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Evaluation of Pretreatments of Biomass for Enzymatic Hydrolysis of Cellulose

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PREFACE

The Solar Fuels Research Division of the Solar Energy Research Institute is responsible for managing a program of research and development for the U.S. Department of Energy Office of Alcohol Fuels. The primary emphasis of the program is the hydrolysis of lignocellulosic feedstock to sugars and their subsequent fermentation to fuel ethanol. One promising way to accomplish this conversion is through an enzymatic hydrolysis process. One critical research issue connected with enzymatic hydrolysis is to find a pretreatment that can render the cellulose susceptible to enzymatic attack yet preserve the other fractions in a usable form for recovery of by-products.

This study begins with an examination of the feedstock, lignocellulosic biomass. This section, which includes both physical and chemical characterization, was prepared by Professor H. A. Schroeder of Colorado State University's Department of Wood Science. The next section examines three pretreatments for their potential to produce an economical feed to enzymatic hydrolysis. Engineering was performed by D. A. Feinberg of the Technical Evaluation and Planning Group, with additional technical material by H. L. Chum, Principal Scientist, Thermochemical and Electrochemical Research Branch. L. J. Douglas, Alcohol Fuels Program Coordinator, was involved in the coordination of the project.

This publication has been thoroughly reviewed by Professor Lennart Johansson from the Department of Chemical Engineering of the University of Washington. Dr. Johansson's comments led to substantial revision and reevaluation of the many processes investigated. We thank both Professor Johansson and Mr. E. Lipinsky from Battelle Columbus Laboratories for their invaluable comments.

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Approved for

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SUMMARY

Objective

To examine the theoretical (scientific-based) and practical (engineering and economic-based) constraints to the pretreatment of lignocellulosic biomass in the enzymatic hydrolysis of cellulose based on available pretreatment data.

Discussion

The pretreatment of biomass is a critical step in the enzymatic hydrolysis of cellulose for the production of fermentation ethanol. To optimize the processes currently being utilized and, if necessary, develop new processes, the physical and chemical characteristics of lignocellulosic materials must be understood. Wood and agricultural residues are heterogeneous materials; variations in characteristics occur between species, among the same species, and from one part of the cell wall to another. The three primary chemical components, cellulose, hemicelluloses, and lignin, occur in varying proportions as well. Each of these constituents has a chemical structure and properties suited for its particular role in the growth of the biomass.

Three pretreatment processes that have undergone some development (under SERI/DOE funding) are organic solvent extraction (organosolv), explosive decompression (steam explosion), and wet oxidation. For each of these processes, heat balances, material balances, and economic summaries were prepared from the available data. The cost of production was determined both in cents per pound of cellulose produced and in dollars per gallon contributed to the cost of ethanol. The effects of variations in such important process parameters as feedstock cost, steam cost, solvent cost, and recovery efficiency were analyzed. A preliminary examination of potential by-product values is also presented.

A wide range of organic solvents has been investigated; this study emphasizes methanol and ethanol. Organosolv has begun to find some use in pulping processes, and similar liquor-to-wood ratios have been used here. Reductions in the liquor-to-wood ratio decrease the liquid loading of most of the equipment, lowering both capital and utility costs. The efficiency of solvent recovery is also critical to the overall economics of the organosolv processes, as are the costs of the feedstock and steam.

The steam explosion pretreatment has had a significant amount of development. Compared to the other pretreatments examined here, this process is the most economical, both in terms of the cellulose pulp produced and its contribution to the ethanol production cost. Under the conditions of the steam explosion reaction, a moderate amount of furfural is also produced, which can further favorably affect the economics of the process. The wet oxidation process achieves a greater degradation of all three fractions of the feed. More feed is therefore required to produce an equivalent amount of cellulose pulp, and the uses of by-product acids from hemicellulose degradation are probably limited to combustion.

