Effect of Biomass Feedstock Chemical and Physical Properties on Energy Conversion Processes

Volume 2 - Appendices

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December 1988

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

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

NTIS Price Codes
Microfiche A01

Printed Copy

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

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SUMMARY

Pacific Northwest Laboratory^(a) has completed an initial investigation of the effects of physical and chemical properties of biomass feedstocks relative to their performance in biomass energy conversion systems. Both biochemical conversion routes (anaerobic digestion and ethanol fermentation) and thermochemical routes (combustion, pyrolysis, and gasification) were included in the study. Related processes, including chemical and physical pretreatment to improve digestibility, and size and density modification processes, such as milling and pelletizing, were also examined.

This report presents an exploration of the relationships between biomass feedstocks and the conversion processes that utilize them. Specifically, it discusses the effect of the physical and chemical structure of biomass on conversion yields, rates, and efficiencies in a wide variety of available or experimental conversion processes. A greater understanding of the complex relationships between these conversion systems and the production of biomass for energy uses is required to help optimize the complex network of biomass production, collection, transportation, and conversion to useful energy products.

The review of the literature confirmed the scarcity of research aimed specifically at identifying the effect of feedstock properties on conversion. In most cases, any mention of feedstock-related effects was limited to a few brief remarks (usually in qualitative terms) in the conclusions, or as a topic for further research. Attempts to determine the importance of feedstock parameters from published data were further hampered by the lack of consistent feedstock characterization and the difficulty of comparing results between different experimental systems. Further research will be required to establish quantitative relationships between feedstocks and performance criteria in conversion.

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

GLOSSARY

Anaerobic Digestion	degradation of organic matter by microbes in the absence of oxygen to produce methane and carbon dioxide.
Ash	inorganic residue remaining after combustion.
Biochemical Conversion	use of biological systems to chemically transform substances.
BOD	biological oxygen demand, quantity of oxygen used in the biological oxidation of organic matter.
Btu	British thermal unit, unit of heat energy.
Carbonization	thermal process of decomposition of biomass which emphasizes the solid product over gaseous or liquid.
Cellulose	principal structural carbohydrate of plants, polymer of d-glucose.
COD	chemical oxygen demand, measure of the amount of oxidizable components in water.
Crack	reduction of molecular weight by breaking of chemical bonds.
EMC	equilibrium moisture content, moisture content at which biomass neither gains or loses moisture to the surrounding air.
Extractives	substances which can be removed by solvent action (water, ether, benzene) without substantially degrading the plant structure.
Heat Release Rate	conceptual measure of combustion energy production rate for a specific feedstock and furnace configuration.
Hemicellulose	noncellulosic polysaccharides of the plant cell wall.
Herbaceous	nonwoody plants, lacking a large portion of lignin.
HHV	higher heating value, potential combustion energy when water vapor from combustion is condensed to recover the latent heat of vaporization.
High-Btu Gas	gas containing mostly methane with a heating value of 800 to 1000 Btu per standard cubic foot.

Holocellulose	total carbohydrate portion of a plant, i.e., cellulose plus hemicellulose.
Hydrolysis	conversion by reaction with water of a complex substance into two or more smaller units.
IEA	International Energy Agency, organizational structure for cooperation and exchange on energy-related issues among participating countries.
IFAS/GRI	Institute of Food and Agricultural Sciences (University of Florida)/Gas Research Institute (Chicago) cooperative project to develop anaerobic digestion.
LHV	lower heating value, potential combustion energy when water vapor from combustion is not condensed.
Lignin	noncarbohydrate structural constituent of plant tissues which encrusts the cell walls and cements the cells together.
Lignocellulose	plant material, made up primarily of lignin, cellulose, and hemicellulose, in its native form.
Low-Btu Gas	gas comprising water, carbon dioxide, carbon monoxide, hydrogen, methane, and nitrogen with a heating value of 90 to 200 Btu per standard cubic foot.
Medium-Btu Gas	gas comprising carbon dioxide, carbon monoxide, hydrogen, methane, and higher hydrocarbons with little or no nitrogen, having a heating value of 300 to 600 Btu per standard cubic foot.
Olefins	light hydrocarbons containing unsaturated carbon-carbon bonds, particularly useful for synthesis of higher hydrocarbons such as diesel or polyethylene.
PNL	Pacific Northwest Laboratory, operated by Battelle Memorial Institute for the U.S. Department of Energy.
Proximate Analysis	determination by prescribed methods of moisture, volatile matter, fixed carbon (by difference), and ash.
Py	pyrolysis number, dimensionless parameter defined as the ratio of heat transfer rate to intrinsic reaction rate.

Pyrolysis	thermal decomposition in the absence of oxygen producing solid, liquid, and gaseous products.
scf	standard cubic foot, a volume of 1 cubic foot at standard conditions.
SER	specific energy requirement, units of work per units of mass of feedstock, as used in size reduction requirements.
SERI	Solar Energy Research Institute, operated by Midwest Research Institute for the U.S. Department of Energy.
Thermochemical Conversion	use of thermal processing to chemically modify substances.
Ultimate Analysis	determination of the elemental composition of a substance by prescribed methods.
VS	volatile solids, all matter that will oxidize and be driven off as a gas at 550°C.
Wood (woody)	solid lignocellulosic material.

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INTRODUCTION

Biomass has been used as a fuel since before recorded history. In pre-industrial civilizations, and for most of the industrial era, optimal utilization of biomass resources was not an issue. The resource base available was always much larger than the demand, and environmental concerns had not yet been raised. For the most part, indigenous biomass was collected from natural growth and burned, with the heat being used for space heating, cooking, and later, industrial applications. The overall efficiency of the supply and distribution system was regarded as unimportant because of the relatively immense size of the resource.

Increased industrialization has led to new issues, and new constraints have been created by a high per capita energy use, competition for resources with food and fiber production, and an increased sensitivity to preserving the natural environment. For biomass to significantly impact the nation's energy supply, attention must be focused on the optimal use of the biomass resource. Otherwise, not only will the amount of energy available from biomass be limited, but costs (economic, social, and environmental) will be greater for the energy produced.

The efficient use of biomass resources relies on the optimization of a very complex system of biomass feedstock supply, transportation, and conversion to energy products. These components of the biomass energy system are interrelated, which further complicates optimization. This report explores, in detail, the relationships between the feedstocks and the conversion processes. A companion report, OVERVIEW, describes the scope and methodology of the study, and provides background and discussion of feedstock/conversion relationships. Furthermore, several recommendations are given for establishing areas of future research.

The effects of the physical and chemical structure of biomass are discussed in both volumes relative to conversion yields, rates, and efficiencies in a wide variety of available or experimental conversion processes. Through

a better fundamental understanding of how these biomass characteristics affect the conversion process, appropriate conversion technologies can be selected for individual feedstocks.

Both biochemical conversion routes (anaerobic digestion and ethanol fermentation) and thermochemical routes (combustion, pyrolysis, and gasification) were included in the study. Related processes, including chemical and physical pretreatment to improve reactivity, and size and density modification processes, such as milling and pelletizing, were also examined.

This volume has been divided into two appendices. Appendix A describes feedstock effects on conversion from a processing perspective and relates information reported primarily by process developers. Appendix B describes feedstock characteristics and relates those characteristics to potential effects on conversion processes from a feedstock perspective.

APPENDIX A

DESCRIPTION OF BIOMASS CONVERSION PROCESSES

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DESCRIPTION OF BIOMASS CONVERSION PROCESSES

With the recent emphasis on interaction between feedstock and process, researchers in the field of biomass production need a basic understanding of the major processes used to convert biomass into usable energy. This appendix describes the major biomass conversion processes, and documents the current understanding of how these processes are affected by variations in the physical and chemical properties of biomass.

MECHANICAL PRETREATMENT AND HANDLING CONSIDERATIONS

All of the processes studied in this report have some set of requirements for the mechanical handling of the raw feedstock. These requirements usually include size reduction and may include the handling characteristics of the feedstock in storage bins, open piles, and transfer lines. In fact, for some processes, moving the biomass into the reactor can be the major consideration for operation (for example, the high-pressure gasification and liquefaction processes now being developed). Drying characteristics can also affect the way a feedstock is handled.

Size Reduction

Size reduction is used to improve the handling characteristics of the feedstock and to facilitate drying. It also lessens the barriers to heat and mass transfer by creating larger surface to volume ratios. The procedure may consist of chopping, crushing, grinding, or other milling operations. The range of size reduction requirements varies considerably by process and feedstock, with particle size requirements ranging from coarse chipping (i.e., 1- to 2-in. particle dimensions) to very fine milling to 40 mesh and smaller. Size reduction considerations by themselves generally will not determine the suitability of a given feedstock for a particular process but can affect the process economics in some instances, and perhaps more importantly, affect the market acceptance of a feedstock.

The primary cost concern typically relates to the energy required to achieve the size reduction. One measure of this energy requirement is called the specific energy requirement (SER), which can be expressed in units of work per unit mass of feedstock. Studies of size reduction equipment using aspen wood, corn stover, corn cobs, and wheat straw indicate that different feedstocks have large differences in the SER (Himmel et al. 1985). For example, the SER for reducing aspen chips from 3/4-in. chips to material passing a 1/16-in. mill screen was reported to be about 16 times that required for a similar size reduction for wheat straw. In this example, the SER obtained for aspen using a knife mill was approximately 120 kW·h/ton of feedstock; this value represents about 2.5% of the thermal energy contained in the aspen (based on a higher heating value, HHV, of 8400 Btu/lb and 6 wt% moisture content). This power must be provided as shaft work to the knife mill (either via electricity or steam power) and actually translates into 6% to 12% of the available energy contained in the biomass.

Moisture content, fiber content, and structure of the feed, as well as harvesting and storage practices, can all affect the suitability of some size reduction methods. Hammer mills, for example, are generally not suitable for size reduction of wet or fibrous materials, while knife mills are very sensitive to the presence of foreign material such as rocks and pebbles which may be present in some feedstocks. Of course, the process requirements also play a role in determining size reduction requirements; a knife mill is well suited for coarse chopping of wet or dry material to particles above about 1/8 in., but finer grinding of dry material will probably require a hammer mill or disk attritor. Very fine grinding of wet feedstocks (above 30 to 50 wt%) is difficult to achieve (and is generally not required) and may require more elaborate methods, such as stone mills or ball mills in conjunction with some pre-reduction with a knife mill.

Bulk Handling and Storage

If a feedstock is difficult to feed or loses an appreciable amount of its energy content during storage, it can create serious problems for the potential user of biomass. Energy loss during storage is almost always a result of microbial action; therefore, feedstocks that are particularly well

suited to biochemical conversion are often the most prone to degradation during storage. Interestingly, the degraded biomass may actually have a higher energy density than the fresh material, but this higher density is always offset by the overall loss in total energy availability.

Herbaceous crops, particularly those with high moisture contents and high free sugar content, are generally the most severely affected by deterioration during storage. Sweet sorghum, for example, begins to deteriorate almost immediately upon cutting, and can show considerable deterioration within 48 h of harvest (Salman, Gascho, and Shih 1980). Storage practices also play a role in determining feedstock stability. Dried biomass (below about 30 wt% moisture) generally is relatively stable with regard to storage. Little has been published regarding the handling and storage characteristics of biomass feedstocks, but Ebeling, Zohns, and Jenkins (1985) emphasize the importance of better characterizing parameters related to these factors.

Drying Characteristics

Drying is a critical consideration in the use of biomass fuels, particularly those destined for thermochemical processes. Drying is a very site-specific process but is also dependent on the feedstock characteristics. The primary feedstock quality associated with drying is the equilibrium moisture content (EMC). The EMC is the moisture content of a material in equilibrium with its surroundings; for biomass, the value of the EMC obtained under normal ambient (field drying) conditions is important. This value alone often will determine the quality and viability of a feedstock, especially for thermochemical processes.

The EMC varies considerably for each feedstock, depending on the harvest techniques and the climate. Most grasses and agricultural residues eventually reach an EMC of 15 to 25 wt%, even in tropical regions (Alexander 1981). Sorghum and similar thick-stalked herbaceous species may reach 30 to 40 wt%. In the case of sorghum, serious degradation may be caused by microbial and insect attack well before the material ever reaches the dry state. For wood, the EMC is very dependent on handling practices, and whole logs or roundwood may remain at 40 wt% moisture for considerable periods of time.

When determining the usefulness of a feedstock, serious consideration should be given to its drying characteristics. Furthermore, harvesting and collection techniques that can minimize moisture content without requiring additional energy inputs should be examined.

THERMOCHEMICAL PROCESSING OPTIONS

A variety of thermochemical processing options exist or are being developed for the recovery of energy stored in biomass. Thermochemical processes differ from each other by parameters such as heating rate, temperature, residence time, and the presence of co-reactants such as oxygen, steam, or reducing gases. Catalysts are also employed in some of these processes. Table A.1 lists the distinguishing characteristics of each type of process. The following section provides an overview of the major technologies proposed for thermochemical conversion of biomass.

Combustion of Biomass

Direct combustion of biomass is the most common means of recovering energy stored in biomass. Equipment for burning biomass can range from small, hand-fed, open fires to continuously fed industrial boilers operating at feed rates in excess of 20 tons/h of wood. Biomass fuels used in combustion systems include wood, hay, straw, agricultural wastes (i.e., corn cobs, rice hulls), and manures. The primary prerequisite for a combustion fuel is a relatively low moisture content (<40 wt%), although the ash content of the

TABLE A.1. Characteristics of Thermochemical Conversion Options

<u>Process</u>	<u>Products</u>	<u>Temperature, °C</u>	<u>Residence Time</u>	<u>Co-reactants</u>	<u>Comments</u>
Combustion	Process heat	>900	Several seconds	Air or oxygen	
Partial oxidation	Synthesis gas, methane, heat	500-1000	Several seconds	Air, oxygen, or steam	
Carbonization	Solid, liquid, and gaseous fuels	<500	1-4 days	None	Primarily pyrolytic
Rapid pyrolysis	Liquid or gaseous fuels	450-1000	Less than 1 s	Inert carrier	Primarily pyrolytic
Liquefaction	Liquid and gaseous fuels	300-450	5-100 min	Steam, reducing gas	Often catalytic

fuel is also a major consideration in most systems. Use of biomass fuels containing more than 40 wt% moisture normally involves a drying operation prior to feeding the fuel to the combustion chamber. Fibrous and other low-density fuels such as straw and other agricultural wastes are often pelletized to improve handling characteristics and reduce problems with fly ash. Feed preparation for all materials depends on the type of boiler being used and the feeding characteristics of the biomass.

