time-resolved studies of the morphological changes in wood during the early stages of pyrolysis under conditions relevant to gasification.

5.2.6 Pyrolysis Mechanisms

5.2.6.1 Cellulose

All of the studies described here have been employed to infer the mechanisms for production of the large variety of products actually observed, including the study of model compounds. Several reviews have discussed the detailed organic reactions leading initially largely to levoglucosan, a primary product of cellulose pyrolysis, and subsequently to a wide variety of decomposition products (e.g., Shafizadeh 1968; Molton and Demmitt 1977). Mechanisms for formation of the lighter gaseous species are almost totally lacking; the time and space resolution of the gas sampling devices, if not the experimental pyrolysis arrangement itself, making intermediates hard to observe. A widely adopted scheme which provides a conceptual framework for many observations has been proposed by Kilzer and Broido (1965).

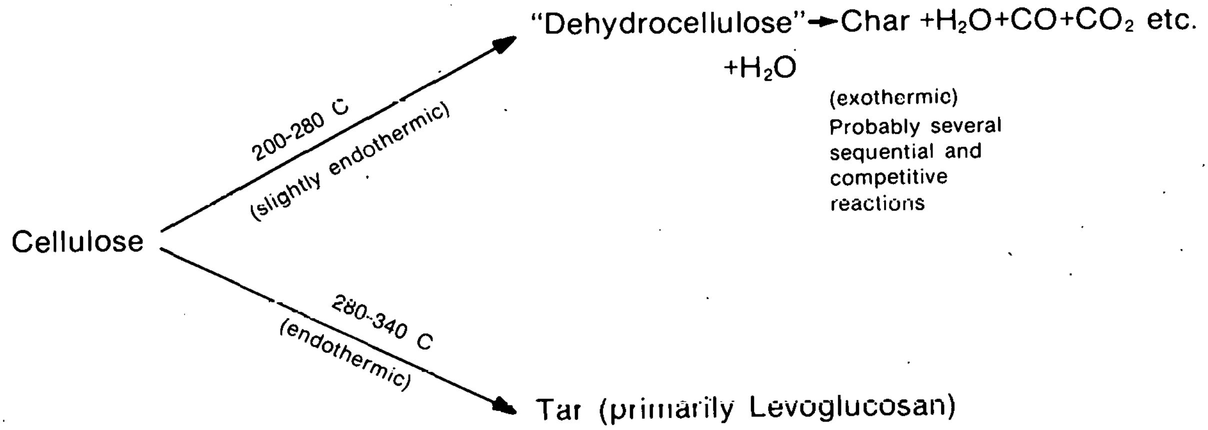
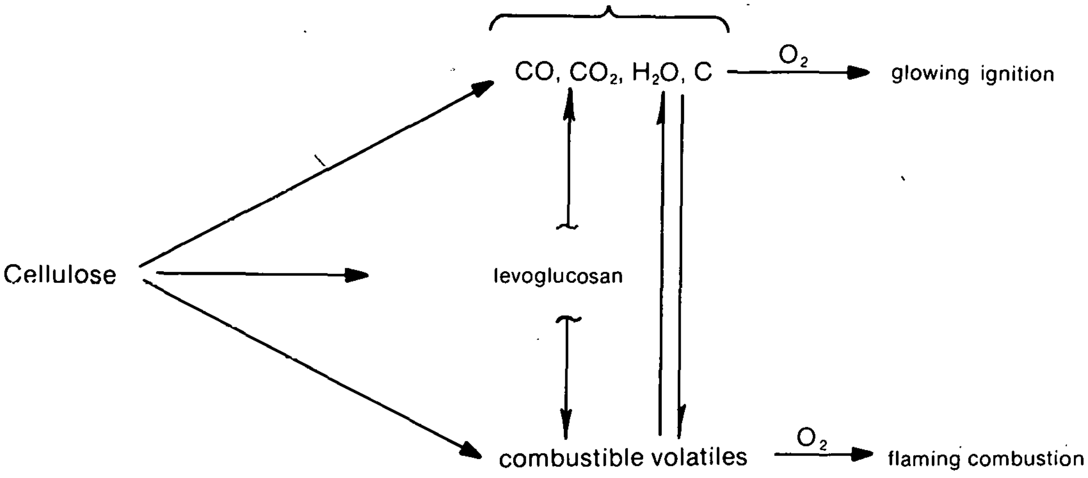


Table 5-5. SELECTED EXAMPLES OF WOOD PYROLYSIS PRODUCTS UNDER CONDITIONS RANGING FROM LONG RESIDENCE TIME TO FAST PYROLYSIS

	Wt % Products		
Species	White Fir (Fast Heating) (Brink & Massoudi 1978)	Pine (Slow Heating) (Knight 1976)	Douglas Fir (Fast Heating (Hileman et al. 1976)
Total Gases	69.0	25	
Char	5.7	32	
Tar	21.0	16	
Water	N/A	27	15.3
H_2	0.1		
CH_4	4.8[a]	2.0	2.0
CO	42[a]	7.3	21.2
CO_2	22[a]	14.2	5.7
C_2H_4			1.0
C_2H_6			0.3
C_2-C_4 HC		2.2	
C_3H_6			1.6
Methanol			0.4
Ethanol			1.4
2-Methyl Propene			0.3
Propenal			0.7
Furan			0.2
2-Oxopropanal			0.5
Hydroxyethanal			0.7
Ethanoic Acid			0.7
2, 3-Butanedione			0.3
2-Hydroxypropanol			0.5
Furfural			0.4
2, 3-Pentanedione			0.1
Furfurylalcohol			0.2
2-Methyl-2-Butenal			0.1
o-Methoxyphenol			0.2
2-Methoxy-4-Methylphenol			0.4
2-Methoxy-4-Methylanisole			0.1
4-Oxophentanoic Acid			0.4
4-Hydroxy Pentanoic Acid			0.2
p-Methoxyacetophenone			0.2
2-Methoxy-4-Propenylphenol			0.1
5-Hydroxymethyl-2-Furaldehyde			0.2

[a] Upper limits.

At low temperatures and slow heating rates, the upper path predominates. Under faster heating, the lower path becomes the more important. Shafizadeh (1968) elaborates on this scheme relative to biomass combustion as follows:



Quoting Shafizadeh:

> Thermal degradation of cellulosic materials proceeds through a complex series of concurrent and consecutive chemical reactions. The [above scheme] provides an outline of the general sets of the degradation reactions of cellulose that could lead to the flaming combustion or glowing ignition of this material. The nature and extent of many individual reactions involved in this process are not known or insufficiently defined. However, it is known that these reactions are highly influenced by: the temperature and period of heating; the ambient atmosphere, oxygen, water, and other reacting or inert gases; and the composition and physical nature of the substrate, especially with respect to inorganic impurities and additives.
>
> The general reactions can be divided into primary and secondary reactions, according to whether they directly affect the cellulosic substrate or one of the intermediate degradation products. Alternatively, two general pathways for degradation of cellulosic materials may be recognized. One involves fragmentation, and formation of combustible volatiles that could feed the flames, and the second mainly involves dehydration and the formation of carbonaceous char that could lead to localized, and relatively slower, glowing ignition. Since these two pathways compete for the same initial substrates, according to the prevailing conditions, one could predominate at the expense of the other.
>
> Heating at the lower temperatures, as discussed later, favors the dehydration and charring reactions. Formation of levoglucosan, which is a principal intermediate compound, takes place at somewhat higher temperatures and leads to further decomposition reactions at the elevated temperatures.

This description, though in the context of combustion, is relevant to gasification as well.

5.2.6.2 Hemicellulose and Holocellulose

Speculations as to reaction pathways for the condensable organics from hemicellulose parallel those for cellulose. Soltes and Elder (1979) reported a postulated two-step decomposition. First, depolymerization to water-soluble fragments occurs, followed by decomposition to volatiles. The expected furan derivatives may be too reactive to survive the usual pyrolysis conditions. Browne (1958) discussed the older literature on hemicellulose pyrolysis behavior. Tang and Eickner (1968) postulated that early pyrolysis of hemicellulose to acetic acid and formaldehyde may affect pyrolysis of cellulose and lignin in wood. Goos (1952) indicated that the pentosans in hemicellulose give the most distinctive products, while little is known of hexosan behavior.

5.2.6.3 Lignin, Bark, and Waste Liquor

The rich structural variety in the hypothesized lignin macromolecule gives rise to many mechanistic pathways to observed condensable organic compounds. Furthermore, each lignin preparation gives a different substrate—with ambiguity as to the nature of the true "native lignin." Soltes and Elder (1979) note that lignin produces more aromatic compounds and char than cellulose. No product predominates as is the case with cellulose. Allan and Mattila (1971) assume that lignin pyrolysis is by homolytic cleavage with phenyl radicals important. Goos (1952) assumes that pyrolysis of lignin in H_2 may give a truer indication of primary fragments by minimizing secondary condensation reactions. The reader is referred to the references above for specific speculations.

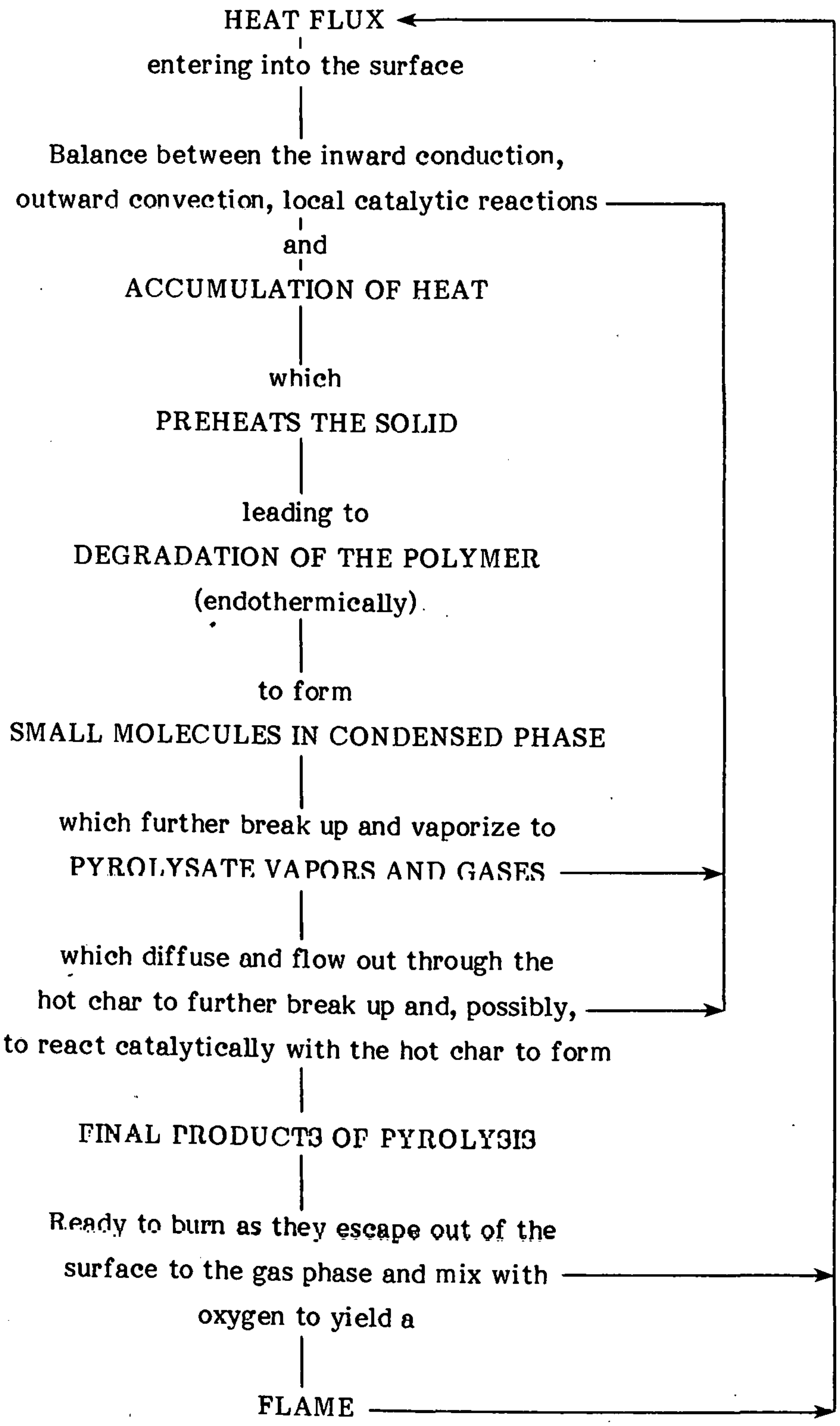
5.2.6.4 Wood and Other Biomass

The general features of wood pyrolysis mechanisms usually have been discussed in terms of the behavior of wood's components, since few interactions or new products found only with wood have been observed. Roberts' (1970) review of the kinetics of wood pyrolysis is still timely. He accepts the prevailing practice of treating wood pyrolysis as a first order process following Arrhenius kinetics. The factors affecting pyrolysis are discussed in terms of composition, autocatalysis, physical structure, pressure, and wood type. His conclusions are:

- The use of a first-order reaction scheme to describe the complex process of wood pyrolysis is questionable theoretically but has empirical advantages.
- Hemicellulose, cellulose, and lignin have pyrolysis reactivities decreasing in the order in which the substances are listed. Most of the lignin will still be present after the bulk of the first two substances has decomposed.
- The cellulose component is extremely sensitive to catalytic and autocatalytic effects, with pure cellulose primary pyrolysis showing a high activation energy and impure or large samples exhibiting a much lower activation energy.
- Lignin pyrolysis shows much smaller effects due to additives or autocatalysis.
- Experiments with small samples may not be representative of large sample behavior to the extent that secondary reactions, autocatalysis, and physical structure play a role.
- Restraints on pyrolysis product movement due to the physical ltructure of the wood are important at low temperature but largely disappear at temperatures of 300 C to 320 C.

- A fully developed pyrolysis wave in wood can be divided into four regions of increasing temperature:
  - wood structure is virtually intact with autocatalytic pyrolysis of most reactive components;
  - wood structure has failed, autocatalysis is reduced, pyrolysis of reactive components occurs;
  - pyrolysis of hemicellulose and cellulose complete and lignin pyrolysis is dominant;
  - all the wood is pyrolyzed to char; and
  - secondary reactions of primary volatiles occur with char residues.
- The choice of suitable kinetics for application to pyrolysis depends on the nature of the problem (e.g., ignition versus complete pyrolysis to char).

This type of sequence has been portrayed schematically for wood combustion by Kanury (1972) and is shown on the following page; in this scheme for gasification, the final step would be gasification and the heat flux might come from an external source as well as from partial combustion.



HEAT FLUX

entering into the surface

Balance between the inward conduction, outward convection, local catalytic reactions

and

ACCUMULATION OF HEAT

which

PREHEATS THE SOLID

leading to

DEGRADATION OF THE POLYMER (endothermically)

to form

SMALL MOLECULES IN CONDENSED PHASE

which further break up and vaporize to

PYROLYSATE VAPORS AND GASES

which diffuse and flow out through the hot char to further break up and, possibly, to react catalytically with the hot char to form

FINAL PRODUCTS OF PYROLYSIS

Ready to burn as they escape out of the surface to the gas phase and mix with oxygen to yield a

FLAME

5.2.7 Discussion

The previous sections are little more than a guide to the kinds of studies that have been done on wood and its components. The reader is referred to the papers, and especially to the reviews, for details. Even had time and space permitted, it is not clear that a detailed comparison of these kinds of studies is warranted in the context of our gasification interests. Many of the studies just cited have involved small samples, slowly heated, with rapid escape of volatile products. In gasifier operation, two conditions will tend to prevail:

- In gasifiers intended to produce a gas tending toward equilibrium, large particles, with attendant slow heating rates, will be subjected to long residence times.
- In gasifiers seeking to maximize production of nonequilibrium gas composition (e.g., olefins), small particles, with attendant fast heating rates, will be subjected to short residence times.

Thus, the conditions of relevance to gasification in laboratory studies will tend toward either large particles at slow heating rates or small particles at fast heating rates. It has been suggested that many of the studies cited above, involving small samples and intermediate heating rates, may have limited applicability to real fire (or gasification) situations (Kanury 1972).

The next section discusses studies relating to pyrolysis gasification of small particles with high heating rates and short residence time.

5.3 FAST PYROLYSIS

Less studied than slow pyrolysis, fast pyrolysis holds the possibility of direct production of products of high value such as olefins, especially ethylene and propylene. A number of studies, usually recent, partially characterize pyrolysis gasification under conditions of rapid heatup, high temperature, or short residence time. These studies can be grouped under four categories:

(1) slow-solid pyrolysis followed by short residence time for re-forming or secondary pyrolysis (Antal et al. 1979);

(2) fast-solid pyrolysis followed by almost instantaneous quenching of primary products in cold gas or vacuum (Lincoln 1965, 1974; Lincoln and Covington 1975; Martin 1965; Lewellen et al. 1976; Hileman et al. 1976; Broido and Martin 1961).

(3) fast-solid pyrolysis followed by relatively short residence times for re-forming or secondary pyrolysis (Brink and Massoudi 1978; Allan and Mattila 1971; Prahacs et al. 1971; Rensfelt et al. 1978; Berkowitz, Mattuck and Noguchi 1963; Diebold and Smith 1979; Kuester 1978; Brink et al. 1973; Mallon 1974).

(4) fast pyrolysis followed by relatively long residence times for re-forming or secondary pyrolysis (Brink 1976; Stern et al. 1965; Barber-Coleman 1975); or very high effective temperatures (Brown 1979; Krieger et al. 1979; Allan and Mattilla 1971).

These studies are summarized and results compared in the following sections, with the emphasis on production of olefins, since these high value products are observed only in fast pyrolysis.

5.3.1 Slow Pyrolysis, Short Residence Time

Antal et al. (1979) seem to be the only researchers to force separation of the slow, low temperature solid pyrolysis from the fast, high temperature gas re-forming/pyrolysis stages in gasification. They have reported results only for cellulose (Whatman filter paper) though studies on wood are in progress. Half gram samples of the cellulose were pyrolyzed at a heating rate of about 100 C/min to 500 C/min in a flow of steam or argon. The volatile pyrolysis products were then swept into a quartz reactor and allowed to react further for 1 to 10 s at temperatures to 750 C. Gaseous components CO, CO_2, H_2, CH_4, C_2H_6, C_2H_4 and C_3H_6 were reported as a function of temperature and residence time. Results in Ar and steam were essentially identical. The results were interpreted to give kinetics of formation of the products, though the composition of the intermediate gases and vapors was not measured completely. (Studies cited above could be used to estimate the likely pyrolysis products.) Table 5-6 shows representative gas compositions from this study and some processes discussed below.

5.3.2 Fast Pyrolysis, Very Short Residence Time

In these studies, pyrolysis was initiated by resistance or flash heating in vacuum or cold transport gases so that the primary pyrolysis should have been rapidly quenched (milliseconds). Lewellen et al. (1976) heated thin strips of cellulose ($\sim$ 0.07% ash filter paper) by resistance heating in vacuum or helium. Residence times from 0.2 to 75,000 s, final temperatures from 250 C to 1000 C, and heating rates from 400 to 10,000 C/s were studied. Volatile products were not measured, but weight loss data could be fit over a surprisingly large range by a simple first-order equation. No char was formed. The rate data at the highest heating rates were interpreted to imply that the critical factor in pyrolysis is the residence time of volatiles in the cellulose matrix.

Lincoln (1965) used flash heating from both carbon arcs (1.5 and 11.0 cal/cm^2-s) and xenon flash lamps (up to 3,000 cal/cm^2-s) to pyrolyze α-cellulose (blackened with 2% carbon black) in both helium and vacuum. Gas chromatography and mass spectrometry were used for product identification. Comparison of slow versus fast pyrolysis showed a big change in primary products, with low energy flash heating producing tar or char. The importance of mineral impurities on pyrolysis also was stressed. Identified products were H_2O, CO_2, CO, two dozen volatile organic compounds, char, and tar (mainly levoglucosan). The higher energy flash heating (3000 cal/cm^2-s) produced virtually no tar or char. A mass balance on the reported products reveals that what Lincoln called "volatile organics" were in reality materials that had the overall empirical formula $CH_{1.24}$, which could have been 71% C_2H_2 and 29% C_2H_4 by volume. These values would represent 20.8 g C_2H_2 and 9.2 g C_2H_4 per 100 g cellulose. The mass spectrometer studies of directly emitted pyrolysis products gave evidence of short-lived intermediates not yet identified.

Berkowitz, Mattuck, and Noguchi (1963) used carbon arc radiation fluxes from 5 to 25 cal/cm^2-s to pyrolyze cotton cellulose in flowing helium. Products were classified into four ranges. Products boiling at -80 C, comprising 5% and 18% of the total at 5 and 20 cal/cm^2-s respectively, were CO, CO_2, CH_4, and C_2H_4. Products condensing between

Table 5-6. PRODUCT RESULTS IN FAST PYROLYSIS OF BIOMASS AND ITS CONSTITUENTS

Reference	Type and Form of Biomass	Rate of Heating	Maximum Temperature of Pyrolysis/ Gasification	Residence Time at Temperature	Environment	Approximate Wt % of Organics											
						Char	Tar	Gases	H_2	CH_4	C_2H_4	CO	CO_2	C_2H_6	C_3H_6	H_2O	Other
Section 5.3.1																	
Antal (1978, 79)	Whatman filter paper (cellulose) 0.125 g	100 C/min to 500 C min	700 C	3.5 s	Hot steam or argon	10	2	88	1.2	7.2	5.5	47.2	11.5	1.0	0.15		0.15
Section 5.3.2																	
Berkowitz-Mattuck and Noguchi (1963)	Cotton cellulose cloth	Carbon-arc radiant at	N A	1 s irradiation	Cold helium												
		5 cal/cm²-s				~20					0	~5	~0				a
		25 cal/cm²-s				~8					0.86	~7.3	~2.1				b
Martin (1965)	α-cellulose + 2% carbon black	Carbon-arc radiant at cal/cm²-s	N A	0.4 - 8 s irradiation	Cold helium												
		4.4				20-35											
		11.6 early		~1 s		4	80		~0.02	~0.02	~0.02	~3	~4			10	c
		11.6 late		~8 s		4	55		~0.5	~0.9	~0.9	~13	~10			15	d
		10^2 - 10^3				0											
Lincoln (1965)	α-cellulose + 2% carbon black	Carbon-arc & Xenon lamp			Cold helium												Volatile Organics
		1.5 cal/cm²-s	~300 C	10 s		33	19	48				3	9			32	3
		11.0 cal/cm²-s	>600 C	4 s		3	51	48	N A	N A	N A	13	11			16	6
		3,000 cal/cm²-s	>600 C	1/2 ms		1	0	99				37	4			28	30
Lewellen et al. (1976)	Cellulose filter paper 0.75 x 2.5 x 0.01 cm. strip	Electrically heated mesh 400-10,000 C/s	250 - 1000 C	0.2 - 75,000 s 400 C/s	Vacuum to 1 atm cold He	No Char		No gas analysis. Wt. loss versus time only.									
Hileman et al. (1976)	Douglas fir 1.5 mg samples	Pyroprobe at ~200 C/s	550 C	3-4 s	Cold argon or air					2.0	1.0	21	5.7	0.3	1.6	15.3	Propane 1.6 Many organics at 0.1-1% level
Section 5.3.31																	
Prahacs (1967)	Na, Ca, Mg-base spent liquors	Atomized spray into hot reactor	600-900 C 5-45 psig	11-100 s	Self-generated steam	Down to 3%			Up to 11%		Illuminants up to 7%						
Prahacs et al. (1971)	Bark, slash wood, and spent liquors	N A. Various reactors up to pilot scale	600-1000 C 0-25 psig	3-60 s	N^2 or self generated												
	Bark	Batch fed	810 C 0 psig	3.6 s				89.5			6.2				0.6		C_2H_2 0.9 Benzene 2.1 Toluene 0.3
Rensfelt et al. (1978)	Poplar wood	~1000 C/s	400-1000 C	~1 s	Steam, H_2					~5	~5 (optimized)						
Brink and Massoudi (1978)	White fir particles 20-40 mesh	~1000 C/s	316-871 C 843 C	3-5 s 3.0 s	N_2	2.5	7.1	92	~1	~10	~5	~62	~13				
Diebold and Smith (1979)	Ecofuel II, 200 μm	10^4-10^5 C/s	500-900 C	50-100 ms	Steam and CO_2	19			1	4	Unsaturates 24	36	16				
Section 5.3.4																	
Stern et al. (1965)	Sawdust 20-30 mesh	Fast	1000 C	long (steel) wool) (Alundum)	Self-generated	22.2	4.4	71.0	4.6	0.3	0	65.5	0.6		2.3		
						14.0	0.4	84.4	4.0	7.1	0.25	68.4	4.8		2.2		
Brink (1976)	Wood, MSW and Kraft Black Liquor	Probably Fast	(475-1125 C) 850 C	Uncertain	6.5% moisture wood				1.8	11.2	7.0	73.0	13.2		45		
					52.5% moisture wood				3.8	7.2	4.2	47.7	35.2				
						Char	Tar	Gases	H_2	CH_4	C_2H_4	CO	CO_2	C_2H_6	C_3H_6	H_2O	Other

[a] Tar fraction, mainly levoglucosan.
[b] Variety of polar organics boiling below 187 C
[c] Acetaldehyde 0.45; acrolein 0.15 acetone, furan, methanole ~0.7.
[d] Acetaldehyde 1.3, acrolein, acetone 0.25 methanol, furan 0.15.

-80 C and room temperature comprised a dozen or so polar organics with boiling points between 14 C and 178 C, including H_2O, acetic acid, acetone, formic acid, formaldehyde, glyoxal, glycolic acid, lactic acid, and dilactic acid. The tar-like material condensing at room temperature was mainly levoglucosan. Chars, constituting about 20% and 10% at fluxes of 7 and 20 cal/cm^2-s respectively, were not characterized.

It was observed that the fast pyrolysis and slow pyrolysis produce similar kinds of products though yields may be very different.

Martin (1965) used a carbon arc to fast pyrolyze α-cellulose containing 2% carbon black (absorptivity 90%) and 0.15% ash. Pyrolysis products were swept away in helium directly to a gas chromatograph. Irradiation at 4.4 and 11.6 cal/cm^2-s for 0.4 to 8 s was used. Heating rates of the cellulose varied with depth of the rather thick specimens used. At the higher irradiation level only 4% char remained. Initially CO, CO_2, H_2O, and tar (mainly levoglucosan) are formed, with subsequent conversion of the tar to acetaldehyde, acrolein, acetone, furan, methanol, methane, ethylene, and H_2 as secondary products postulated to arise from the further cracking of the tar at the char layer. At 100 to 1,000 cal/cm^2-s no char is produced. Martin concluded that levoglucosan is the principal pyrolysis product.

Hileman et al. (1976) used rapid heating of 1.5-mg samples in a commercial pyrolyzer (Pyroprobe) coupled with the most sophisticated gas analysis equipment reported to date for such studies. Samples were heated in streams of Ar gas or air to 550 C in 3 to 4 s, with direct coupling to either a chemical ionization mass spectrometer or a gas chromatograph-mass spectrometer. Materials studied were Douglas fir, α-cellulose, and Bolker lignin, at estimated heating rates of 200 C/s. Tables of products are shown, with no single organic species dominating. At 400 C, fast pyrolysis gave the same product distributions as pyrolysis at 45 C/min. Also, fast pyrolysis at 400 C in air gave the same results as in argon. No levoglucosan is reported in the products, perhaps because it condensed before entering the mass spectrometer. Whether the Pyroprobe involves contact with metal and the possibility of catalytic effects is not known to us. The products of pyrolysis of lignin were deduced by subtracting the products of cellulose from those observed in wood. These derived products showed no resemblance to those produced by direct pyrolysis of an isolated lignin, raising questions about the effects of isolation and about the material interactions of components in pyrolyzing wood.

5.3.3 Fast Pyroloysis, Short Residence Time

In a number of studies both rapid heating and short residences times were employed in a single step pyrolysis/re-forming/gasification.

Allan and Mattila (1971) quote results of Goheen and Henderson on the extremely high-temperature pyrolysis of lignin. They blew powdered lignin, Douglas fir, and cellulose in He into an electric arc, achieving in each case about 14% conversion to C_2H_2. With a tungsten coil at 2000 C to 2500 C, 23% C_2H_2 was produced. In a small pilot plant as much as 40% C_2H_2 was formed but only about 12% could be quenched during extraction. It is possible that such extreme, costly heating conditions are reflecting very high temperature equilibrium compositions rather than pyrolysis kinetics. In fact, C_2H_2 is seldom reported in pyrolysis studies at lower temperatures. Recently plasma arc reduction of biomass has been reported (Brown 1979) as well as pyrolysis in microwave induced plasmas (Krieger et al. 1979).

Prahacs et al. (1971) pyrolyzed bark, slash, fir, pine, and various pulping liquors in several reactors. Conditions were: 0 psig to 25 psig; 600 C to 1000 C; residence times, 3 to 60 s. The exact conditions of heatup of particles and sprays are not given but probably exceed 100 C/s. Results of hydrocarbon gas production are shown as a function of operating variables. In general, although conversions were fairly low, olefins increased with increasing dilution in steam, with decreasing pressure, and with decreasing residence time. An optimal temperature existed for each set of other pyrolysis conditions. Bark gave a little more ethylene than α-cellulose and much more than black liquors. Investigation of continuous pyrolysis systems was recommended.

Prahacs (1967) reports pyrolysis results in an "atomized suspension technique" reactor in which pulping liquors are sprayed into a 1-ft diameter by 15-ft high reactor. Temperatures of 600 C to 900 C, pressures of 5 psig to 45 psig, water/organics ratios of 1.2 and 2.4, and residence times of 11 to 100 s were studied. The size distribution of the spray was not given, but it is assumed that heatup rates were quite fast. Ethylene and acetylene were maximized in Mg-based liquors while H_2 was maximized in Na-based liquors, presumably due to catalytic destruction of pyrolysis intermediates in the latter case.

Rensfelt et al. (1978) pyrolyzed powdered (500 μm) wood, peat, and municipal solid waste (MSW) in a vertical quartz tube in a furnace at 500 C to 1000 C. Heating rates of 1000 C/s were estimated with residence times of less than a second possible. Similar results were obtained in N_2, steam, and H_2. CH_4 and C_2H_4 production from MSW and wood are comparable. The results are interpreted as showing the importance of secondary reactions of the primary heavy hydrocarbons produced during rapid heating. For wood heated to 800 C, 70% conversion to gas occurs in 0.7 s.

Brink and Massoudi (1978) pyrolyzed fir-wood particles (400 μm to 840 μm) in a N_2 flow in an entrained flow furnace reactor. Suspension densities of 0.05 to 0.5 g/l were tested at 316 C to 871 C and residence times of 3 to 5 s. Calculations show that the largest particles reach 80% of the reactor temperature in 0.4 s. H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, char, and tar are shown as a function of system variables.