Conclusions

Lignocellulosic biomass is a complex feedstock; it is therefore a challenge to develop economical biochemical processes for its conversion to alcohol fuels. Three pretreatments are under investigation that can render the feedstock susceptible to enzymatic hydrolysis. Steam explosion, organosolv, and wet oxidation can all produce cellulosic materials at costs competitive with those of current industrial practices. The major contributors to production costs are the wood feedstock and steam.

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SERIO 

SECTION 1.0

INTRODUCTION

The conversion of lignocellulosic biomass into fuels and chemicals offers great potential for extending the dwindling supplies of nonrenewable fossil resources (coal, oil, and natural gas). The conversion of lignocellulosic materials into ethanol would serve a dual purpose because the product is both a fuel and a potential chemical feedstock. The industrial chemistry of two-carbon compounds is well developed, and ethanol as an initial source is easily adaptable.

Hydrolysis of the cellulosic fraction to glucose for subsequent fermentation to ethanol can be accomplished using either acid or enzyme catalysts. If an industrial alcohol fermentation is to be preceded by an acid hydrolysis process, no pretreatment is required, except possibly a size reduction step. Mineral acids are quite nondiscriminating toward lignocellulosic material, compared to living organisms with specific metabolic needs. Another disadvantage of a mineral acid pretreatment is that some sugar degradation to substances detrimental to fermentation occurs. In addition, possible utilization of the other lignocellulosic constituents—the hemicelluloses and lignin—is made more difficult by a mineral acid treatment.

Enzymatic hydrolysis of cellulose would be preferred, and a pretreatment is therefore essential to render the cellulose accessible to the enzyme. Such a pretreatment could be either mechanical, chemical, or both. It could result in fractionation of the lignocellulosic material into its three constituents—cellulose, hemicelluloses, and lignin—or in partial removal of one of the latter two. Although this separation of the constituents is not critical as long as hydrolysis is strongly enhanced and fermentation is not inhibited, it does provide the possibility of utilizing these other constituents that are available in the biomass. This additional utilization could help defray some of the costs involved, thereby increasing the overall cost-effectiveness of the process.

In the past, a variety of pretreatments have been investigated that make lignocellulosic material more nutritious to ruminant animals than roughage. In the pulp and paper industry, a number of pretreatments have been evaluated to increase yield. Only those that provide easier and more complete delignification would have any relevance and generally are similar to those pretreatments used to increase the nutrient value of lignocellulosic material for ruminants.

The scope of this report is limited to those processes that are evaluated specifically for industrial fermentation. For a few of these processes, sufficient scientific and engineering research (primarily SERI-sponsored) has been done to justify a more detailed analysis. This report is limited to those processes but includes a brief discussion of a few others. Much of the information is based on bench-scale data, with pilot-plant data used where available. Assumptions are clearly noted and justified. The objective is to stimulate further discussion and suggest areas for further research.

SECTION 2.0

LIGNOCELLULOSIC BIOMASS

So the reader may better appreciate the requirements for and difficulties encountered in pretreatments, we provide a description of the physical structure and chemical composition of lignocellulosic material. Since the predominant biomass available is wood, it will be emphasized accordingly. Where appropriate, agricultural residues will also be discussed.

2.1 PHYSICAL CHARACTERIZATION

2.1.1 Summary of Physical Characterization

One of the problems inherent in biomass utilization is the complex structure of the feedstock, which evolved to perform the functions of the living plant. Depending on the source of biomass, this material consists of structural elements for strength (i.e., some type of fiber), vascular elements for liquid conduction (such as vessels in hardwoods), storage cells (primarily in rays), and specialized cells. Most of the substance in biomass is present in the fibers that, because of their function, tend to have thicker cell walls, especially toward the end of a growth ring when latewood is deposited.