For most industrial applications, biomass is burned in specially designed boilers to provide steam for process heating. Combustion chambers may be suspension fed, grate fed, or operated as fluidized beds. The waste heat available in the flue gas may also be used to provide additional process heat or to dry the raw biomass feedstock. The primary performance criteria in such combustion systems include the heat release rate (a measure of rate at which biomass can be burned), the combustion temperature, and the feeding and ash-handling characteristics of the feedstock. Environmental considerations, including particulate production and production of noxious gases such as nitrogen oxides and ammonia, must also be considered. A related criterion is the amount of carryover, or unreacted biomass, that leaves the furnace. Such carryover adversely affects both the efficiency of the furnace and the cost of cleaning up the flue gas. Each of these factors is affected by the system configuration, operating conditions, and the feedstock itself.

Combustion of biomass is generally considered to be the most "brute force" approach to the utilization of biomass because of the high temperatures involved. It is clear, however, that many characteristics of the fuel affect the performance of combustion systems.

Heat Release Rate

The heat release rate is used to determine the size of furnace required to provide a given power capacity. It is a function of both the fuel characteristics and the furnace design. Differences between biomass fuels can be expected to create substantial variation in heat release rate. Several feedstock characteristics can influence this rate, including the amount and nature of the volatiles contained in the fuel, the heating content of the

fuel, the chemistry of the bulk components (lignin and cellulose), and the reactivity of the char produced after devolatilization of the fuel.

The chemistry of the biomass influences the release rate by determining the rate and mode of combustion. This influence stems from two basic mechanisms being at work during the combustion of biomass. Volatile components, including volatile pyrolysis products (derived primarily from cellulose and less so from lignin), burn in a radiant gaseous flame (flaming combustion) at relatively high rates; the remaining biomass char reacts within a fairly shallow region on the surface at a lower rate (glowing combustion). The exact balance between gaseous combustion and surface combustion is influenced by such feedstock-dependent properties as volatile content, lignin content, cellulose content, the presence of alkali salts or other inorganic ash components affecting volatilization pathways, and the inherent reactivity of the biomass char (Shafizadeh 1981). Physical characteristics such as porosity, density, and thermal conductivity would also seem to be likely influences on combustion characteristics. The relative importance of each of these factors is uncertain and most likely depends on the conditions present in the furnace, as well as the feedstock characteristics themselves.

The effect of energy content on heat release rate is much less complex. For a given combination of feedstock and furnace, the feed rate is established by the need to burn all of the biomass fed to the furnace. Thus, the feed rate is determined by the kinetics of the combustion. For a fixed feed rate, the heat release rate is directly proportional to the available energy content of the feedstock (usually expressed as HHV). As will be discussed in Appendix B, there is a wide variation in HHV among different feedstocks.

The net effect of variations in heat release rates is that furnaces designed for use with one type of biomass feedstock may have to be derated when a new feed with a lower heat release rate is substituted. The heat release rate can also affect the furnace operating temperature, which is discussed below. The presence of flammable volatile materials (such as terpenes) in biomass can also contribute to ignitability of the material.

Combustion Temperature

The feedstock properties most affecting combustion temperatures are chemical in nature. In addition to the operating characteristics of the boiler itself (such as the amount of excess air used, etc.), the primary determinant of flame temperature in a combustor is the heat of combustion. This value, in turn, depends on the chemical composition of the feedstock. In contrast to its negative impact on heat release rate, the presence of lignin actually contributes to the overall energy content of the biomass. Shafizadeh and DeGroot (1976) published heat of combustion data for several biomass components; holocellulose yielded a value of 7,527 Btu/lb, while lignin isolated from Douglas fir yielded 11,479 Btu/lb. Some extractive compounds have heats of combustion in the range of 10,000 to 15,000 Btu/lb.

Ash Characteristics

Since ash does not contribute to the heating value of the feedstock, the bulk energy density of a given material is inversely proportional to the ash content of the feed. An upper limit on acceptable ash content cannot be established a priori. Feedstocks such as rice hulls and other agricultural wastes have been burned in some systems despite ash contents of 25 wt% or more. For practical purposes, however, ash contents should be as low as possible for optimal combustion system performance.

Ash density may play a role in determining the amount of ash carried over into the flue gas and also affects the degree of effort required to collect the ash. Generally, high-density ash is more desirable. Ash density is not well characterized in the literature.

The thermal characteristics of ash at the high temperatures commonly found in combustion systems are also important. Low ash fusion temperature and the presence of volatiles in ash, such as alkali compounds, can plug ash removal systems, entrain noncombusted carbon, and reduce heat transfer efficiency by deposition of ash components on boiler tubes. In at least one advanced application of biomass combustion (Hamrick 1987a), the deposition of ash on the blades of a gas turbine has posed significant problems. The

mechanism of ash deposition has not yet been determined, but differences in deposition rates were observed when the fuel was switched from pine to oak (Hamrick 1987b).

Ash fusion temperatures have been well characterized in the literature for some feedstocks (Wilen, Ståhlberg, and Sipilä 1987). The ash deformation and fusion temperatures reported for several straws (wheat, rye, oat, barley, and turnip rape) exhibited a span of over 400°C from lowest to highest, indicating that there is enough variability for this property to warrant its inclusion in any thorough characterization of feedstocks. Fusion temperatures are a function primarily of ash composition. Ash that is high in alkali content (potassium and calcium) and low in silica and alumina tends to have a relatively low fusion temperature.

Ash hardness may affect some combustion systems. Flue gases exit most combustion systems at relatively high linear velocities, and may also pass through centrifugal separation equipment (cyclones) in which high velocities are reached. In these environments, erosion of equipment may present serious maintenance problems. Very little data are available regarding the effect of ash hardness on erosion rates, and comparing the data is difficult because information is specific to the equipment used for each system.

The chemistry of the ash has long been thought to play a role in determining the rate of combustion. Certain ash components, such as alkali metal salts, are known to promote gasification reactions which are critical to the combustion process. Other ash components, including boron compounds, act as flame inhibitors and may work against the complete combustion of the fuel. The effect of these materials on combustion and gasification has been well documented by Susott, Shafizadeh, and Aanerud (1979).

Single-Particle Combustion Dynamics

Much attention has been given to modeling and measuring the single-particle combustion dynamics of biomass and coal (Chan, Kelbon, and Krieger 1985; Simmons and Ragland 1985). The rate at which particles are consumed is determined in order to understand how various parameters influence it. This information can be useful in determining what amount of material will leave the furnace in an unreacted state, either in the grate ash or in the

flue ash. The information can further be used to determine proper feeding rates for different feedstocks and to develop new feeding mechanisms to prevent the loss of carbon to ash.

The most common parameters studied in single-particle combustion dynamics include particle size and shape. Studies carried out by Huff (1985) involved the effects of particle density as well as more conventional parameters. Density was varied by selecting different species of wood (balsa, pine, and oak). The effect of density on burning time was reported. Plots of burning time versus particle density were approximately linear, with the magnitude of the (positive) slope exhibiting a strong dependence on the combustion temperature. The report did address the possibility of purely kinetic differences among these feedstocks.

Gasification by Partial Oxidation

The effects of feedstock properties on gasifier performance are similar in many ways to those described for combustion systems. Gasification processes represent a form of partial combustion, in which the biomass is heated in the presence of air, steam, and/or oxygen to produce a fuel gas consisting of carbon monoxide, hydrogen, methane, ethane, and carbon dioxide. Gasification reactions take place at relatively high temperatures (usually above 600°C) and involve relatively simple chemical entities (in addition to the products mentioned, elemental carbon, oxygen, and steam are all involved in gasification). The process heat is usually provided by burning a portion of the biomass, usually within the gasifier vessel itself. In some cases, process heat is provided by burning a supplemental fuel.

Gasification processes are employed where direct combustion of biomass is not practical. For industrial users of biomass in particular, economic studies have shown that it is generally more economical to build a gasifier and burn the product gas than to retrofit a liquid or gaseous fuel boiler to burn solid biomass (Reed et al. 1981). The solid biomass can be more conveniently gasified at the user site or in central facilities. The gaseous fuel product has numerous advantages over solid biomass fuel as it can be

transported economically for short distances and used in many industrial applications. The gases can be burned more efficiently and usually with less environmental concern.

Biomass has several advantages over coal as a feedstock for gasification. Of major importance is its high reactivity compared with that of coal and other solid fuels. Biomass contains high portions of volatile material, 70% to 90% for wood compared with 30% to 45% for a typical coals. This high volatility allows biomass to be volatilized/gasified at relatively low temperatures and has potential to open new gasification pathways which can lead to improved processes. The chars produced from biomass are more easily gasified than coal chars and also lead to lower temperature processes (Schiefelbein, Stevens, and Gerber 1986).

Wood has been the primary biomass feedstock used in gasification systems for the reasons listed above and because of its availability, physical handling characteristics, and moisture content. Wood is a denser fuel than most other biomass feedstocks and thus can be collected and transported more economically. Depending on the gasifier, wood can be fed to a gasifier as chips, as a sawdust, or as a powder, and therefore has more versatility than the agricultural residues, which require certain types of gasifiers or feed preparation. Moisture contents vary among types of biomass, with wood having relatively low moisture compared with many other feedstocks. The moisture content is important in determining drying cost and the as-received fuel value of the feed. Moisture values are available for many woods; however, very little data are available for other potential biomass feedstocks. Additional problems occur because the moisture content of each biomass also depends on the species, time of year harvested, length of aging or field drying, and climatic conditions.

A number of operating and design parameters can be used to characterize gasifiers. Figure A.1 illustrates some of the more critical parameters. In the broadest sense, gasifiers can be classified low-Btu gasifiers (air-blown gasifiers) and medium-Btu gasifiers (usually steam or oxygen blown). The names refer to the energy content of the product gas. Low-Btu gases contain

FIGURE A.1. Parameters Affecting Gasifier Design

80 to 150 Btu/scf; medium-Btu gases contain 300 to 450 Btu/scf. Gasifier products containing more than about 500 Btu/scf are sometimes referred to as high-Btu gases.

A limited number of commercial air gasifiers are available in a wide range of capacities and have been employed in less-developed countries for many years. As with most other thermochemical conversion processes, the most commonly used biomass fuel is wood, although a number of agricultural wastes including mill wastes, orchard prunings, bagasse, coconut shells, walnut

shells, corn cobs, fruit pits, rice hulls, coffee husks, palm hulls, and straw have also been used. Low-Btu gasification of biomass is considered to be commercial or near-commercial technology (Schiefelbein, Stevens, and Gerber 1986) and can be substituted for natural gas and oil to fire boilers (Schiefelbein, Stevens, and Gerber 1986; Reed et al. 1981), subject to the following limitations:

- Low-Btu gasifiers must be close-coupled to boilers to take advantage of the high temperature of the gas leaving the gasifier.
- Burning low-Btu gas in a boiler designed for oil or natural gas will frequently result in boiler derating unless expensive modifications are made to the boiler.

Low-Btu gas can also be used instead of gasoline and diesel oil to fuel internal combustion engines, provided that the gas is sufficiently cleaned and cooled (Schiefelbein, Stevens, and Gerber 1986). However, the efficiency of the engine will be reduced by about 20%. Although low-Btu gasifiers are commercially available, questions about overall reliability remain.

Medium-Btu gas is produced by eliminating the nitrogen that dilutes the energy value of gases produced in air-blown gasifiers. Instead of air, oxygen or steam is used to gasify the biomass. Depending on the method used, a gas containing between 300 and 550 Btu/scf is produced. The gas is often relatively rich in hydrocarbon gases, including methane and ethane and heavier tars and oils. These components are produced by pyrolysis, rather than true gasification reactions. Medium-Btu gas is much more versatile than low-Btu gas, and Schiefelbein, Stevens, and Gerber (1986) list the following advantages over low-Btu gas:

- Medium-Btu gas can be substituted for natural gas or oil in most retrofit applications without significant derating problems.
- Medium-Btu gas produces a higher flame temperature than low-Btu gas, making it suitable for retrofitting processes where this is a critical factor.
- Medium-Btu gas has two to five times the energy density of low-Btu gas, allowing it to be transported moderate distances by pipeline at a reasonable cost.
- Medium-Btu gas can be used for synthesis of high-value products such as pipeline gas or liquid transportation fuels.

It is through optimization of reactor conditions, including temperature, pressure, gasifying agents (steam, O_2 , H_2 , etc.), catalysts, and selection of reactive feedstocks that desired products can be produced efficiently. Methods to optimize these conditions vary greatly from process to process depending on many of the previously described variables. Much has been accomplished in defining potential improvements in biomass gasification systems in the research sponsored by the DOE Biomass Thermochemical Conversion Program. A description of the program has been provided by Schiefelbein, Stevens, and Gerber (1986) and a survey of gasifier research, types of gasifiers and gasifier design considerations, manufacturers, and recommendations for future gasification research and development has been provided by Reed (1981).

Biomass gasifiers exist in a wide variety of types and styles and are classified by various methods used to achieve gasification. Gasifiers are most often classified by the method of contacting the biomass with the gasifying medium, and over the years many different types of gasifiers have been constructed for experimental and commercial use. However, most gasifiers fall into one of three distinct categories. The main types of gasifiers are fixed-bed (downdraft, updraft, and crossdraft), fluidized-bed, and entrained-flow, referring to the motion of the solids in the gasifier. This section discusses fixed-bed and fluidized-bed gasifiers. Entrained-flow gasifiers are primarily employed for rapid pyrolysis processes and are discussed separately. Each type of gasifier is associated with different operating parameters that result in significantly different product and byproduct yields. Figure A.2 illustrates some of the various options available to carry out biomass gasification.

For fixed-bed gasifiers, a further distinction is generally made between the thermal regions, or zones, present within the gasifier (see Figure A.3). Each of the zones within an operating gasifier defines a region where particular types of reactions occur. The usual names assigned to these zones are descriptive of the predominant processes within that particular zone. Thus, the principal zones within a fixed-bed gasifier are the drying/heating zone; the pyrolysis (thermal cracking) zone; the gasification (reduction) zone; and the combustion (oxidation) zone. These zones are not always physically well

FIGURE A.2. Types of Biomass Gasifiers

FIGURE A.3. Reaction Zones in a Fixed-Bed (updraft) Gasifier

defined, but are useful in discussing the role of physical and chemical properties in gasification processes. In a fluidized-bed gasifier, the thorough mixing of the bed eliminates the distinction.