Kuester (1978) has obtained high olefin yields in a dual-fluidized bed pyrolysis reactor while Mallon (1974) reports the flash pyrolysis of a municipal solid waste rich in plastics.

Diebold and Smith (1979), using ECO FUEL-II in an entrained flow reactor, have obtained the most spectacular olefin production so far reported (see Table 5-6). The 250 μm powder (composition not reported but derived from MSW in a proprietary chemical comminution process) was entrained as a dilute phase in steam or CO_2, passing through a 1.9-cm diameter, 2- to 6-m long, externally flame heated tube in 50 ms to 150 ms. Heating rates of 10^4 C to 10^5 C/s are estimated. Gaseous products are shown as a function of temperature, residence time, and dilution. The latter parameter is especially important in olefin production. Under optimal conditions, from 700 C to 860 C, short residence time, and high degrees of dilution C_2+ hydrocarbons were 24% of the feedstock (by weight) and contained 53% of the original feedstock energy. Experiments are underway to test cellulose, lignin, and wood in this reactor to determine to what extent the olefin yields are an anomaly of the ECO FUEL-II, possibly due to the plastics content of the municipal solid waste from which ECO FUEL-II is derived (Diebold 1979).

Shock tube studies on biomass dust may provide information on pyrolysis (Lester 1979) as may the mostly older literature on dust explosions.

5.3.4 Fast Pyrolysis, Long Residence Time

Stern et al. (1965) pyrolyzed 20 to 30 mesh sawdust by dropping the material continuously on a packed bed of steel wool or Alundum maintained at 1000 C. The gases were forced through the bed and collected for analysis. Heating rates are probably fast, but residence times for secondary reactions are probably long. The steel wool experiments gave mainly H_2 and CO in 1:1 ratio at 1000 C, while the Alundum gave significant CH_4 yields but only a trace of C_2H_4.

Brink (1976) reports pyrolysis results for wet and dry wood, wet MSW, and Kraft black liquor. The exact reactor conditions are not given in this report nor are the particle size, heatup rate, or residence time. (Presumably, these are available in the primary references.) Gaseous compositions are given from 475 C to 1125 C, in some cases showing significant C_2H_4 yields.

Moderate olefin yields and large benzene yields were reported by Barber-Coleman (1975) in pyrolysis of simulated solid waste on a molten lead bath. An interesting study, the conditions of which are hard to classify, was carried out by Sanner et al. (1970), yielding moderate ethylene conversion from wet solid waste.

Table 5-6 presents an overview of typical product compositions for many of the above cited studies. It may be concluded that fast pyrolysis, coupled with dilute-phase, high-temperature, short residence time, secondary reactions can yield large quantities of olefins. Several of the cited studies continue to be active and new results can be expected to further shed light on the sequence of pyrolysis secondary reactions for a variety of biomass materials and components.

CONCLUSIONS

From all the evidence cited it appears that the products of primary pyrolysis are a sensitive function of physical size and state of the material, inorganic impurities, heating rate, and final temperature. Gaseous environment seems to be relatively unimportant. Secondary reactions are a function of contact with char, temperature, pressure, dilution, and residence time, with gaseous environment again perhaps secondary (air excluded). The "ideal" fast pyrolysis/gasification study should permit time resolved measurement of both the residue and gaseous species during the entire course of the reaction, with millisecond time resolution, in a realistic gaseous process environment at pressure and with particle sizes and loadings of practical interest. SERI's own approach to this ideal will involve coupling a high-pressure, free-jet, molecular beam, mass spectrometric sampling system with some form of entrained-flow laboratory reactor (Milne and Soltys 1979).

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SERI

Chapter 6

Thermodynamics of Gas-Char Reactions

R. Desrosiers
SERI

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CHAPTER 6

THERMODYNAMICS OF GAS-CHAR REACTIONS

6.1 INTRODUCTION

The products of the pyrolytic reactions described in Chapter 5 do not conform to chemical equilibrium because gas phase reactions are very slow below 500 C. However, at temperatures above about 500 C, chemical equilibrium is approached fast enough so that thermodynamic calculations can predict important trends and in some cases the gas compositions to be expected.

The temperatures, residence times, and gas-solid contacting methods employed in gasification equipment strongly affect the degree of attainment of equilibrium. In downdraft fixed bed gasifiers, products of pyrolysis and combustion are drawn over a bed of charcoal at temperatures between 700 and 1000 C and approach equilibrium closely. In updraft fixed bed gasifiers, initial combustion gases also filter through a hot char bed, but then they are mixed with the products of low temperature pyrolysis and the exit gas analysis bears little relation to equilibrium. The uniformly high temperatures in a fluidized bed offer favorable conditions for equilibrium, but the degree attained depends on gas residence time.

Reliable predictions of product compositions for any gasifier may be obtained only from a detailed kinetic model for that reactor incorporating global reaction rates, which may be strong functions of gas velocities, particle sizes, etc. These kinetic restrictions limit the quantitative significance of an equilibrium calculation; nevertheless, such an exercise is of considerable predictive value in estimating the effects of changes in the major thermodynamic variables: temperature, pressure, and composition.

In this chapter, the results of equilibrium calculations are presented which illustrate the predicted effects of temperature, pressure, feed moisture content, and oxidant/fuel ratio on gasifier performance; the results have been plotted and are discussed in detail below. The purpose of the discussion is not to present an exhaustive parametric study but to extract as much information as possible from a set of salient examples.

6.2 MAJOR PROCESSES AND REACTIONS

The processes occurring in any gasifier are oxidation, reduction, pyrolysis, and drying. The unique feature of the updraft gasifier is the sequential occurrence of these processes: they are separated spatially and therefore temporally. For this reason, the operation of an updraft gasifier will be used in the following discussion. The reaction zones and a schematic temperature profile for an updraft gasifier are illustrated in Fig. 6-1. Several reactions of importance in char gasification are listed in Table 6-1.

In the lowest zone, oxidation of char with oxygen occurs; the heat released here drives subsequent processes. In this zone, the oxygen pressure is high enough to favor CO_2 formation. This reaction (e) is very fast, probably being mass-transfer limited, and the thickness of this zone may vary in magnitude from one to tens of centimetres.

The gas stream issuing from Zone One is hot and rich in CO_2 (and H_2O if the blast contains steam). The high temperatures favor, kinetically and thermodynamically, the

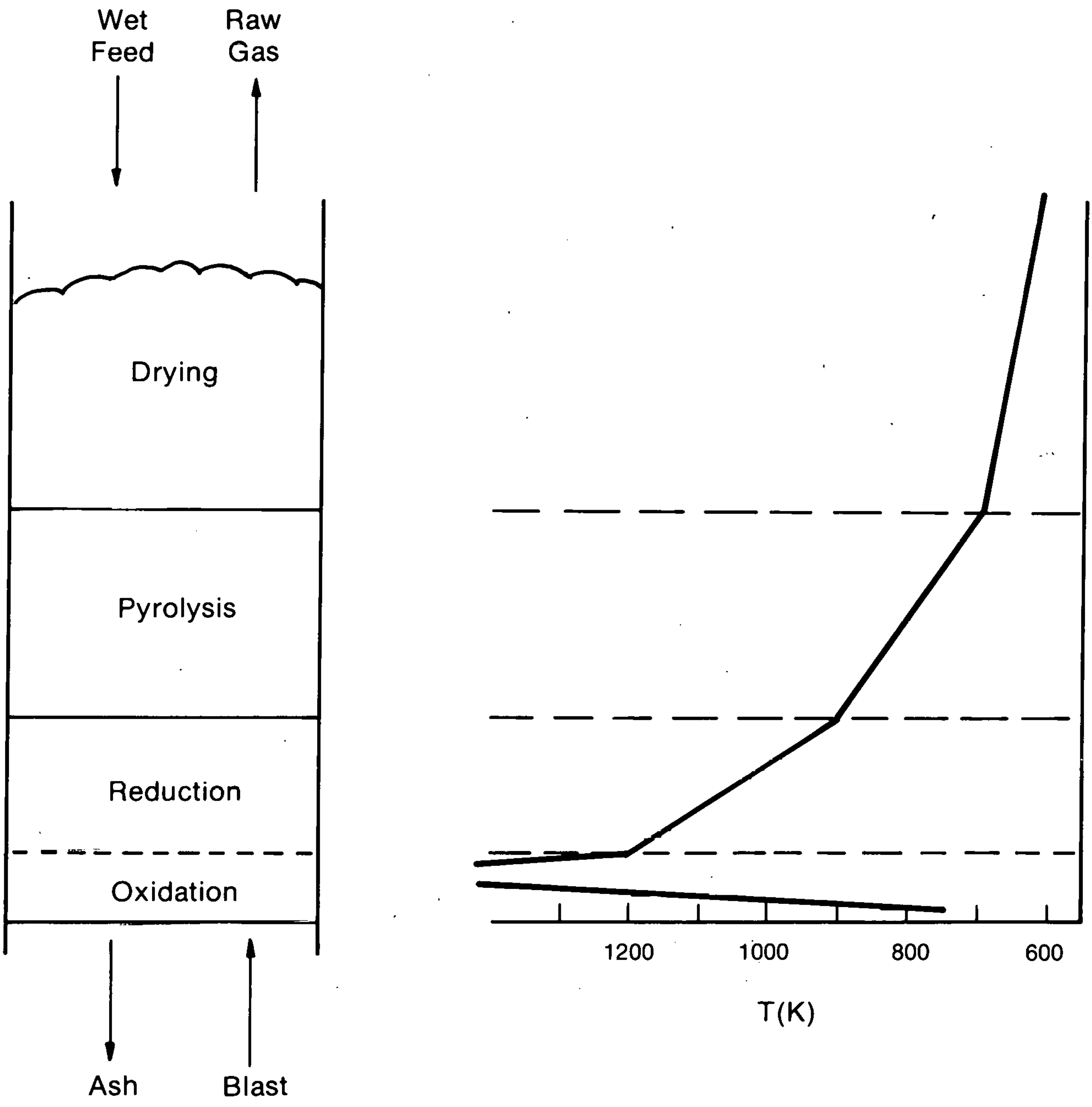


Figure 6-1. Major Processes Occurring in an Updraft Gasifier

Boudouard (d) and water-gas (c) reactions which are highly endothermic. These control the upper limit of temperature in the reduction zone. (A dramatic example of this effect has been observed in a downdraft gasifier. If pure oxygen is used in the blast, the temperature does not rise more than a hundred degrees or so above that for the air blast except in the immediate vicinity of the tuyeres.)

This temperature stabilization phenomenon may be explained with reference to Fig. 6-2 in which the log of the mass action expression (Q)* for the reactions (1) through (4) is plotted against the reciprocal of temperature.

In Fig. 6-2 (a), consider a point near the intersection of curves (b), (c), (d). If the system attempts to attain a temperature higher than this, then the endothermic reduction reactions (c), (d) are thermodynamically favored and begin to moderate the temperature. These reactions are too slow to be controlling, however, until the temperature nears 1400 K. Above this temperature, they constitute an effective energy sink and limit further rise in temperature. Conversely, the exothermic methanation reaction could provide a temperature floor for the reduction zone of a fixed bed gasifier. However, this reaction is probably too slow to be important in controlling bed temperature. Figure 6-2 (b) illustrates the effect of increased pressure, which is to raise the level of the "stable" temperature interval.

Table 6-1. IMPORTANT REACTIONS IN GASIFICATION

		H (kJ/mole)	
	Reaction	298 K	1000 K
(a)	$CO + H_2O = CO_2 + H_2$	-41.2	-34.77
(b)	$C + 2H_2 = CH_4$	-74.93	-89.95
(c)	$C + H_2O = CO + H_2$	131.4	136.0
(d)	$C + CO_2 = 2CO$	172.6	170.7
(e)	$C + O_2 = CO_2$	-393.8	-394.9

As the gases rise beyond the reduction zone, they come into contact with cooler, solid feed. The temperature falls below 900 K and the reduction and shift reactions are frozen. The gas composition at this point may be reasonably close to the equilibrium com position for some temperature within the reduction zone.

---

[*] For reaction $\Sigma \nu_i X_i = 0$ among ideal gases X_i, we have

$$K = P^{\nu} \Pi y_i^{\nu_i} = P^{\nu} Q$$

$$\text{or } \log Q = \log K - \nu \log P$$

where

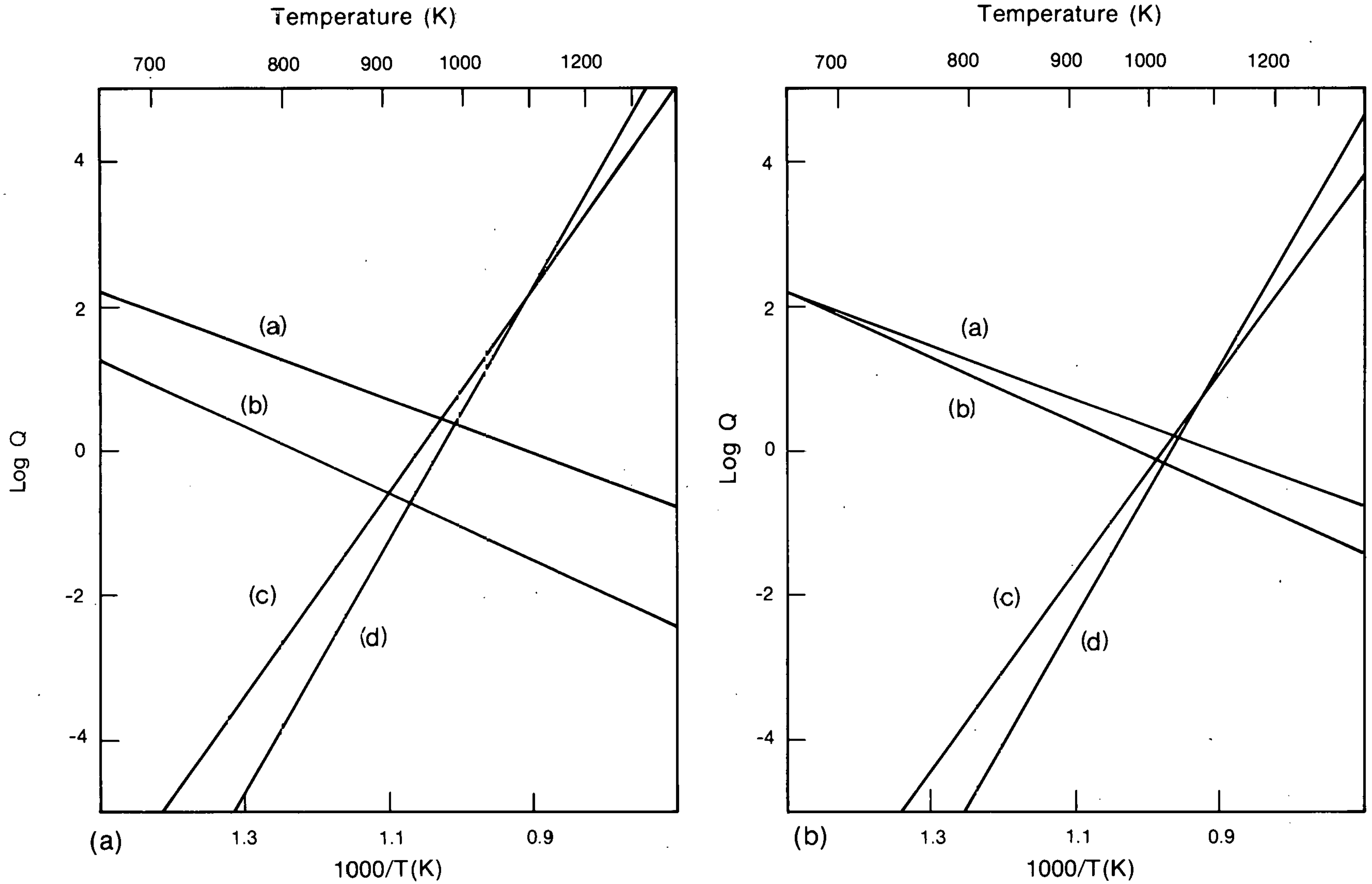
$K = K(T)$ equilibrium constant

$Q = Q(P,T)$ mass action quotient

ν_i = stoichiometric coefficient

$\nu = \sum_{\text{gases}} \nu$

y_i = mole fraction



(1) $CO + H_2O = CO_2 + H_2$ (2) $C + 2H_2 = CH_4$

(3) $C + H_2O = CO + H_2$ (4) $C + CO_2 = 2CO$

Figure 6-2. Mass Action Quotient Vs. Reciprocal Temperature for Gasification Reactions at (a) 1 and (b) 10 atm

The partially dried feed above the char bed is pyrolyzed by the rising, hot gas stream; the immediate products are low molecular weight hydrocarbons, alcohols, acids, oils, and tars, as well as CO, H_2, CO_2, H_2O, and CH_4. The hydrocarbons undergo cracking and re-forming to H_2, CO, and CO_2. The temperature near the top of the bed is too low for this re-forming to be completed, and the raw gas stream exiting the reactor is laden with products which are not characteristic of the equilibrium established in the reduction zone or of the primary pyrolysis products.

The downdraft gasifier is operated so that the final gas-solid contact is one involving hot char rather than volatile-laden feed, and a near-equilibrium product distribution is achieved. The degree to which other types of gasifiers approach equilibrium is related to residence time. Thus, a fluidized bed with recycle can approach equilibrium very closely while equilibrium concepts may have no relation to a fast pyrolysis process with millisecond residence times.

6.3 THE EQUILIBRIUM CALCULATION

The equilibrium calculations were made using a computer program called "GASEQ". The algorithm is based on that developed by D. R. Cruise (1964) at the Naval Ordnance Test Station at China Lake. A large thermodynamic data file compiled from the JANAF (Stull and Prophet 1971) tables is required. The program will "burn" any feed for which a composition is specified. All gaseous products are assumed to behave ideally, and all condensed products are treated as pure phases. The user can specify the temperature or allow an iterative calculation of the adiabatic flame temperature; in the latter case, a heat of formation for the feed must be supplied. Usage of the program is described in detail in Desrosiers (1977).

The calculations were based on the typical analysis for dry, sulfur- and ash-free wood shown in Table 6-2.

In each calculation the following species were considered as possible products:

H, H_2
N, N_2, NH_3, NO, NO_2, CN, HCN
O, O_2, H_2O, OH
C, CO, CO_2, CH_4, C_2H_2, C_2H_4, CH_2O
C_s

No attempt was made to model "char" or "tar". Carbon (as graphite) was the only solid product considered. For all conditions investigated, the only products present in significant amounts ($>10^{-4}$ mole %) were C_s, H_2, H_2O, CO, CO_2, CH_4, and N_2. It is important to note that no hydrocarbon other than CH_4 is thermodynamically stable under gasification conditions. Acetylene, ethylene, and higher hydrocarbons (as well as oils and tars) are produced by most gasifiers: these are nonequilibrium products. A gasifier can be designed to inhibit or promote the production of these materials, and this behavior may be correlated roughly with residence time and temperature in the pyrolysis and reduction zones.

Table 6-2. **TYPICAL ANALYSIS FOR DRY SULFUR- AND ASH-FREE WOOD**

Composition	C	52.50wt %		
	H	6.16		
	O	41.24		
	N	0.10		
High Heating Value (HHV)[a]		-22.21	kJ/g	(-9550 Btu/lb)
Low Heating Value (LHV)		-20.9	kJ/g	(-8987 Btu/lb)
Heat of Formation		- 3.74	kJ/g	(-1609 Btu/lb)
Formula				
C_6 basis	$C_6H_{8.39}O_{3.54}N_{0.1}$	(FW = 137.27)		
C_1 basis	$C\,H_{1.4}\,O_{0.59}\,N_{0.017}$	(FW = 22.86)		
Stoichiometric Oxidant Ratio				
Molar O_2/dry wood C_1 basis		1.055		
Weight O_2/dry wood		1.476		
Weight air/dry wood		6.364		

[a] HHV (LHV) = Heat of Combustion with product water in liquid (vapor) form.

$$\text{LHV (kJ/g)} = \text{HHV (kJ/g)} - 0.2122 \times \text{wt \% H}$$

6.4 RESULTS

The calculations are organized into five related sets in which the effects of one or two variables are investigated. The results are presented visually in the form of plots; each plot is described separately. The entire set of plots for a series immediately follows the discussion in the text.

6.4.1 Series 1 — Pyrolysis, Gasification, and Combustion Partitioned by the Equivalence Ratio

A concept widely used in the study of hydrocarbon fuel combustion is the equivalence ratio (ER), which is defined as the oxidant to fuel weight ratio divided by the stoichiometric ratio. Thus ER must be greater than or equal to 1.0 for complete combustion of the fuel to carbon dioxide and water. The equivalence ratio is used here to describe wood pyrolysis, gasification, and combustion. Complete combustion of wood (as defined in Table 6-2) with oxygen requires 1.476 g O_2/g wood or 6.364 g air/g wood.

The first series of plots introduces the kind of information which is readily calculable from the equilibrium composition. The results of 20 calculations for an adiabatic system of dry wood with varying quantities of air are illustrated in Figs. 6-3 (a) through 6-3 (e). Along the abscissa in each case is plotted the equivalence ratio:

$$\mathrm{ER} = \frac{\text{weight oxidant/weight dry wood}}{\text{stoichiometric oxidant/wood ratio}}$$

The curve in Fig. 6-3 (a) is the adiabatic flame temperature (AFT) as a function of equivalence ratio. The intersection with the axis at ER = 0 occurs at 913 K (640 C). This point corresponds to pyrolysis, the reaction of wood in the absence of oxygen. Notice that as air is added to an ER of 0.255 (1.62 g air/g wood) the AFT rises very slowly from 913 K to 1025 K. As air is added beyond this point, however, the AFT rises dramatically to combustion temperatures (2300 K). This break in the curve corresponds to the point at which carbon disappears. Carbon formation in g/g dry wood is plotted in Fig. 6-3 (b). (Note the expanded scale for ER). Since carbon is the only condensed product formed, the gas production in g/g dry wood is obtained easily from

$$\text{Gas production (g/g dry wood)} = 1 + \text{ER X (stoich. oxidant ratio)} - C_s \text{ formation}$$

The dry gas composition appears in Fig. 6-3 (c). The curves for each component display an extremum or an inflection point at ER = 0.255.

The reaction corresponding to the calculated product distribution at ER = 0 (pyrolysis) is:

$$CH_{1.4}O_{0.59} = 0.64C_s + 0.44H_2 + 0.15H_2O + 0.17CO + 0.13CO_2 + 0.005\ CH_4$$

For a point just beyond the carbon stability region at ER = 0.275 (gasification), the stoichiometry is:

$$CH_{1.4}O_{0.59} + 0.29O_2 + 1.1N_2 = 0.63H_2 + 0.07H_2O + 0.90CO + 0.10CO_2 + 1.1N_2$$

Further addition of air results in consumption of H_2 and CO until combustion conditions are approached at ER = 1.0:

$$CH_{1.4}O_{0.59} + 1.05O_2 + 3.99N_2 = 0.15H_2 + 0.67H_2O + 0.11CO + 0.89CO_2 + 3.99N_2$$

The low heating value (LHV) of the dry gas is plotted in Fig. 6-3 (d). The initial rapid decrease in LHV correlates with the disappearance of CH_4. Beyond ER = 0.255, the LHV approaches zero as CO and H_2 are consumed. [To convert from Btu/SCF (60 F, 1 atm) to MJ/Nm^3 (0 C, 1 atm), divide by 25.39].

The three curves in Fig. 6-3 (e) illustrate the variation of chemical, sensible, and total energy in the gas. The chemical energy stored in the gas is maximal at ER = 0.255, corresponding to complete carbon uptake. This is the point at which one should operate an air-blown gasifier. (Note that in most of the figures, calculated points are simply connected by straight lines. The gas composition data were interpolated in some cases to yield smooth curves).

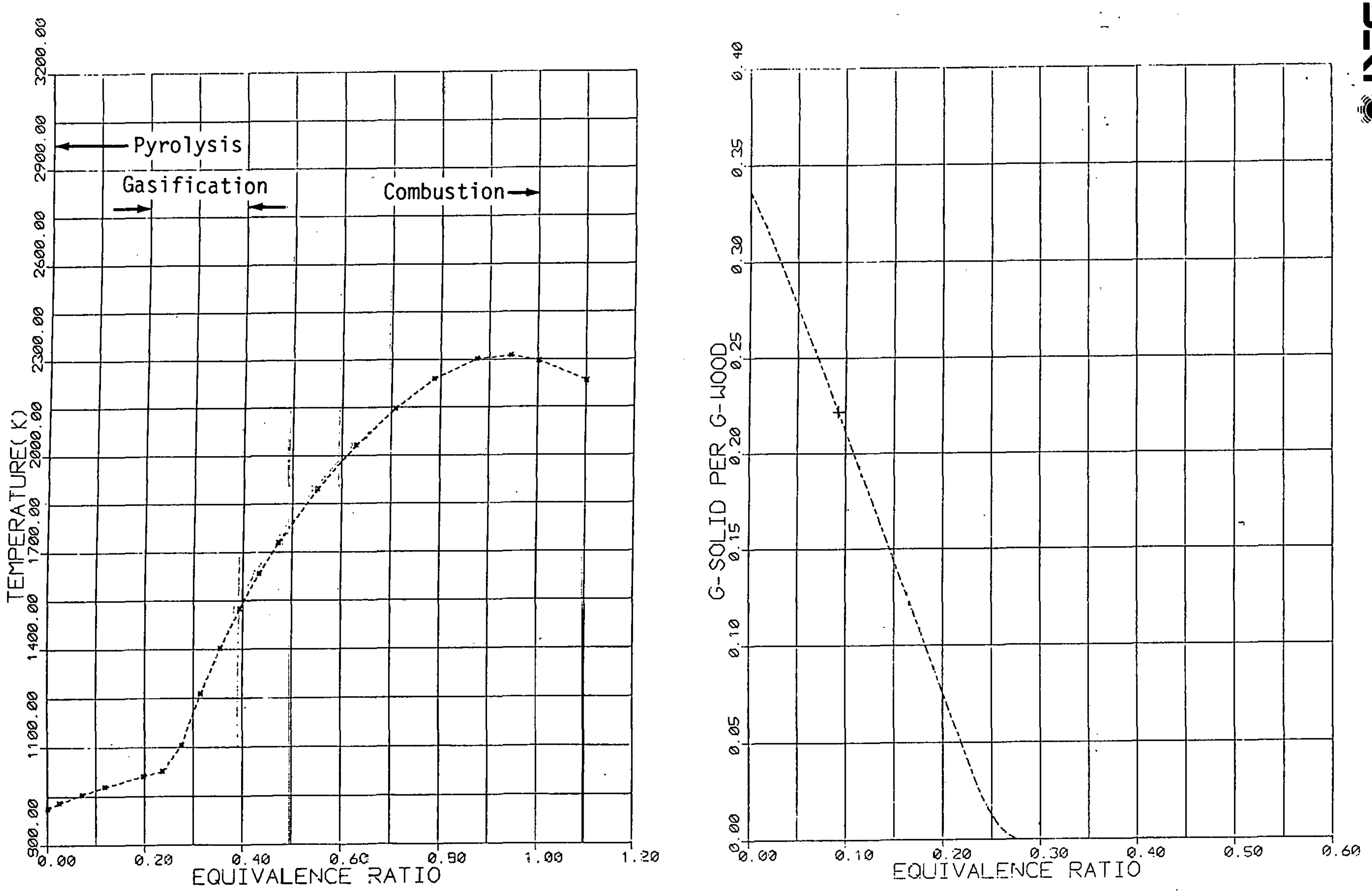
The AFTs for a variety of systems are plotted in Fig. 6-4. (The lines appear more broken because fewer points were plotted.) Curve f is the AFT for air. The more dramatic temperature rise with oxygen (a) is readily apparent for ER = 0.26 and higher. The very small AFT difference (<150 K) for equivalence ratios below 0.26 is a consequence of the temperature stabilizing reduction of CO_2 and H_2O in the presence of hot carbon. This effect is extended to higher ER values by the addition of excess char, as illustrated by curve e (Fig. 6-4).

Curves a, b, c (Fig. 6-4) correspond to oxygen gasification of dry wood at 0, 100, 300 psig (1, 6.8, 20.4 atm). In the combustion region (high ER) significant temperature differences are observed. In the region of interest, gasification (ER = 0.2 to 0.3), however, negligible changes in AFT are induced by a twentyfold change in pressure. In fact, the dry gas compositions for oxygen gasification at 1 atm and at 300 psig [Figs. 6-8 (b,d)] can almost be superimposed for ER < 0.50. Pressure has a negligible effect on the gasification of dry wood. Curves d and g (Fig. 6-4) are AFT versus ER profiles for the adiabatic gasification of wet wood. The lowering of both pyrolysis and combustion temperatures is significant as expected.

The carbon formation curves d, f (Fig. 6-5) for these two cases illustrate the extreme effect of water addition on carbon consumption.

The LHV and energy distribution curves for the cases of oxygen/air gasification of dry wood and oxygen with wet wood are plotted in Figs. 6-6 and 6-7. Curve b for wet wood initially lies above curve a for dry wood due to enhanced methane formation at the lower temperatures. Beyond ER = 0.15, however, the LHV for wet wood is lowered due to shifting of CO to CO_2 with added water. (The LHV is calculated for the dry gas composition.) The initial increased uptake of carbon with added water results in more chemical energy being stored in the gas (curve c, Fig. 6-7).