The individual cell walls are also not homogeneous but instead are highly structured. The cells are cemented together by a true middle lamella consisting entirely of lignin. Adjacent to the true middle lamella is the original primary wall, which consists in the mature cell of considerable lignin and pectin with minor amounts of cellulose and hemicelluloses. The combination of two primary walls and the true middle lamella between them is known as the compound middle lamella. Its dimensions are fairly constant regardless of cell type, position in the growth ring, or biomass classification (hardwoods or softwoods). In fibers the compound middle lamella is responsible for only a small fraction of the total material available. The secondary cell wall contains most of the woody substance and usually consists of three separate layers differentiated by the orientation of microfibrils. The middle secondary wall layer is the most dominant; this layer varies in thickness between early- and latewood.

The specific gravity of woody substances is rather constant at 1.5; therefore, the specific gravity of biomass is actually an indirect measure of the amount of void volume present in the material. Density is important in biomass utilization because it determines digester capacity and influences liquor-to-wood ratios. Density varies considerably within a growth ring, and although the light earlywood might occupy most of the volume, the latewood contains most of the material and determines reaction parameters.

Wood-liquid interactions are also important for biomass utilization. The rate of liquor penetration into wood is highly species-dependent. Sapwood is normally readily accessible, especially if never dried, whereas the heartwood may be almost impregnable. Penetration of the cell wall is controlled by bound-liquid diffusion, and in thick-walled latewood fibers of some species the diffusion rate controls the rate of reaction. The pore size or exclusion limit of the cell wall may affect the rate of reaction where larger molecules are involved, such as in the removal of lignin fragments during delignification.



The effect of other than normal wood, such as reaction wood, branch wood, and juvenile wood, which are constituents of biomass, is also discussed. These wood types differ from normal wood in their density and wood-liquid interactions. Specific problems related to agricultural residues are also discussed.

2.1.2 Gross Features of Wood

When trees are harvested, even in whole-tree logging, the predominant biomass obtained is the trunk. The trunk is composed of three parts: the xylem or wood, the cambium, and the bark. The cambium is a thin layer, at most only a few tenths of a millimeter thick, containing growing cells that eventually result in more wood and inner bark or phloem being formed. Most xylem cells are longitudinal and are formed in concentric layers outside the older wood. In the spring when growth is rapid, cells with thin walls and wide cavities or lumens are formed; in the fall growth is slower, producing cells with thicker walls and narrow lumens. The former cells are called springwood or earlywood, the latter summerwood or latewood. A year's growth, especially in softwood, is easily seen and is called a growth or annual ring. Growth rings vary in thickness and in the ratio of earlywood to latewood. Growth rings can be so narrow that several hundred occur in a linear inch and contain less than a dozen concentric layers of cells each. Fast growth may contain several hundred concentric layers of cells per annual ring and yield only a few annual rings per inch.

Besides xylem or wood, the cambium also forms phloem or inner bark in the other direction. The ratio of phloem to xylem formed is 1 to 6-8. The inner bark, which is active in photosynthate transport and nutrient storage, is light colored and similar to wood in appearance when freshly cut. The inner bark is usually 3-15 mm wide in smooth- or thin-barked species and is by far the dominant total bark material. Its presence often does not interfere with chemical utilization of wood and may actually contribute biomass.

All trees will eventually develop a thick outer bark due to activation of a cork cambium. The age at which this occurs is highly species-dependent, with so-called thick- or rough-barked species developing a pronounced outer bark layer after only a few years. The outer bark is normally a mixture of cork cell layers with varying amounts of included phloem cells and is often rich in extractives. Cork cells are highly impervious to liquids and therefore tend to present problems when present in appreciable amounts in chemical utilization processes.

The xylem can also be divided into two components: sapwood and heartwood. The sapwood is active in conduction of water, trace amounts of minerals, and nutrients upward to sites of photosynthesis. Formation of heartwood is highly species-dependent, with some species such as the pines having wide sapwood bands. The heartwood may be indistinguishable as in aspen, spruce, and fir, or it may be readily visible due to the presence of appreciable phenolic extractives, primarily tannins. Generally the heartwood is not as permeable as the sapwood, and in some species it is almost impervious to liquids. This is one reason thinnings or short rotation material are preferred for chemical utilization, because often the heartwood has not yet been formed.