The types of performance criteria that are affected by feedstock properties are similar to those listed for combustion: ash handling characteristics, tar production and volatile content, gasification kinetics, environmental emissions, and size reduction. All of these properties vary with the

different feedstocks, and their influence on conversion and product formation and yield depends to differing degrees on the gasification system and processing conditions selected.

Feeding and Ash Handling

In fixed-bed gasifiers, solid biomass is fed into the top of the reactor by lock hoppers or feeders. The fuel bed is supported by a grate at the bottom of the reactor which rotates in some systems. The biomass must be in the form of chips or pellets because fine particles often result in plugging. Some feedstocks, such as wheat straw, corn stover and corn cobs, tend to create large quantities of fines during primary milling or shredding (Himmel et al. 1985). This tendency must be taken into account when a new feedstock is being considered. For such feedstocks, pelletization of the fines may be possible, although the additional step adds cost and complexity to the process. While fines can be more readily accommodated in fluidized-bed gasifiers, it is important that particle size be relatively uniform, since particle size and density are the primary determinants of fluidization behavior. Very broad particle size distributions in feedstocks can lead to problems in bed stability and in the efficiency of the bed.

Solid streams exiting the gasifiers are in the form of solid ash or slag (melted ash) and particulates in the gas stream. The form of the ash depends on the bed temperature and the thermomechanical properties of the ash. In general, a gasifier is designed for only one type of ash removal (solid or slag) and a change in ash form can cause serious operating problems. The use of feedstocks with low fusion temperature ash can cause problems with ash removal if the bed is operated at temperatures high enough to cause slagging or ash softening. Feedstocks with very high ash contents may also pose problems if the gasifier was not designed with a sufficient ash-removal capacity.

Fluidized-bed gasifiers are less susceptible to ash melting problems because relatively low operating temperatures are employed (generally under 900°C). Because fluidized-bed gasifiers have a relatively flat temperature profile throughout the entire bed, ash softening and/or deposition is generally not a problem unless the ash has an exceptionally low softening

temperature. Depending on the design, ash and char may be removed from the top of the reactor with the product gases, from the bottom of the reactor, from the top of the bed, or a combination of all three. Ash density and agglomeration properties are expected to play a role in determining the most appropriate means for ash removal, and may need to be considered when a gasifier is to be operated with feedstocks other than the one for which it was designed. Numerous references provide details on design and operation of fluidized-bed, biomass gasifiers (Datin, LePori, and Parnell 1981; Flanigan, Findley, and Sineath 1983; Feldmann, Paisley, and Appelbaum 1983; Goldbach et al. 1983; Miller 1983; Mudge et al. 1983; Murphy 1984; and Oliver 1982).

Ash content plays a critical role in the amount of particulate produced, and its composition dictates the disposal requirements. Elemental compositions of the ash for selected biomasses are spread out in the literature, and reviews with consistent analytical methods describing ash content for biomass are not available. Biomass ashes range from about 0.1% to 40%.

Tar Production and Volatile Content

In many biomass gasifiers, the production of condensible tars and oils can cause a number of problems with downstream processes and usually require very close coupling between the gasifier and the user (Baker et al. 1986). The amount of tar produced greatly depends on the type of gasifier employed, and to a lesser extent, the type of feedstock used. Tar production is particularly high in updraft gasifiers, which allow the tars created when the product gases pass through the pyrolysis and drying zones to escape without passing through the reduction and oxidation zones. Downdraft gasifiers exhibit very low tar yields that depend on combustion zone temperatures. In downdraft and crossdraft gasifiers, tars and oils are drawn through the reduction zone and cracked to lighter components. Fluidized-bed gasifiers produce relatively low tar yields because of the turbulent mixing and uniform temperature distribution within the bed.

The effect of feedstock properties on tar production is secondary to the effect of reactor configuration. Nonetheless, for a given set of gasification conditions, variations in tar production can be expected among feedstocks. Work reported by Kuester et al. (1985) studied more than 50

feedstocks, including herbaceous energy crops, woody residues, and solid wastes, and demonstrated a significant range among the different feedstocks in gaseous olefinic hydrocarbon production and hydrogen to carbon monoxide product gas ratio. Multivariate analysis using a quadratic regression technique indicated that the strongest correlation between feedstock characteristics and olefin production and H_2/CO resulted from the combination of quantity of ash (inverse), heating value, and extractable content. Other combinations that correlated strongly ($R^2 > 0.95$) with olefin production only included fiber (inverse), heating value, and quantity of ash (inverse), as well as temperature. The experiments were conducted in a steam-blown, dual-bed gasifier; inert solid material (generally sand) was used as a heat transfer agent.

Gasification Reactivity

The rate of gasification reactions is an important factor in determining the reaction vessel size required for a given throughput of biomass. Since the cost of the gasification reactor is usually the largest single cost item in a gasification plant, rate can play a significant role in determining process economics.

The chemical composition of woods and miscellaneous plant materials is reported by Graboski and Bain (1981) and scattered literature sources. Information usually consists of cellulose, lignin, holocellulose, and sometimes, extractable content. The contribution of these contents of biomass to overall conversion rate (including pyrolysis steps) has not been related to any significant degree except to demonstrate the relative rate (ease) of char gasification (Nandi and Onischak 1985) and the relative reactivity of feedstock constituents (Sealock et al. 1981). The studies of char gasification rate indicated that reaction rate constants for char gasification varied almost by a factor of 2 between maple and jack pine. In a review of pyrolysis kinetics, Roberts (1970) reported the relative sequence of reactivity as:

hemicellulose > cellulose > lignin.

The same review stressed the importance of catalytic and autocatalytic effects, particularly for cellulose. Many authors cite alkali metal salts as particularly effective in the promotion of cellulose gasification reactions. The implications of these findings for biomass production need to be further explored.

The role of catalysts in biomass gasification using alkali catalysts and alkali/nickel catalysts combinations has been studied in detail, and considerable research has been conducted dealing with the catalytic effects of various alkali carbonates on the reaction of carbon with steam (Sealock et al. 1981). Little research involving catalyst has been directed at the actual biomass structure. Research with high-moisture feedstocks at PNL (Butner, Elliott, and Sealock 1986) has demonstrated that low-temperature catalytic pathways have potential for new gasification approaches. Utilization of selected inorganic material specifically incorporated into the biomass structure has potential to further increase the reactivity of the biomass and could potentially replace unwanted inorganics in the biomass structure.

Gasification Temperature

Gasification temperatures employed in the various gasifiers have been described above. Feedstock properties that influence the selection of a gasification temperature are mainly based on their reactivity. The more reactive the biomass, the lower the gasification temperature required. Preliminary data at PNL indicate that nonwoody feedstocks demonstrate high reactivity even at gasification temperatures below 450°C. In general, these feedstocks are not suitable for conventional systems because of a high moisture content, low energy density (high transportation costs), and feeding difficulties. However, new processes are developing that can gasify high-moisture feedstocks (Sealock et al. 1988).

Emissions

Gasification of biomass is better characterized than most processes for the conversion of biomass, mainly because of its similarity to coal gasification and the combustion of biomass. However, effluents from the biomass gasification process have not been well defined and documented.

Furthermore, a number of factors are related to these systems that make an environmental assessment of the processes and process streams difficult. Many of the gasification systems have not operated at a commercial scale and are developmental systems concerned with proving the conversion concept and feasibility. Environmental issues are treated as secondary issues, and effluents vary as processing parameters are varied and optimized.

Biomass gasification processes are expected to have many of the same environmental problems as coal gasification technology. The chemical composition of the biomass feedstock will have a direct role in the pollutants produced during gasification. Solid streams exiting the gasifiers include ash or slag and particulates in the gas stream. Ash content plays a critical role in the amount of particulate produced, and its composition dictates the required disposal method.

Gaseous air effluents from biomass gasification are also directly related to the inorganic material in the biomass feedstock. Pollutants such as SO_x , H_2S , NO_x , and particulates can be generated from the S, N, and metals present in the feedstock.

It is expected that many of the pollutants present in the product stream will be scrubbed and collected in the wastewater. High amounts of organics (phenols, aromatics, light oxygenates) and inorganic compounds (CO_2 and NH_4) are expected, and, therefore, wastewaters will likely be high in BOD and COD. Information is limited on the properties of tars and particulates produced during biomass gasification (Elliott 1986; 1987), and there is almost no documentation of the effectiveness of gas cleaning systems for biomass-derived gas, particularly for tar removal (Baker et al. 1986).

Destructive Distillation (Carbonization)

After direct combustion, destructive distillation (i.e., carbonization) is the oldest and probably the simplest thermochemical conversion process for biomass. The primary product from this type of processing is an improved solid fuel (charcoal), which has a higher energy density, less smoke formation, and better storage stability than the original biomass. The process is relatively inefficient, producing a considerable quantity of liquid and gaseous byproducts. The low efficiency of the process has helped to restrict

the domestic use of carbonization processes to the preparation of cooking fuels and other specialty products. Although charcoal is not commonly used as a fuel in most developed countries, its use is widespread in some developing nations where biomass is plentiful and access to modern technology is limited. Research in carbonization is mostly incidental to investigations of fundamental pyrolysis processes.

Destructive distillation of biomass is accomplished by heating in the absence of air to temperatures in the range of 500°C (Emrich 1985). Traditionally, the processing has been performed batchwise with a slow heatup to temperature and an extended residence time at the end temperature. Newer technology, including multiple hearth furnaces, allows for continuous processing, while more stringent process control allows for optimizing the yield of a uniform-quality product. The furnaces are typically sized at 40 to 50 tons per day (wet wood). The products of the process include a solid charcoal fuel, a combustible gaseous mixture, and a liquid product typically recovered as two phases. The two phases are an aqueous solution of oxygenated organics and a denser organic tar, which is a complex mixture of oxygenated organics with some dissolved water. Optimal yields of charcoal from wood are in the range of 25 wt%.

The normal feedstock for traditional destructive distillation consists of wood logs or coconut shells, although other types of biomass have been used. Although round wood has been the traditional feedstock for destructive distillation, in recent years other waste materials have been found to be acceptable. These materials include tops and limbs from forestry harvesting, sawdust, wood shavings and offcuts from lumber mills and furniture factories, and bark and residues from the pulp and paper industry. No significant differences are reported for product yields from residues (tops and limbs, sawdust, wood stumps, etc.) compared with round wood (Emrich 1985). The use of other residues has also been reported (Emrich 1985; Reger 1985), including husks and shells of nuts, plantation and orchard residues, sugarcane bagasse, straws and grasses, bamboo and reeds, cactus, forest underbrush, and discharges from farm cropping and food processing. The qualities and yields of charcoal (and pyrolysis liquids) from these residues vary greatly. Charcoal yields vary from 15% to 45%. Nut shells, for example, produce a high-quality

char useful for activated charcoal. On the other hand, other types of these feedstocks (forest underbrush, for example) are very high in ash and produce a high-ash charcoal with low heating and commercial value.

The heating value of the charcoal is determined by the fixed carbon content of the solid residue and is reduced in cases where high-ash-content feedstocks are employed. The ash and other inorganic element composition is directly derived from the feedstock; for example, a higher amount of bark in the feedstock will result in a higher ash content in the charcoal. Bark contains high levels of ash, and, therefore, debarking the feedstock results in a higher quality fuel.

Other aspects of the feedstock can affect the quality of the fuel product. Wood degraded by mildew or fungi gives a lower yield, and the charcoal produced is less dense and more friable. Moisture content affects the processing rate, and feedstocks with lower moisture contents show more effective carbonization and higher yields of solid product.

The difference between charcoals produced from softwoods and hardwoods can be detected in a number of areas. Softwoods tend to produce a more friable, less dense product. The resins contained in softwoods can also remain in the charcoal and then be volatilized during the combustion of the fuel. This effect can result in unpleasant flavors if the charcoal is used to barbecue food. Differences in the pyrolytic oil composition are more significant. The resin content in the softwoods results in an oil of higher calorific value, and good yields of naval stores (turpentine and pine oil) can be extracted from it. Hardwood pyrolysis can result in significant yields of methanol, acetic acid, acetone, and methyl acetate. There are lesser yields of these products from softwood.

Rapid Pyrolysis

Rapid pyrolysis processes are currently under development for the production of liquid and gaseous fuels from biomass feedstocks. Laboratory studies are limited to about 12 tons per day. In most of these studies, wood has been the primary feedstock. Recent emphasis on rapid pyrolysis research

has been focused on the production of liquid fuel precursors, which generally must be further treated prior to practical integration into other fuel inventories.

All rapid pyrolysis processes depend on the same fundamental phenomena. The objective in designing a rapid pyrolysis system for liquid production is to obtain high enough heat fluxes and reaction temperatures that the biomass is completely degraded to gases and vapors at short residence times. The primary production of pyrolysis tars can be maximized through control of the reaction temperature and processing time (500°C and ≤ 1 s). Alternatively, the primary products can be more severely processed so as to maximize gaseous product formation ($\geq 750^{\circ}\text{C}$ and ≤ 3 s). In either case, the chemistry involved is primarily thermal decomposition as no reactants other than steam are mixed with the biomass in the reactor.

Performance criteria for rapid pyrolysis systems include the quality and yield of the liquid produced, the yield of char produced, and the standard requirements of material feeding and handling. The quality of the liquid fuels is determined by its density, its nitrogen and oxygen content (both of these should be low), its aromaticity, and its stability with respect to oxidation. Feedstock parameters likely to influence these criteria include heat and mass transport properties of the feed, feed chemistry, moisture content, and density. Rapid pyrolysis processes also have relatively stringent size reduction requirements.

Size Reduction

Because rapid pyrolysis processes typically depend on entrained flow of biomass particles through the reaction zone and into a quench zone, particles being fed must be small enough to be readily entrained in a carrier gas (typically nitrogen, flue gas, or steam). The use of small particles also facilitates the rapid release of primary decomposition products from the reacting particle and permits the rapid intraparticle temperature rise needed to avoid secondary cracking of the tars to gaseous products. Particle sizes are below 0.25 in., and the use of much finer material (40 mesh and below) is common. Thus, size reduction properties of the biomass, particularly energy requirements for size reduction, are of great importance. As

discussed earlier, these requirements exhibit large variations among feedstocks. Particle density, which can vary by a factor of 3 to 4 among feedstocks, is also expected to affect size reduction requirements by its influence on minimum entrainment velocities required in the gas.