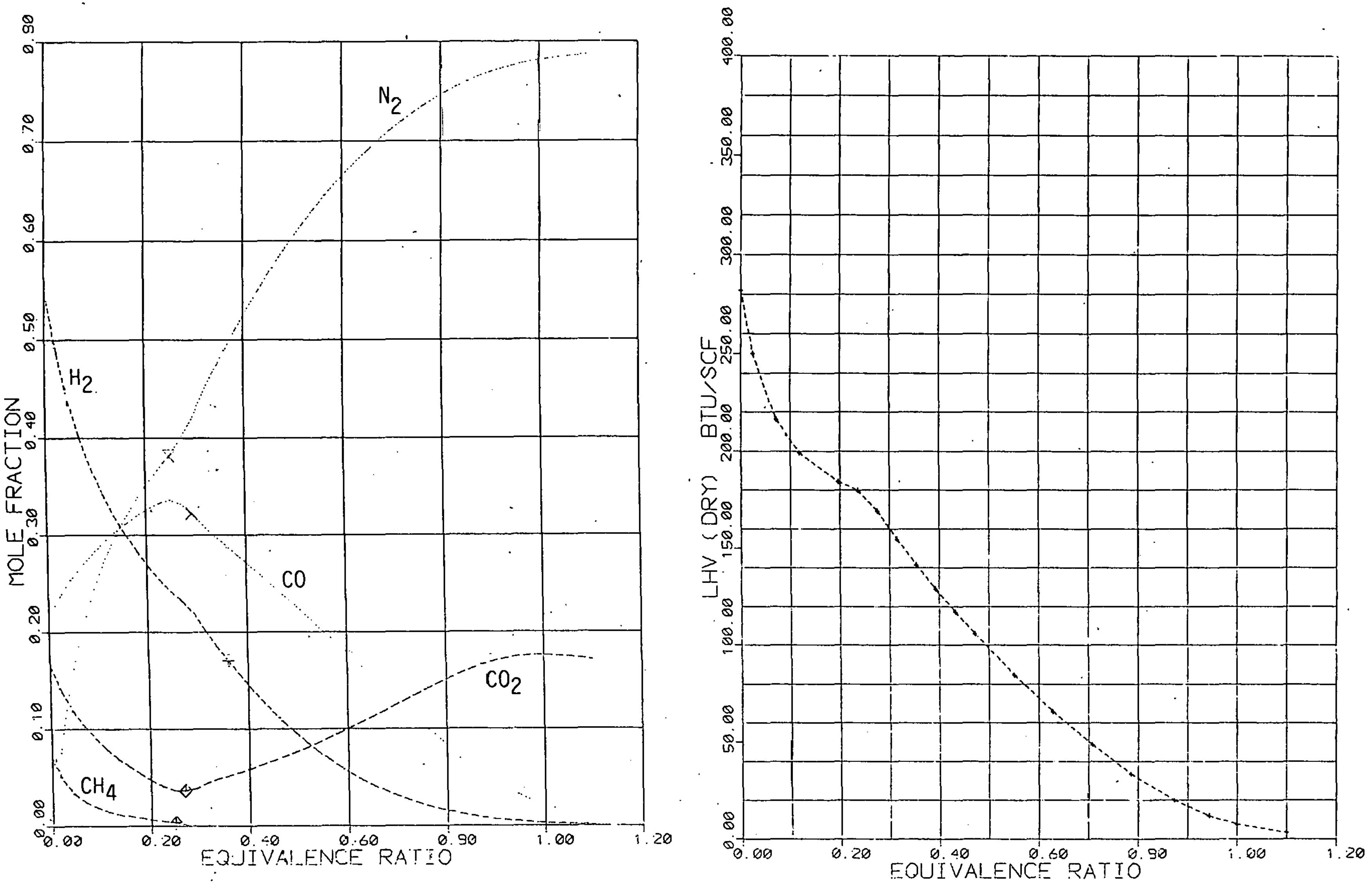
The dry gas compositions for four of the cases discussed above appear in Figs. 6-8 (a) through 6-8 (d). (Dry gas compositions are more easily compared with the gas analyses reported by investigators.) Stoichiometric reactions for some cases are listed in Table 6-3. The extent of water formation, which is not apparent in the gas composition plots, is readily inferred from the table.



(a) Adiabatic Flame Temperature

(b) Carbon Formation

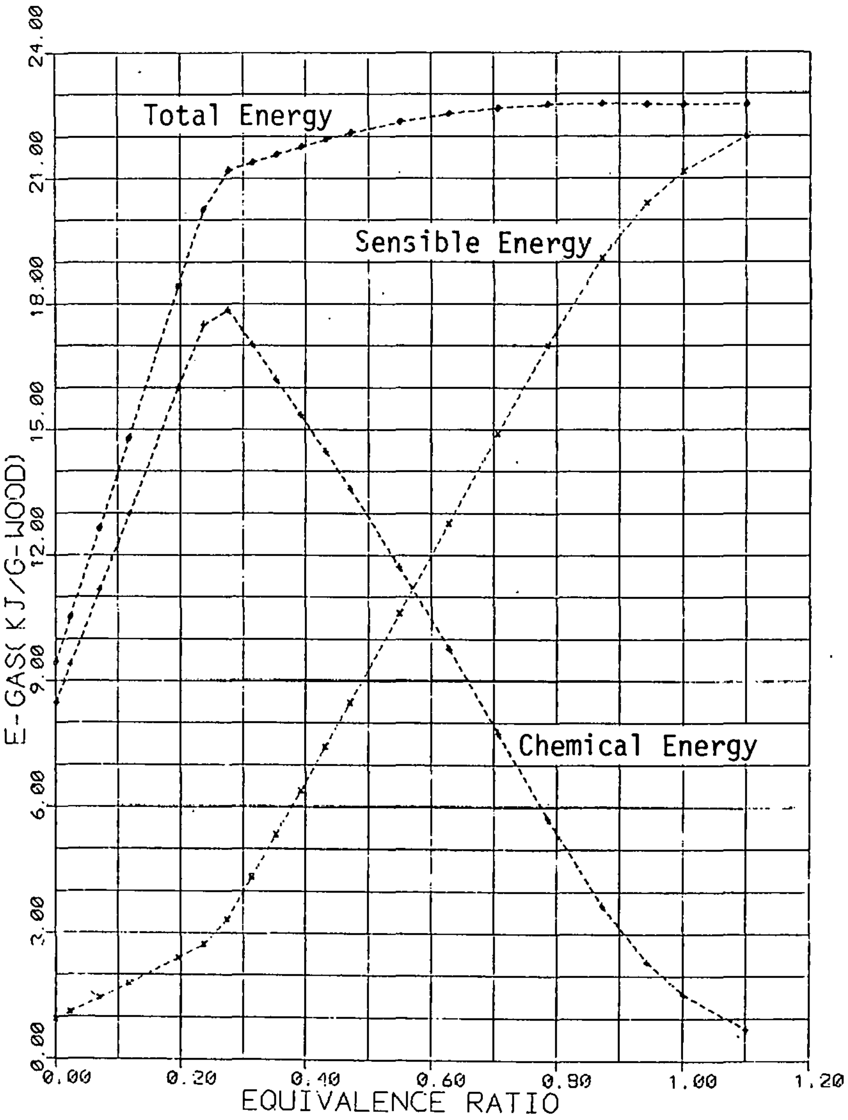
Figure 6-3. Adiabatic Air Gasification of Dry Wood at 1 atm



(c) Dry Gas Composition

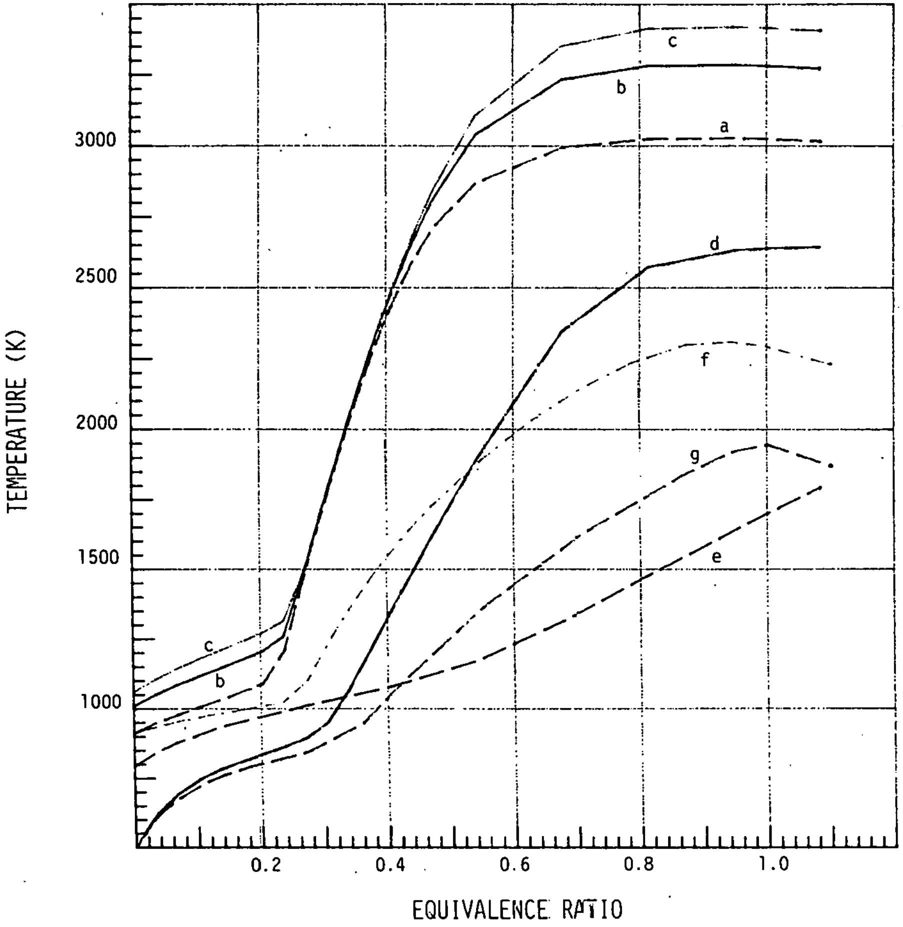
(d) Low Heating Value

Figure 6-3. Adiabatic Air Gasification of Dry Wood at 1 atm



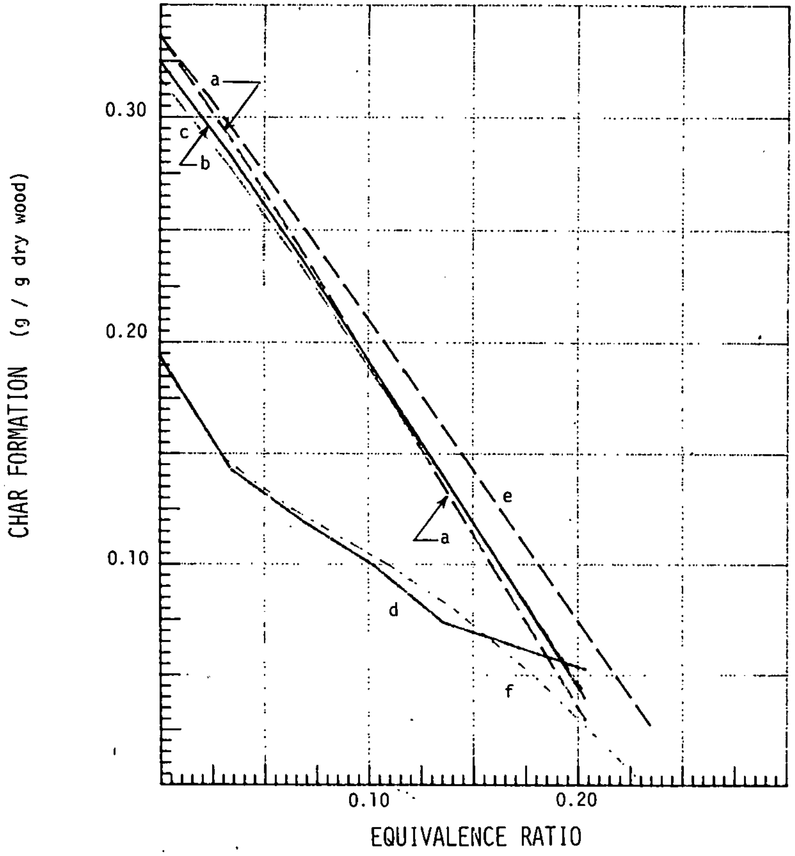
(e) Energy in Product Gas

Figure 6-3. Adiabatic Air Gasification of Dry Wood at 1 atm



	a	b	c	d	e	f	g
Oxidant	O_2	O_2	O_2	O_2	O_2	Air	Air
Pres. (psig)	0	100	300	0	0	0	0
Water (g/g)	0	0	0	.80	0	0	.80
Added Char (g/g)	0	0	0	0	2.00	0	0

Figure 6-4. Adiabatic Flame Temperature Vs. Equivalence Ratio



	a	b	c	d	e	f
Oxidant	O_2	O_2	O_2	O_2	Air	Air
Pres. (psig)	0	100	300	0	0	0
Water (g/g)	0	0	0	.80	0	.80

Figure 6-5. Char Formation Vs. Equivalence Ratio

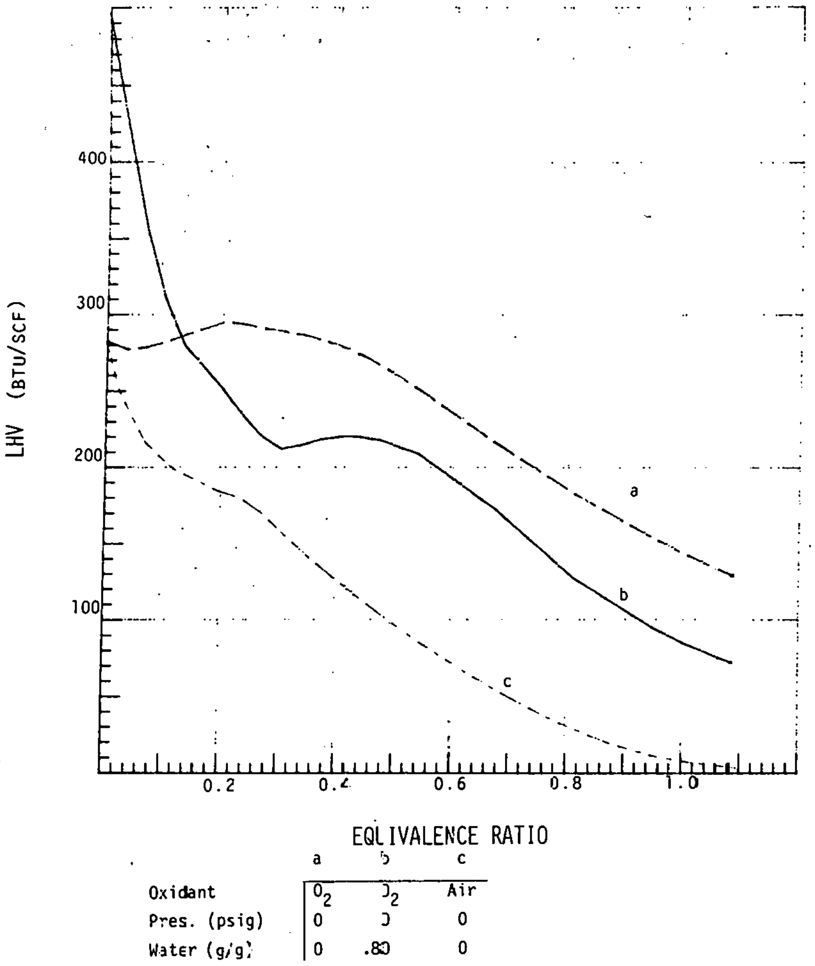


Figure 6-6. Low Heating Value Vs. Equivalence Ratio

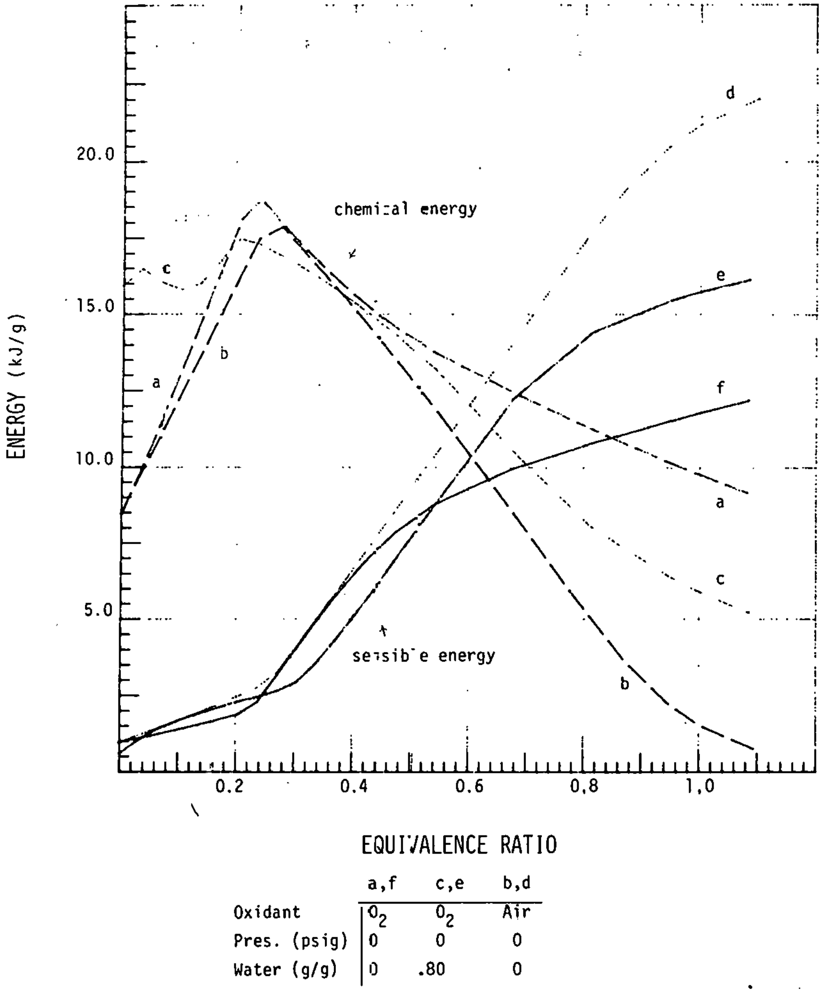
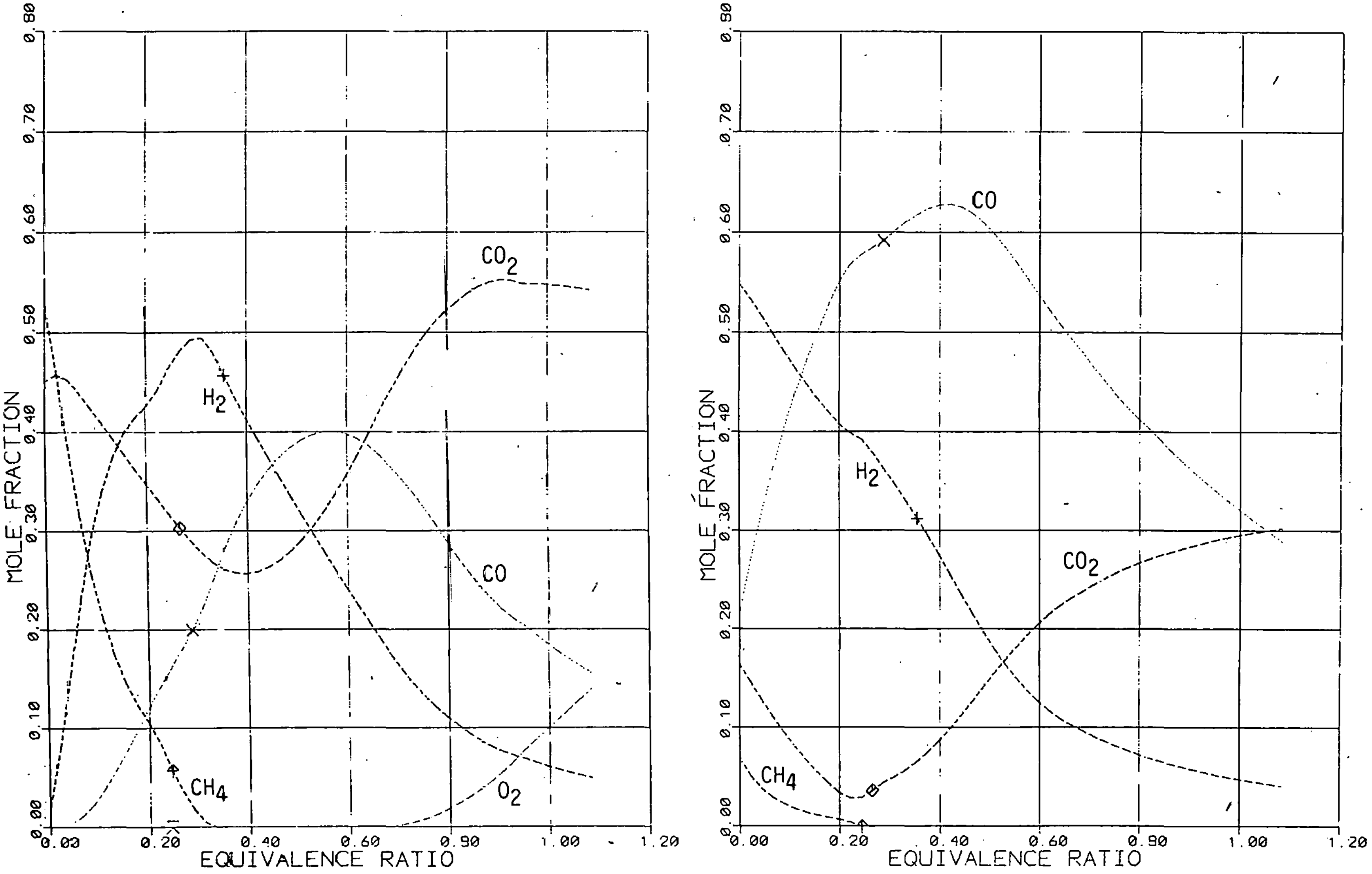


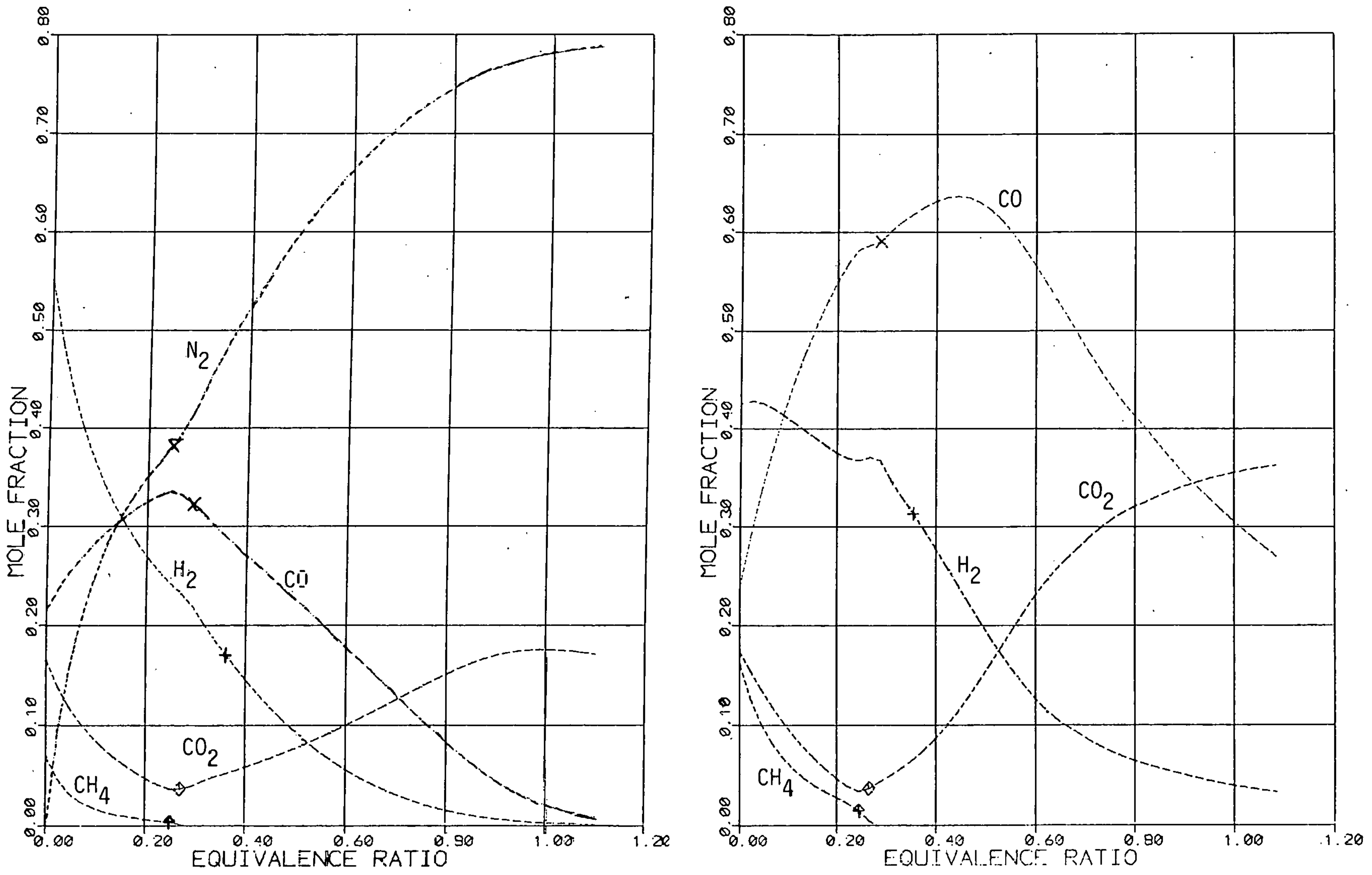
Figure 6-7. Energy Distribution Vs. Equivalence Ratio



(a) Oxygen Gasification of Wet (80%) Wood at 1 atm

(b) Oxygen Gasification of Dry Wood at 1 atm

Figure 6-8. Dry Gas Composition Vs. Equivalence Ratio



(c) Air Gasification of Dry Wood at 1 atm

(d) Oxygen Gasification of Dry Wood at 300 psig

Figure 6-8. Dry Gas Composition Vs. Equivalence Ratio

Table 6-3. ADIABATIC REACTIONS OF WOOD UNDER PYROLYSIS AND GASIFICATION CONDITIONS

$$CH_{1.4}O_{0.59} + yO_2 + zN_2 + wH_2O = x_1C_s + x_2H_2 + x_3H_2O + x_4CO + x_5CO_2 + x_6CH_4 + x_7N_2$$

Oxidant	Pressure (psig)	Water (g)	ER	T (K)	y	z	w	x_1	x_2	x_3	x_4	x_5	x_6	x_7
O_2	0	0	0	913	0	0	0	0.64	0.44	0.15	0.17	0.13	0.005	0
O_2	0	0	0.1016	1005	0.11	0	0	0.36	0.57	0.08	0.52	0.11	0.023	0
O_2	0	0	0.2709	1497	0.29	0	0	0	0.60	0.10	0.94	0.062	0	0
Air	0	0	0.2750	1105	0.29	1.1	0	0	0.63	0.07	0.90	0.10	0	1.1
O_2	0	80	0	502	0	0	1.02	0.37	0.014	1.03	0	0.29	0.34	0
O_2	0	80	0.2709	897	0.29	0	1.02	0	0.95	0.66	0.36	0.59	0.059	0
O_2	300	0	0	1060	0	0	0	0.61	0.30	0.19	0.17	0.12	0.11	0
O_2	300	0	0.2709	1502	0.29	0	0	0	0.60	0.10	0.94	0.06	0	0

6.4.2 Series 2 — Oxygen Gasification of Dry Wood at Fixed Temperature and Pressure

The calculations described here are for systems held at constant temperature and pressure. In Figs. 6-9 (a) and 6-9 (b), dry gas compositions are plotted versus equivalence ratio for several temperatures. The range of ER values extends from 0 to 0.30, the region of interest in gasification. In Fig. 6-9 (a), curves a and b are for H_2 at 900 and 1400 K, respectively. The weak temperature dependence is evident. Curves c, d, e, f are CO_2 concentrations at 900, 1000, 1100, and 1200 K. In Fig. 6-9 (b), the curves a, b, c, d are for CO at 900, 1000, 1100, 1400 K in the order listed; curves e, f, g and are for CH_4 at 900, 1000, and 1100 K. Methane is a minor component above 1100 K.

In a fluidized bed gasifier, temperature and equivalence ratio may be adjusted nearly independently: externally heated and recirculated inert bed material can influence the temperature level, and bleeding a variable amount of oxidant into a recycle stream will affect the ER. In a fixed-fuel-bed gasifier, however, the ER is not adjusted easily. Simply increasing the air rate, for example, will not necessarily have any effect on the ER. Introducing more air may simply expand the active portion of the bed, resulting in more throughput and leaving unchanged the ratio of air to wood consumed. One of the most sensitive tests of any kinetic model will be to predict the effect of air rate on bed temperature and equivalence ratio.

Given that the ER for a fixed bed gasifier may not be an adjustable parameter, it is interesting to observe the variation of composition with temperature for fixed ER. Figures 6-10 (a) and 6-10 (b) are plots of this type:

Figure 6-10 (a): H_2 Curves a, b, c, d: ER = 0.00, 0.068, 0.169, 0.284
CO_2 Curves h, g, f, e: ER = 0.00, 0.068, 0.169, 0.284

Figure 6-10 (b): CO Curves d, c, b, a: ER = 0.00, 0.068, 0.069, 0.284
CH_4 Curves e, f, g : ER = 0.00, 0.115, 0.284

Carbon formation in g/g dry wood and low heating value in Btu/SCF are plotted versus ER in Figs. 6-11 and 6-12:

Figure 6-11: C_s Curves a, b, c, d, e: T = 900, 1000, 1100, 1200, 1400 K

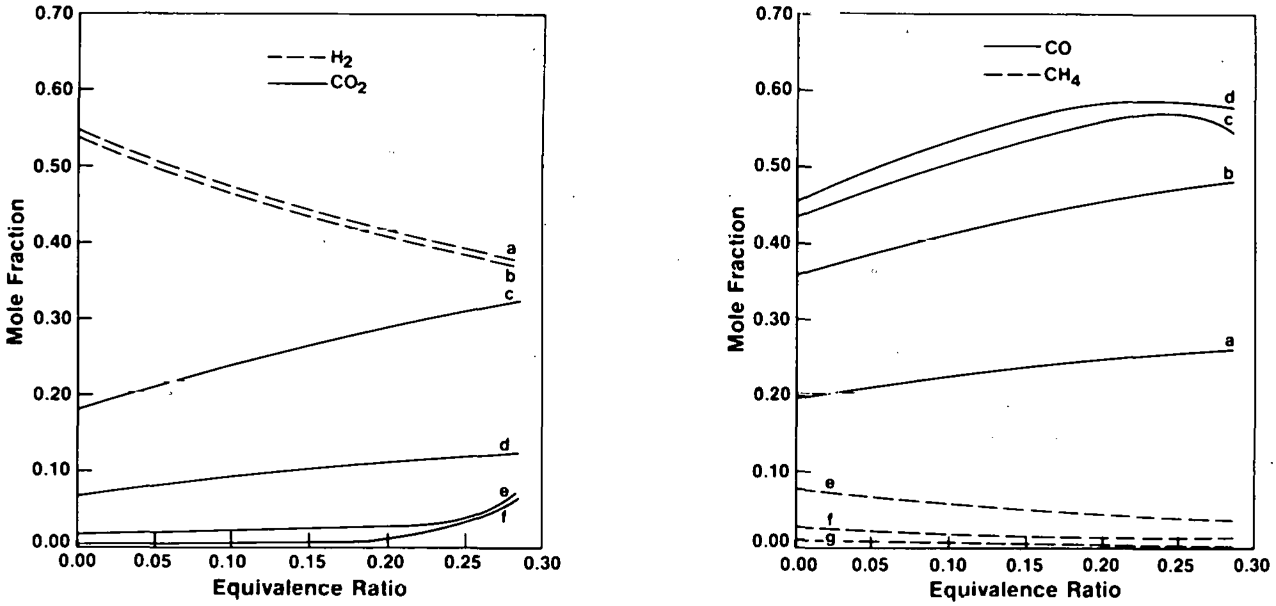
Figure 6-12: LHV Curves d, c, b, a : T = 900, 1000, 1100, 1400 K

Figures 6-13 through 6-16 are also fixed temperature runs but at 200 psig:

Figures 6-13 (a), 6-13 (b):	Dry gas compositions versus ER are plotted for H_2, CO_2, CO, and CH_4. There are five curves for each species corresponding to T = 900, 1000, 1100, 1200, and 1400 K. The direction of increasing temperature for each set of curves is indicated by an arrow.
Figures 6-14 (a), 6-14 (b):	Dry gas concentrations are plotted as functions of temperature. There are seven curves for each species corresponding to ER = 0.000, 0.034, 0.068,

	0.115, 0.169, 0.224, 0.284, with an arrow indicating the direction of increasing oxygen input.
Figures 6-15, 6-16	Carbon formation and LHV are plotted versus ER for five temperatures: T = 900, 1000, 1100, 1200, 1400 K.