Mass and Heat Transport Properties

Besides particle size, several other feedstock-dependent parameters appear to have a role in determining the performance of rapid pyrolysis systems. The required rapid heating of the particle to high temperatures means that such factors as the moisture content of the feed, the heat capacity of the particle, and the thermal conductivity of the biomass are all expected to affect reactor performance. Mass transfer limitations, particularly barriers to the release of primary tars from within the particle, should also play a part in determining product distribution. No tests evaluating the effect of these factors are reported in the literature within the context of the rapid pyrolysis of biomass. As with other thermal conversion processes, the lack of transport-related data (such as porosity, diffusivity, and thermal conductivity data) for particles at high temperature limits the ability to model these systems.

Pyrolysis Chemistry

The pyrolysis chemistry, which causes the formation of the product components, is entirely dependent on the feedstock composition. As a result, both yield and composition of the product will be determined by the feedstock composition. Pyrolysis of biomass components has been studied extensively in the past several decades, yet an understanding of the complex maze of chemical mechanisms involved in biomass pyrolysis has not been clearly demonstrated.

Reviews of this information have been presented by a number of authors (for example, Shafizadeh 1980; Soltes, Wiley, and Lin 1981), who conclude that the importance of the carbohydrate structures in the pyrolysis mechanism is the overriding determinant of the product distribution. Cellulose, the most abundant component, has received the most emphasis in pyrolytic studies. Trace inorganic component effects have been studied to evaluate their impact on volatilization of the biomass during pyrolysis and hence its

flammability (DeGroot and Shafizadeh 1984). Soltes and Elder (1981) describe the reported differences in the pyrolysis products generated from hardwoods versus softwoods yet conclude "... (pyrolysis) is a leveling process in which the many physical forms of lignocellulosic waste materials can be transformed into similar gases, liquids, and solids."

In addition to the abundant studies of pyrolysis of biomass and biomass components by thermogravimetric analysis, several more detailed pyrolytic studies have been undertaken which demonstrate the effect of feedstock composition on the product composition from pyrolysis. Microwave heating has been applied to several types of biomass and biomass components (Krieger 1980). Analysis of the products resulted in a correlation of the amount of char product and the composition of the gas with the carbon/hydrogen/oxygen ratios of the feedstock. Tar components included fragments of the original biomass structure as has been reported in other pyrolysis studies. The addition of sodium salts was also noted to lead to higher char yields. Fundamental pyrolysis studies have also been undertaken at the Solar Energy Research Institute with a free-jet, molecular-beam mass-spectrometric sampling system (Evans and Milne 1986). These studies also demonstrated the difference in the pyrolysis products of the major components of biomass, cellulose, lignin, and hemicellulose, but no study was made of other constituents, such as protein, which are more important in biomass materials other than wood. Whole wood was determined to act essentially as the sum of its major components with little, if any, interaction among the pyrolysis products from the wood components. In addition, physical effects such as particle size, moisture content, and heating rate had only secondary effects on the composition of the oil product, although the effect on yield of oil was in some cases dramatic.

Chemistry of Flash Pyrolysis at Low Temperatures

Process development in low-temperature flash pyrolysis can be traced back about 20 years to the pioneering work of Garrett Research and Development Company (later Occidental Research Corporation). Although municipal waste was the primary feedstock of interest, other biomass feedstocks such as Douglas fir bark, rice hulls, grass straw, animal manure, and rubber were

also tested (Chang and Preston 1981). High-quality synthetic fuels were reportedly obtained from all the feedstocks except the animal manure, which yielded a high-nitrogen oil and char containing high concentrations of sodium and potassium.

The current process development of pyrolysis systems for liquids production at Georgia Tech Research Institute began with tests in porous-bed, countercurrent flow reactors in 1968. Product yields and qualities have been reported to be feedstock dependent without further details given (Knight et al. 1980). Although several types of feedstock (wood wastes, agricultural wastes, and municipal waste) were tested over the years in the Georgia Tech systems, little has been concluded as to the effects of feedstock composition on the yields and qualities of the products.

More extensive experimental studies of feedstock effects have been made at the University of Waterloo, Ontario, Canada, in a fluidized-bed reactor system. Among those feedstocks tested were hardwoods (poplar, maple, aspen, aspen bark), agricultural residues (wheat straw, corn stover, sugarcane bagasse), cellulose, and peat. From this work, Scott, Piskorz, and Radlein (1985) have determined that oil yield responds in inverse proportion to the ash content of the feedstock and in direct proportion to the amount of cellulose. Particle size was also reported to be an important factor related to oil yield. The effect was attributed to the heating rate of the particle and the residence time of the particle in the fluidized bed (Scott and Piskorz 1982). The optimal particle size range was reported to be between 105 and 250 μm . In this vein, the importance of particle density can also be hypothesized, at least for certain reactor configurations in which particle density affects residence time. Such a dependency was not tested in the Waterloo work.

Pyrolysis of biomass under vacuum has also been reported. This type of processing produces a highly oxygenated, primary pyrolysis oil similar to that produced in flash pyrolysis. Product distribution (oil, char, gas, water) has been suggested to be a function of feedstock composition (Roy, deCaumia, and Chornet 1982) with the major factor being the distribution of cellulose, hemicellulose, and lignin (which varied in the different age and

species of tree samples studied). Later work on the specific components separated from biomass suggested that the pyrolysis products of the whole biomass may correlate with the sum of the pyrolysis products of the individual components (Roy et al. 1985). Hemicellulose was found to be a good source of oil but also produced large amounts of gas and water; the primary product from lignin was char.

Chemistry of High-Temperature Pyrolysis

Intuitively it seems that at more severe processing conditions the effects of the feedstock composition should become less discernible. However, important effects are still noted by researchers. One of the most detailed studies of feedstock composition effects was performed by Kuester et al. (1985) in a steam-blown pyrolysis unit. Modeling attempts were made to relate feedstock composition factors to product composition. Heating value, ash, fiber, protein, and polyphenol-oil-hydrocarbon extracted fractions along with temperature were correlated with olefin content and H_2/CO ratio of the product gas. The best correlations were found between heating value, extractants, and the inverse of ash with the olefin content and H_2/CO ratio. The more cellulosic feedstocks produce lower levels of olefins, while materials containing hydrocarbons (oil, latex) produce higher olefin yields (Kuester 1980). Others have also noted the effect of feedstock composition on olefin production by high-temperature pyrolysis but have drawn no conclusions as to how the biomass structure relates to olefin production (Hanley and Benham 1981).

Cellulose content has also been connected with total gas yield under these processing conditions. Raman, Walawender, and Fan (1981) draw data from several sources (Antal, Friedman, and Rogers 1977; Beck and Wang 1980; Howell 1979; Walawender, Raman, and Fan 1980) to demonstrate the widely published belief in the correlation of gas yield with cellulose content in the feedstock, including woods, paper, manure, agricultural waste, and coal.

One study has compared hardwood and softwood in this type of reaction environment (Feldmann, Paisley, and Appelbaum 1982). Higher carbon conversion to gas and higher heating value of the gas from softwoods was attributed to the higher volatile matter content. However, the yield of condensable

organic byproducts did not show a similar increase with the softwood feedstock. In this case the softwoods would be considered a more suitable feedstock.

High-Pressure, Low-Temperature Processes

High-pressure, low-temperature processes have been developed with the general intention of maximizing liquid product yields from biomass (Beckman and Elliott 1985). Further developments have shown that these environments can also be used for substantial yields of methane when appropriate catalysts are used (Sealock et al. 1988). These processes are in the experimental development stages. The largest facility operated to date is the 3-ton-per-day, wood-to-oil, Biomass Liquefaction Experimental Facility in Albany, Oregon. This facility, which was built by the federal government and operated by Bechtel National Corporation and Rust Engineering Company from 1977 to 1981, has since been dismantled.

Four main areas exist in which feedstock composition would affect biomass processing in high-pressure, low-temperature conversion systems: feeding properties; pyrolytic chemistry; subsequent chemistry; and catalytic effects. Although feeder system constraints have been recognized since early in the development of the high-pressure systems, detailed determination of the feedstock effects on high-pressure feeders has not been made. Much of the effect of feedstock on pyrolytic chemistry has been presented in the previous section. The subsequent chemistry occurring at low temperatures and high pressures is also affected by the feedstock composition. In almost all cases, the effect of feedstock composition on the catalysts, which are used in some of these conversion systems, is known only by extrapolation from other reported catalytic systems.

Feeding Properties

High-pressure liquefaction has been reported by Lindemuth (1981) to be applicable "to any biomass material that can be dried, pulverized, and slurried ... (including) wood, grasses, agricultural residues, municipal solid waste, and peat." This reference is interesting because it defines the feedstock in terms of ability to feed the material with a high-pressure positive displacement pump. The high-pressure solids feeding system has long

been recognized as a weak area for high-pressure biomass conversion processes. The facility at Albany, Oregon, the only large-scale, high-pressure processing unit ever built for biomass, was constructed with two different feeder systems with the hope that at least one could be made to work. In practice, the positive displacement pump system was the only feeder used and the lock-hopper system was never tested (Thigpen and Berry 1982). We have found no recorded testing of a high-pressure (above 1000 psia) lock-hopper feeder for biomass. A third type of feeder currently under development with DOE funding is the extruder at the University of Arizona (White, Wolf, and Zhao 1987). The extruder and pump systems take advantage of the liquid phase reaction environment and have undergone the most extensive testing.

The question of feedstock effects on feeding different biomass materials in either pumps or extruders has never been studied in great detail. Limited tests of feeding wood and peat (Kjellström et al. 1988) have been reported for a positive displacement pump, but there is no reference to other types of biomass nor is there any basis for predicting behavior of other biomasses based on this study. Extruder tests have also been limited to two types of wood (White, Wolf, and Zhao 1987) and a peat (Kjellström et al. 1988). Both of these tests were performed with finely ground biomass and suggest, as reported by Lindemuth (1981), that any biomass that can be finely ground can be fed to a high-pressure system. In both cases the biomass was well-dried prior to the grinding. This drying step would be energy-intensive for moist biomass.

High-pressure feeding systems may be more readily achievable for high-moisture biomass (<20% dry solids) by directly feeding them without drying. Wet-milling may produce a water slurry that can be pumped to high pressure directly. This tactic has been investigated in a bench-scale system constructed at PNL (Sealock et al. 1988).

Pyrolytic Chemistry

The high pressures (2000 to 5000 psig) and low temperatures (300°C to 400°C) used in liquefaction processes generally result in the presence of a liquid phase in the reactor. Residence times on the order of minutes are

required so that sufficient conversion to liquid or gaseous products is achieved. Regardless of the presence of a liquid phase, the high pressures ensure that fluid phase densities are much higher than in other pyrolysis systems, and secondary reactions between the primary products can proceed more readily. Secondary reactions, often in the presence of a catalyst, result in the formation of the desired product from the primary pyrolysis products.

The initial pyrolytic chemical mechanisms involved in high-pressure conversion processes are essentially those earlier described for the pyrolytic processes; high pressure itself having little demonstrable effect on the initial products of pyrolysis. The low temperatures involved may play a role in redirecting some of the normal pyrolytic pathways, and almost certainly promote the formation of larger degradation product molecules. Because of the relatively long residence times in high-pressure systems (generally on the order of 10 to 60 min), subsequent reactions of the pyrolysis products are believed to play a much greater role.

Subsequent Chemistry

The long residence times, chemically reducing environments, and often, the presence of catalytically active material in high-pressure systems magnify the importance of the reactions that occur subsequent to initial pyrolysis. These reactions result in more stable products through condensation of reactive pyrolytic fragments and the removal of reactive side chains by scission or condensation. The overall effect of these reactions is to produce a product that is less like the feedstock. Therefore, the effects due to feedstock differences become less pronounced than those encountered with fast pyrolytic processes.

A number of studies have attempted to determine the effects of feedstock differences on the product yield and quality from high-pressure processes. In considering this work in total it can be determined that even in the high-pressure systems involving significant chemical reaction following the initial pyrolysis, the effect of feedstock on the product composition can still be evident. Although the bulk of the product may consist of chemicals

similar to those produced from other types of biomass, unique chemical species generally survive to provide evidence of the original biomass.

Most of the work on feedstock effects has been aimed at determining the composition of liquid products. The difference in the product oil from different feedstocks was not obvious to early researchers. For example, Appell, Wender, and Miller (1970) described the conversion of such diverse feedstocks as newsprint, sewage sludge, and pine needles. While differing elemental compositions were reported for products of each feedstock, only one oil component description was presented, as if all three products contained the same compounds. These early workers also identified the difference in processing temperature required to optimize oil yield and quality from different feedstocks (Appell et al. 1971; Appell et al. 1975). High lignin content and high degree of crystallinity of the cellulose were determined to inhibit the liquefaction reactions of different biomasses. An independent review of these data and others available in the literature at the time^(a) emphasized the need for better definition of the feedstock to make sense of the data for product yield and quality. Lignin was identified as a major contributor to the oil production chemistry, although it required more severe processing conditions.

Studies since that time have been careful to demonstrate an understanding of feedstock effects on the product composition (Wilhelm, Kam, and Stallings 1981), with various oil components attributed to different biomass carbohydrate structures. The most common statement of this type is that phenolics in the oil are derived from lignin structures. Although this statement is true to some degree based on some of the specific phenolic structures found in the oils, i.e., methoxyl side groups, it is also true that phenolics are derived from cellulosic structures in base-buffered systems as described in the next subsection on catalysts (Molton et al. 1978). Other studies have surveyed the effects of feedstock through

(a) Work performed (in 1976) by Pacific Northwest Laboratory to determine optimal use of Albany, Oregon, pilot plant for advancement of processes for conversion of cellulosic materials to liquids.

comparative tests of different biomasses. From these studies, we can conclude that cellulose, starches, and sugars are converted more readily than lignins, but the crystallinity inhibits conversion as does larger particle size and low surface to volume ratio (Elliott and Giacoletto 1979). Although the cellulose result in higher conversion (less solid residue), they actually produce less oil than the lignins (Meier, Larimer, and Faix 1986). Meier, Larimer, and Faix also reported that the molecular weight of oil is lower when produced from barley and sugarcane, bark, and isolated carbohydrates than when produced from whole wood or lignins. Furthermore, they identified the presence of large amounts of ethylphenol as resulting directly from the lignin structure of the grasses containing considerably less methoxyl substitution. The ethylphenol could be useful as a chemical commodity but may also be a useful indicator of less methoxyl content in the product oil, which suggests a higher stability toward thermal processing such that catalytic hydrotreating to gasoline may be more easily accomplished. Another study of biomass feedstocks included peat and sewage sludge (Russell, Molton, and Landsman 1980). This paper reports the presence of nitrogen- and sulfur-containing compounds and suggests their production from protein molecules in the biomass. Further evidence of this type of product was found by Elliott, Sealock, and Butner (1987), and a direct correlation was made between the product components and the nitrogen content of the feedstock.