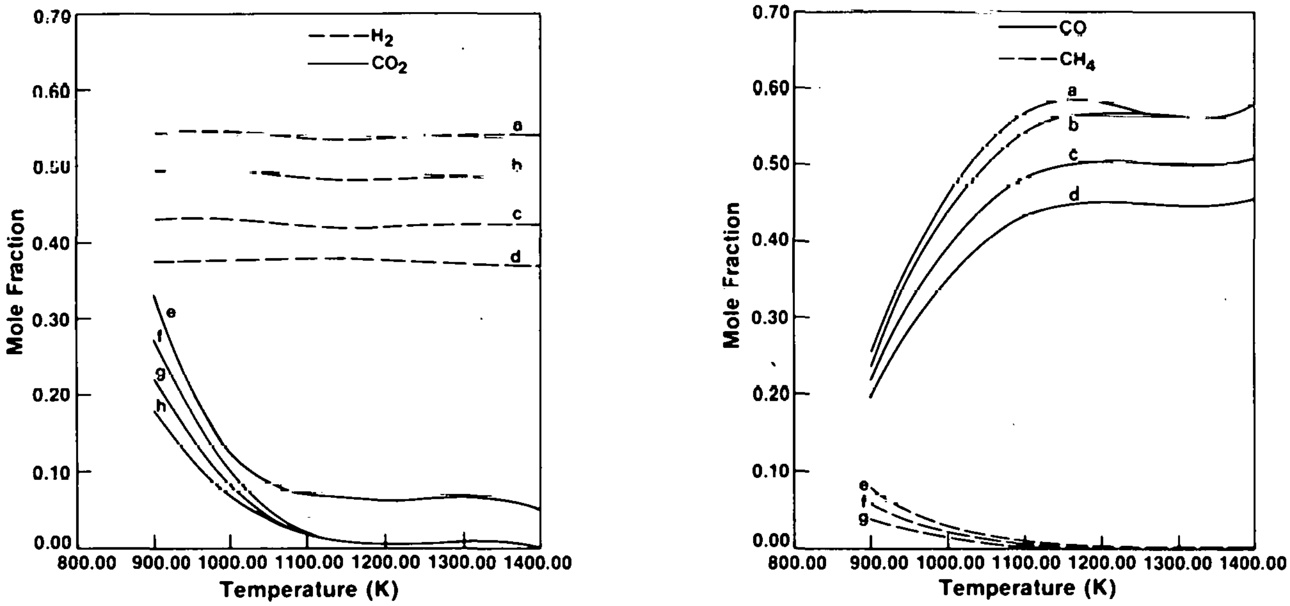
Stoichiometric reactions for several conditions are listed in Table 6-4.



(a) H_2 and CO_2

(b) CO and CH_4

Figure 6-9. Gas Composition Vs. Equivalence Ratio at Specified Temperatures and 1 atm



(a) H_2 and CO_2

(b) CO and CH_4

Figure 6-10. Gas Composition Vs. Temperature at Specified Equivalence Ratio and 1 atm

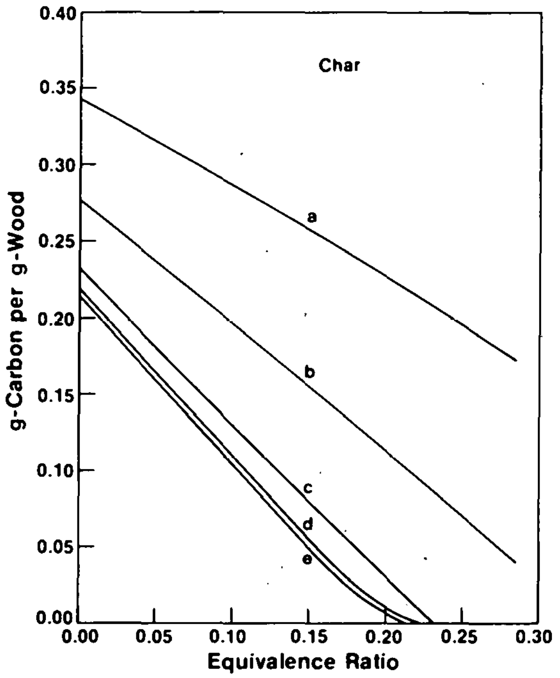


Figure 6-11. **Carbon Formation Vs. Equivalence Ratio at Specified Temperatures, 1 atm**

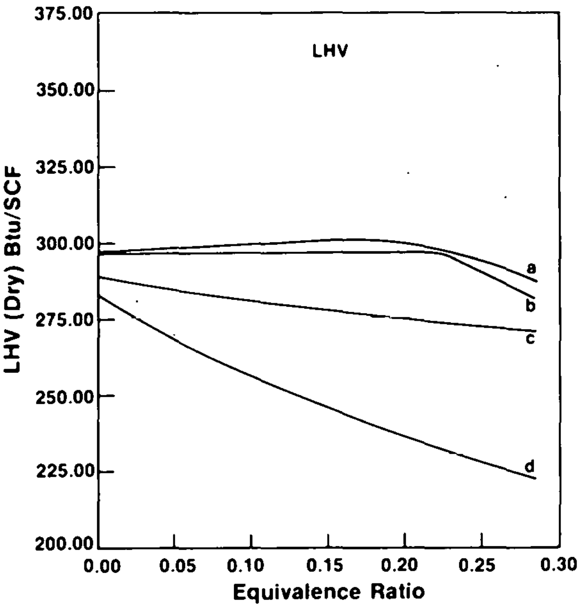
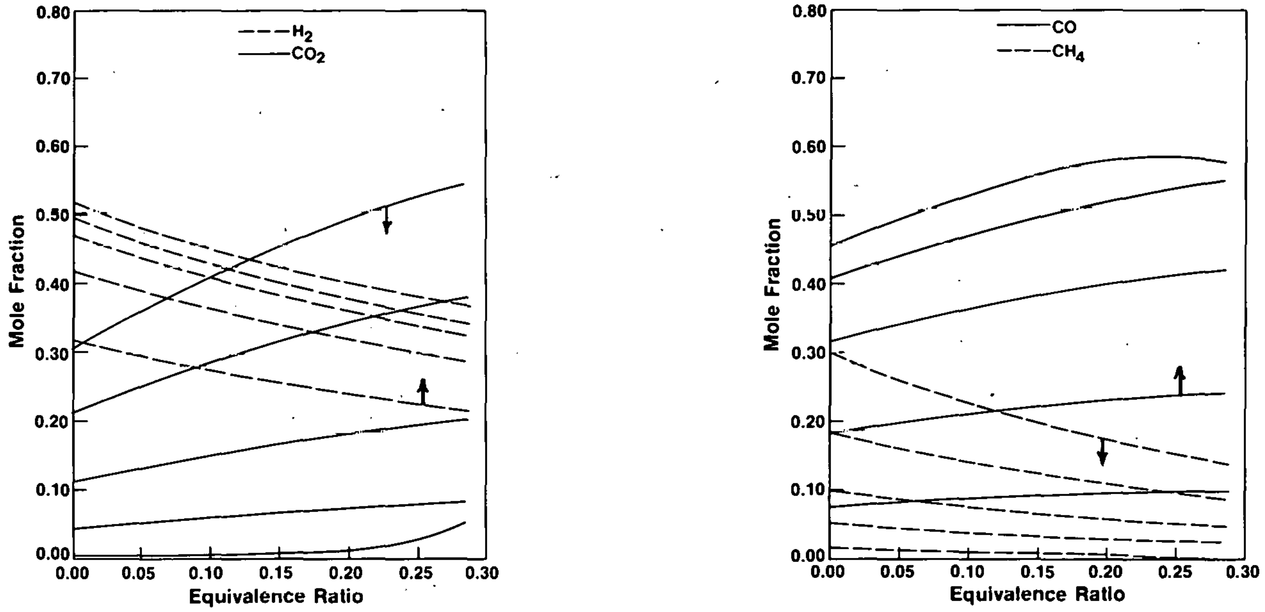


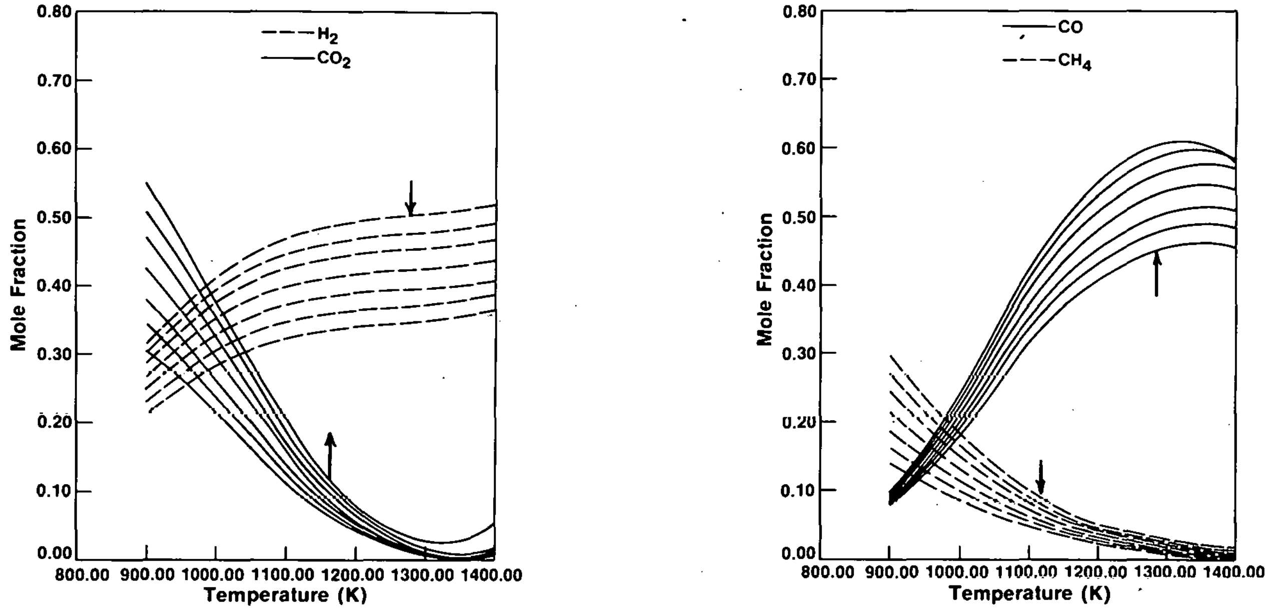
Figure 6-12. **Low Heating Value Vs. Equivalence Ratio at Specified Temperatures, 1 atm**



(a) H_2 and CO_2

(b) CO and CH_4

Figure 6-13. **Gas Composition Vs. Equivalence Ratio at Specified Temperatures and 200 psig**



(a) H_2 and CO_2

(b) CO and CH_4

Figure 6-14. Gas Composition Vs. Equivalence Ratio at Specified Temperatures and 200 psig

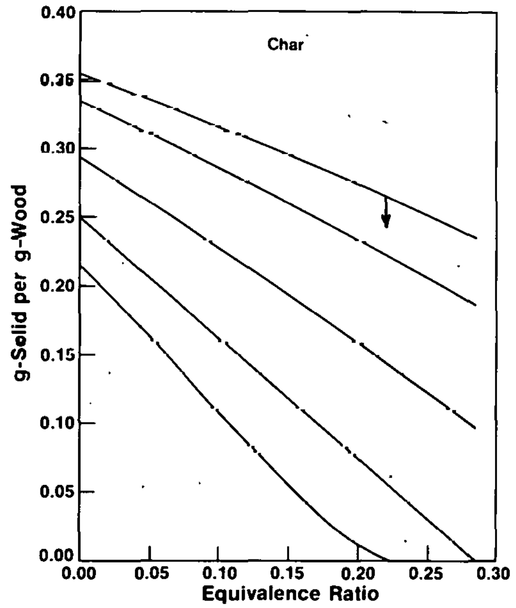


Figure 6-15. Carbon Formation Vs. Equivalence Ratio at Specified Temperatures, 200 psig

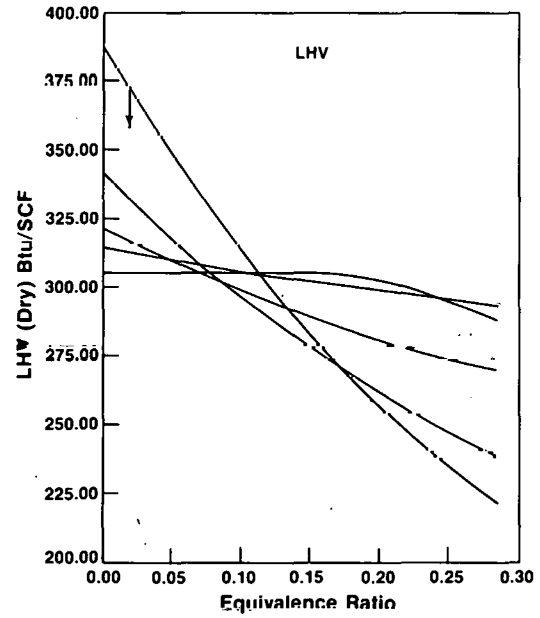


Figure 6-16. Low Heating Value Vs. Equivalence Ratio at Specified Temperatures, 200 psig

Table 6-4. OXYGEN GASIFICATION OF DRY WOOD AT FIXED TEMPERATURE AND PRESSURE

$$CH_{1.4}O_{0.59} + yO_2 = x_1C_s + H_2 + x_3H_2O + x_4CO + x_5CO_2 + x_6CH_4$$

Temperature (K)	Pressure (psig)	ER	y	x_1	x_2	x_3	x_4	x_5	x_6
	pyrolysis								
900	0	0	0	0.65	0.42	0.16	0.15	0.14	0.059
1000		0		0.53	0.57	0.08	0.37	0.07	0.028
1200		0		0.42	0.68	0.008	0.57	0.005	0.006
1400		0		0.41	0.69	0.001	0.59	0.0005	0.002
	gasification								
900	0	0.284	0.30	0.33	0.40	0.22	0.28	0.35	0.040
1000		0.284	0.30	0.08	0.56	0.10	0.72	0.19	0.019
1200		0.284	0.30	0	0.61	0.09	0.90	0.10	0.0003
1400		0.284	0.30	0	0.59	0.11	0.92	0.08	—
	pyrolysis								
900	200	0	0	0.67	0.15	0.26	0.036	0.15	0.14
1000		0		0.64	0.26	0.21	0.11	0.13	0.11
1200		0		0.48	0.51	0.075	0.42	0.045	0.055
1400		0		0.41	0.64	0.016	0.56	0.006	0.021
	gasification								
900	200	0.284	0.30	0.45	0.15	0.35	0.07	0.38	0.10
1000		0.284	0.30	0.35	0.26	0.28	0.22	0.34	0.08
1200		0.284	0.30	0	0.52	0.10	0.84	0.12	0.04
1400		0.284	0.30	0	0.58	0.11	0.92	0.08	0.002

6.4.3 Series 3 — Water Addition to Gasification

Nearly all gasifiers produce char. Some processes use all effluent char to raise steam, while others produce a surplus. The char is not a particularly attractive boiler fuel since it is low in volatiles. If the char is not recycled in the gasification plant, it cannot be considered a product of high value; in these cases, complete gasification of char should be promoted.

The controlling variables in char formation are moisture and temperature. Biomass feedstocks occur with varying amounts of moisture, depending on extent of pretreatment and method and duration of storage. For some gasification schemes, this inherent moisture may be an advantage. Those reactors with the capability of recycling a portion of the product gas may be particularly suited for handling wet feeds, because the recycled steam may significantly increase gas yields and is easily removed from the raw gas product. If hot gas is not recycled, then superheated steam may be used to promote char gasification.

The adiabatic flame temperatures for several conditions of interest in gasification are plotted in Fig. 6-17 (a). Abscissa values are equivalence ratios and range from 0 to 0.30. In all cases, oxygen is used in the blast; thus, for example, ER = 0.2 refers to

$$0.20 \times 1.476 = 0.295 \text{ g } O_2/\text{g dry wood} .$$

Curves a, b, c, d [Fig. 6-17 (a)] are all calculated for 1 atm of pressure. The first curve is for dry wood, while increasing amounts of water are added in cases b, c, d. The water is added either as liquid water at ambient temperature or as steam at 1000 K (1340 F). The large separation between curves a and b illustrates the effect of moisture on the adiabatic flame temperature. Further water addition was made as steam to minimize temperature differences to isolate the effect of moisture on gas composition and char consumption. Curves e, f are for elevated pressure. The quantities of water and steam listed in the tables below each figure are in g/g dry wood.

The influence of water/steam addition on gasification of char is illustrated in Fig. 6-17 (b,c). As more char is consumed, more chemical energy is stored in the gas [Fig. 6-17 (b)]. The breaks in the gas energy curves coincide with the stability limits of carbon. It appears from comparing curves c, e and d, f in Fig. 6-17 (c) that increasing pressure promotes char takeup. Most of this effect is a result of a temperature increase, however. When excess water is present, only the methanation reaction is pressure-dependent. The CO produced in the water gas reaction ($C + H_2O = CO + H_2$) is shifted by steam to $CO_2 + H_2$, resulting in the net reaction

$$2C + 2\,H_2O - CH_4 + CO_2 ,$$

which would exhibit a negligible pressure dependence.

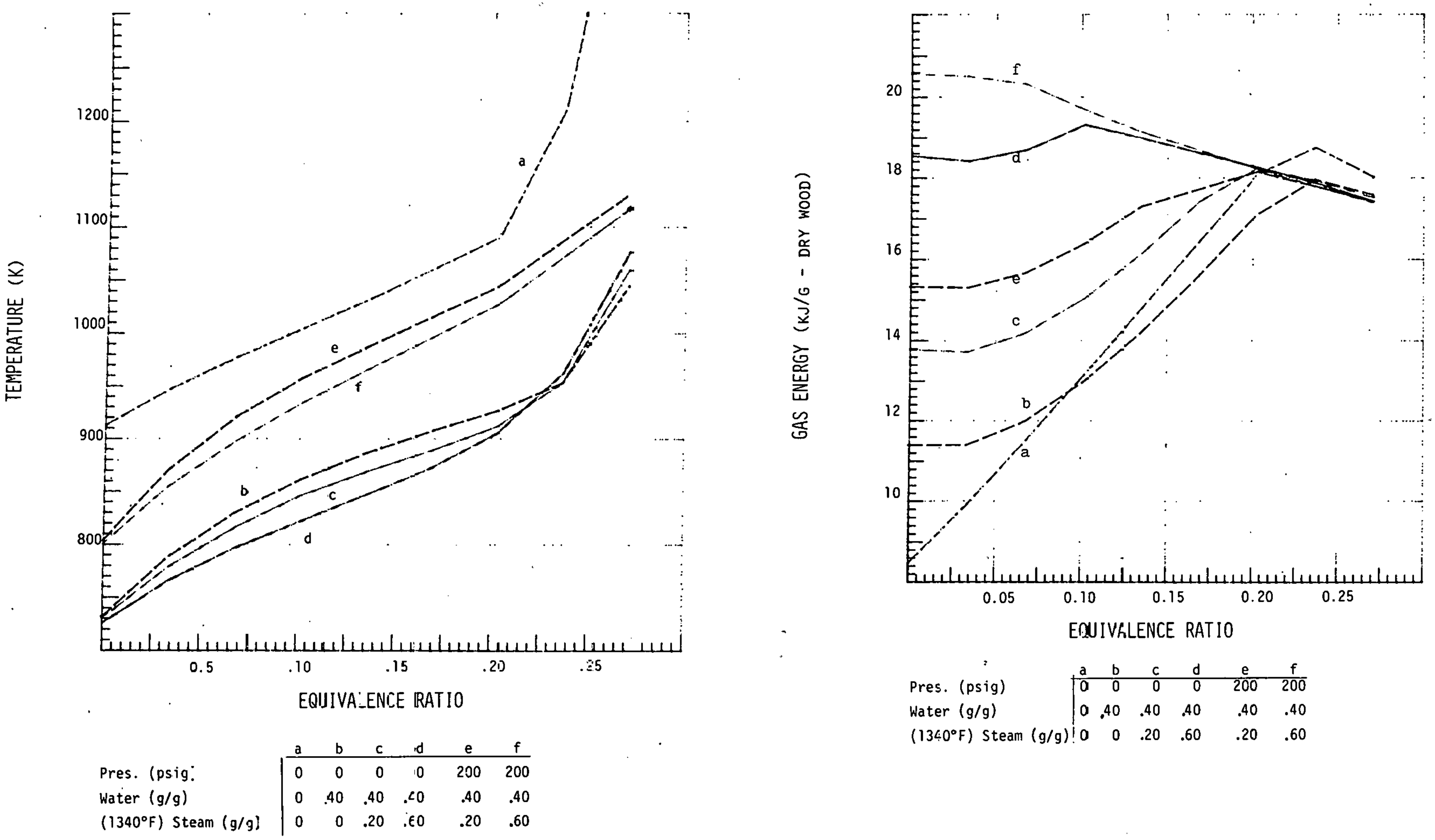
Whenever a steam blast is used in gasification, it is important to know under what conditions the steam can be considered inert: whether it acts as a diluent or as a reactive species. Net water formation is plotted in Fig. 6-17 (d).

$$\text{Net } H_2O \text{ formation} = \frac{\text{weight } H_2O \text{ in product} - \text{weight } H_2O \text{ in feed}}{\text{weight dry wood in feed}} .$$

Since curves b through f are below 0, it is apparent that water is not just a diluent under gasification conditions. All the curves turn upward after their break points, the latter coinciding with the limiting equivalence ratios for carbon stability. This upward trend at higher ER values agrees with experience since water is a diluent (thermodynamically, not kinetically) under combustion conditions.

The dry gas composition for these six cases is plotted in Figs. 6-17 (e) through 6-17(h). In all these figures, the curves for case (a), for dry wood, always lie well separated from the others. The effect on the CO shift reaction of increasing water addition is evident in Fig. 6-17 (g). The partitioning of these conditions into three sets a; b, c, d; and e, f is especially evident in the AFT plot [Fig. 6-17 (a)] and in the LHV plot [Fig. 6-17 (i)].

Stoichiometric reactions for several conditions at ER = 0.2032 are listed in Table 6-5.



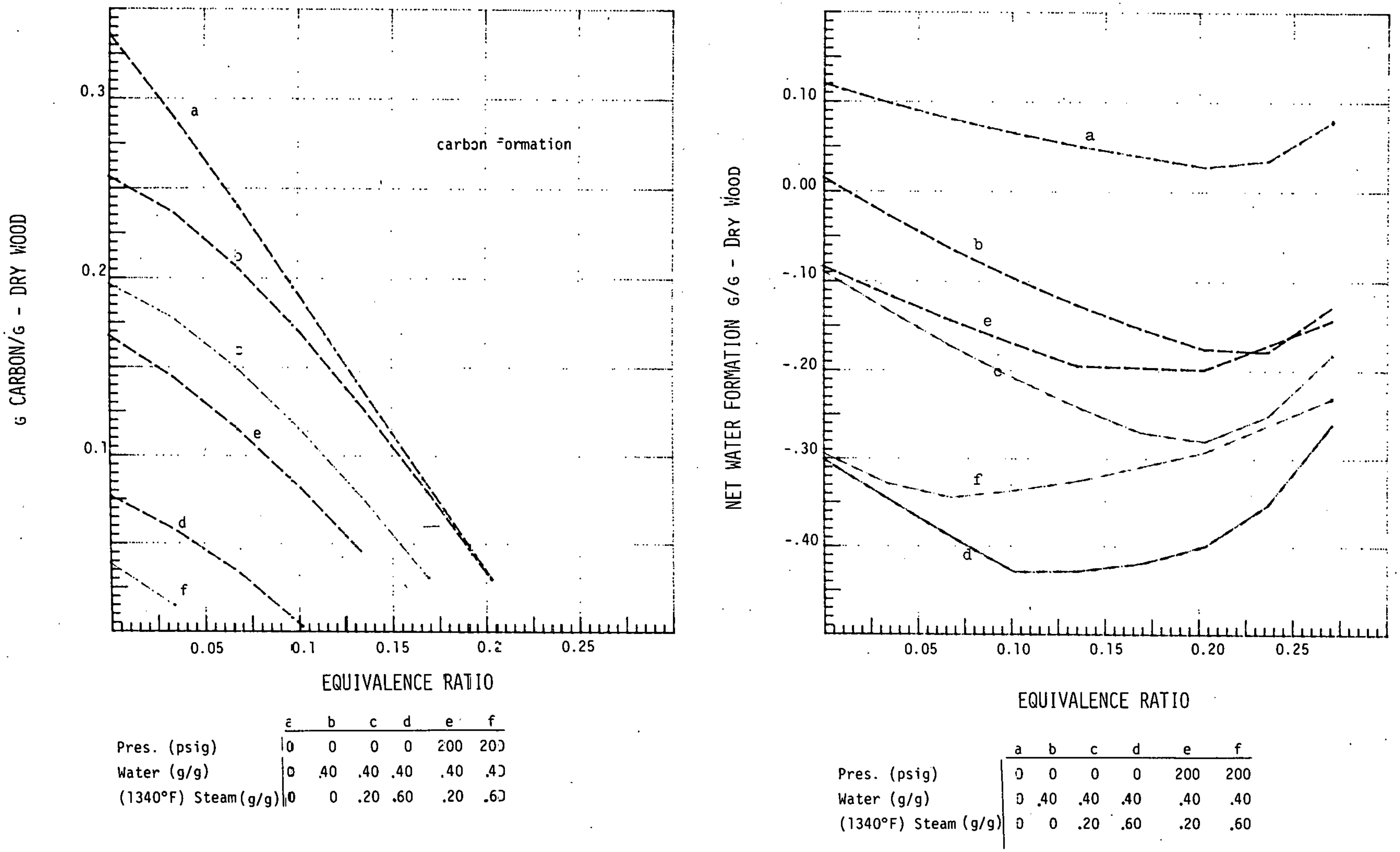
	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(a) Temperature Vs. Equivalence Ratio

(b) Energy Distribution Vs. Equivalence Ratio

Figure 6-17. Water Addition to Gasification



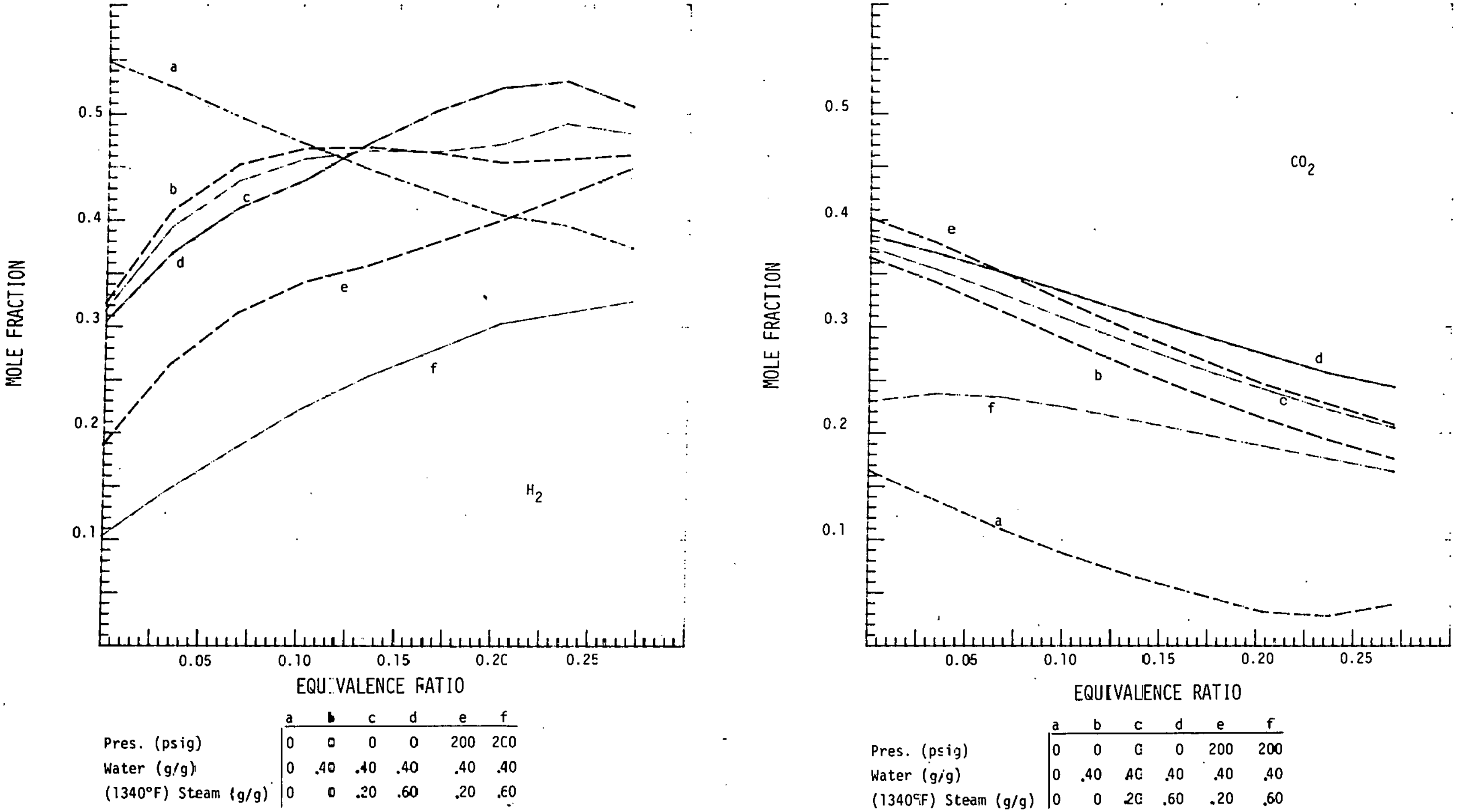
	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(c) Carbon Formation Vs. Equivalence Ratio

	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(d) Net Water Formation Vs. Equivalence Ratio