Although the subsequent chemical reactions found in high-pressure conversion processes can tend to mask the chemical identity of the feedstock through condensation of pyrolysis products to a common product mix, numerous examples have been reported of product components directly attributable to the feedstock chemical structure. The ratio of lignin to cellulose in the feedstock has a decided effect on oil yield and on oil composition under certain conditions. Other structures in the biomass, such as protein, can also be represented in the product oil. Crystallinity, compactness of structure, and particle size have also been linked to product oil yield. Inorganic components have not been studied but would be expected to be evident in the product oil following high-pressure processing.

Catalytic Effects of Biomass Composition

Catalysts used in high-pressure processing generally have been one of two types, either aqueous bases, such as alkali carbonates and hydroxides, or metal hydrogenation catalysts, such as nickel. Feedstock effect studies have been limited for both catalyst systems.

Base-catalyzed conversion of biomass must be considered both in the cases of added base and for biomasses containing significant amounts of alkali and alkaline earth metals, such as potassium or calcium. The addition of base has been reported to be useful to maximize oil production at low temperatures (275°C to 375°C) (Appell, Wender, and Miller 1970; Appell et al. 1971, 1975; Elliott and Giaccolletto 1979; Molton et al. 1978). At least part of the oil-forming mechanism is related to the condensation of cellulosic pyrolysis products to phenolics (Molton et al. 1978; Nelson et al. 1984). At higher temperatures (375°C to 475°C), alkali has been used to maximize biomass conversion to gas in a manner analogous to, although mechanistically different from, the alkali catalysis of the carbon-steam reaction (Elliott and Sealock 1985). Similar tests with biomass containing high levels of alkali (sorghum containing 2.04% K and 0.42% Ca) have also shown that the base need not be added and is, in fact, inhibitory in such cases (Butner, Elliott, and Sealock 1986). Further studies at PNL, in which model compounds were tested with catalysts, determined gasification characteristics (Baker and Sealock 1988). Results of this work showed that sodium carbonate was not a good gasification catalyst for methylisobutylketone in a pressurized aqueous environment at 400°C, whereas nickel metal was highly effective. Nickel was also useful in the gasification of para-cresol, naphthalene, benzene, n-hexane, and mixtures of these compounds. No other effective catalysts were found in the group tested (nickel oxide, cobalt/molybdenum oxide, cobalt metal, iron oxide, and Y-zeolite).

The use of metal hydrogenation catalysts for biomass conversion to both liquids (Boocock, Mackay, and Lee 1982; Meier, Larimer, and Faix 1986) and gases (Sealock et al. 1988) has been reported. In the case of liquids production, little feedstock interaction with the catalyst has been determined. The hypothetical mechanism has been suggested as the stabilization of

the reactive pyrolysis fragments to produce a stable oil. At higher temperature, nickel is seen as a reforming and methanation catalyst. Comparative studies showing the greater reactivity of cellulose versus lignin under these conditions also have been reported (Elliott and Sealock 1985). The use of metals raises issues related to deactivation with sulfur or halides, and the use of supported metal catalysts allows for catalyst deactivation through laydown of other metals or carbon formations. Even traces of metals, halides, and sulfur in biomass may lead to catalyst deactivation.

BIOCHEMICAL PROCESSING OPTIONS

Biochemical routes for the production of energy products from biomass rely on relatively low-temperature, enzymatically catalyzed conversion of the biomass substrate to simpler, more readily usable products. In comparison with thermochemical systems, biochemical processes have high selectivity towards the desired product and operate under relatively mild conditions. These advantages are offset to varying degrees by relatively slow, incomplete conversion of the substrate, and some susceptibility to poisoning or inhibitory action by trace compounds which may be present in some biomass feedstocks. This balance between process advantages and disadvantages helps to emphasize the importance of feedstock properties in the selection of appropriate conversion technology.

The major energy products that can be produced biochemically from biomass are ethanol (by fermentation of sugars derived from carbohydrates) and methane (by anaerobic digestion of structural and nonstructural carbohydrates and proteins). There has also been considerable interest in recovering the unused lignin from these processes and chemically treating it to produce useful energy byproducts such as octane enhancers (Johnson et al. 1986). This is actually just one of several schemes proposed that would integrate thermochemical and biochemical processing in the same facility to take advantage of both systems. Another example is the combination of thermochemical and biochemical gasification (Butner et al. 1988).

In most bioconversion systems, the key to increasing yield is overcoming the natural defense systems to microbial attack which have evolved in most

plants. In this sense, feedstock effects play a major role in determining the usefulness of a particular species as a feedstock for biochemical conversion. Understanding these effects is critical both to the development of new conversion processes and to the ongoing efforts to develop new feedstocks. With regard to selection and development of new feedstocks, this means that the mechanisms of these defense systems must be understood so that plants can be selectively bred to minimize these defenses.

Some properties of paramount importance in thermochemical processes are of relatively little importance in biochemical systems. For example, the moisture content of a feedstock is not a factor in biochemical conversion, since most of the operations take place at higher moisture contents than are present in most terrestrial crops. The thermal properties (i.e., fusion temperature, melting temperature) of biomass-derived ash, which were important to many thermochemical processes, do not appear consequential to biochemical processes because low temperatures (35°C to 55°C) are used. The composition of inorganic material present in the biomass may, however, have either beneficial or adverse impact on biochemical systems, particularly for high-ash feedstocks.

The complex and highly specialized nature of the biochemical pathways leading to energy products places a greater emphasis on the chemistry of the biomass substrate than is typified in thermochemical processes. Also, the relative inertness of some biomass components (principally lignin) places a high economic priority on obtaining the highest possible yield from the remaining fractions of the biomass that can be biochemically converted. There has also been a general recognition that the entire plant must be used. This recognition places a high priority on byproduct recovery and utilization. Nonetheless, biochemical conversion offers a highly selective means of producing higher-valued fuels from biomass.

Anaerobic Digestion to Produce Methane

Documented observation of anaerobic digestion dates back at least 200 years (Stafford, Hawkes, and Horton 1980) to "marsh gas," or "swamp gas," which is the result of naturally occurring anaerobic digestion of biomass in

swampy areas. The digestion is carried out by a rather complex series of biochemical reactions, which culminate in methane generation by a group of bacteria known as methanogens.

Reactor design for anaerobic digesters is generally a compromise between high methane production rates and high methane yields. Both affect the economics of methane production but in most cases methane yield is the more critical parameter. Other criteria, which are of lesser importance in most cases, include the susceptibility of the anaerobic culture to possible toxic and/or inhibitory effects of some biomass components, and the ability of the biomass feedstock to provide the anaerobic culture with all or part of the required nutrients for cell growth and enzyme production. Feedstock-related properties have an impact on each of the above criteria.

Methane Yield

Methane yield in biochemical systems is determined by the amount of biodegradable carbon present in the biomass and by the oxidation state of the carbon, which affects the relative distribution of degradation products. In anaerobic digestion, the principal products are methane and carbon dioxide, which are produced in a ratio of approximately 60:40 (Chynoweth et al. 1984). The distribution of products from anaerobic systems can be predicted from empirical composition data (Symons and Busewell 1933).

The stoichiometric limit for methane yield varies somewhat with the elemental composition of the plant material but is typically about 8.5 scf/lb volatile solids (VS) (Chynoweth et al. 1983). In actual systems, the cells require approximately 15% of the total carbon available for cell maintenance so the actual upper limit of biogas yield if all biomass were digestible would be about 7.2 scf/lb VS. Practical conversion levels are about 50% to 65% of the volatile solids converted to gaseous products.

The availability of degradable substrates in the biomass determines the methane yield, and the composition of these substrates also plays a role in determining the methane to carbon dioxide ratio. These two parameters are closely related, since carbon dioxide and methane are the only major products of an anaerobic digestion system. The ratio of carbon dioxide to methane can be correlated with the stoichiometry of the feedstock.

In addition to the stoichiometric limits on biomass conversion to methane, limits are imposed by the chemical structure of the biomass itself. Lignin is poorly degraded in an anaerobic environment. Some aromatic compounds can be degraded, including lignin precursors and low molecular weight degradation products of lignin. Unsubstituted aromatics are generally difficult to degrade, whereas partially oxidized aromatics are more easily degraded. Phenol, for example, can be degraded anaerobically, but not benzene. Because lignin is resistant to degradation in an anaerobic environment (Zeikus 1980), lignin remains unaffected while the carbohydrate fraction is broken down. The residual lignin markedly affects the rate of methane production (Fan, Lee, and Beardmore 1981). A linear relationship was established between reduction efficiency and lignin content (Chandler 1980).

While a substantial fraction of the holocellulose present in biomass can be converted to methane following the fermentive action of the other organisms in the consortium, a portion may be inaccessible and therefore go unreacted. The rate of cellulose conversion is affected by the degree of crystallinity, capillary structure, and degree of polymerization (Cowling 1985). In actual practice, however, the amount of lignin and its degree of association with the cellulose governs the conversion rate to a greater extent than the state of the cellulose (Fan, Lee, and Beardmore 1981).

Methane Production Rate

Relatively little data are available concerning the relative kinetics of different biomass substrates, since most research is concerned with increasing yield, rather than reaction rate. It is logical to assume, however, that due to the wide variability in substrate chemistry and the potential for various transport limitations posed by cell ultrastructure, some intrinsic differences in reactivities of different substrates would be observable. This assumption must be couched against the observation that the rate-limiting step in anaerobic digestion is the metabolism of fatty acids and lipids (Zeikus 1980). This observation places the rate-determining step apart somewhat from basic properties of the feedstock. There is no

indication that this work took into account such substrate-related limitations as mass transfer effects, which can affect the observed, as opposed to intrinsic, kinetics.

In the absence of empirical data, kinetic modeling can sometimes be of use in predicting the impact of intrinsic kinetic differences on reactor design and cost. This approach, which was used in the discussion of thermochemical systems, is of relatively little use here. The utility of conventional kinetic models developed for biochemical systems (such as the Monod model) is severely limited by the lack of model parameters that can be directly related to the individual properties of a particular biomass feedstock.

Toxic and Inhibitory Effects

Some natural constituents of biomass are present as defense mechanisms against decay. Other potentially toxic compounds such as pesticide residues are present as a result of production practices. These compounds can reduce the efficiency of an anaerobic system by poisoning the cell culture or by inhibiting some part of the metabolic pathway. In both cases, methane production can be severely affected, or even stopped completely.

The presence of chlorinated hydrocarbons appears in many cases to be inhibitory to the production of methane from acetate intermediate (McCarty 1964), even in concentrations as low as 3 μM . The widespread use of these compounds as both carriers and active agents in many pesticides indicates a need for examining existing agricultural practices when energy crops are being grown for anaerobic digestion.

The presence of heavy metals in solution may also be inhibitory to anaerobic processes above certain threshold levels. The data in Table A.2 present toxicity levels for heavy metals commonly encountered in some feedstocks.

As in most biochemical processes, intermediate products of the biochemical production of methane are themselves inhibitory or toxic to methane production. One mechanism for this self-regulation is the inhibitory effect of lowered pH, which can be brought on by overproduction of volatile acids,

TABLE A.2. Toxicity Levels for Various Metals (Anaerobic Digestion)

<u>Element</u>	<u>Toxic Concentration</u>
Na ⁺	8000 mg/L ^(a)
Mg ⁺⁺	3000 mg/L ^(a)
Cu	150-500 mg/L ^(b)
Ni	200-1000 mg/L ^(b)

(a) McCarty (1964).

(b) Kugelman and Chin (1971).

the major metabolic intermediate in methane production. While this effect can be controlled by the addition of alkali to control pH, the alkaline nature of the inorganic content of some feedstocks indicates a potential advantage for some high-ash feedstocks, which may in effect contribute to the pH control of the system automatically. In any event, the effect of high ash contents on the growth rate and stability of anaerobic cultures is worthy of further investigation.

Nutrient Effects

Biochemical systems need continuing supplies of materials other than carbon, hydrogen, and oxygen to continue to produce the enzymes responsible for biomass degradation. These nutrients include many elements present in biomass, such as nitrogen and phosphorus, as well as several trace metals. The ability of the biomass to provide these nutrients can play an interesting, albeit minor, role in determining the suitability of a feed for anaerobic digestion.

Nitrogen is present in all biomass to some extent, but the actual ratio of carbon to nitrogen varies considerably among feedstocks, as shown in Table A.3. Insufficient nitrogen in the feedstock indicates the need to add nitrogen to the digester in some form; ammonium salts are often used. The reported value of the optimal carbon to nitrogen ratio varies widely but is generally in the range of 20:1 to 30:1 (on an atom basis) (Meynell 1976). This value is considerably lower than that found in most woody materials but is in the range of many high-nitrogen biomass materials, including grasses

TABLE A.3. Carbon to Nitrogen Ratios for Several Biomass Feedstocks^(a)

<u>Feedstock</u>	<u>Carbon: Nitrogen Ratio, Atom Basis</u>
Napier grass	>500.0
Sorghum	260.8
Sunflower stalks	28.5
Macrocystis kelp	26.2
Water hyacinth	9.0

(a) Elliott, Sealock, and Butner (1987).

and other herbaceous materials. Nitrogen contents much in excess of this level may be inhibitory in some cases, although very few materials contain such high levels of nitrogen.

Ethanol Fermentation and Related Pretreatment Processes

Ethanol production is arguably the oldest known biochemical process used by man, although the production of ethanol for fuel uses is a relatively new venture. Ethanol is produced by fermentation of five- or six-carbon sugars, which can be native to the biomass or derived from starch or holocellulose. A number of feedstocks have been utilized for ethanol production, including sugarcane juice, blackstrap molasses, sugar beet, sweet sorghum, and fruit-cannery waste. Typical sources of starch for ethanol production include corn, wheat, oats, rice, etc.; sweet potatoes; and cassava. Domestically, most of the fuel ethanol produced is made from corn (Wright and Power 1985). The following discussion is primarily concerned with conversion of lignocellulosic materials such as bagasse, straw, grasses, and wood, since this category includes most potential energy crops.

The production of fuel ethanol from biomass is an established industry in the U.S. and other countries. Most existing fuel ethanol facilities rely on agricultural surpluses, particularly of corn, to provide a ready supply of

easily fermentable sugars and starch. Efficient utilization of nonfood biomass such as wood and herbaceous energy crops depends on further advances in fermentation and pretreatment technology; the relatively high priority given this work by government and private agencies makes it likely that these advances will occur.

Fuel ethanol production is similar in most respects to the production of potable alcohol. Figure A.4 illustrates the basic components of a fuel ethanol process.

There are many variations on the generalized process schematic shown in Figure A.4. For example, the pretreatment operation (which is a part of any practical fuel ethanol operation) may consist of a single step or several steps, or may even be incorporated into the fermentation reactor. This pretreatment process may be chemical, physical, or thermal, or (as is usually the case) a combination of the three. Although a number of techniques have been described in the literature, the principal pretreatment processes under development today are acid hydrolysis (Barrier and Moore 1986), steam explosion (Bungay 1982), and enzymatic hydrolysis (Wyman 1986). Of these processes, enzymatic hydrolysis is the least developed and shows the most potential for improving the total bioconversion process. The role that feedstock properties play in determining the type of pretreatment required is discussed in more detail later in this section.

FIGURE A.4. Overall Process Schematic of Fuel Ethanol Production from Biomass

Byproduct recovery has been recognized for some years as critical to the economic viability of fuel ethanol processes, particularly under current energy price structures. The byproducts of ethanol production vary considerably depending on the feedstock used, the processing conditions, and the type of pretreatment process selected. In most cases, the byproducts contain (at a minimum) the unreacted lignin and other nonfermentable materials; they may also contain degradation products from acid hydrolysis, protein, unreacted cellulose, and spent yeast cells. In many cases, the byproducts contain a considerable portion of the nitrogen that was originally in the feedstock, often in a form that allows the byproducts to be fed to cattle and other livestock as a high-protein supplement. Proposed processes for recovering these byproducts vary in complexity, from simple collection and dewatering of stillage to extensive chemical pretreatment (i.e., via the Organosolv process) to recover relatively pure lignin and hemicellulose fractions with potential for high value-added chemical uses. The latter processes are currently in the development stage.

In existing processes, the fermentation step utilizes the six-carbon sugars (hexosans) almost exclusively. For most feedstocks, the amount of free sugar in the native plant is relatively small, making the pretreatment of the cellulosic fractions to produce glucose very important to the development of a viable process. In recent years, progress has been made in the development of microbial and enzymatic agents which would allow the production of ethanol from five-carbon sugars (pentosans), particularly xylose. Much of this work has concentrated on increasing the ethanol tolerance of microorganisms that are known to carry out this fermentation. Since xylose is the primary hydrolysis product of most hemicelluloses, progress in this area is seen as key to the widespread utilization of most energy crops in ethanol processes.

The ethanol recovery step was once considered the major barrier to the economic production of high-purity, fuel-grade ethanol from biomass. Advances in membrane separation technology and other more conventional recovery processes have helped somewhat, but recovery still remains an important and potentially costly part of the process. Since the cost of

separation depends to some degree on the final concentration of ethanol produced in the fermentation reactors, the role of the feedstock cannot be ignored here either.

Current research efforts in support of ethanol production from biomass are concentrated on improving the yield and efficiency of the pretreatment processes. Byproduct recovery and utilization are also high priorities. There is also some interest in developing improved ethanol recovery processes.

Several key factors should be discussed when considering the effect of feedstock properties on ethanol production. These factors include the availability of fermentable substrate, amount and type of byproduct, consumption of pretreatment reagents by the feedstock, and the rate of various reactions comprising the overall process. Toxic and inhibitory effects can be expected to be involved in ethanol processes as well. Indeed, because ethanol production processes are carried out by a single-cell species, these factors could logically be expected to be even more significant than in anaerobic digestion, where the diversity of the microbial consortium provides a more tolerant cell culture. Unfortunately, little documentation was found to either dispel or support such an assumption. These factors, along with nutrient considerations are not discussed in the context of fermentation because of a lack of reported information. This omission indicates an important area for future research.

Yield of Fermentable Sugars

Fermentation of biomass to produce ethanol requires the availability of relatively simple monomeric sugar units that are derived from the raw biomass either directly or by hydrolysis of complex structural carbohydrates, such as cellulose or starches. The five-carbon sugars (i.e., xylose, mannose) that are obtained by hydrolysis of hemicellulose are not used efficiently in fermentation cultures and contribute little, if at all, to the ethanol yield. This limitation restricts the maximum yield of ethanol that can be produced from the most feedstocks, since hemicellulose can account for up to 35% of the carbohydrate fraction of many plants.

The development of processes for the fermentation of five-carbon sugars (Jeffries 1985; Lastick, Tucker, and Grohmann 1986) offers considerable promise to dramatically increase the yield of ethanol available from many biomass feedstocks now being grown. In the short term, however, process development efforts have largely concentrated on maximizing the yield of six-carbon sugars during biomass production and preprocessing.

Six-carbon sugars are primarily derived from either cellulose or starch, although the sugars are also present to some degree as monomeric units, as low-molecular-weight oligomers, and as repeating units in side chains attached to the hemicellulose backbone. The nonstructural carbohydrates are the most readily accessible to fermentation, and their presence in significant quantities will generally lead to easier processing of the feedstock.

Although hemicellulose does not contribute greatly to the yield of fermentable sugars, it can play an important role in affecting both yield and rate of hydrolysis processes via its physical/chemical association with cellulose. This is particularly true with enzymatic hydrolysis, where the close association of hemicellulose with cellulose can lead to diffusional resistances towards transport of enzymes to sites on the cellulose chain. Grohmann, Torget, and Himmel (1985) reported that mild pretreatment of biomass with acid (effectively hydrolyzing much of the more reactive hemicellulose while leaving the cellulose intact) led to a significant increase in the rate of enzymatic hydrolysis of the pretreated material. Evidence presented indicated that the increase is due (at least in part) to the creation of larger pore volumes by the selective removal of hemicellulose (Grethlein 1986), although alternative explanations exist, including the possibility of thermal and/or chemical modification of lignin.

In the event that a practical process for the utilization of five-carbon sugars is developed, the hemicellulose composition will become even more important. Unlike cellulose, hemicellulose exhibits a great deal of variety in its composition. Xylose is the main monomeric unit in hemicellulose derived from most herbaceous feedstocks and hardwoods, while mannose is the principal unit in softwoods (Rydholm 1965). Since most of the research

efforts are directed at xylose utilization, crops with high xylose concentrations are more desirable than those containing other hemicellulose building blocks.

Consumption of Hydrolyzing Reagent

Most commercial hydrolysis is carried out either by a combination of autohydrolysis and steam explosion or by acid-catalyzed hydrolysis. A number of acids have been employed, including hydrofluoric and hydrochloric (Wright and Power 1985), but sulfuric acid is the most commonly employed, largely because of its low cost. Acid hydrolysis produces glucose from cellulose and a mixture of pentoses (primarily xylose) from hemicellulose. Mild hydrolysis tends to make the unhydrolyzed cellulose more accessible to further treatment by removing the hemicellulose, which is much more easily hydrolyzed than cellulose.

Although the acid used in hydrolysis processes acts as a catalyst, and is therefore not chemically consumed by the hydrolysis reaction itself, some of the acid is consumed during the process. There are two main mechanisms for acid loss in the process, dilution and adsorption/absorption on the residual solids and in the associated water. No studies were found that examined the effect of feedstock choice on these losses. Such differences are possible, but variations in the process conditions themselves probably play a much greater role in determining acid loss than any feedstock-related property. For feedstocks with a high inorganic content, an added mechanism is represented by loss of acid, which is consumed by basic cations present in the biomass. Variations in the inorganic content and composition therefore represent a possible influencing factor (albeit probably a minor one) in determining the economics of acid hydrolysis.

A potentially greater problem regarding reagent consumption during hydrolysis is that caused by the adsorption of cellulase enzyme on lignin and other residual biomass solids leaving enzymatic hydrolysis reactors. One of the conclusions of a study of this question (Sutcliffe and Saddler 1986) is that the degree of adsorption and/or deactivation is dependent on the chemical nature of the lignin. Although the authors addressed chemical differences due largely to the lignin isolation methods employed, significant

differences are known to exist among native lignins derived from various kinds of feedstocks. Until the question of how these natural variations affect adsorption properties is answered, the nature of cellulase adsorption by residual lignin should be considered when comparing the performance of new or different feedstocks.

Byproduct Recovery

Several schemes for recovering nonfermentable byproducts from biomass fermentation processes have been proposed. The major byproducts for most feedstocks include lignin, hemicellulose or hemicellulose-derived sugars, and furfural and other byproducts of acid hydrolysis. In some cases, byproducts may also contain unhydrolyzed cellulose, proteins, and other biomass constituents.

The recovery and utilization of lignin from fermentation processes is a subject of great importance to biochemical conversion. Lignin-bearing residues or lignin extracted from the pretreated biomass by chemical means has a number of potential uses (Chum et al. 1985), including use as a low-grade fuel, a surfactant, a filler for plastics and rubber, an asphalt substitute, and an adhesive. Chemically treated lignin also has potential as a fuel or as an octane enhancer for gasoline and other transportation fuels.

The specialized nature of some of the potential chemical applications of lignin point to the potential importance of native lignin chemistry. Lignin characterization work reported by Chum et al. (1987) indicates that significant interspecies variations exist in the molecular weight distribution of Organosolv lignins from beech, birch, and oak. These differences may be significant for some potential lignin utilization schemes. Differences in the distribution of the coniferyl, sinapyl, and p-coumaryl alcohols (Fincher and Stone 1981; Higuchi 1981), which are the monomeric units in most lignins, may also play a role in determining the suitability of lignin for some applications. One type of application that could be particularly affected is based on the chemical processing of lignin to produce low-molecular-weight chemicals such as methylaryl ethers.

Recovery of the pentose fraction resulting from mild hydrolysis of hemicellulose was discussed above, with proposed uses for the materials ranging

from use as livestock feed supplements to use as a boiler fuel. With the advancement of enzymatic processes that would allow pentose utilization as a fermentation substrate, it is likely that this fraction will no longer be treated as a "byproduct."

A related issue of importance in acid hydrolysis processes is the production of furfural and hydroxymethylfurfural as a result of the acid-induced degradation of xylose and glucose, respectively. While there is a limited chemical market for these products (indeed, most furfural produced in the U.S. is produced from either corn or sugarcane bagasse), they are toxic to the yeasts used to produce ethanol, and represent a potential liability to a facility designed to produce ethanol as its primary product.

Finally, a potential near-term use of fermentation residues is as a feed supplement for livestock. This use adds little to the value of the residue (typically only a few dollars per wet ton) but in exchange requires little additional processing or handling. Also, this use of fermentation byproducts capitalizes on existing markets. Of course, the suitability of the residue for this use will depend largely on the pretreatment processes involved, but feedstock selection will also have a great impact on the digestibility, nutrient value, and many other more subjective criteria which must be met in order to permit feeding of the fermentation byproducts.

Reaction Rates in Ethanol Production

Each of the steps in the conversion of lignocellulosic material to ethanol (cellulose hydrolysis, glucose fermentation) is carried out at a rate that is affected to some degree by the nature of the original feedstock. Certainly, hydrolysis rates are limited by the close association of cellulose with hemicellulose and to a lesser degree, lignin; it is also thought that the degree of polymerization and the degree of crystallinity of the cellulose each can affect hydrolysis rates by acid-catalyzed or enzymatic processes. The pore size distribution in the raw and pretreated biomass has been reported to have a significant effect on enzymatic hydrolysis rates.

The fermentation rate of glucose to ethanol is concentration-dependent; thus the concentration of fermentable sugars that can be obtained from a feedstock can affect reaction rate as well as yield. The concentration of

glucose in biomass hydrolyzate is probably much more dependent on the hydrolysis process used than the feedstock, but for a given set of process conditions, feedstock effects are still significant.

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APPENDIX B

CHEMICAL AND PHYSICAL CHARACTERISTICS OF BIOMASS FEEDSTOCKS

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CHEMICAL AND PHYSICAL CHARACTERISTICS OF BIOMASS FEEDSTOCKS

This appendix summarizes the critical chemical and physical parameters that appear to influence conversion processes. Applicable analytical procedures are identified where possible.

IMPORTANCE OF FEEDSTOCK CHEMISTRY

Throughout this report we have tried to demonstrate that the performance of even the most severe conversion processes is affected by the chemistry of the biomass feedstock. The problem of correlating the effect of feedstock conversion with individual feedstock characteristics is complicated by the chemical complexity and diversity of the feedstocks themselves, and by a lack of clear consensus on methods for performing chemical characterization. This section describes the importance of understanding the chemistry of the feedstock.

Elemental Composition (Ultimate Analysis)

The elemental composition of biomass (often reported as the "ultimate analysis") is typically understood to include the elements constituting most of the organic fraction of the biomass: carbon, hydrogen, oxygen, and nitrogen. While other elements are always present, these four elements constitute the overwhelming portion of most feedstocks. The range of compositions found in the literature is depicted in Table B.1.

Standardized methods for determining the elemental composition of biomass are derived from coal methods. Experimentally, the analysis for carbon, hydrogen, and nitrogen is performed by burning the material in a controlled atmosphere and analyzing the resulting gaseous compounds. Often, the process is automated on a microanalytical scale. In commercial units the biomass is burned at high temperature in an oxygen environment. The product gases are then sent through a tube packed with catalyst (to ensure complete combustion), through a reduction tube to regenerate elemental nitrogen, and then

TABLE B.1. Range of Elemental Compositions Reported
for Biomass Feedstocks^(a)

<u>Element</u>	<u>Percent Dry Weight</u>	
	<u>Low</u>	<u>High</u>
Carbon	34.6	54.4
Hydrogen	3.9	6.2
Oxygen	30.4	46.6
Nitrogen	0.0	3.0
Sulfur	0.0	0.2

(a) Jenkins and Ebeling (1985).

along to a series of "traps" or through a chromatographic column, where the individual gases (CO_2 , H_2O , and N_2) can be measured. The quantity of each gas can then be used to calculate the weight fraction of each of the target elements. Alternate chemistries have been derived and automated for analysis of sulfur and oxygen, as well. Analysis for elements other than C, H, N, O, and S is usually conducted as part of the ash analysis.