Figure 6-17. Water Addition to Gasification



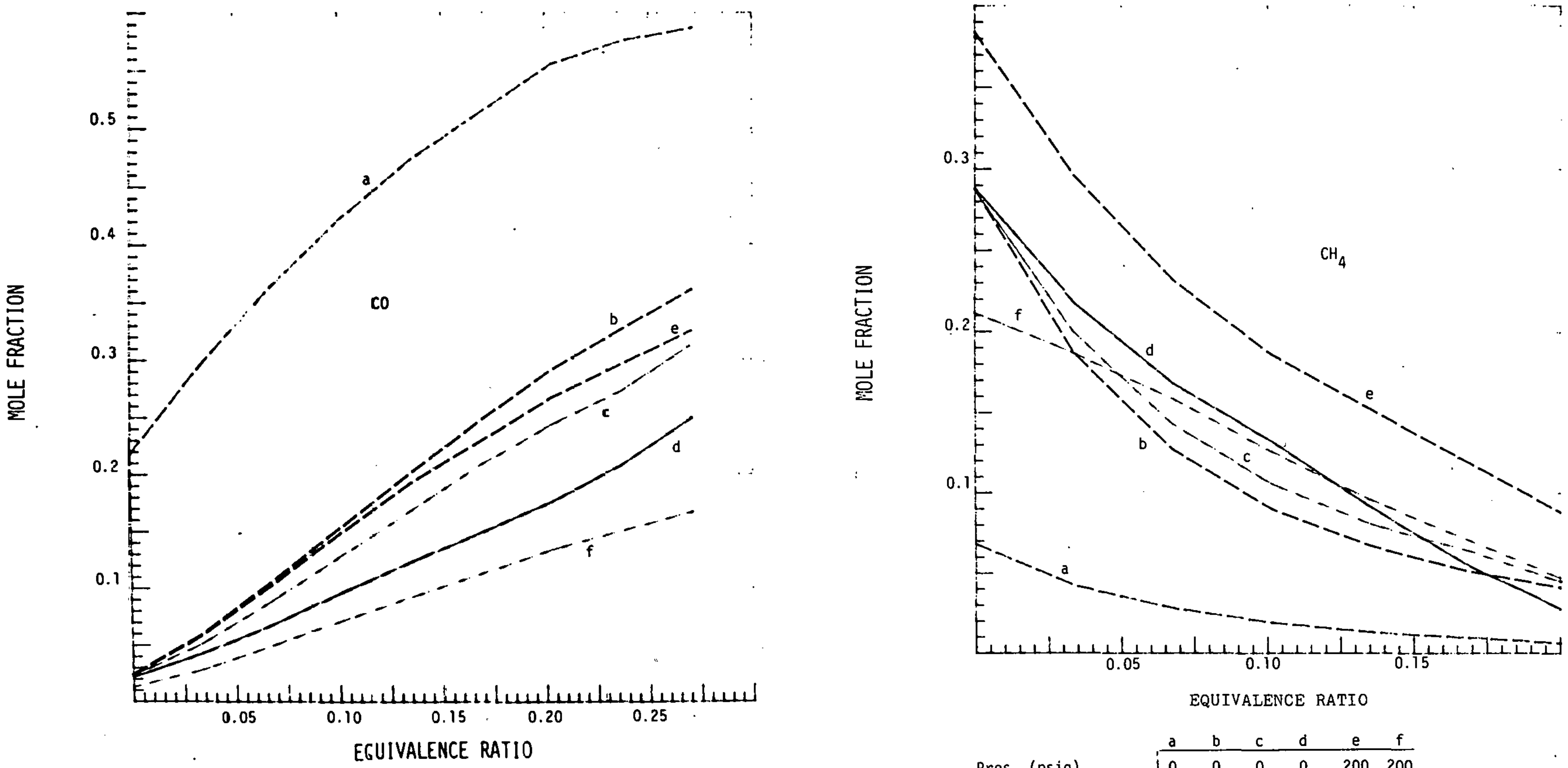
	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(e) Gas Composition (H_2) Vs. Equivalence Ratio

(f) Gas Composition (CO_2) Vs. Equivalence Ratio

Figure 6-17. Water Addition to Gasification



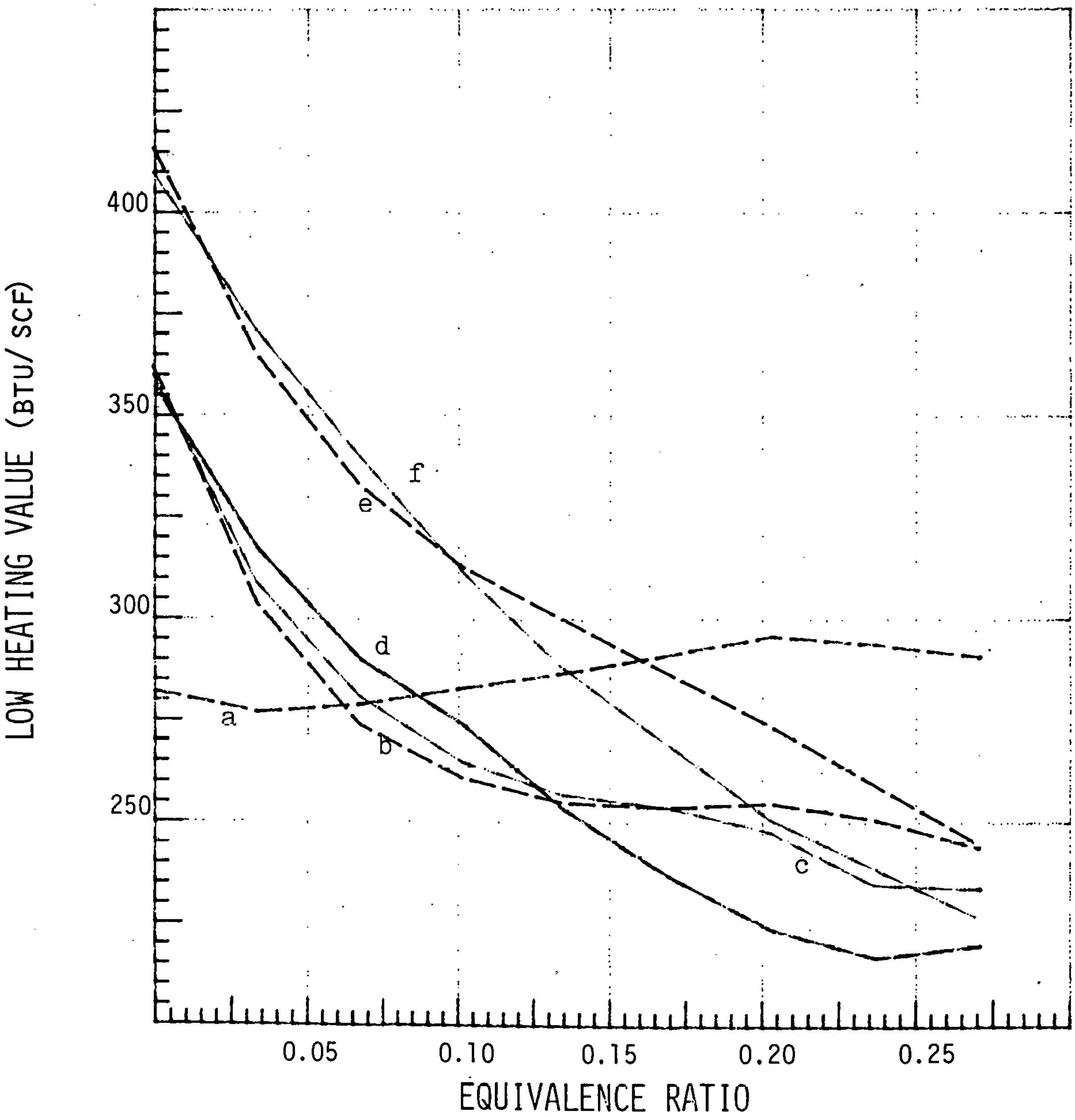
	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(g) Gas Composition (CO) Vs. Equivalence Ratio

	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(h) Gas Composition (CH_4) Vs. Equivalence Ratio

Figure 6-17. Water Addition to Gasification



	a	b	c	d	e	f
Pres. (psig)	0	0	0	0	200	200
Water (g/g)	0	.40	.40	.40	.40	.40
(1340°F) Steam (g/g)	0	0	.20	.60	.20	.60

(i) Low Heating Value Vs. Equivalence Ratio

Figure 6-17. Water Addition to Gasification

Table 6-5. ADIABATIC OXYGEN GASIFICATION REACTIONS OF WOOD UNDER STEAM (1000 K, 1340 F)

$$CH_{1.4}O_{0.59} + yO_2 + wH_2O = x_1C_s + x_2H_2 + x_3H_2O + x_4CO + x_5CO_2 + x_6CH_4$$

Pressure (psig)	Temperature (K)	Water (g/g-dry wood)	Steam (g/g-dry wood)	ER	y	w	x_1	x_2	x_3	x_4	x_5	x_6
0	1091	0	0	0.2032	0.21	0	0.06	0.64	0.036	0.88	0.05	0.01
0	927	0.40	0	0.2032	0.21	0.51	0.06	0.78	0.29	0.50	0.37	0.07
0	912	0.40	0.20	0.2032	0.21	0.76	0	0.89	0.41	0.46	0.46	0.08
0	906	0.40	0.60	0.2032	0.21	1.27	0	1.10	0.76	0.37	0.58	0.05
200	1045	0.40	0.20	0.2032	0.21	0.76	0	0.67	0.51	0.45	0.41	0.14
200	1028	0.40	0.60	0.2032	0.21	1.27	0	0.83	0.90	0.36	0.51	0.12

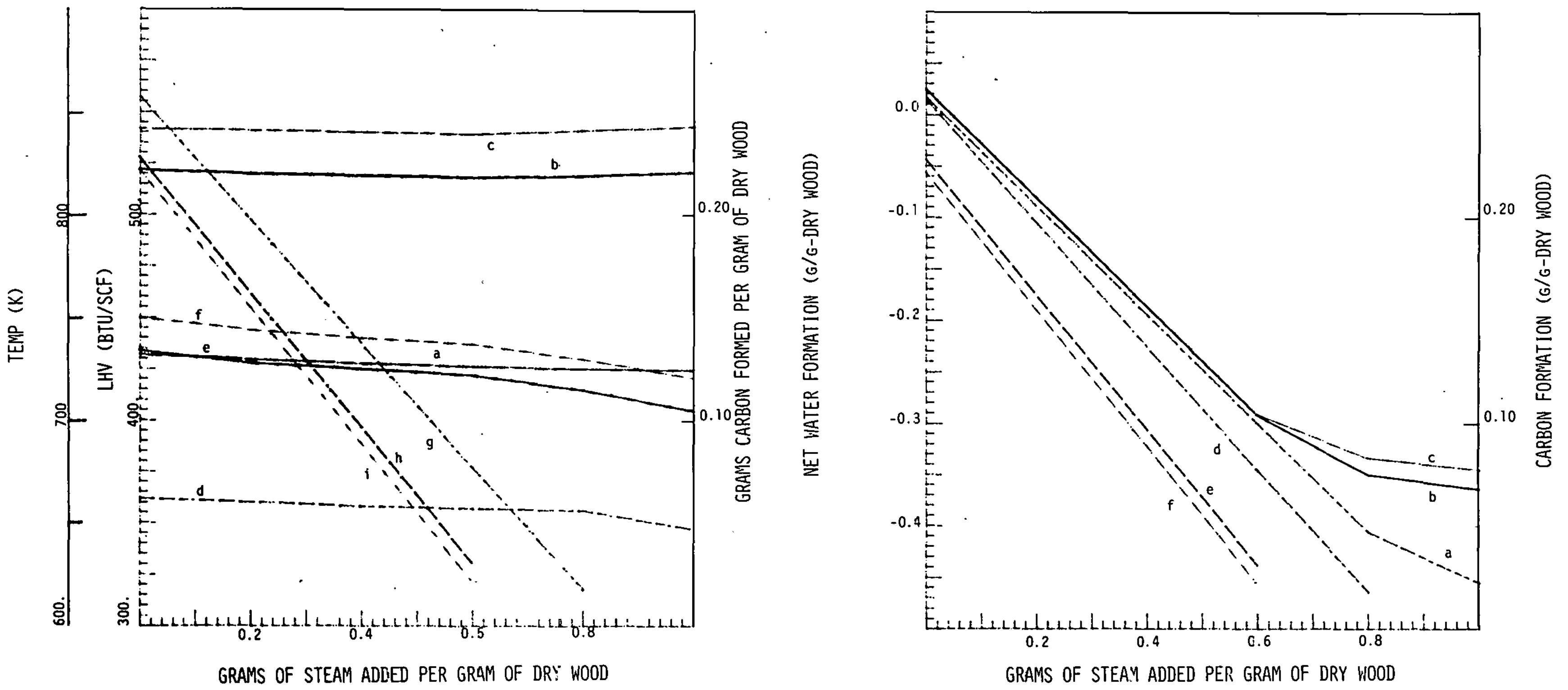
6.4.4 Series 4 — Steam Addition to Pyrolysis

Pyrolysis offers the advantage of producing a medium energy gas without the requirement of an oxygen plant. The results of pyrolysis for the conditions considered to this point are all represented by points on the left hand axis at ER = 0. In this series of plots we consider the effect of steam addition [steam temperature 1000 K, (1340 F)] on pyrolysis. In Figs. 6-18 (c) and 6-18 (d), dry gas compositions are plotted for three different pressures (0, 400, and 1000 psig) as a function of steam addition. The feed is wet wood (40% moisture, dry basis). The values on the x-axis of each figure represent the weight of steam added per unit of dry wood. Thus the system at a point with x-coordinate 0.6 is composed of 100 g of wood, 40 g of water, and 60 g of steam. As observed previously, pressure strongly affects the concentration of H_2 and CH_4 but has little effect on CO or CO_2. Carbon formation is superimposed on each figure. Steam addition affects the quantity of gas produced but the composition is fixed by the water-gas shift and methanation reactions.

The AFT and LHV curves are plotted in Fig. 6-18 (a) and net water formation in Fig. 6-18 (b).

A higher steam temperature (1144 K, 1600 F) has a negligible effect on the results, as can be seen by comparing Figs. 6-18 (e) and 6-18 (f) with Figs. 6-18 (a) through 6-18 (d). [Notice that steam addition is plotted on an expanded scale in Figs. 6-18 (e) and 6-18 (f).] This observation highlights the difficulty of introducing sufficient sensible heat in a pyrolysis scheme to significantly affect the system composition. Some designs rely on recirculating hot solids to fluidized or entrained beds. The solid is usually char or sand that is withdrawn from the bed and heated externally. The thermal duty of the process is supplied easily by providing a sufficiently high solids/gas ratio; design problems arise only in the solids handling area. Pyrolysis schemes which rely on heating a recycled gas stream, however, have more stringent equipment limitations because of the volume of gas that must be handled. Consider the example illustrated in Fig. 6-19, in which 100 g wood, 40 g water, and 67 g steam (at 1600 F) are fed to a pyrolysis reactor equipped with a gas recycle stream which is reheated from the adiabatic reactor temperature (T_{aft}) to a reheat temperature (T_{rh}) of 1300 K (1880 F). The computer program used in these calculations includes the option of introducing an enthalpy adjustment for heat losses or additions. For several enthalpy additions (ΔH) in kcal, the system composition and T_{aft} were calculated. Then, using the heat capacity of the product gas stream, the quantity of gas which would have to be recycled to provide the stipulated heat input within the temperature rise $T_{rh} - T_{aft}$ was determined. The results of a series of such calculations for the system pictured are listed in Table 6-6. For the level of reheat considered, over 72% of the reactor effluent would have to be recycled in order to effect a change in temperature of 100 K.

The stoichiometry of the pressure-steam pyrolysis reactions considered in this section are listed in Table 6-7. The methane concentrations achieved under steam pyrolysis can be as high as 48%. The Wright-Malta process operates under conditions similar to those described here and offers a very attractive route to SNG and a medium energy boiler fuel.



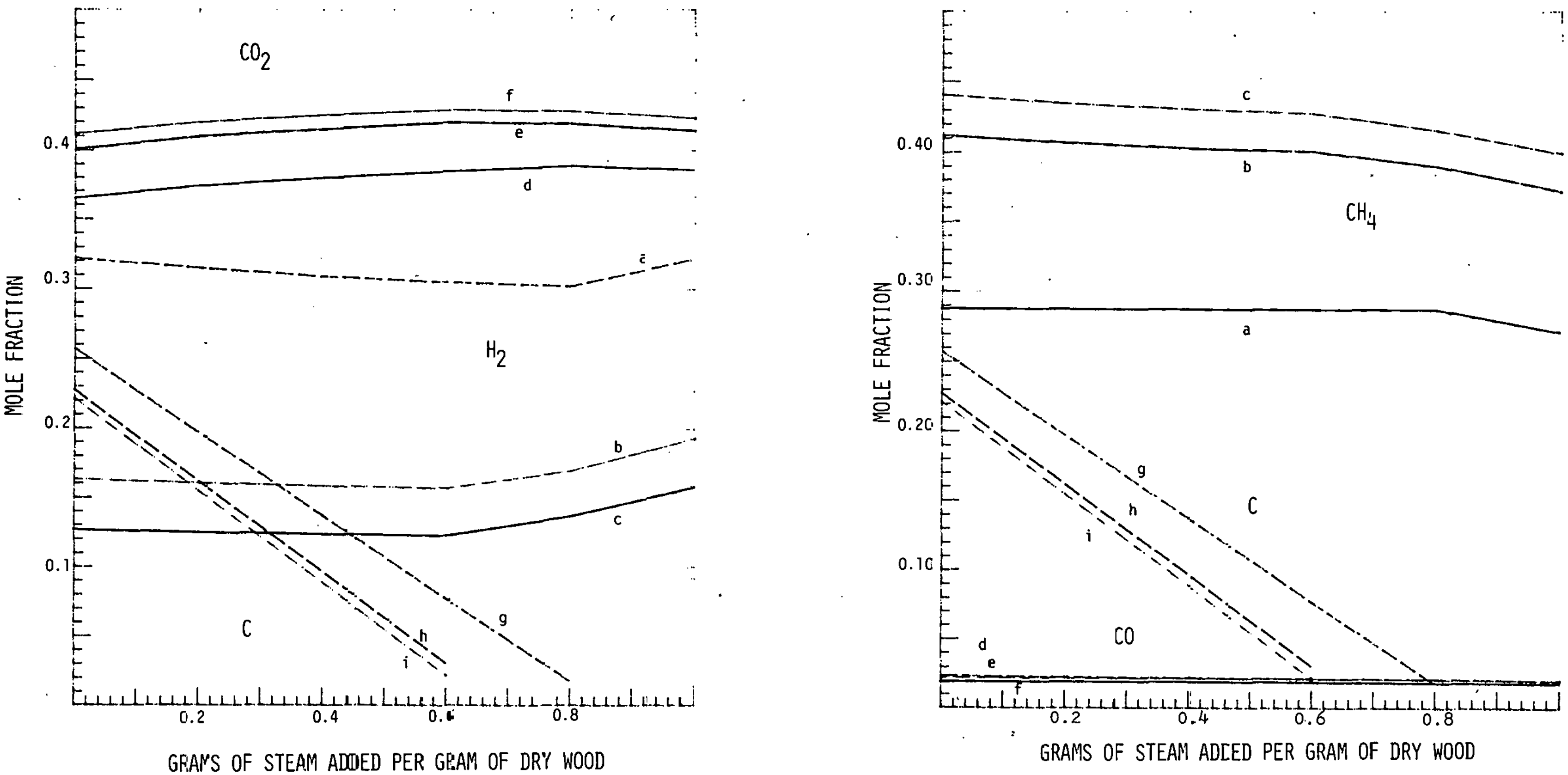
Pres (psig)	0	400	1000
Temp. (K)	a	b	c
LHV (BTU/SCF)	d	e	f
Carbon Formation	g	h	i

Pres (psig)	0	400	1000
Water formation	a	b	c
Carbon formation	d	e	f

(a) Adiabatic Flame Temperature, Low Heating Value and Carbon Formation

(b) Net Water Formation and Carbon Formation

Figure 6-18. Steam Addition to Pyrolysis



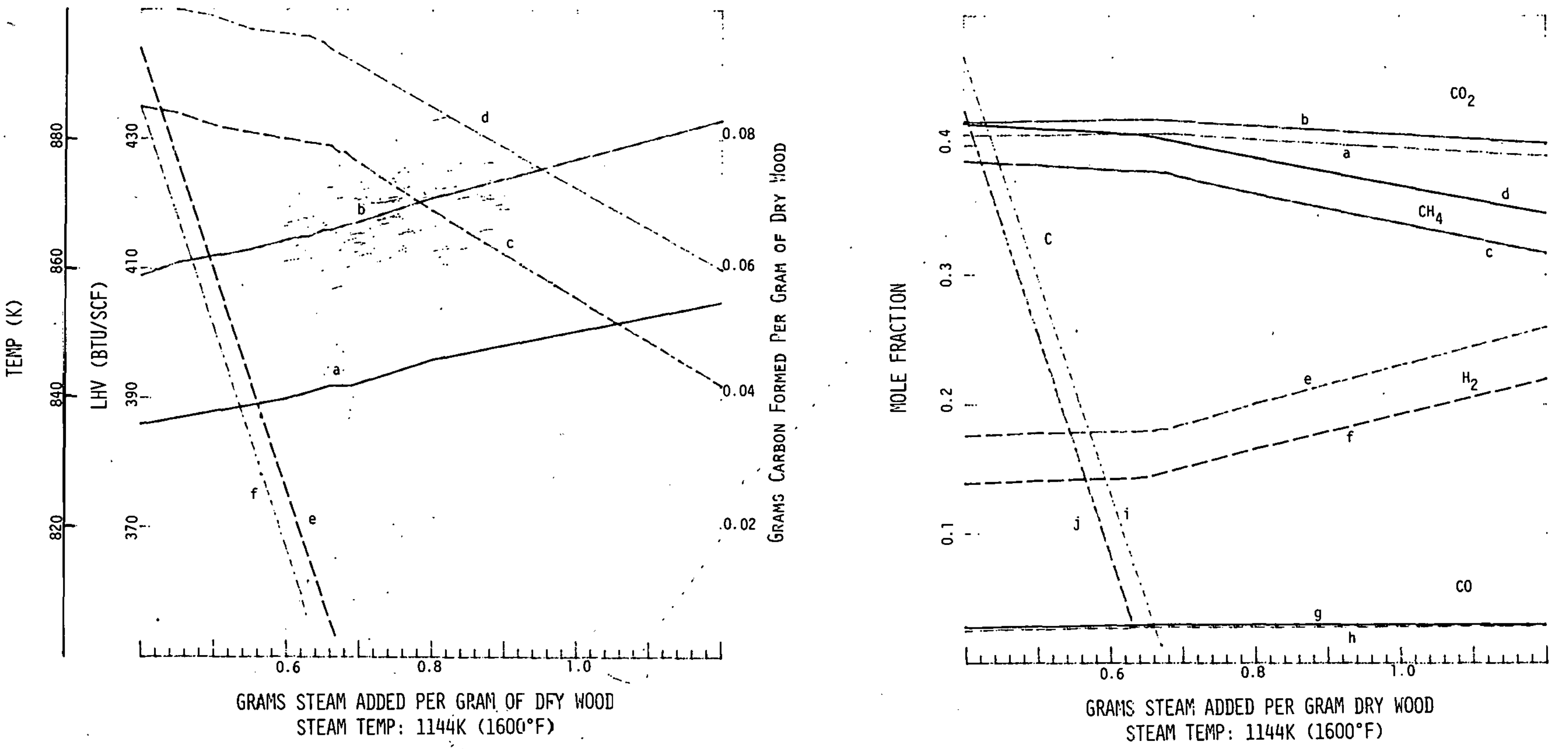
Pres (psig)	0	400	1000
H_2 Mole Fraction	a	b	c
CO_2 Mole Fraction	d	e	f
C g/g-Dry Wood	g	h	i

(c) Gas Composition (CO_2, H_2)

Pres. (psig)	0	400	1000
CH_4 Mole Fraction	a	b	c
CO Mole Fraction	d	e	f
C g/g-Dry Wood	g	h	i

(d) Gas Composition (CH_4, CO)

Figure 6-18. Steam Addition to Pyrolysis



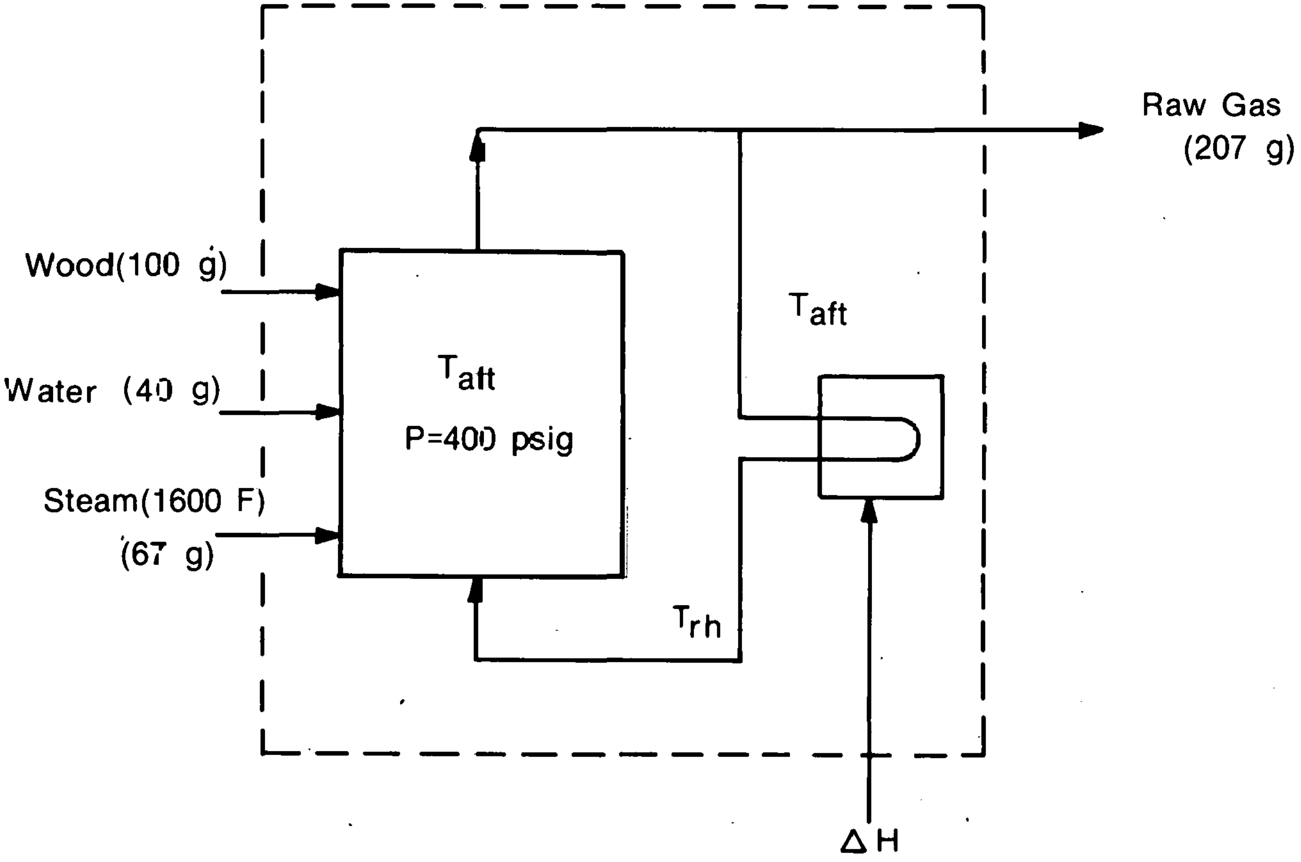
Pres (psig)	400	1000
Temp. (K)	a	b
LHV (BTU/SCF)	c	c
Carbon Formation	e	f

Pres. (psig)	400	1000
CO_2 Mole Fraction	a	b
CH_4	c	d
H_2	e	f
CO	g	h
C g/g-Dry Wood	i	j

(e) Adiabatic Flame Temperature, Low Heating Value, and Carbon Formation, Steam at 1144 K

(f) Gas Composition, Steam at 1144 K

Figure 6-18. Steam Addition to Pyrolysis



T_{aft} =adiabatic flame temperature
T_{rh} = recycle reheat temperature

Figure 6-19. Pyrolysis with Recycle Reheat

Table 6-6. HEAT ADDITION IN PYROLYSIS

$$h = \bar{c}\,(T_{rh})\,(T_{rh} - 298) - \bar{c}\,(T_{aft})\,(T_{aft} - 298)$$

$$\text{Recycle \%} = \Delta H \times 10^5 / h \times 207$$

ΔH	T_{aft}		Products (mole %)				H_2O	LHV	$\bar{c}(T_{aft})$	$\bar{c}(T_{rh})$	h	Recycle
(kcal)	(K)	(F)	H_2	CO	CO_2	CH_4	(g)	(MJ/Nm^3)	(cal/g C)		(cal/g)	(%)
0	842	1056	18.05	3.03	40.94	37.91	72.27	15.96	—	—	—	0.00
5	862	1092	20.24	3.92	39.79	35.98	70.95	15.62	0.445	0.493	243	9.94
10	881	1126	22.47	4.89	38.57	34.01	70.08	15.27	0.449	0.495	234	20.65
20	914	1186	26.58	6.98	36.08	30.29	68.50	14.65	0.457	0.497	216	44.73
30	943	1238	30.29	9.20	33.60	26.86	67.10	14.10	0.463	0.499	201	72.10

Table 6-7. ADIABATIC PYROLYSIS REACTIONS OF WOOD[a] UNDER STEAM (1000 K, 1340 F)

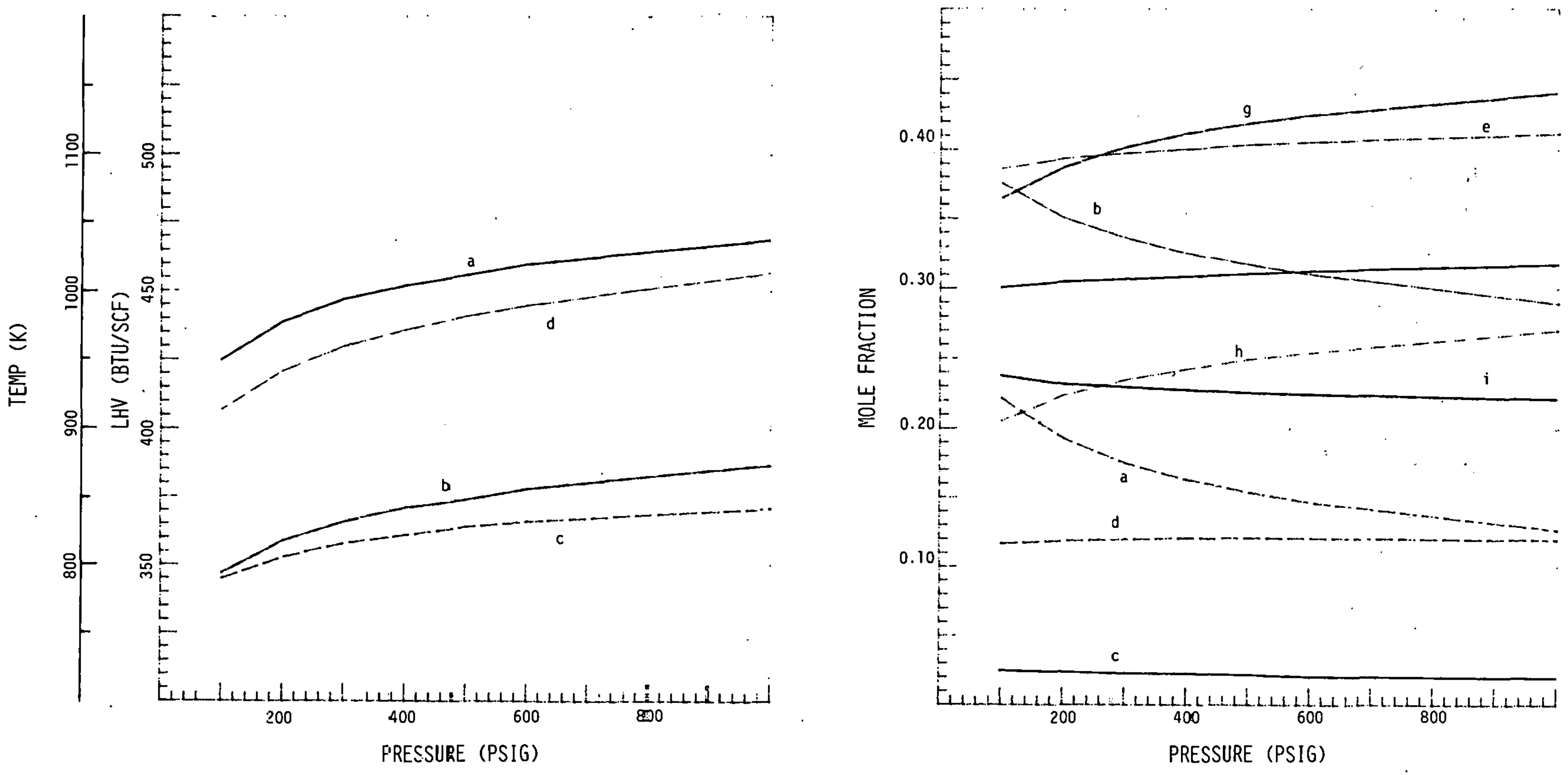
$$CH_{1.4}O_{0.59} + wH_2O = x_1C_s + x_2H_2 + x_3H_2O + x_4CO + x_5CO_2 + x_6CH_4$$

Pressure (psig)	Temperature (K)	Steam (g/g-dry wood)	w	x_1	x_2	x_3	x_4	x_5	x_6
0	732	0	0.51	0.49	0.24	0.53	0.018	0.28	0.22
	728	0.40	1.02	0.26	0.33	0.77	0.024	0.41	0.31
	725	0.80	1.52	0.03	0.42	1.01	0.029	0.54	0.40
400	822	0	0.51	0.43	0.11	0.54	0.015	0.27	0.28
	819	0.40	1.02	0.18	0.15	0.78	0.021	0.40	0.39
	819	0.80	1.52	0	0.20	1.08	0.026	0.50	0.47
1000	842	0	0.51	0.42	0.08	0.54	0.013	0.27	0.29
	840	0.40	1.02	0.17	0.12	0.78	0.019	0.40	0.41
	841	0.80	1.52	0	0.16	1.10	0.022	0.50	0.48

[a] Wood at 40% moisture, dry basis.