Correlation of Ultimate Analysis with Performance Criteria

While ultimate analysis data do not provide the detailed chemical description of the feedstock that might be obtained by other methods, ultimate analysis is a fairly reliable predictor of the energy value of a feedstock. It is a relatively fast and simple test and can provide enough information to accurately predict the heat of combustion of the biomass, which, in turn, is a primary determinant of combustion temperature. The ultimate analysis can also be used in some instances to predict gasifier product composition, and is a critical data requirement for calculating carbon conversion, an important measure of combustion and gasification efficiency. A few of the published correlations between ultimate analysis and heating value are shown in Table B.2. As can be seen by examining the correlations in Table B.2, carbon and hydrogen both exert positive influences on the HHV. The presence of oxygen would logically cause a reduction in the HHV; however, regression of data from 51 different biomass samples yielded a small, positive coefficient for oxygen. This is contrary to the effect that

TABLE B.2. Correlations for the Prediction of Biomass Heat of Combustion

$$\begin{aligned}\Delta H_c \text{ (MJ/kg)} &= 0.341 C + 1.322 H - 0.12(O + N) - 0.0153 A + 0.0686 S^{(a)} \\ \Delta H_c \text{ (MJ/kg)} &= 2.549 + 0.349 C^{(b)} \\ \Delta H_c \text{ (MJ/kg)} &= -0.763 + 0.301 C + 0.525 H + 0.064 O^{(b)} \\ \Delta H_c \text{ (MJ/kg)} &= 0.230 + 0.394 C^{(c)}\end{aligned}$$

NOTE: C, H, N, O, A and S are the weight percents of carbon, hydrogen, nitrogen, oxygen, ash, and sulfur, respectively.

(a) Reed (1986).

(b) Jenkins and Ebeling (1985).

(c) Shafizadeh (1980).

would be predicted on a theoretical basis and is likely an artifact of the statistical methods used (Jenkins and Ebeling 1985). Reed (1986) reports a correlation showing the more normal negative effect. Nitrogen is sometimes factored into these correlations and exerts a weak, negative influence. Any sulfur has a small, positive effect on the heat of combustion.

Two common indexes of heating value are used in engineering practice, the higher (gross) heating value (HHV) and the lower (net) heating value (LHV). The HHV is the value that is typically determined experimentally, and represents the energy released in burning all of the biomass to CO_2 and H_2O , with the product and the reactant enthalpies both referenced to their standard states at $25^\circ C$. Nitrogen in the feedstock is assumed to form molecular N_2 . The LHV represents a corrected form of the HHV, with the water formed during the combustion assumed to be a vapor at $25^\circ C$. Thus, the LHV is lower than the HHV by an amount related to both the amount of hydrogen present in the feedstock and the moisture content of the feedstock. Jenkins and Ebeling (1985) presented a simple formula for converting HHV to LHV:

$$LHV = (1 - MC_{wb})(HHV - \Delta H_v(MC_{db} + 0.09H)) \quad (B.1)$$

where MC_{wb} = moisture content on a wet basis

ΔH_v = latent heat of vaporization (water)

MC_{db} = moisture content on a dry basis

H = weight percent hydrogen from elemental analysis.

The HHV is most likely to be reported; but LHV is probably a more meaningful value, since the latent heat of condensation for any water present in the reaction products is not likely to be recovered.

Some general relationships between ultimate analysis and product quality have been observed for the various thermal liquefaction processes. In particular, the presence of nitrogen and oxygen is detrimental in these processes, since they must be removed from the liquid fuel produced. Work performed by Elliott, Sealock, and Butner (1987) indicates that in some instances the nitrogen contained in the feedstock manifests itself as nitrogen heterocyclics in the liquids produced during high-pressure aqueous liquefaction. The presence of these compounds raises concerns about the stability and the toxicity of fuels containing them. Due to the difficulty of removing nitrogen from the ring structure, this is an unfavorable characteristic for liquefaction feedstocks.

Ultimate analysis data have also been used to predict the stoichiometric methane to carbon dioxide ratio in anaerobic digestion. Typically, the ratio of methane to carbon dioxide is 60:40 for biomass substrates. Since the carbon dioxide to methane ratio is determined by the oxidation state of the carbon present in the substrate, it can be estimated from the ultimate analysis data. Chynoweth et al. (1984) proposed the following empirical correlation between the ultimate analysis of the feedstock and the theoretical maximum gas yield and gas composition in anaerobic digestion:

Table B.3 gives the predicted stoichiometric methane yields and methane to carbon dioxide ratios of several feedstocks. While this approach represents a gross simplification, its utility lies in the relative ease of obtaining ultimate analysis data, and thus it provides a quick means of qualitatively assessing the relative digestion potential of a new feedstock.

TABLE B.3. Predicted Methane Yields Based on Chynoweth et al. (1984)

<u>Feedstock</u>	Coefficients from Eq. (B.2)			<u>Mole Methane/ Mole C in Feed</u>	<u>Methane/ CO₂</u>
	<u>n</u>	<u>a</u>	<u>b</u>		
Sunflowers	3.88	6.02	2.96	0.503	1.01
Napier grass	4.01	6.34	2.84	0.521	1.09
Douglas fir	4.38	6.33	2.56	0.534	1.15
Sorghum	4.23	6.54	2.66	0.536	1.15
Water hyacinth	4.62	7.68	2.30	0.583	1.40

In practice, lignin and some aromatic extractives are not biodegradable in anaerobic systems, so these yields are not obtained with native biomass. Nonwoody materials, for example, are generally 60% to 80% convertible. Hardwoods can be bioconverted to methane without pretreatment at yields up to 60% (Jerger, Dolenc, and Chynoweth 1982; Jerger et al. 1982). Bjorndal and Moore (1986) correlated digestibility with composition for more than 2000 samples and reported a mean digestibility of 70% (based on volatile solids) for sorghum leaves (variety not specified). Digestibility correlated best with the sum of neutral-detergent fiber analysis and lignin (by permanganate).

Examination of Equation (B.2) indicates that (at least in a qualitative sense) for anaerobic digestion, methane yield will be favored by selecting feedstocks low in oxygen and with a high hydrogen:carbon ratio. Unlike the case with combustion, however, the use of elemental composition to predict product yield and composition from biochemical processes is seriously limited by the overriding importance of chemistry at the molecular level.

Structural Carbohydrates

The term "structural carbohydrates" is generally used interchangeably with the word "holocellulose," i.e., the sum of the cellulose and hemicellulose fractions of the biomass. Taken together, these compounds, which are naturally produced polymers of simple five- and six-carbon sugars, represent between 65 and 90 wt% of most biomass materials. They are important in

determining the biodegradability of biomass in biochemical systems, and are believed to influence the rate and product yield from thermochemical processes as well.

Cellulose

Cellulose is a stiff, ribbon-like polymer of D-anhydroglucose subunits linked by beta-1,4 bonds. Cellulose is synthesized on or near the outer region of the plasma membrane, and the polymer as such does not pass through the cytoplasm. One basic biological function of the cellulose is to sheath the plant protoplast to provide resistance to hydrostatic pressure and thereby prevent rupture. This sheath forms the primary cell wall material, which is about 50% cellulose.

Cellulose is also present in the secondary cell wall material and helps to form a continuum between cells to provide structural support to maintain plant shape. Individual cellulose molecules do not run the course of the plant but rather combine with other cellulose molecules to form microfibrils, which constitute the basic structural unit. Microfibrils vary in size with plant species, location in the plant, season, etc. A typical size is 5 to 6 nm in diameter. Collections of cellulose molecules generally form either crystalline regions or amorphous regions.

The cellulose content of a feedstock may be determined gravimetrically after selectively removing the hemicellulose, lignin, and extractive fractions by "wet chemistry" procedures. Chemical characterization of native cellulose to determine such factors as degree of polymerization and crystallinity is complicated by the fact that isolating the cellulose generally changes these parameters. The actual monomeric units and linkages involved in natural cellulose do not vary between plant species, however.

Hemicellulose

Unlike cellulose, hemicellulose is a heterogeneous group of polysaccharides consisting of β -(1,4) linked xylose, glucose, or mannose subunits. Xyloglucan, however, is the predominant hemicellulose polysaccharide. The main hemicellulose chains are linear and often, but not always, homopolysaccharides. The polymers have short side chains attached that are composed of

xylose, glucose, arabinose, fucose, rhamnose, and glucouronic acid groups. The number, length, and composition of side chains vary with species. The main dicot hemicellulose is xyloglucan.

Influence of Holo-cellulose Content on Thermochemical Conversion

The pyrolysis and combustion characteristics of cellulose and hemicellulose are quite different from those of other biomass constituents. The relatively high oxidation state of cellulose and hemicellulose results in a heat of combustion (approximately 4100 cal/g) considerably lower than that of lignin (approximately 6400 cal/g). Thus, in combustion systems, highly cellulosic fuels will tend to produce less heat per unit mass of fuel.

On the other hand, cellulose and hemicellulose are much more reactive than lignin, as demonstrated by thermogravimetric and differential thermal analysis data presented by Shafizadeh (1981). As a result, much of the volatile material evolved during combustion and gasification comes from the holo-cellulose fractions of the biomass. These volatile materials burn at much higher rates than the remaining solid chars, increasing the overall rate of conversion that can be obtained.

The role of cellulose content and hemicellulose content on pyrolysis product yield and distribution in gasification and pyrolytic processes has been a subject of much investigation. The extension of this work to a larger number of feedstocks and the use of native materials should increase the understanding of these materials.

Influence of Holo-cellulose on Biochemical Conversion

It is nearly axiomatic that, in the absence of a significant contribution of nonstructural carbohydrates, a high cellulose content is required in order to have an effective feedstock for biochemical production of fuels. This is particularly true in ethanol production, where cellulose is the principal source of fermentable sugars, which are produced by hydrolysis of the cellulose, although, eventually, development of xylose fermentation technology should reduce dependence on cellulose. While cellulose content alone is not a reliable indicator of potential methane or ethanol yields from a feedstock, it is nonetheless a useful screening parameter when new feedstocks are being considered.

A second issue is the morphological form of the native cellulose and its effect on conversion rate and yield. Variations in degree of polymerization, crystallinity, and association (through hydrogen bonding) with other biomass constituents are thought to influence the reactivity and accessibility of cellulose in both enzymatic and acid hydrolysis processes. The degree of association between cellulose and hemicellulose in the native feedstock is believed to be particularly important in determining the rate of enzymatic hydrolysis. While these parameters have been studied in some depth, it has generally not been in the context of fuel production but rather in the area of fiber utilization, i.e., pulp and paper manufacture.

The amount and chemical composition of hemicellulose is probably one of the most important variables in biochemical conversion. Hemicellulose can be converted by acid or enzymatic hydrolysis to sugars. Some of these sugars can be fermented to ethanol by using conventional yeasts. Research progress in alternative fermentation systems and enzymatic transformation of xylose makes the distinction between fermentable and unfermentable substrate somewhat hazy. An analysis of hemicellulose composition (expressed in terms of constituent sugars) would, when coupled with cellulose content, allow relatively accurate prediction of maximum ethanol yields from most feedstocks.

Nonstructural Carbohydrates

Nonstructural carbohydrates, which include free sugars, starches, and pectins, typically comprise between about 1 and 20 wt% of biomass dry matter. Both the sugar and the starch are readily converted to energy products, and are desirable constituents within the constraints established by the structural requirements of the growing plant. The role of pectins in both biochemical and thermochemical conversion processes is unclear. It is known, however, that pectins are capable of yielding biodegradable substrate and therefore contribute to yield in biochemical processes. High-pectin feedstocks may require specially modified hydrolysis conditions (particularly in enzymatic hydrolysis-based processes) to produce optimal yields and rates of hydrolysis (Coughlan et al. 1985).

Lignin

Lignin comprises 17% to 33% of wood, with the remainder mainly cellulose and hemicellulose. Lignin is less plentiful in herbaceous species, typically comprising less than 10%. Lignin from soft wood, such as spruce, is a dehydrogenation polymer of coniferyl and sinapyl alcohol. Hard-wood lignin is a dehydrogenation polymer of sinapyl, coniferyl, and p-coumaryl alcohols (Fincher and Stone 1981; Higuchi 1981). Lignification in herbaceous species generally occurs as the plant reaches full maturity, leading to large variations in lignin content as a function of maturity, species, and position on the plant.

In woods, lignin content is most often determined by the Klason method, which is essentially a hydrolytic treatment to solubilize the holocellulose fraction. In many herbaceous species, interference from nonstructural carbohydrates and proteins limits the usefulness of the Klason method, and other methods must be employed.

While lignin serves a valuable structural function in most plants, its value in conversion processes is somewhat questionable. In thermochemical conversion, lignin is less reactive than the carbohydrates, leading to slower rates of reaction. The high energy content of lignin, on the other hand, tends to increase the total energy availability of the biomass, thereby increasing the energy density. In gasifiers prone to char formation, lignin is thought to be the precursor.

In biochemical conversion, lignin is only marginally reactive. In conventional biochemical processes, lignin must be recovered as a byproduct from the process and utilized either as a fuel or a chemical precursor in order to improve the process economics. More work must be done to facilitate the use of lignin and lignin byproducts to make these processes more competitive. The chemical properties of lignins are subject to variation among species, and the extent of these variations is not well documented. The role of lignin chemistry in determining its suitability for byproduct utilization needs to be further investigated.

The question of whether or not lignin plays a significant role in impeding hydrolysis of biomass does not yet appear to be resolved. While most researchers seem to agree that the associations between lignin and cellulose or hemicellulose present (at least in principle) a barrier to hydrolysis, many of the papers surveyed indicate that this effect is not as important as the association of cellulose with hemicellulose.

Volatiles and Extractives

Volatiles and extractives include a number of minor constituents in biomass, many of which are specific to a particular species. They may include fats, fatty acids, terpenes, phenolics, and a host of other organic compounds. In wood, they are often concentrated in the bark, where they serve a protective function.

Extractive material, especially the more volatile compounds such as terpenes and lipids, can contribute to the combustion of biomass by providing a source of relatively low-temperature volatile material with a high heat of combustion. This fraction of biomass appears to contribute to the ignitability of biomass, and most certainly makes a small contribution to the rate of combustion and the total energy content of the biomass. In some gasification systems, such as updraft gasifiers, the extreme volatility of these materials can contribute to the production of tars and may be more of a liability than an asset.

The effect of these materials cannot be so readily determined for biochemical conversion systems. While some of the fats and fatty acids can be broken down and eventually converted to product, the protective function of some extractives leads to the conclusion that some of these materials may be inhibitory to bioconversion processes. Determining the importance of this effect is important to the development of "whole-tree" conversion processes.

Inorganic Matter (Ash) Composition

The term "ash" is often used to describe the inorganic content of biomass, even in biochemical processes where temperatures are never high enough to create a true ash. This usage probably results from the methods for determining inorganic content, which involve heating to extreme temperatures

to drive off the organic material (i.e., "ashing"). The inorganic content of biomass varies considerably among feedstocks, from negligible amounts to more than 35 wt% for some aquatic species. In general, wood is low in inherent ash (typically below 1%), although the dirt and sand often incorporated during harvesting and collection can add to the amount substantially. Herbaceous species tend to have much higher inorganic content, often up to 10 to 20 wt%.

Most biomass ash is silica, although alkali and alkaline earth (K, Ca, Na) cations are also common and are the most abundant cations in wood. Many of the cations are believed to be chemically associated with acid groups on various carbohydrates in the biomass. Other important elements, such as phosphorus, magnesium, and sulfur, are also found in the ash. Metals such as aluminum and iron are also usually present. A number of techniques can be used for chemical characterization of biomass ash.

The ash is thought to play a role in determining the rate and pathways of gasification and pyrolysis reactions during combustion and gasification. Alkali and alkaline earth cations in the ash can act as catalysts and improve the reaction rate and lower char yields. Other materials (some ammonium salts, for example) are inhibitory to those reactions which lead to flaming combustion. This leads to increased char yields and reduced reaction rates. Other trace elements such as nickel, present in some biomass ash, also have the potential for catalyzing certain reactions.

In biochemical systems, the ash chemistry has the potential to influence the system pH (an important parameter in determining the performance of most biochemical systems) and can also influence the acid uptake in acid hydrolysis processes. Some ash components, particularly metals, can also have a toxic or inhibitory effect on conversion, even at relatively low concentrations. Toxicity data presented by Kugelman and Chin (1971) showed copper and nickel to be toxic to anaerobic systems at concentrations as low as 150 to 250 mg/L. Toxic effects were also noted at higher concentrations of chromium and zinc. Such considerations are likely to be important only in systems using high-ash feedstocks.

PHYSICAL CHARACTERISTICS OF BIOMASS FEEDSTOCKS

Physical properties of the feedstock also should be considered for determining conversion performance. This section discusses several key physical parameters of feedstocks that appear to affect conversion.

Structure of Lignocellulosic Materials

Many of the physical properties of biomass are a result of the plant structure at the cellular level. Although different plants exhibit considerable variation in the fine structural details, the basic structure is similar for nearly all plants. Plant cells are immeshed in cell wall and intercellular material, which provides support and protection to individual cells. Different plant organs have varying requirements for intercellular material. The leaf must have somewhat open areas between cells for gas exchange. The tree trunk and branches have a more substantial mechanical requirement. Between these extremes is a continuum of tissues with varying mechanical requirements. The composition of the intercellular material varies accordingly.

The cell wall provides a restraining force that prevents plant cells from bursting from turgor pressure. Turgor is due to cells being in the presence of a hypotonic medium. Turgor provides much of the rigidity of unignified tissues (Ray, Green, and Cleland 1972). Lignin is most frequently deposited in walls of cells with water-conducting or support functions.

Plant cell walls provide a semipermeable barrier between cells and the external environment. The matrix material between the cells is hydrated, being about 60% water (Roelofsen 1965), but contains pores of about 3.5 to 4.0 nm (Carpita et al. 1979) that allow diffusion of hormones, salts, sugars, and amino acid but not large molecules. Bulk movement of water and solutes through the plant occurs by flow through a continuous system of cell walls and intercellular spaces called the apoplast. Apoplastic channels are formed by selective deposition of lignin and suberin in cell walls (Fincher and Stone 1981; Higuchi 1981).

An important function of cell wall material is to provide a barrier against invading pathogens. Lignified secondary walls are particularly important in this regard (Albersheim and Anderson-Prouty 1975). Wall glycoproteins may recognize specific sugar residues on the cell wall of invading pathogens and trigger defense mechanisms (Kosuge 1981). Fragments of wall polysaccharides formed by degradative enzymes are thought to act as signals for activating defense mechanisms (Ryan et al. 1981).

Plant cell walls consist of cellulose, lignin, hemicellulose, pectic polysaccharides, and structural protein. The cell wall composition varies with the organism, but as a general rule lignin is about 60% of the dry weight of cellulose and in wood can account for as much 24% of the dry weight. The close association of lignin and holocellulose in the plant cell walls is believed to be a factor in determining the kinetics of biochemical conversion.

Moisture Content and Drying Characteristics

The moisture content of biomass reflects the amount of surface, inter-cellular, and intracellular water that may be driven off by drying at low temperatures. It may be reported in either wet weight percentage or on a dry weight basis. Standard methods for measuring moisture content of biomass samples involve heating the material in air at 50°C to 110°C for 12 h, or until it reaches constant weight. In general, the lower temperatures (50°C to 60°C) are used for herbaceous and other nonwoody feedstocks, while the higher drying temperatures are used for wood.

The moisture content of biomass materials is affected by the type of biomass, the climatic conditions, and the handling considerations. For most freshly cut mature wood, moisture content ranges from 40 to 60 wt% (wet basis). Sapling growth or wood samples rich in leaves may have somewhat higher moisture contents. Many grasses may have moisture contents as high as 80 wt% when green, but may drop to as low as 15 wt% or less after drying in the field. Table B.4 lists the reported range of moisture contents for several biomass materials.

Drying characteristics include such factors as the degree of bonding of surface water, the resistance to movement of water through the biomass, and

TABLE B.4. Moisture Content of Several Biomass Materials

<u>Feedstock</u>	<u>Typical Moisture Content, %</u>
Napier grass	60 to 85
Sorghum (green)	70 to 80
Sorghum (field dry)	20 to 40
Douglas fir	30 to 60
Water hyacinth	90 to 95
Wheat straw	less than 15

the amount of intracellular water. These factors manifest themselves in the equilibrium moisture content (EMC). The EMC, in addition to being dependent on the biomass itself, is also a function of the temperature and relative humidity of the drying medium. Accordingly, reported values of the EMC are of little use for making comparisons between feedstocks, except when the values were obtained under similar conditions.

Most thermal conversion systems need relatively dry feedstocks. Drying is of relatively little importance to most biochemical processes. The difficulty and cost of drying feedstocks to acceptable levels can directly affect process efficiency and economics. The moisture content of the feedstock can also indirectly affect the product distribution and quality by influencing other feedstock properties such as heat transfer rates and thermal capacity. Moisture content also plays a major role in determining the equipment and power requirements for size reduction processes, with dry feedstocks generally being much easier to reduce.

Ash Characteristics

The physical properties of ash at high temperatures are critical to determining the suitability of a feedstock in several types of gasifiers and combustion systems. Critical ash characteristics include ash softening and fusion temperatures, which are measured using standardized methods derived from coal ash characterization.

Ash fusion temperatures are influenced by the chemistry of the ash itself, and are generally lower for ashes containing potassium and sodium

salts. Data taken from the coal literature indicate that ash containing these elements can also be volatilized, leading to depositions of scale and mineral material on downstream equipment. In the case of combustion coupled with gas turbines, disastrous results could follow. In other cases, the volatilized ash can lead to reduced heat transfer efficiency and corrosion problems. It is unclear whether the problems related to volatilization of ash results from entrainment of softened ash particles in an aerosol or true deposition of gaseous species. In some cases, both mechanisms partly may be responsible.

Ash can act as a diluent and as a heat sink, which in the extreme can reduce the thermal efficiency and flame temperature of combustion and gasification systems. Ash in the form of particulate emissions also poses a considerable environmental liability in fluidized-bed and downdraft gasification systems, as well as in combustion systems. The ash must be removed from the flue gas in these processes. The removal is accomplished by a number of technologies, including cyclones, filters, wet scrubbing, and electrostatic precipitation. In the latter process, the electrical conductivity of the ash is involved in determining the effectiveness of precipitation. Ash density also is involved in cyclone removal systems, since the efficiency of a cyclone is determined in part by the density differential between the solid and gaseous phases.

Although it is not well documented, the hardness of the ash may also be expected to affect the erosion characteristics of the biomass in some conversion systems. Erosion is typically a problem in processes where high linear velocities are present, including entrained flow pyrolysis, combined-cycle gasification, and close-coupled combustion/turbine systems.

Heat Transfer Effects in Biomass Conversion

The temperature profile and history of a biomass particle undergoing heating may be of importance whenever the time required for heating is comparable to the time required for reaction in a conversion process. This is true of physical transformations, such as volatilization, and chemical reactions, such as pyrolysis or gasification. Depending on the process involved, the temperature profile of a biomass particle can affect conversion rate,

product yield, and product distribution. Thermal properties are relatively unimportant in biological conversion processes, which all operate at relatively low temperatures.

The heat transfer properties of biomass are very difficult to characterize because of the anisotropic nature of the material and because these properties change as the material is affected by the conversion process. These properties are also dependent on the physical condition and prior history of the biomass. As a result, little useful information on thermal characteristics of biomass is available from the literature.

Modeling studies have demonstrated that the effective thermal conductivity is a key parameter in determining the temperature profile through a biomass pellet subject to external heat flux (Chan, Kelbon, and Kreiger 1985). The thermal conductivity of a biomass particle is a function of the particle density, moisture content, and temperature. Under actual pyrolysis conditions, the thermal conductivity is often replaced by an effective conductivity, which factors in the effects of nonconductive heat transfer. In particles that evolve volatile compounds as they are heated (as is the case with biomass), convective heat transfer caused by the bulk movement of the hot reaction gases through the porous particle is an important mechanism for heat transfer. Under these conditions, the effective thermal conductivity is generally an anisotropic property and can be influenced by biomass ultrastructure. As would be expected, measured conductivities are higher in the direction of the grain than in the direction normal to the grain.

Other thermal properties of biomass that appear to be important in some conversion processes include the heat capacity, and to a lesser degree, the thermal emissivity. Heat capacity is a measurement of the ability of the particle to act as a heat sink. The heat capacity measurement helps to determine the amount of energy required to heat a particle, and, when coupled with the thermal conductivity, plays a significant role in determining the temperature history of biomass particles subjected to sudden heating or cooling. Thermal emissivity plays a role in determining the rate at which energy can be transferred into the particle.

Qualitatively, the effects of thermal properties of biomass would be expected to play a major role only in those processes where heatup times are comparable to the reaction rates. Fast pyrolytic processes are particularly suspect, although combustion and gasification processes may also be affected where large particles or very short residence times are involved. Buekens and Schoeters (1985) presented an excellent discussion of the importance of thermal effects. The discussion was based on kinetic modeling of wood gasification and introduced the concept of the Pyrolysis number (Py). This dimensionless parameter is defined as the ratio of heat transfer rate to intrinsic reaction rate and is derived from density, thermal conductivity, particle size, and pyrolysis rate data. Taken with the Biot number, which relates surface convection heat transfer rates to internal conduction heat transfer, the Py was used to characterize gasification reactions as either kinetic controlled, heat transfer controlled, or a hybrid of both. While external factors such as heat flux and particle size are the principal determinants of Py in real systems, variations in Py as a function of biomass properties are important. Unfortunately, this approach requires fairly extensive experimental work to determine the biomass properties as a function of temperature and degree of reaction.

Indirect experimental evidence for the importance of thermal characteristics of biomass may be found in the literature. For example, fundamental pyrolysis studies undertaken at the Solar Energy Research Institute with a free-jet, molecular-beam, mass-spectrometric sampling system (Evans and Milne 1986) have indicated that physical effects such as particle size, moisture content, and heating rate had only secondary effects on the composition of the oil product, although the effect on yield of oil was dramatic in some cases. The fact that each of these parameters is related to the time/temperature profile in the biomass particle indicates that thermal properties may play an important role in determining yield in pyrolytic processes. Unfortunately, these studies have included a relatively limited number of feedstocks, and thermal properties generally have not been determined.

Particle size was also reported to be an important factor related to oil yield in a fluidized-bed reactor operated by the University of Waterloo

(Scott and Piskorz 1982). The effect was attributed to the heating rate of the particle and the residence time of the particle in the fluidized bed. This study found that an intermediate particle size (105 to 250 μm) was needed to optimize product distribution. It was postulated that the larger particles were not heated quickly enough, while the smaller particles were either overheated or else blown out of the bed too soon.

Thermal effects in bioconversion processes are not expected to play as great a role as chemical composition in determining process performance, primarily because of the relatively low temperatures and long residence times employed. Some thermal hydrolysis processes, however, may be affected by thermal conductivity variations to the extent that temperature profiles within individual particles are affected. A more general consideration is the role of heat capacity of the feedstock in determining the energy requirements for preheating the feedstock to hydrolysis temperatures. The range of these parameters has not been adequately determined to allow a conclusion regarding their importance in these processes.

Mass Transfer Effects in Biomass Conversion

Mass transfer in biomass particles manifests itself in two ways: 1) the resistance to mass flux of reaction products and volatile materials out of the biomass particle and 2) the resistance to the mass flux of reactants and enzymes into the particle. Movement is by both convective and diffusive mechanisms.

Mass transfer properties are affected by a number of measurable parameters, including porosity, pore dimensions, and diffusivity. In contrast to heat transfer properties, discussions of mass transfer properties are most often found in the biological processing literature. Although they are rarely treated in the literature, mass transfer phenomena may also be important in thermochemical processes. Like heat transfer characteristics, mass transfer properties are thought to be dependent on the feedstock type, history, and moisture content. In thermochemical processes, mass transfer can affect the time required for primary pyrolysis products to migrate from the interior of a heated particle of biomass to the outside, where these products can further react or leave the reactor vessel.

In biochemical processes, mass transfer can impose limitations on the measured conversion rate and affect total yield. Mass transfer can be a particularly important consideration in enzymatic hydrolysis of feedstocks as a precursor to ethanol production. The relatively large size (approximately 50 Å) of the typical cellulase enzyme requires correspondingly large pores to permit realistic yields and rates of hydrolysis. Other issues related to mass transfer include the possibility of gel formation and cellulose swelling during hydrolysis processes, both of which can close off pore volume and limit the yield of hydrolyzate.

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