6.4.5 Series 5 — Pyrolysis Equilibria Versus Pressure

Although pressure has been considered as a parameter in several cases discussed in previous sections, the effect of pressure has not been presented from a global perspective. The major advantage of high pressure operation in gasification is the diminished compression required for downstream gas processing. A second benefit is an enhanced rate of reaction. The effect on equilibrium conversion is very small, as is demonstrated in Figs. 6-20 (a) and 6-20 (b). In these figures the calculated equilibrium properties for two systems are plotted: wood and water (0.4 g/g) and wood with steam (1 g/g, at 1600 F).



Water (g/g)	40	100 (as 1600°F steam)
LHV (BTU/SCF)	a	b
TEMP (K)	c	d

Water (g/g)	40	100 (as 1600°F steam)
H_2 Mole Fr.	a	b
CO " "	c	d
CO_2 " "	e	f
CH_4 " "	g	h
C_s g/g-dry wood	i	-

(a) Adiabatic Flame Temperature and Low Heating Value

(b) Gas Composition

Figure 6-20. Pyrolysis Equilibria Vs. Pressure

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Chapter 7

Kinetics of Char Gasification Reactions

M. Graboski
Colorado School of Mines

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CHAPTER 7

KINETICS OF CHAR GASIFICATION REACTIONS ABOVE 500 C

Biomass chars, like coal chars, are composed principally of carbon. Chars produced by pyrolytic reactions can be oxidized to synthesis gas through heterogeneous reactions with carbon dioxide, steam, oxygen, and hydrogen. The reactivity of chars in gaseous atmospheres is a complicated function of temperature, particle structure, carbon source, and thermal history of the char. The overall rate of char gasification may be affected not only by chemical kinetics but also by intraparticle and external mass transfer resistances. Additionally, the gasification reactions have large associated heat effects, making possible a significant temperature gradient within the particle. Therefore, any discussion of kinetics must include the effects of mass and heat transfer. Many early studies on gasification kinetics have been invalidated because they ignored these effects.

This chapter introduces some of the fundamental concepts of heat and mass transfer in chemical reactions. The true kinetics of the important gasification reactions are then summarized in terms of mechanisms and the effects of pertinent variables on the observed rates of gasification.

7.1 CHEMICAL REACTION SCHEMES

The principal objective in char gasification is to produce from the carbon-containing char a mixture of gases containing a substantial quantity of carbon monoxide and hydrogen. The reaction scheme usually involves the coupling of the exothermic oxygen combustion reaction with a number of endothermic gasification reactions to produce the synthesis gas. In order for the overall process to occur at a significant rate, temperatures in excess of 500 C are required, and more likely the process will operate at temperatures on the order of 800 C. The energy content of the synthesis gas will depend on the mode of heat addition to the gasification reactions. Oxygen gasification will yield a medium energy gas of 300 Btu/SCF or higher depending on the amount of methane produced during gasification. Air gasification, on the other hand, will yield a low energy gas of 150 Btu/SCF or less with little or no methane in the product. The lower energy content is due mainly to the nitrogen content of the air. In either case, the principal reactions are:

$$C + O_2 \rightleftharpoons 2CO, \qquad \Delta H_R = -26 \text{ kcal/mole} \tag{7-1}$$

$$C + H_2O \rightleftharpoons CO + H_2, \qquad \Delta H_R = +31 \text{ kcal/mole} \tag{7-2}$$

$$C + CO_2 \rightleftharpoons 2CO, \qquad \Delta H_R = +41 \text{ kcal/mole} \tag{7-3}$$

In many gasification systems, the gasifying medium is a mixture of air or oxygen and steam. Equation 7-2, termed the carbon-steam reaction, is the principal endothermic step in such systems. In the absence of steam, as in partial oxidation, Eq. 7-3, termed the Boudouard reaction, converts CO_2 produced by oxidation to CO. The rates of reactions 7-2 and 7-3 are similar (the carbon steam reaction being several times faster) for most carbons. Thus reaction 7-3 can serve as an indicator of the activities of different chars. It is much easier to study the kinetics of reaction 7-3 in comparison to reaction 7-2, since in reaction 7-2 parallel competing reactions can occur when the hydrogen generated reacts with other species.

Reaction 7-3 is very important in downstream heat transfer equipment and piping, where steel surfaces can promote the reverse reaction and deposit soot.

Since the combustion and gasification reactions produce carbon monoxide, the water-gas shift reaction can take place in the presence of steam:

$$CO + H_2O \rightleftarrows CO_2 + H_2, \Delta H_R = -10 \text{ kcal/mole} \quad (7\text{-}4)$$

This reaction is thought to occur as a result of heterogeneous catalysis by the carbon surface at temperatures below about 2000 F. At higher temperatures it may occur as a homogeneous reaction.

Methane formation by the hydrogasification reaction,

$$C + 2H_2 \rightleftarrows CH_4, \Delta H_R = -17 \text{ kcal/mole} , \quad (7\text{-}5)$$

is important in oxygen gasification for two reasons: (1) The energy content of the synthesis gas is increased; (2) the oxygen required is reduced because of the heat released in methane generation. For coal chars, two methane-forming processes have been observed (for example, Johnson 1974). Freshly devolatilized char is highly reactive and forms methane at a high rate in the first seconds of its existence. After that time, the char becomes graphitized (or stabilized) to some degree and, subsequently, methane is formed at a very slow rate. To have significant production rates of methane relative to the rate of carbon gasification by the steam carbon reaction, rapid heating and high pressure operation are necessary since the kinetics of reaction 7-5 are strongly dependent on hydrogen partial pressure. Air gasification is usually carried out at low pressure. This fact, coupled with the dilution effect of the nitrogen in the air, all but eliminates methane production from char by reaction 7-5.

In fixed bed gasifiers, there are different kinetic regions depending on whether the gasifier is operated in the updraft or downdraft mode (Fig. 7-1). In downdraft gasifiers, the steam and oxidant are fed directly to the gasifier with the fresh biomass. Pyrolysis and combustion occur simultaneously; tars are gasified to CO, CO_2, and H_2. The hot gases are swept downward over the remaining char to yield a relatively hydrocarbon-free, low energy gas at the gasifier outlet.

In the updraft mode, steam and oxygen contact spent char. Combustion occurs at the base of the gasifier, and above the combustion zone the slower gasification reactions take place. In the top zone, the biomass is devolatilized to produce a synthesis gas containing substantial quantities of hydrocarbons.

The operating mode depends on the use of the synthesis gas. The downdraft method is especially useful for conversion of biomass materials to methanol and ammonia synthesis gas. Updraft gasification yields a fuel gas suitable as a boiler fuel or feedstock for manufacture of synthetic natural gas.

7.2 EFFECT OF MASS TRANSFER ON REACTION RATE

Figure 7-2 shows a porous char particle typical of biomass materials, such as wood, which contain negligible quantities of ash. In char gasification, the following reaction steps are considered to occur in series:

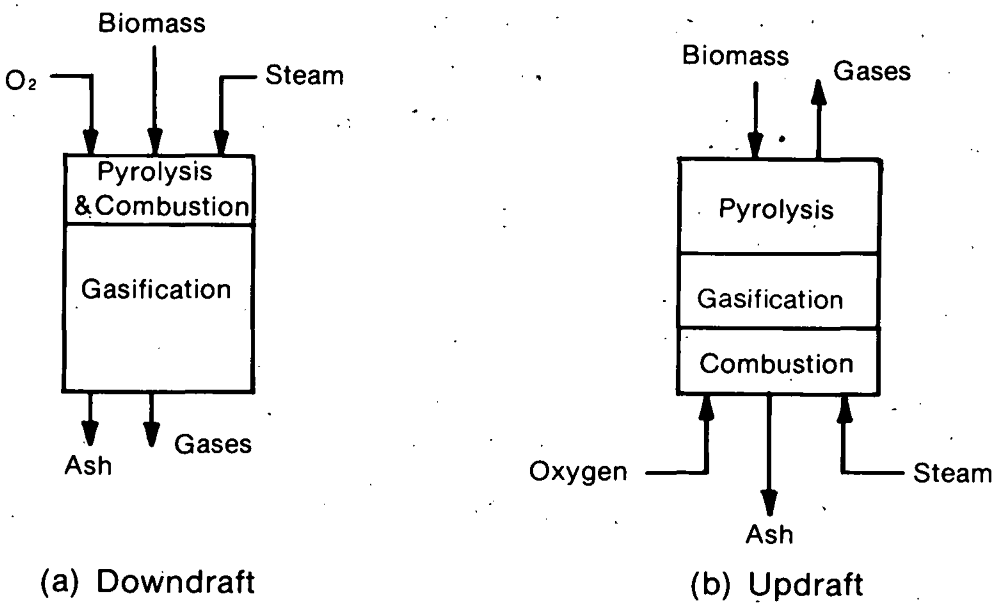

Figure 7-1. Modes of Gasifier Operation

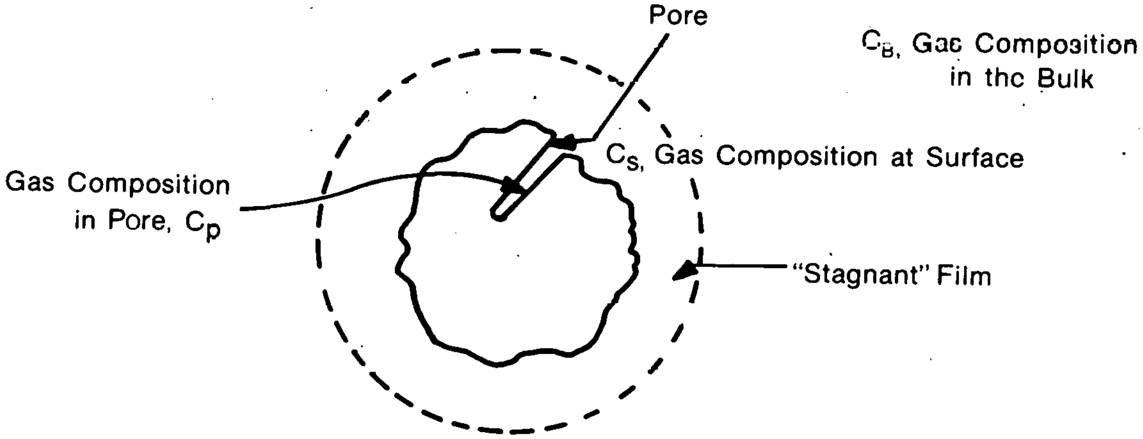

Figure 7-2. Model of Porous Char Particle

- diffusion of reactants across the stagnant film to the external char surface;
- diffusion of gas down the pore toward the center of the particle;
- adsorption, surface reaction, and desorption on the pore wall;
- diffusion of products out of the pore; and
- diffusion of products across the stagnant film to the gaseous reaction environment.

Depending on the temperature, pressure, gas composition, and extent of reaction, any or all of these steps may be important.

7.2.1 External Mass Transport and Heat Transfer

Diffusion across the film is termed external mass transport. At steady state, the rate of transport to the surface is given by the standard mass transfer expression:

$$W = k_m A_p C(Y_B - Y_S) = k_m A_p (C_B - C_S) \ , \tag{7-6}$$

where

W = transfer rate, moles/time/weight of solid;
k_m = mass transfer coefficient, length/time;
A_p = external surface area per weight of solid;
Y_B = bulk gas concentration, mole fraction units;
Y_S = concentration of gas adjacent to surface, mole fraction units;
C = total gas concentration, moles/volume;
C_B = concentration of component in the bulk, moles/volume; and
C_S = concentration of component adjacent to surface, moles/volume.

The mass transfer coefficient is a weak function of absolute temperature and velocity, as is shown later in this section. The total concentration C is given approximately by the ideal gas law:

$$C = P/RT \ ,$$

where

P = absolute pressure,
R = gas constant, and
T = absolute temperature

The external heat transfer process by convection across the film is described by the following equation:

$$Q = hA_p (T_B - T_S) \ , \tag{7-7}$$

where

h = heat transfer coefficient, energy/area/temperature;
A_p = external surface area per mass of solid;
T_B = absolute bulk temperature, R;
T_S = absolute particle surface temperature, R; and
Q = total heat flow to the gas per mass of particle.

Equation 7-7 assumes that there is minimal heat transfer by conduction between particles and negligible radiation exchange. The total heat flow Q is given by the following expression:

$$Q = (W)(\Delta H_R) \ , \tag{7-8}$$

where

H_R = heat of reaction, energy/mole.

In fixed-bed operation, Satterfield (1970) recommends correlations for heat and mass transfer coefficients based on the Colburn j factor defined as follows:

$$j = \frac{k_m}{V} (Sc)^{2/3} = \frac{h}{C_p(\rho * V)} (Pr)^{2/3} \ , \tag{7-9}$$

where

j = Colburn j factor, dimensionless;
k_m = mass transfer coefficient, length/time;
h = heat transfer coefficient, energy/time;
C_p = heat capacity, energy/mole temperature;
$\rho*$ = molar density, moles/volume;
V = superficial velocity, length/time based on empty tube;
Sc = Schmidt number, $\mu/\rho D$, dimensionless;
Pr = Prandtl number, $C_p\mu/k_T$, dimensionless;
μ = viscosity, mass/length/time;
ρ = mass density, mass/volume;
D = diffusivity through the film, $(\text{length})^2$/time; and
k_T = thermal conductivity of the film, energy/length/time/temperature.

The j factor depends on the external bed porosity ϵ, and the Reynolds number, $Re = D_pV\rho/\mu$, where D_p is the particle diameter as follows:

$$j = \frac{0.357}{Re^{0.359}} \qquad 3 \le Re \le 2000 \quad . \tag{7-10}$$

The appropriate particle diameter is given as:

$$D_p = \frac{6V_{ex}}{S_{ex}} \quad , \tag{7-11}$$

where

V_{ex} ≡ volume of particle, and
S_{ex} = surface area of particle.

In fluidized beds, Chu et al. (1953) recommend the j factor as follows for mass and heat transfer:

$$j = 5.7 \left(\frac{Re}{1-\epsilon}\right)^{-0.78} \qquad 0 < \frac{Re}{1-\epsilon} < 30 \quad , \tag{7-12a}$$

$$j = 1.77 \left(\frac{Re}{1-\epsilon}\right)^{-0.44} \qquad 30 < \frac{Re}{1-\epsilon} < 10{,}000 \quad . \tag{7-12b}$$

Equations 7-9 and 7-12 show that the heat and mass transfer coefficients vary with velocity, gas density, and particle size due to the Reynolds number dependency.

For fixed beds:

$$k_m h = f(V^{0.641})$$

For fluid beds:

$k_m h = f(V^{0.22})$ low Reynolds numbers

$k_m h = f(V^{0.56})$ high Reynolds numbers

By definition, the j factor for mass transfer and for heat transfer are identical. In terms of temperature dependency, the mass transfer coefficient behaves like a diffusion coefficient. Therefore:

$$\frac{k_m(2)}{k_m(1)} = \left(\frac{T_2}{T_1}\right)^{1.75} \tag{7-13}$$

For a temperature change from 800 C to 1000 C, $k_m(2)/k_m(1) = 1.35$. If an Arrhenius behavior were assigned to the mass transfer coefficient:

$$k = k_o \exp(-E/RT) \ , \tag{7-14}$$

a value of about 4 kcal is obtained for the temperature change from 800 C to 1000 C. Thus the mass transfer process has a very low activation energy; that is, the rate of mass transfer is not affected significantly by temperature.

External mass transfer reduces the concentration of reactant gas close to the particle surface and thus reduces the overall process rate. To demonstrate this phenomenon, consider gasification to be a first order reaction. Then at steady state, the rate of gasification equals the rate of mass transfer:

$$kC_S = k_m A_p (C_B - C_S) \ . \tag{7-15}$$

Solving for the surface concentration yields:

$$C_S = \frac{k_m A_p C_B}{k + k_m A_p} \ . \tag{7-16}$$

The process rate is given by $-r_c = kC_S$:

$$-r_c = \frac{kk_m A_p C_B}{k + k_m A_p} \ . \tag{7-17}$$

If the mass transfer rate constant k_m is large, $k_m > k$, the rate reduces to:

$$-r_c = KC_B ; \tag{7-18}$$

that is, the true kinetic rate is based directly on the bulk concentration. At high temperatures, $k \geq k_m$ since the activation energy for k is typically 50 kcal and the process becomes controlled by mass transfer. Due to the low activation energy for the mass transfer coefficient, the process rate becomes almost independent of temperature at high temperatures.

External mass transfer effects can be minimized by increasing the velocity (v) or mass flux (ρ v) and decreasing the particle size (D_p). The mass transfer coefficient increases with an increase in particle size according to Eqs. 7-9 through 7-12 as $k \propto D_p^n$ with $0.22 \leqq n \leqq 0.641$. Since the particle external surface area per unit weight is inversely proportional to D_p, decreasing the particle size increases the $k_m A_p$ product by D_p^m with $0.359 \leqq m \leqq 0.78$.

Similarly, for heat transfer:

$$T_S = T_B - \frac{(-r_c)(\Delta H_r)}{hA_p} \ . \tag{7-19}$$

For large reaction rates, high heats of reaction, large particles, or low velocities the solid temperature may be significantly different from the bulk gas temperature. For endothermic reactions the particle is cooler whereas for exothermic reactions the particle temperature is higher. The effect of velocity and particle size on h are the same as for k_m.

7.2.2 Pore Diffusion

The gasification reaction occurs principally within the particle. Except at very high temperatures, reactants must diffuse into the pore to the reacting surface. The average reaction rate within the particle may be related to the rate based on the surface concentration in terms of the effectiveness factor (for example, Satterfield 1970) defined as follows:

$$\eta = \frac{(r_{avg})}{r_{surface}} \quad . \tag{7-20}$$

The effectiveness factor is a function of a dimensionless group termed the Thiele modulus, which depends on the diffusivity in the pore, the rate constant for reaction, pore dimension, and external surface concentration C_S.

The effectiveness factor for a wide range of reaction kinetic models differs little from the first order case. For an isothermal particle, the first order reaction effectiveness factor is given as follows:

$$\eta = \frac{\mathrm{Tanh}\ \phi}{\phi} \quad , \tag{7-21}$$

where ϕ is the Thiele modulus,

$$\phi = L_p \left(\frac{k C_s^{\ m-1}}{V_p D} \right)^{1/2} \quad , \tag{7-22}$$

and

L_p = effective pore length, cm = R/3 for spheres (R = particle radius);
k = reaction rate constant, $(\mathrm{cc/mole})^{m-1} s^{-1}$;
C_S = external surface concentration, moles/cc;
m = reaction order;
V_p = pore volume, cc/g; and
D = diffusivity, cm^2/s.

When diffusion is fast relative to surface kinetics, $\phi \to 0$, $\eta \to 1$, and $r_{avg} = r_{surface}$. Under these conditions all of the pore area is accessible and effective for reaction. When $\phi \to \infty$, that is, diffusion is slow relative to kinetics, the reaction occurs exclusively at the particle external surface; reactant gas does not penetrate into the pores.

For the process controlled by pore diffusion, the apparent reaction rate constant k_{app} is given as follows based on the Thiele modulus:

$$k_{app} \propto (kD)^{1/2} . \tag{7-23}$$

Therefore, the apparent activation energy is given by Eq. (7-24), under the assumption that the activation energy for diffusion is much less than that for reaction.

$$E_{app} = \frac{E_{diff} + E_{act}}{2} \cong \frac{E_{act}}{2} \tag{7-24}$$

The effect of pore diffusion is to halve the activation energy for the process.

7.2.3 Surface Kinetics

The surface kinetics depend on the reaction and carbon species under consideration. Kinetic models are presented in the following sections. The activation energies for gasification reactions are on the order of 50 kcal/mole.

7.2.4 Global Kinetics

The global kinetic expression combines the effects of mass transfer, pore diffusion, and kinetics. Thus at steady state:

$$W = (-r_{surface}) = \text{overall process rate.} \tag{7-25}$$

At low temperatures, the kinetic rate constant approaches zero. Thus the pore diffusion and mass transfer processes are very fast relative to the kinetics; the kinetic step is rate-limiting. As the reaction temperature increases, pore diffusion tends to be important and, at sufficiently high temperatures, external mass transfer dominates. The effects of these processes on the activation energy are shown in Figure 7-3.

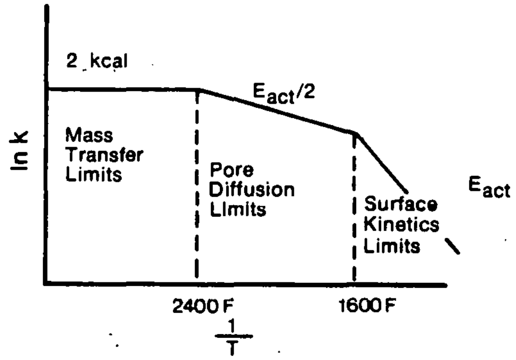

Figure 7-3. The Effect of Temperature on Reaction Rate of Heterogeneous Processes

7.2.5 Estimates of Pore Diffusion Effects

As an example, consider a biomass char with a pore volume and surface area of 0.5 cc/g (0.008 ft^3/lb) and 200 m^2/g, respectively. This translates to a mean pore radius of 50 Å. The Knudsen diffusivity controls the diffusional transport process at low pressure, and a value of the diffusion coefficient is estimated as 0.06 cm^2/s (0.004 ft^2/min). For a steam concentration of 1.1 x 10^{-5} gmole/cc (6.86 x 10^{-7} lbmole/ft^3) at 1 atm, and pore length of one-third the particle radius, the data presented in Table 7-1 were generated.

Table 7-1 shows that for biomass chars with the assumed properties, particles smaller than 20 mesh will be free of pore diffusion effects at gasification temperatures. Chars undergoing combustion may be diffusion-limited.

Table 7-1. EFFECTIVENESS FACTORS FOR BIOMASS CHARS

	Kinetic Rate (g char/g-min)			
Particle Diameter	0.01 (700 C)[a]	0.10 (800 C)[a]	1.00 (900 C)[a]	240 Combustion (900 C)[a]
1/4 in.	0.413	0.133	0.042	0.0027
20 mesh	0.968	0.765	0.317	0.021
200 mesh	0.999	0.998	0.975	0.233

[a] Approximate temperature at which the rate will be observed for biomass chars for gasification with CO_2 or steam.

7.2.5.1 Gasification Reactions

For coal chars, the rate of steam gasification is on the order of 0.01 g/g-min to 0.05 g/g-min at 900 C (1650 F). Thus for coal chars having the same properties used to construct Table 7-1, pore diffusion limitations appear to become important for particles larger than 20 mesh at 900 C.

For a variety of bituminous coal chars, Dutta et al. (1975) found that pore diffusion became important above 980 C for particles of -35 + 60 mesh size and larger for CO_2 gasification.

Hedden and Lowe (1965) claim that pore diffusion is unimportant for graphite particles smaller than 35 mesh at 900 C.

Walker and Hippo (1975) examined the effect of particle size on gasification rate for lignite and bituminous chars. At 900 C (1650 F), pore diffusion mass transfer appeared to be important at particle sizes of 325 mesh, at least during the initial stages of gasification. Since coal chars contain some very fine pores, elimination of pore diffusion is probably not possible but smaller particle sizes tend to minimize the effect.

For biomass materials, the reactivity is such that comparable gasification rates for wood chars are obtained at temperatures 100 C to 200 C lower than those required for coal. Thus, diffusion mass transfer may be important for 20 mesh particles at temperatures on the order of 700 C to 800 C (1300 F to 1475 F). For fluidized-bed gasification of biomass chars, smaller particles are used and thus mass transfer within the particles does not tend to affect the process rate. However, for the large particles (1/4 in.) used in fixed bed operations, intraparticle mass transfer may decrease the process rate significantly even at 700 C (1300 F). At present there is insufficient information to quantify more fully the diffusional effect; data on the structure, effect of particle size, and rate for a variety of biomass chars are limited and none are available for pelletized materials.

7.2.5.2 Combustion Reactions

The combustion reaction occurs at a much more rapid rate than gasification. For Saran chars, Tomita et al. (1977) show that the rate of combustion in air at 550 C is comparable to the rate of CO_2 gasification at 900 C. The gasification rate of the char was 1 g/g-min, which is typical of biomass chars.

Thring and Essenhigh (in Lowry [1963]) report an activation energy of about 30 kcal for the carbon combustion reaction. At 900 C, the approximate ratio of the kinetic combustion rate to gasification is estimated to be:

$$\left(\frac{r_{\text{combustion}}}{r_{\text{gas}}}\right)_{900\text{C}} = 240 \ . \tag{7-26}$$

Based on the relative rate data, an estimated intrinsic combustion rate would be 240 g/g-min for biomass chars at 900 C. The combustion reaction rates for various particle sizes, including the effects of pore diffusion, are given in Table 7-2.

Table 7-2. THE EFFECT OF PORE DIFFUSION ON GASIFICATION AND COMBUSTION RATES FOR BIOMASS CHAR

	Pore Diffusion Corrected Rate, (g/g-min at 900 C)		
Particle Diameter	Combustion	Gasification	$r_{\text{combustion}}/r_{\text{gas}}$
1/4 in.	0.648	0.042	15.4
20 mesh	5.04	0.317	15.9
200 mesh	55.9	0.975	57.3

The effect of pore diffusion is to bring the rates closer together. The combustion reaction, however, is still more than an order of magnitude faster than the gasification reaction.

7.2.6 Estimates of External Mass Transfer Effects

External mass transport generally becomes dominant at temperatures higher than that at which pore diffusion limits the gasification rate. For small particles, $D \leq 20$ mesh, mass transfer limitations generally are not important because these particles have external surface areas that are large compared to their unit volume. Furthermore, mass transfer coefficients are greater in fluid bed operations due to the motion of the solid particles. Thus in fluid bed operations, external mass transfer limitation in the temperature region below 900 C to 1100 C is never important. For fixed bed operation, mass transfer to large particles can be important.

In fixed beds, the mass transfer coefficient is given by the following expression resulting from Eq. (7-9) and (7-10):

$$k = \frac{j\ (\rho *V)}{(Sc)^{2/3}} = \frac{0.357\ Re^{-0.359}\ (\rho *V)}{(Sc)^{2/3}} \quad . \tag{7-27}$$

Table 7-3 presents mass transfer calculations for a fixed-bed gasifier operating at 1 atm and 1 ft/s gas velocity with 1/4-in. particles. For a kinetic gasification rate of 1.0 g/g-min (see Table 7-1), the observed rate, limited by pore diffusion mass transfer, would be 0.014 g/g-min. Using the external mass transfer rate constant from Table 7-3, the mole fraction drop, Δy, across the external film would be:

$$\Delta y = \frac{0.014\ \text{g/g-min}}{1.15\ \text{g/g-min}} = 0.012 \quad .$$

If relatively pure steam or CO_2 were being used in gasification, external mass transfer again would not limit the process.

From this analysis, it may be concluded tentatively that particle size is important in terms of diffusional limitations during gasification but may not be in terms of external mass transfer effects. This conclusion is dependent on the structural properties of the feedstock. For biomass chars, the process rate can be increased significantly by using small particles that tend to eliminate pore diffusion mass transfer.

For combustion, the mole fraction drop at 900 C is more significant:

$$\Delta y = \frac{0.648\ \text{g/g-min}}{1.15\ \text{g/g-min}} = 0.56 \quad .$$

The combustion reaction may become limited by external mass transfer for larger particles at 900 C. Thus, combustion is predominantly a surface phenomenon at the higher gasification temperatures whereas gasification occurs more uniformly throughout the particle. For smaller particles, as in a fluidized bed, external mass transport has a lesser effect on the combustion rate.

7.3 Mechanistic Considerations for CO_2 and Steam Gasification

Considerable information is available concerning the mechanisms of the gasification reactions. The C-CO_2 reaction has been the most extensively studied of the gasification reactions because its products do not enter into side reactions. The steam-C reaction is technically the more important of the two reactions; it has been found that both reactions are similar in their kinetics.

Table 7-3. EFFECT OF MASS TRANSPORT ON THE OVERALL GASIFICATION RATE IN A FIXED BED GASIFIER

Reaction Rate = 0.014 g/g-min = 0.014 lb/lb-min

Particle Size, D_p = 1/4-in. cylinders

Gas Superficial velocity, v = 1 ft/s

Pressure = 1 atm CO_2 or steam

Sc (Schmidt Number) = 0.7, dimensionless

Gas Density, ρ = 5.54×10^{-4} lbmoles/ft^3

Viscosity of gas, μ = 0.035 cP

Bed Voidage, ϵ = 0.5 ft^3 of voids/ft^3 of bed

Re (Reynolds Number) $= \dfrac{\rho D_p V}{\mu} = 21.6$

Particle Density (ρ_p) = 30 lb/ft^3

j_D (Colburn j Factor) = 0.237, dimensionless

$\bar{k}_m = k_m C$ $= 0.01 \dfrac{\text{moles}}{\text{ft}^2\text{-min}} \times 12 \text{ lb/mole} = 0.12 \dfrac{\text{lb carbon}}{\text{ft}^2\text{-min}}$

A_p, Specific External Particle Surface Area, $= \dfrac{S_p}{V_p} \cdot \dfrac{1}{\rho_p} = \dfrac{\left[2 R_p^2 + 2 R_p (2 R_p)\right]}{R_p^2 (2R_p)} \times \dfrac{1}{\rho_p}$

$= \dfrac{3}{R_p \rho_p} = 9.60 \text{ ft}^2/\text{lb}$

$k_m A_p$ = 1.15 lb/lb-min = 1.15 g/g-min

7.3.1 Gasification with CO_2

Mentser and Ergun (1973) recently reviewed the literature on the C-CO_2 reaction and performed a number of isotope experiments on spheron carbon to learn about the reaction mechanism. The mechanistic studies indicate:

- The exchange of oxygen by Eq. (7-28) occurs reversibly at all temperatures investigated, including those below that required for gasification:

$$C_f + CO_2 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} C(O) + CO \quad . \tag{7-28}$$

  C(O) represents a surface oxide, not adsorbed oxygen. C_f are free carbon sites.

- Interchange of carbon between CO and solid carbon occurs only at temperatures on the order of 1500 C.

- Deposition of carbon on the surface by decomposition of CO_2 occurs at an insignificant rate.

Bonner and Turkevich (1951) found that during the initial stages of reaction 7-28, 95% of the radioactive CO_2 charged was converted to radioactive CO with no increase in system pressure. This result further substantiates reaction 7-28. During later stages of the reaction, the gas pressure increased, suggesting surface decomposition of the oxide species:

$$C(O) \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} CO + nC_f \tag{7-29}$$

In several studies (Bonner and Turkevich 1951; Orning and Sterling 1954), it was found that the oxygen exchange reaction (Eq. 7-28) was potentially faster than the oxide decomposition reaction (Eq. 7-29) at low temperatures, suggesting that the oxide decomposition was rate controlling.

Assuming that Eqs. 7-28 and 7-29 in the forward direction apply, the reaction rate is given by the following kinetic expression if it is assumed that the reactions are far from equilibrium:

$$-r_c = \frac{k_1 C_{tot} \; P_{CO_2}}{1 + \frac{k_1'}{k_2} P_{CO} + \frac{k_1}{k_2} P_{CO_2}} \quad . \tag{7-30}$$

According to the rate equation, CO_2 and CO may suppress the reaction. CO can decrease the gasification rate by reversibly removing the surface complex C(O) by Eq. 7-28. At high CO_2 partial pressures, the reaction becomes independent of CO_2 pressure because the surface sites become saturated with CO_2. The oxygen exchange reaction (Eq. 7-28) limits the rate at high temperatures due to its lower activation energy. The surface oxide decomposition reaction (Eq. 29) has a large activation energy and is much more temperature sensitive than the exchange reaction. Grabke (1966) estimated that in pure CO_2 gaseous environments, and at temperatures above 1000 C, reaction 7-28 becomes rate controlling; in environments with equal CO and CO_2, reaction 7-28 does not become limiting until about 1200 C for the carbon he used. Mentser and Ergun (1973) suggest that the forward exchange reaction has an activation energy of about 53 kcal; the reverse exchange reaction 36 kcal; and the oxide decomposition reaction 58 kcal. In Eq. 7-30, the temperature dependence of the ratios k_1'/k_2 and k_1/k_2 are such that these terms become negligible at the high temperatures at which the rate equation goes to a first order form:

$$-r_c = k_1 C_{tot} P_{CO_2} \cdot \tag{7-31}$$

At the lowest temperatures, in pure CO_2 atmospheres, the gasification rate varies from zero order to first order:

$$-r_c = \frac{k_1 C_{tot} P_{CO_2}}{1 + \frac{k_2}{k_1} P_{CO_2}} \cdot \tag{7-32}$$

Equation 7-32 explains the observation that at moderate pressures and temperatures the reaction varies by about $(P_{CO_2})^{1/2}$.

Equation (7-30) also states that the rate is proportional to C_{tot}, the total number of active carbon sites available. C_{tot} is not the total surface area of the carbon; it has been proposed that only edge carbon atoms, atoms present along crystal defects, and atoms adjacent to mineral matter deposits (particularly CaO, MgO, and FeO_4) are sufficiently reactive to be gasified. Thus C_{tot} is only a small fraction of the surface atoms.

In studies where oxygen, hydrogen, and carbon monoxide chemisorption areas and total surface areas of chars were compared (Laine et al. 1963a, b; Menster and Ergun 1973), it was found that the chemisorption area amounted typically to only several percent of the total surface area. Thus the number of exposed reactive carbon sites is small compared to the total number of exposed sites. Further, Ergun (1956) and Menster and Ergun (1973) showed that the activation energies of the elementary steps are independent of char type. Thus the reaction rate at a given temperature is dependent on the number of active sites only.

The mechanistic equation (7-32) can be extended to consider the reversible approach to equilibrium by adding in the reverse reaction from Eq. 7-29. Under these conditions, the gasification rate equation becomes:

$$-r_c = \frac{k_1 C_{tot} (P_{CO_2} - P^2_{CO}/k_{eq})}{1 + \frac{k_1 + k_2'}{k_2} P_{CO} + \frac{k_1}{k_2} P_{CO_2}} \cdot \tag{7-33}$$

At pressures substantially above 1 atm Blackwood and Ingeme (1960) report that the rate varies with a CO_2 partial pressure order somewhat greater than unity.

7.3.2 Kinetics of Carbon-Steam Reaction

The kinetics of the carbon-steam reaction are in many respects analogous to those for the carbon-CO_2 reaction. The carbon-steam reaction is made more difficult to analyze by possibly competitive reactions resulting from the generation of H_2 and CO_2 by side reactions.

Lowry (1963) reports general agreement that the products of the carbon-steam reaction at low pressures are CO and H_2:

$$C + H_2O \longrightarrow CO + H_2 \ . \tag{7-34}$$

Carbon dioxide is produced through the water-gas shift reaction which is catalyzed by the carbon surface.

As with CO_2, water vapor deposits oxygen on the carbon surface at temperatures below gasification temperatures. This oxygen may be removed by reaction with either carbon monoxide or hydrogen at temperatures below gasification temperatures. At gasification temperatures the surface oxide readily decomposes to liberate carbon monoxide.

A plausible mechanistic model is the following:

$$C_f + H_2O \underset{k_6'}{\overset{k_6}{\rightleftarrows}} C(O) + H_2 \tag{7-35}$$

$$C(O) \underset{k_7'}{\overset{k_7}{\rightleftarrows}} CO + nC_f . \tag{7-36}$$

In Eq. 7-35, C_f represents free carbon sites for reaction while C(O) is the surface oxide. Assuming this two-step mechanism, at steady state the rate expression is:

$$-r_c = \frac{k_6 \ C_{tot} \ P_{H_2O}}{1 + \frac{k_6'}{k_7} P_{H_2} + \frac{k_6}{k_7} P_{H_2O}} \ . \tag{7-37}$$

According to the model, steam and hydrogen may suppress the reaction. Hydrogen can reduce the reaction rate by removing the surface oxide by the reverse reaction in Eq. 7-35. Thus the number of complexes available to decompose to CO is reduced. At sufficiently high steam partial pressures, the surface becomes saturated with the oxide complex and the decomposition of the oxide by Eq. 7-36 becomes rate controlling.

The rate is also dependent on C_{tot}, the number of carbon sites available on the surface for reaction. These sites are the same as those that are capable of reacting with CO_2.

The rate constant (k_6) exhibits an Arrhenius dependency and thus increases with temperature. The ratios of rate constants in the denominator of Eq. 7-37 can exhibit a positive or negative temperature dependence depending on the activation energies (E) of the individual rate constants. Since the surface oxide is identical in both CO_2 and steam gasification reactions, the activation energy for k_7 should be on the order of 58 kcal. For graphite tubes, Lowry reports $E_6 = 32.7$ kcal, $E_6' = 14.2$ kcal, and $E_7 = 46.6$ kcal. While the activation energy E_7 is lower than for the CO_2 reaction ($E_2 = 58$ kcal) the difference is probably within experimental error.

An appropriate extension of the rate expression as Eqs. 7-36 and 7-37 approach equilibrium is:

$$-r_c = \frac{k_6\, C_{tot} \left(P_{H_2O} - P_{CO} P_{H_2O} / k_{eq} \right)}{1 + \frac{k_6'}{k_7} P_{H_2} + \frac{k_6}{k_7} P_{H_2O}} \quad . \tag{7-38}$$

The reactivities of the chars are affected by thermal annealing or graphite formation; the pretreatment and thermal history of the char are important. If freshly prepared char and char thermally stabilized (annealed) at the reaction temperature are reacted under the same conditions, the fresh char will have a higher initial reactivity than the stabilized char. The rates will tend to become the same at longer reaction times, after the fresh char has stabilized. Thermal annealing becomes important at temperatures above 700 to 1100 C. During thermal annealing, carbon active sites (edges and dislocations) are lost due to surface reorganization, and the char structure becomes more graphitic. Additionally, thermal annealing causes a decrease in porosity of the char that reduces the accessibility of the internal surface to reacting gases. The overall effect of pretreatment on yield is not extremely significant since the carbon-steam reaction is relatively slow. If the pretreatment is conducted at a temperature higher than the reaction temperature, the reactivity of the char will be lower than that of the char prepared at the reaction temperature. Table 7-4 shows the specific rate data for a coal devolatilized at two different temperatures. The rate of gasification was reduced by a factor of two to three by thermal annealing.

Table 7.4. RATE OF GASIFICATION OF COAL CHAR IN STEAM AT 850 C (Jolley et al. 1953)

	Rate (g/g-min)	
	Pretreatment Temperature	
Burnoff (%)	850 C	1000 C
0	0.0041	0.0014
30	0.0059	0.0026
60	0.0087	0.0038

At high temperatures, the thermal stabilization becomes rapid enough to interfere with the rate of gasification. Figure 7-4 from Yang and Steinberg (1977) shows that above about 1200 C thermal annealing tends to make the rate insensitive to temperature for a variety of carbons; above 1400 C, the rate decreases with increasing temperature due to the very rapid loss of active sites.

The water-gas shift reaction is considered to occur catalytically on the carbon or ash surface at sites not undergoing gasification and always occurs during gasification.

It has been found experimentally that the rate equation (7-39) correlates catalytic water-gas shift data:

$$-r_{CO} = \frac{k_8 \; P_{CO} P_{H_2O} - P_{H_2} \; P_{CO_2}/k_{eq}}{(1 + k_9 \; P_{CO_2} + k_{10} \, P_{CO}} \quad . \qquad (7\text{-}39)$$

7.4 RELATIVE REACTIVITIES OF CARBONS DURING GASIFICATION

A number of recent studies have examined the relative reactivities of carbons to carbon dioxide and steam. All of the studies discussed in this section used chars that were devolatilized by slow heating in nitrogen to a temperature from 900 C to 1000 C; the chars were held at the higher temperature for at least 30 min to stabilize (graphitize) the char.

7.4.1 Reactivity in CO_2 at 1 atm, 900 C

Considerable data have been reported on the reactivity of chars with CO_2 at 900 C and 1 atm pressure. Most runs were made for -40 mesh particles. The reactivity data (Table 7-5) show clearly the effect of carbon rank (degree of aromatization) on gasification reactivity. In carbon dioxide lignites are, on the average, ten times more reactive than the bituminous chars at the same conditions.

Baird et al. (1976) report relative reactivities for biomass and coal chars based on the approach to equilibrium of the C-CO_2 reaction. In their fixed bed reactor using pure CO_2, the ratio of exit CO to CO_2 is a measure of reactivity at steady state. The materials studied included paper board, wood chips, lignite, and subbituminous coals. Each was pyrolyzed at reaction temperature prior to reaction. The wood chips consisted of chips and branches of 1/8 in. by 3/4 in. size. The paper board, composed of compressed paper and plastic, had a density of 60 lb/ft^3 and was charged in 1-in. squares. No particle size was reported for the coals. Because of the variability in particle sizes, it is not possible to rate the feedstocks quantitatively. Table 7-6 shows the qualitative rating of data taken at the lowest temperatures of the study, where mass transport is least important.

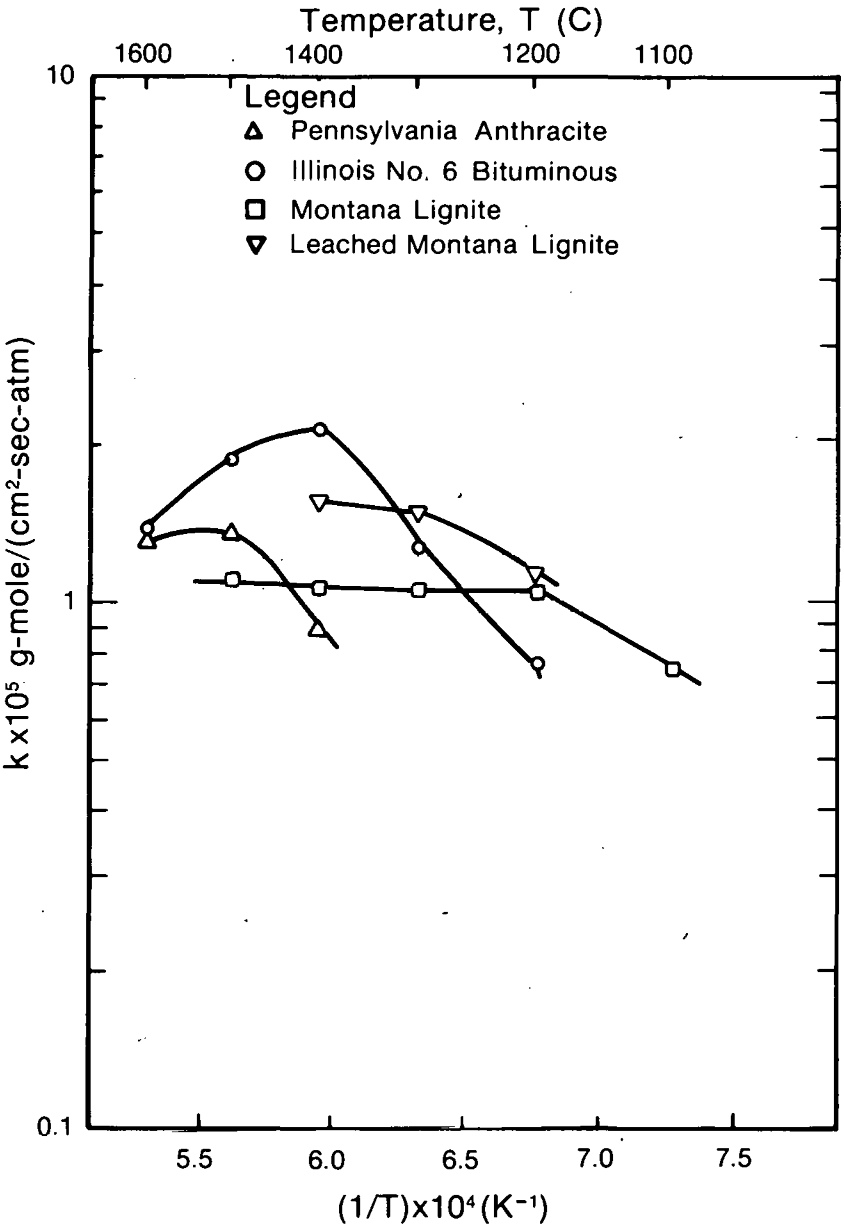

Figure 7-4. Rate Constant as a Function of Temperature for Coal Chars

Table 7-5. COMPARISON OF CHAR REACTIVITY IN C-CO_2 REACTION AT 900 C

	Reference	Reactivity (g/g-min)	Method
Montana Lignite	Walker and Hippo 1975	0.058	TGA
ND Lignite (1)	Walker and Hippo 1975	0.060	TGA
ND Lignite (2)	Walker and Hippo 1975	0.045	TGA
Wyoming Sub C	Walker and Hippo 1975	0.055	TGA
Wyoming Sub A	Walker and Hippo 1975	0.028	TGA
Illinois HVC	Walker and Hippo 1975	0.011	TGA
IGT No. 155 (ILL 6)	Dutta et al. 1975	0.0107	TGA
Hydrane No. 49 (ILL 6)	Dutta et al. 1975	0.0117	TGA
Synthane No. 122 (ILL 6)	Dutta et al. 1975	0.0129	TGA
Hydrane Char (ILL 6)	Fuchs and Yavorsky 1975	0.011[a]	Fluid bed
Hydrane Char (HVA)	Dutta et al. 1975	0.0063	TGA
High Vol A (KY)	Walker and Hippo 1975	0.0032	TGA
Graphite From Pitch	Peterson and Wright 1955	0.002	TGA
Coconut Shell Charcoal	Lowry 1963 (See Table 7-13)	0.01	—

[a] Corrected to 1 atm assuming rate is related by $(P_{CO_2})^{1/2}$.

Table 7-6. **QUALITATIVE COMPARISON OF THE REACTIVITY OF BIOMASS AND COAL CHARS IN CARBON DIOXIDE**

	Activity Ratio $\left(\frac{CO}{CO + CO_2}\right)$		
Feedstock	500 C	600 C	700 C
Wood chips	8.2	11.8	21.2
Lignite	2.3	6.4	16.6
Pressed paper	2.3	1.5	7.9
Subbituminous coal	1.7	4.9	8.8
Equilibrium	9.1	34.0	71

According to the study, the wood chips exhibit a reactivity greater than lignite, but a quantitative ranking in terms of weight loss of carbon is not possible. The paper exhibits an activity close to that of the subbituminous char, a result which is probably unreasonable. No physical property data for the chars or explanation of the reactivity is given.

7.4.2 Reactivity in Steam

A number of char reactivity studies have been conducted in steam. The same general pretreatment policy was followed; that is, slow devolatilization of the char to be tested at the reaction temperature. Table 7-7 summarizes a number of these gasification studies. Data are available for several biomass chars from Rensfelt et al. (1978). The rates have been adjusted to 900 C and 1 atm of steam with the assumptions that the reported activation energy is correct where applicable and that the rate is proportional to $(P_{H_2O})^{1/2}$. Table 7-7 shows that the data for the bituminous coal chars from Friedman (1975) and Lowry (1963) are consistent. The rates for biomass gasification appear to be four to ten times greater than those for the lignite chars, which are the most reactive coal chars available.

A comparison of Tables 7-5 and 7-7 shows that the gasification rate in pure steam is greater than that in pure CO_2 by a factor of about 3 to 5. Thus for rating chars on a relative basis, kinetic studies in CO_2 are satisfactory.

In coal chars, rank is a measure of the degree of aromatization or graphitization of the carbon. As rank increases, reactivity decreases. Since biomass chars are much more reactive than even lignite, the degree of aromatization resulting from pyrolysis may be less than that in the coal chars. Such a hypothesis is consistent with the monoaromatic structure of lignin. The difference in reactivity also may be partly explained by differing pore structures; biomass pore structures are much more open than coal pore structures.

7.5 EFFECT OF BURNOFF AND SURFACE AREA

Numerous studies have been conducted on the effect of burnoff (% weight loss, sometimes called burnout) on gasification rate in carbon dioxide and steam atmospheres; they

Table 7-7. REACTIVITY OF CHARS IN STEAM AT 900 C

	Reactivity (g/g-min at 900 C)		
	Reference	Reported	Corrected to 1 atm steam
Illinois COED	Friedman 1975	0.0027	0.0027
Utah COED	Friedman 1975	0.0054	0.0054
WKY COED	Friedman 1975	0.0069	0.0069
Pittsburgh	Friedman 1975	0.0093	0.0093
Pittsburgh oxidized[a]	Friedman 1975	0.0037	0.0037
Lignite 247	Nandi et al. 1975	0.020	0.132
Lignite LLL	Nandi et al. 1975	0.0159	0.105
Montana Lignite[b]	Linares et al. 1977	0.045	0.296
ND Lignite	Linares et al. 1977	0.044	0.290
Wy. Sub C	Linares et al. 1977	0.0390	0.257
Wy. Sub A	Linares et al. 1977	0.0156	0.103
Sub BC 2A8	Nandi et al. 1975	0.005	0.033
Ill HVC	Linares et al. 1977	0.0070	0.046
MVB 274	Linares et al. 1977	0.0004	0.0027
Coconut Shell	Linares et al. 1977	0.070	0.070
Solid Waste[b]	Rensfelt et al. 1978	0.318	0.372
Poplar Wood[b]	Rensfelt et al. 1978	0.942	1.102
Straw[b]	Rensfelt et al. 1978	0.463	0.542
Bark[b]	Rensfelt et al. 1978	0.725	0.849
High Moor Peat[b]	Rensfelt et al. 1978	0.152	0.178

[a] Oxidized during pyrolysis; corrected to 900 C using 18 kcal activation energy.
[b] Measured at 45% burnout, 0.73 atm steam.

show that the rate is dependent on burnoff in a complicated and somewhat confusing manner. Some materials show little change of rate with burnoff while others show marked changes, either positive or negative. Burnoff alters the pore size distribution, pore volume, and hence surface area available for reaction. It is logical, therefore, to believe that the rate of reaction should depend on the burnoff to the extent that burnoff alters the porous structure of the solid. In studies by Hedden and Lowe (1965), the chars to be gasified were produced by slow heating (20 C to 50 C per minute) to a temperature of 900 C. The graphites used to produce the chars were commercial products, and it is assumed that at some point during their preparation they were exposed to temperatures higher than 900 C. The maximum temperature and timing of exposure are important in that the stabilization or graphitization process is sensitive to the highest temperature experienced by the char. Any rate studies carried out at or below the temperature of manufacture will not be affected by major changes in the char structure due to thermal annealing.

Hedden and Lowe (1965) examined the rate of gasification of two graphites at 1030 C and 1 atm of CO_2 as a function of burnoff. The BET surface area based on liquid nitrogen was also determined at each burnoff level. Table 7-8 summarizes their results.

Table 7-8. COMPARISON OF BURNOFF SURFACE AREA AND RELATIVE RATES FOR BURNOFF OF GRAPHITES[a]
(Nitrogen BET)

% Burnoff (X)	Specific Surface (S)	Surface Area Ratio [S(O)/S(X)]	Reactivity Ratio [R(O)/R(X)]
Graphite G-S			
0	1.7	1.00	1.00
2	4.2	2.47	—
5	7.4	4.35	2.41
12	9.3	5.47	3.88
20	10.0	5.88	4.49
38	9.8	5.76	4.97
60	9.6	5.65	4.65
Graphite G-9			
0	1.6	1.00	1.0
5	7.3	4.6	2.5
9	10.5	6.6	3.4
21	14.5	9.1	3.8

[a] From Hedden and Lowe 1965.

There is a direct relationship between BET surface area and reaction rate. However, the rate is not directly proportional to the measured area of the particle, indicating that the low temperature BET surface might not be the "correct" area for correlating reaction rates.

Turkdogan and Vinters (1969) report N_2 BET areas and kinetic rates for the gasification of a coconut shell charcoal and a graphite at 900 C. The surface areas and rates were reported for a 10% burnoff. The data are presented in Table 7-9.

Table 7-9. GASIFICATION RATES AND SURFACE AREAS AT 10% BURNOFF FOR TWO CARBONS[a]
(Nitrogen BET)

Carbon	Surface Area (S) (m^2/g)	Gasification Rate (R) (g/g-min)
Graphite	4	8×10^{-5}
Coconut shell	850	0.014
Ratio	200	175

[a] From Turkdogan and Vinters (1969).

For the two very different carbons, the ratio of gasification rates and surface areas is essentially the same, indicating a proportionality between area and rate. The gasification rates reported are unusually low for the carbons investigated.

Dutta et al. (1975) investigated the relationship between N_2 BET area and reactivity at 900 C for four different coal chars. Their results are given in Table 7-10.

Table 7-10. RELATIONSHIP BETWEEN SURFACE AREA AND GASIFICATION RATE FOR COAL CHARS[a]
(Nitrogen BET)

Coal Char	Total Surface Area(S) (m^2/g)	Surface Area r_p 27.5 Å	Rate (R) (g/g-min)	$\frac{R}{S(27.5)}$
Hydrane No.150	18.75	18.75	0.067	3.57×10^{-3}
IGT No. HT155	423.87	25.43	0.113	4.44×10^{-3}
Hydrane No. 49	171.69	34.42	0.123	3.57×10^{-3}
Synthane No. 122	280.87	38.06	0.136	3.57×10^{-3}

[a] From Dutta et al. (1975).

There was no correlation between the reactivity and total BET surface area. Based on the pore size distribution, Dutta et al. found a strong correlation between the area for pores greater than 27.5 Å and the reactivity. At 900 C and 1 atm the bulk diffusion coefficient is about 1.7 cm^2/s while the Knudsen diffusion coefficient is 0.014 cm^2/s. Thus the diffusion process is pure Knudsen diffusion. Since the Knudsen diffusion coefficient is directly proportional to the pore radius, diffusion limitations in the fine pores might be responsible for making part of the surface completely inaccessible.

Wen et al. (1977) investigated the effect of burnoff on CO_2 BET surface area and on reactivity, on the assumption that the CO_2 surface area would be a better parameter against which to correlate reactivities. Table 7-11 shows the results of this study based on a lignite char. The char was prepared by devolatilization at 1000 C for 30 min. The reactivity was determined at 900 C.

Table 7-11. EFFECT OF BURNOFF ON SURFACE AREA AND REACTIVITY FOR LIGNITE CHARS
(Carbon Dioxide BET)

% Burnoff (X)	CO_2 Surface Area (S) (m^2/g)	Rate Ratio [R(O)/R(X)]	Surface Area Ratio [S(O)/S(X)]
0	137	1.0	1.0
21.4	186	1.4	1.34
45.0	281	2.03	2.05
56.3	306	2.35	2.24
71.4	404	2.50	2.95

These data indicate a strong correlation between the CO_2 reactivity and CO_2 surface area for the lignite char.

Rensfelt et al. (1978) studied the gasification of biomass and coal chars at various temperatures and burnoffs. Figure 7-5 shows the influence of burnoff on the gasification rate at constant temperature for various chars. Biomass materials such as bark and wood exhibit a rate that is strongly dependent on burnoff. This suggests that gasification is generating major increases in surface area in these materials. Figure 7-6 shows that the temperature also affects the rate dependency on burnoff for poplar wood. This might suggest that activated diffusion in molecular size pores contributes significantly to the gasification rate at higher temperatures. Activated diffusion is a transport process that occurs in molecular size pores. The diffusion coefficient is very small and highly temperature-dependent due to molecular interactions between the gas and surface. No surface area or pore size data were reported.

A number of conclusions can be drawn from these studies. Surface area and reaction rate are related during gasification. Furthermore, it is suggested that the percentage of active sites on the total surface remains constant during gasification. Most of the studies suggest that the N_2 BET surface is not a correct measure of the reactive surface. For low area solids (solids with a large mean pore radius), the nitrogen areas correlate reasonably well with reactivity. For high area solids where the bulk of the area is associated with fine micropores, the N_2 BET area is not related to reactivity. Nitrogen cannot penetrate micropores readily; the CO_2 can more readily diffuse into the micropores due to polar interactions with the char surface. The only study not consistent with this conclusion is that of Turkdogan and Vinters (1969), which shows a direct correlation between areas and rates for two solids, one of which has a significant area tied up in micropores.

For correlating reactivities, the CO_2 surface area is probably a better measure of reactive surface area than the N_2 surface area. No comprehensive studies of this type have

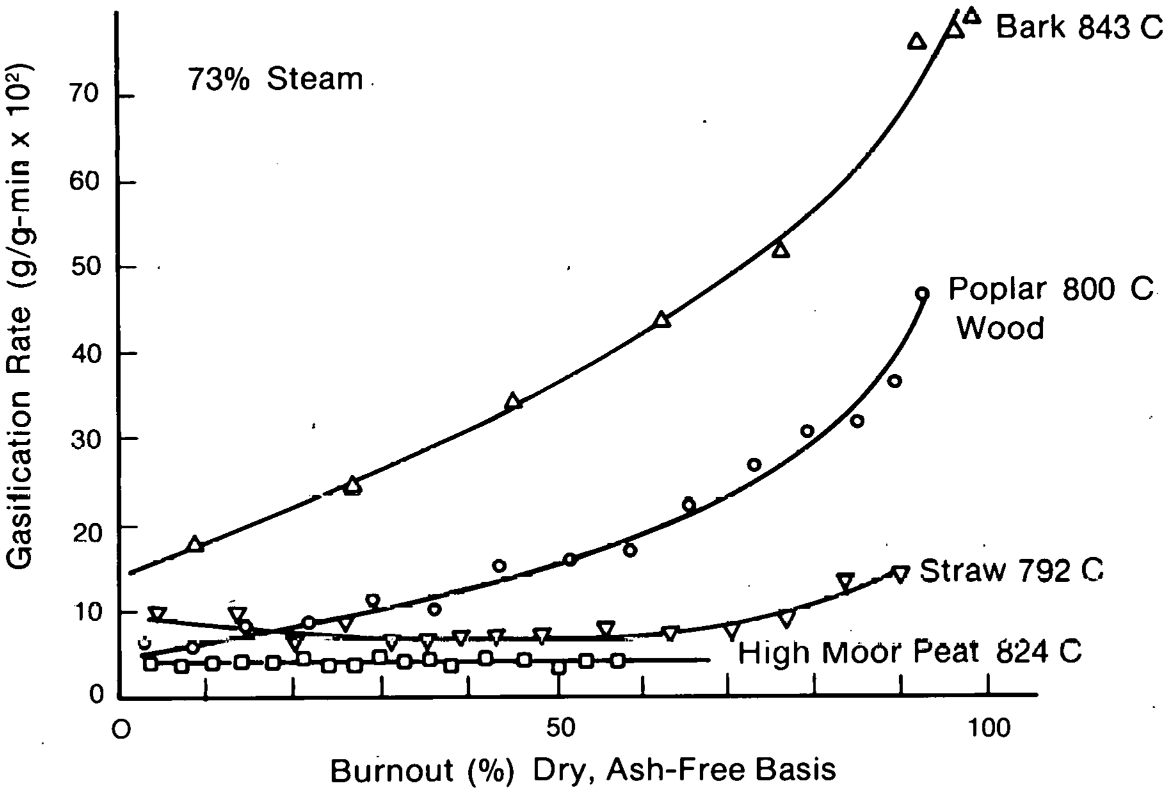

Figure 7-5. Influence of Burnout on the Gasification Rate of Different Fuels in a Steam-Argon Mixture

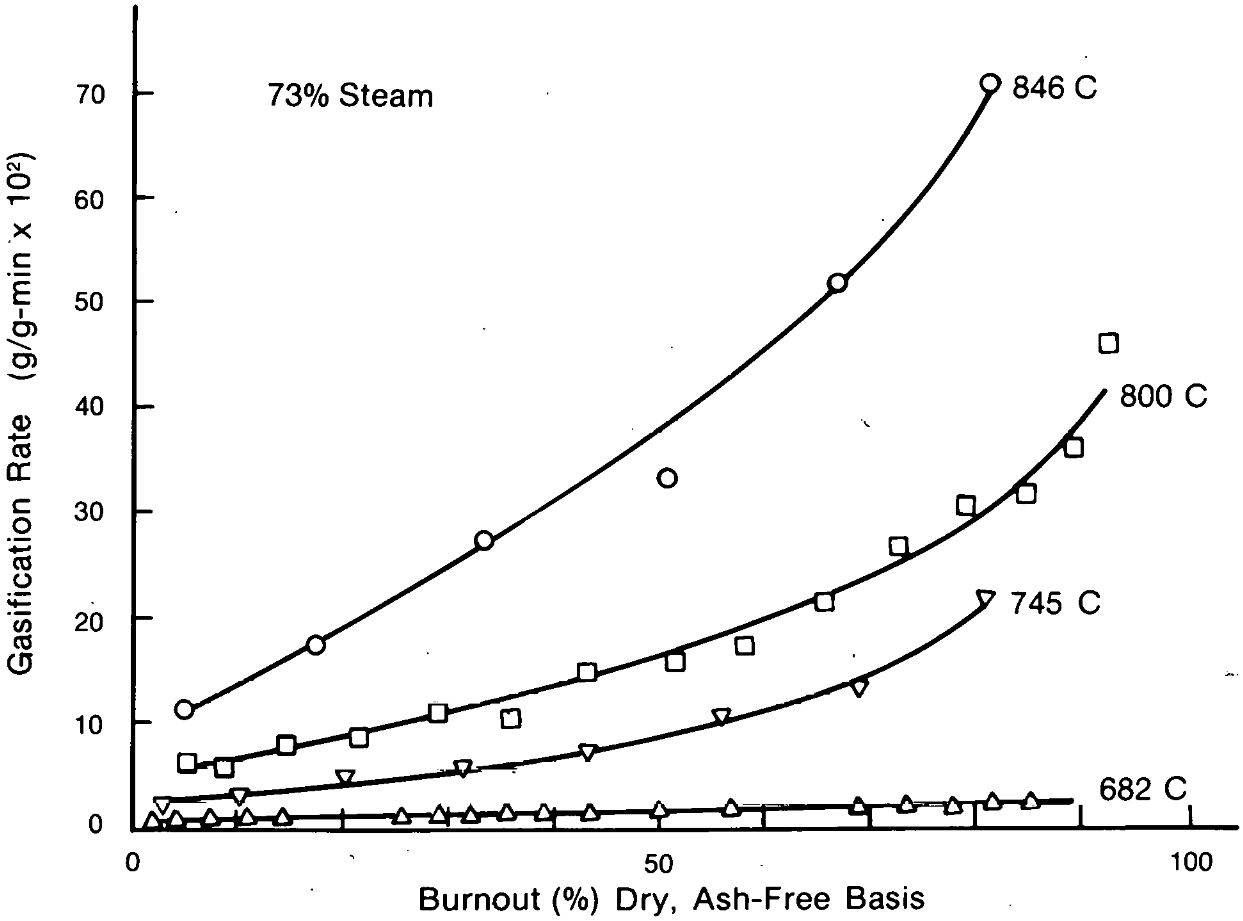

Figure 7-6. Influence of Burnout on the Gasification Rate of Poplar Wood in Steam-Argon Mixture

been done for biomass materials. Since the kinetic rates for the C-H_2O reaction and C-CO_2 reaction are similar, it is expected that similar conclusions could be drawn for the carbon steam reaction. Since steam is a smaller molecule and is more polar than CO_2, it can penetrate more micropores, a fact which may explain the difference in reactivity.

No data are available in the literature which relate surface area to gasification rate for biomass chars.

7.6 RATE CONSTANTS FOR BIOMASS CHARS

Most of the available studies ranking gasification reactivity are based on a constant gas composition. Researchers infer an activation energy based on the rate of carbon gasification from such data. These activation energies are apparent values in as much as there is an effect of temperature on the composition factor as discussed in Section 7-3. The only data available for biomass chars were reported by Rensfelt (1978). Table 7-12 shows apparent activation energies and frequency factors for biomass chars gasified in 0.73 atm of steam.

Table 7-12. KINETIC PARAMETERS FOR BIOMASS AND COAL CHARS
$[k=k_o \exp(-E_{act}/RT)]$

Fuel	Activation Energy (E_{act}) (kcal/mol)	Frequency Factor (k_o) (g/g-min)
Solid waste	59.5	3.9×10^{10}
Poplar wood	43.4	1.2×10^{8}
Straw	43.4	5.9×10^{7}
Bark	37.0	5.8×10^{6}
Peat	40.4	5.1×10^{6}
Bituminous coal	48.8	5.9×10^{7}

Except for the solid waste, the apparent activation energy is essentially constant at 42.6 ± 3.1 kcal/mole. The constancy of activation energy for a variety of charcoals and graphites has been observed by a number of researchers, particularly Ergun as cited earlier. The nature of the carbon is apparent in the frequency factor, which generally decreases with rank for the carbons investigated. The frequency factor is related to the number of active sites, while chemical activity of the sites is related to the activation energy. Thus there appear to be more energetically similar reactive sites available in biomass chars than in coal chars, suggesting either more available surface area or a less ordered structure.

No data are available for the effect of the ambient gas composition on the reactivity of biomass chars. Hedden and Lowe (1965) found that their data and data from other are studies could be fit to Eq. 7-30 over a wide range of conditions. Table 7-13 presents rate constant data for several studies from Lowry (1963). Paralleling the apparent rate data, the frequency factor and activation energy data show the appropriate trends with rank; that is, E_{act} is constant and k_1 decreases with increasing rank. The constant k_1/k_2, which accounts for the retardation of CO_2, is essentially independent of the carbon type. The constant k_1'/k_2 indicates that retardation by CO is strong and more variable

Table 7-13. ARRHENIUS CONSTANTS FOR THE CARBON-CARBON DIOXIDE REACTION

	Temperature Range (C)	k_1 $\left(\frac{\text{g-mole}}{\text{g-min-atm}}\right)$	E_{act} (kcal)	k'_1/k_2 (1/atm)	E_1-E_2 (kcal)	k_1/k_2 (1/atm)	E_1-E_2 (kcal)	Value at 800 C	
								k'_1/k_2	k_1/k_2
Coconut shell charcoal	734-830	6.3×10^8	58.8	1.26×10^{-8}	-45.5	3.16×10^6	30.1	23.37	2.34
New England coke	800-1090	6.9×10^5	47.6	1.4×10^{-2}	-15.0	0.21	-6.3	15.91	4.03
New England coke	--	3.16×10^7	61.7	4.0×10^6	-40.3	3.16×10^{-2}	-6.1	647.3	0.55
Electrode carbon	--	1.0×10^6	50.1	3.16×10^9	-60.6	0.16	-6.6	697.9	3.54
Pitch coke	926-1150	1.05×10^7	40.1	2.0×10^9	-55.1	--	--	33.5	--

than for CO_2. Using the rate constant data, the following equation applies at 800 C for coconut shell charcoal:

$$-r_c = \frac{0.00796\ P_{CO_2}}{1 + 23.37\ P_{CO} + 2.34\ P_{CO_2}} \ . \tag{7-40}$$

Figure 7-7 shows the effect of gas composition on rate for the coconut shell carbons relative to the rate in pure CO_2 at 1 atm. The rate is relatively independent of CO_2 pressure above 1 atm and is strongly inhibited by carbon monoxide. Thus, at 1 atm pressure, the rate in the gaseous environment of one third CO_2 is about one fifth that in a CO_2-free gaseous environment. For more active chars like the biomass materials, the behavior of coconut shell char should be typical. Thus, for biomass chars, changing the pressure should have little effect on gasification rate with CO_2.

Rate data were determined by Long and Sykes (1948) for coconut shell charcoal in steam.

At 800 C,

$$-r_c = \frac{0.0387\ P_{H_2O}}{1 + 33\ P_{H_2} + 2.54\ P_{H_2O}} \ . \tag{7-41}$$

This equation is also plotted in Figure 7-7. In a gaseous environment of one third hydrogen, the rate is depressed by a factor of five as compared to a H_2-free atmosphere. The rate in water is roughly five times as great in steam as in CO_2. Data for coal chars show a similar behavior.

From these data, it is evident that the rate is extremely sensitive to the partial pressure of the products CO and H_2. In practice, the gaseous environment may contain appreciable amounts of both CO and H_2.

7.7 CATALYTIC EFFECTS

A number of investigations have studied the effects of catalysis on gasification. Most metals, their oxides, and salts are more or less catalytic. Tingly and Morrey (1973) report that iron, calcium, and magnesium have the greatest potential effect on reactivity. Surface impurities can also affect the water-gas shift reaction. Biomass is essentially ash-free. Therefore, any catalyst to promote reaction would have to be added from an external source, increasing the ash disposal problem.

As an example related to biomass chars, Rensfelt (1978) investigated the C-steam gasification of peat char with and without a 2% K_2CO_3 catalyst. The alkali tripled the rate of C-steam gasification.

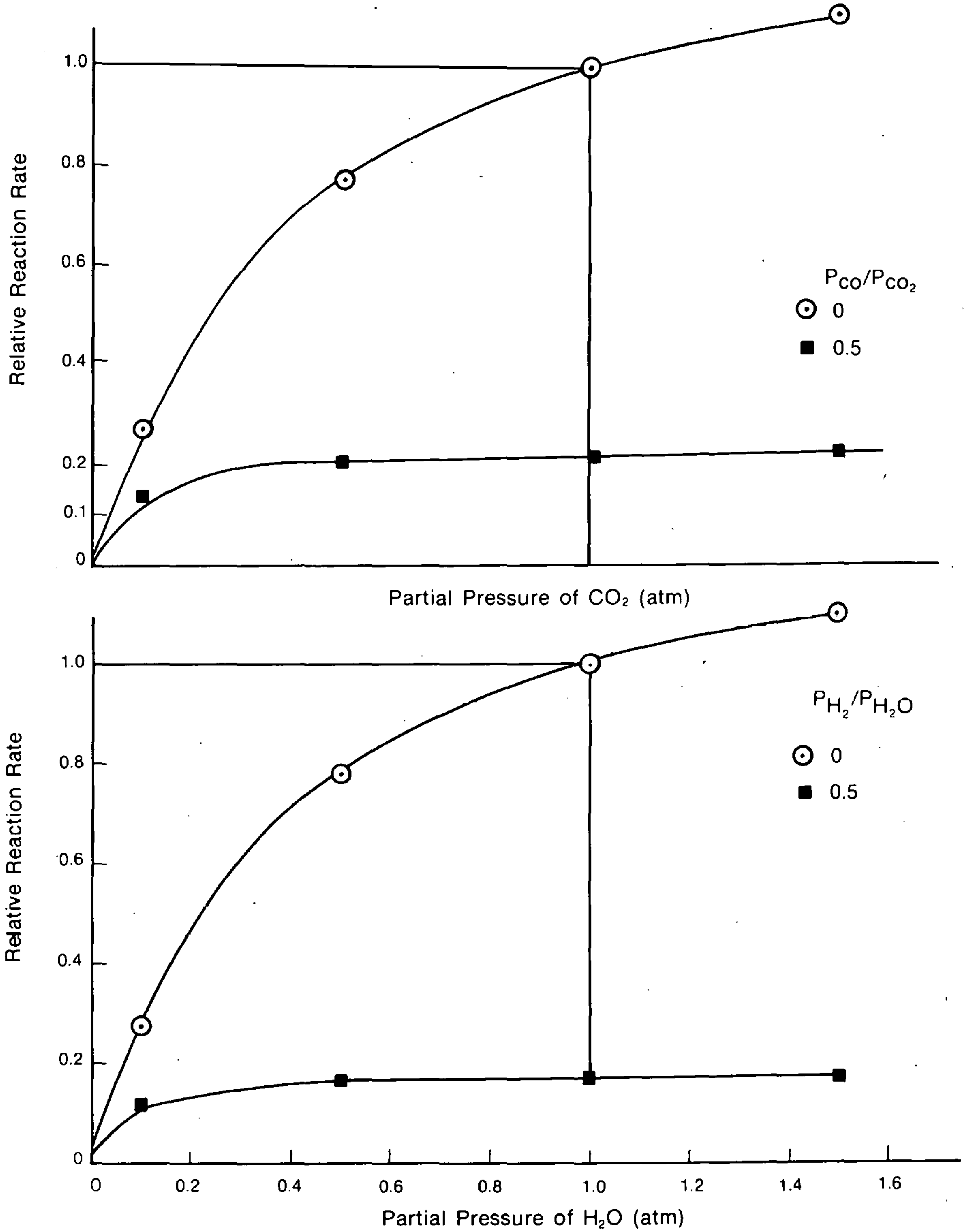

Figure 7-7. Reactivity of Coconut Shell Charcoal in H_2O and CO_2 at 800 C

7.8 MECHANISM AND KINETICS OF COMBUSTION

It is generally believed that the combustion mechanism involves attack of the same active sites as in gasification. Also as in gasification, the reaction is thought to proceed through an intermediate surface oxide that decomposes at a characteristic rate. At low temperatures, the surface oxides are stable and essentially cover the surface. The reaction is zero order under these conditions. At high temperatures, the rate of decomposition is so fast that the rate becomes limited by the formation of surface oxides and the reaction order approaches unity.

At intermediate temperatures, the rate is typically 1/2 order. It also has been determined that both CO and CO_2 are primary products of combustion. However, at all temperatures of interest, CO production is the dominant reaction, with CO_2 being produced in the film surrounding the particle.

A possible mechanism summarized by Laurendeau (1978) is the following:

$$2C_f + O_2 \underset{k_{11}}{\overset{k_{10}}{\rightleftharpoons}} 2\,C'(O) \quad , \qquad (7\text{-}42)$$

$$C'(O) \xrightarrow{k_{11}} C(O) \quad , \qquad (7\text{-}43)$$

$$C(O) \xrightarrow{k_{12}} CO + nC_f \quad , \qquad (7\text{-}44)$$

$$C'(O) \xrightarrow{k_{13}} CO + nC_f \quad , \qquad (7\text{-}45)$$

$$2\,C'(O) \xrightarrow{k_{14}} CO_2 + C_f \quad . \qquad (7\text{-}46)$$

In this mechanism, C'(O) are primary mobile surface oxides while C(O) are immobile complexes. Such a two-site adsorption helps explain the rapidity of the combustion process since the most active sites are constantly regenerated while, as reaction proceeds, the less reactive sites are removed by the oxide decomposition. Equation 7-46 accounts for primary CO_2 production. Since the number of active sites is small compared to the total surface, the probability that reaction 7-46 will proceed, to produce significant quantities of CO_2, is very small. Equations 7-42 to 7-46 lead to a rate expression of the form:

$$-r_c = k' \; C_{tot} \; P_{O_2}^{m} \qquad (7\text{-}47)$$

where m can be 0, 1/2, or 1 with the appropriate simplifications. At combustion temperatures of interest in biomass gasification, m of 1/2 should apply.

Experimental studies have shown that thermal annealing of the carbon is important at temperatures above about 1300 K. Below that point, k exhibits an Arrhenius behavior with an activation energy of 30-40 kcal. Above 1300 K, the rate becomes independent of temperature and, at very high temperatures, falls to a low value. The annealing or graphitization phenomenon is a stabilizing reaction that eliminates the necessary defects or surface active sites for combustion.

It is generally observed that the primary products of combustion are CO and CO_2. Arthur (1951) has shown that the product mixture is a function of temperature but probably not of carbon type. Between 460 C and 900 C, the primary product distribution is given as follows:

$$\frac{[CO]}{[CO_2]} = 10^{3.4} \exp\left[-12{,}400/RT\right], \text{ T in K} \quad . \tag{7-48}$$

7.9 HYDROGASIFICATION

Pyrolysis is normally carried out in an inert gaseous environment. When the pyrolysis is conducted in hydrogen, with rapid heating (>1000 C/s), it is possible to increase the devolatilization of the feedstock and enhance the hydrocarbon yield. Recently, Anthony and Howard (1976) reviewed the state of the art for hydrogasification of coals.

The hydrogasification reaction takes place in two stages. If the char is prepared and stabilized in an inert atmosphere, the rate of hydrogasification is very low. On the other hand, if hydrogen is in direct contact with the freshly formed char during pyrolysis, the rate of gasification is several orders of magnitude greater. Figure 7-8 from Gray et al. (1975) shows the effect of heating on the hydrogasification rate. For rapid heating, the gasification rate is almost 100 times faster than for the slow heating case.

The rate of hydrogasification depends on temperature, hydrogen pressure, and time. As an example of a rate model, Gray et al. (1975) propose that a parallel sequence occurs.

$$\begin{aligned} &\text{Char} + H_2 \rightarrow CH_4 + \text{Oil} + \text{Light hydrocarbons} \\ &\text{Char} \rightarrow \text{Stabilized char} \quad . \end{aligned} \tag{7-49}$$

The rate of reaction of stabilized char with hydrogen is negligible during normal residence times. The stabilization reaction is assumed to consume only a fraction of the char available for hydrogasification. The proposed rate equation then, is:

$$-r_c = \frac{1}{W}\frac{dW}{dT} = KP_{H_2}\left(\alpha - \frac{W}{W_o}\right) \quad . \tag{7-50}$$

The parameter α is a function of temperature, coal type, and heating rate. The rate constants plotted in Figure 7-8 are based on the model given in Eqs. 7-49 and 7-50. Hydrocarbon production in atmospheric gasifiers by direct hydrogenation of char is slow, even in comparison to the steam gasification reaction.

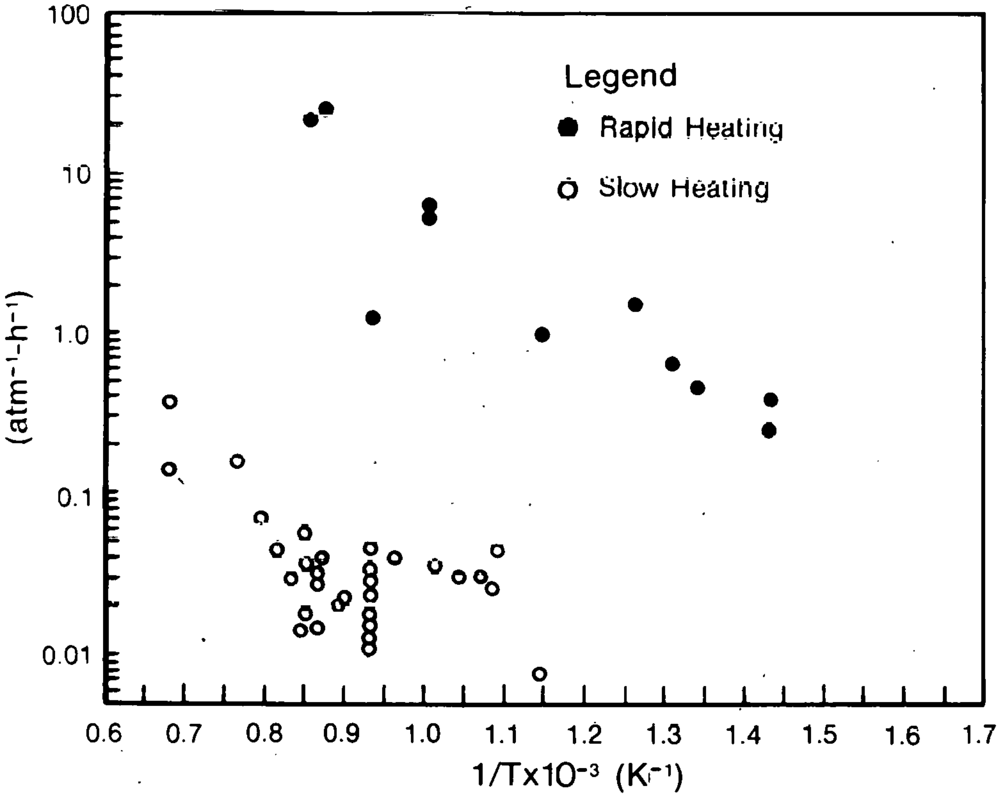

Figure 7-8. Temperature Dependence of Hydrogasification Rate Constants for Coal and Char

The only published hydrogasification studies on biomass have been conducted for a naturally occurring peat. Punwani et al. (1978) and Weil et al. (1978) recently investigated the hydrogasification of peat with a volatile content of 63.2%. Figure 7-9 shows the effect of hydrogen pressure on the rapid heating gasification of peat. At 60 atm of hydrogen in 4 s to 7 s at 1400 F, the amount of carbon gasified increased by roughly 40% over that for pyrolysis in an inert atmosphere.

Figure 7-10 compares the effect of pretreatment on conversion. The base carbon is the fixed carbon, as determined from the proximate analysis. With char devolatilized and stabilized in nitrogen, the additional gasification in steam and hydrogen at 1500 F is minimal even for long residence times. For the raw peat, the initial extra gasification is significant, representing 70% of the fixed carbon after 10-min residence time.

Hydrogasification of other biomass feedstocks is presently being investigated (Babu 1979), and it is believed that a considerable quantity of hydrocarbons can be derived from such materials under high hydrogen pressures and rapid heating.

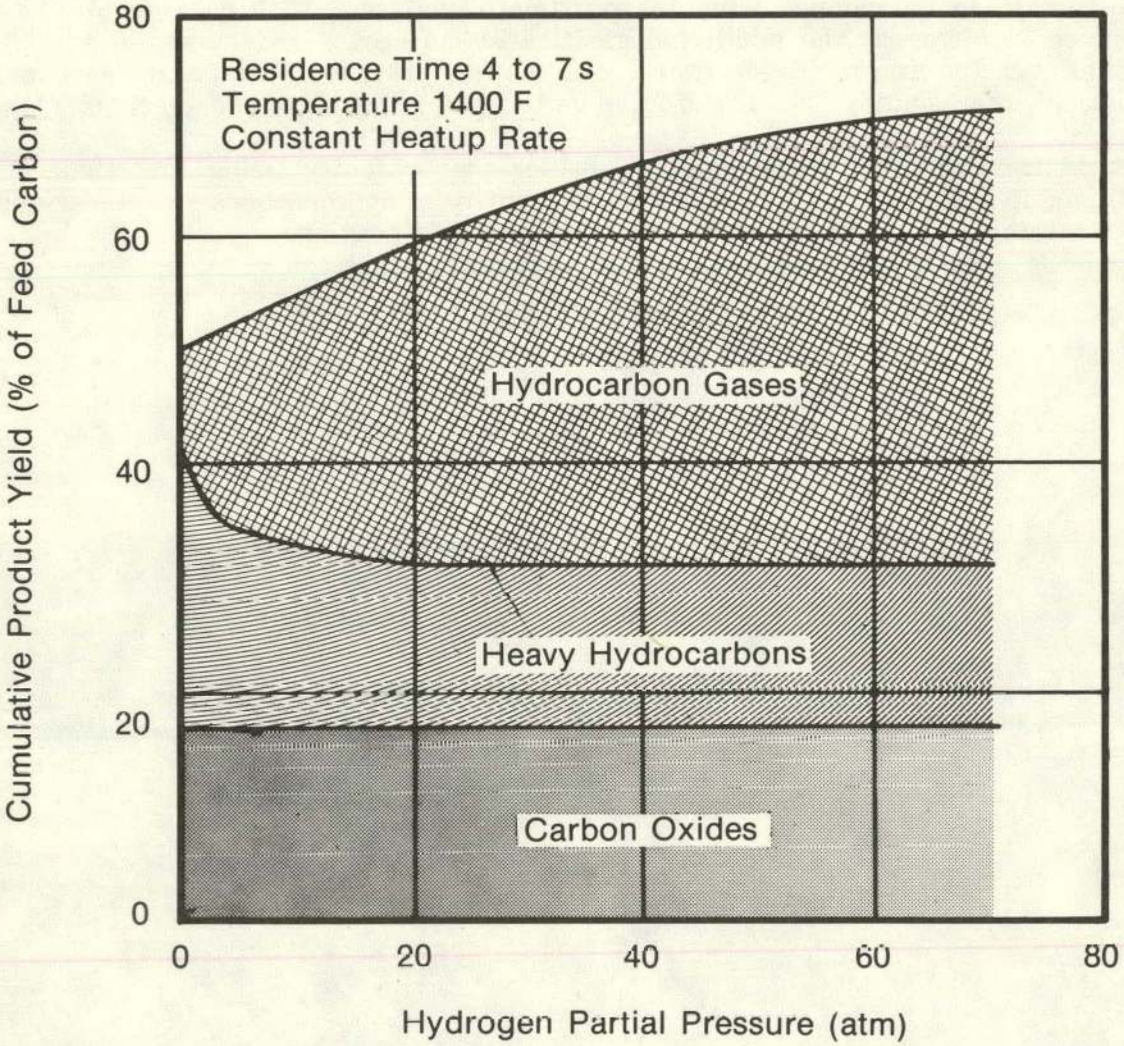

Figure 7-9. Effect of Hydrogen Partial Pressure on Product Yields Obtained During Peat Gasification

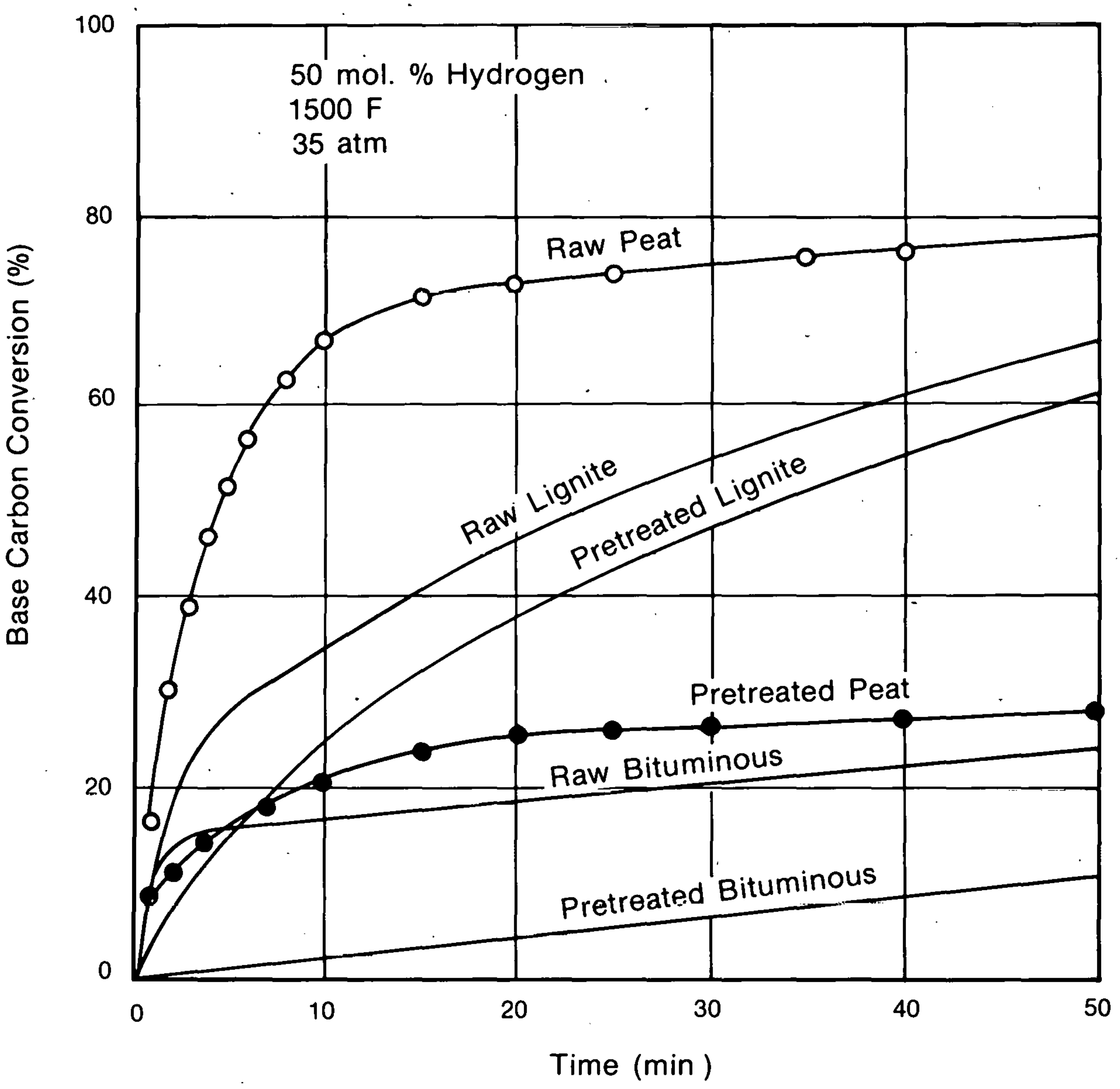

Figure 7-10. Comparison of Carbon Conversions for Peat, Lignite, and Bituminous Coal During Gasification with a Steam-Hydrogen Mixture

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Document Control Page	1. SERI Report No. TR-33-239	2. NTIS Accession No.	3. Recipient's Accession No.

4. Title and Subtitle

Survey of Biomass Gasification
Volume II - Principles of Gasification

5. Publication Date
July 1979

6.

7. Author(s)
T.B. Reed, et al.

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Solar Energy Research Institute/DOE
1536 Cole Boulevard
Golden, Colorado 80401

10. Project/Task/Work Unit No.
Task #3322

11. Contract (C) or Grant (G) No.
(C)
(G)

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered
Technical Report

14.

15. Supplementary Notes

Volume II 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 Rd.
Springfield, VA 22161

19. No. of Pages
241

20. Price
$9.50

Form No. 8200-13 (6-79)

☆U.S. GOVERNMENT PRINTING OFFICE: 1979-0-677-083/55