Other gross features of wood include rays, which differ from most elements in not being longitudinally aligned but instead going from the center or pith outward radially. The function of rays is transverse transport of liquids and possibly gases, and nutrient storage. They are more predominant and species-characteristic in hardwoods. Hardwoods also have pores, actually vessels, which in ring porous species such as oak, elm, ash, and

hickory are much larger in earlywood. In diffuse porous species such as aspen and maple, the pores are smaller and have less size variation throughout the growth ring. Some softwoods contain resin canals, and in pines the oleoresin present in them is the source of naval stores, i.e., turpentine and resin.

2.1.3 Structural Elements of Wood

Wood is a cellular, porous material in which the cells show a great diversity depending on their main functions in the living tree; i.e., either supporting the crown, conducting liquid, or storing food reserves.

Parenchyma cells are primarily involved in storage of food reserves, although their secondary activity appears to be synthesis of secondary metabolites or extractives. Rays contain considerable parenchyma cells; often the term "ray cells" is used instead, although it is not completely correct. The cells are living and contain protoplasm in sapwood, but they die at the heartwood/sapwood boundary. Parenchyma cells are thin-walled and a minor component in wood, but are more prevalent in hardwoods. Table 2-1 presents dimensions and relative amounts present in wood and grasses.

The major cellular component of softwoods is tracheids, more commonly called fibers. They serve the dual functions of providing rigidity through strength and upward transportation of liquids. Tracheids constitute over 90% of the volume of softwoods and because they have thicker walls than parenchyma cells may contribute 98% or more by weight. Tracheids in normal wood average 3-5 mm in length. Their length-to-width ratio often exceeds 100 to 1, which is why they are such good papermaking fibers. The tracheids in softwoods vary in cross-sectional area, cell wall thickness, and lumen size between earlywood and latewood. In earlywood the cells have a larger cross-sectional area, thinner cell walls, and larger lumens. But even in latewood the lumen is usually several times wider than the cell wall. Pits are present in the walls of the tracheids and generally exist in pairs between adjacent cells in the wood where they facilitate movement of liquid between the cells. The total number of pits in a given tracheid varies considerably, but in the earlywood of some species may exceed 200.

Table 2-1. Relative Amounts of Cells Present in Biomass (%)

Biomass	Fibers	Vessels	Parenchyma
Softwoods			
Volume	90-95	None	5-10
Weight	95-98	—	2.5-4
Hardwoods			
Volume	40-65	20-50	10-20
Weight	70-85	10-15	4.5-7.0
Grasses			
Volume	25-60	1-10	30-70

Hardwoods are anatomically more complex than softwoods. The functions of liquid conduction and mechanical support are generally separate, but a few minor cell types perform both functions. Vessels, more commonly known as pores, are responsible for liquid conduction. The vessels are composed of individual vessel elements, which are open-ended cells that have a much larger lumen diameter than any other cell type found in wood, but have thinner cell walls than fibers. In some species, vessels may account for more than 50% of the volumetric composition of the wood, but generally less than 10% by weight.

Associated with the vessel elements are hardwood tracheids; three types are apparently involved in some secondary liquid conduction activity and are usually present in small amounts. The major woody substance in hardwoods is libriform fibers—cells adapted for strength and support rather than conduction. Libriform fibers have a smaller cross-sectional area and thicker walls than softwood tracheids, with the lumen occupying less than one-half of the cell diameter. Hardwood fibers are shorter than softwood tracheids, averaging 1.2 mm in length. The length of hardwood fibers is highly species-dependent, ranging from 0.5 to 2.5 mm. The amount present is also variable—25%–75% by volume and 75%–90% by weight.

Hardwoods also have a greater array of parenchyma cell types than softwood, including both longitudinal varieties and transverse types in rays. The rays themselves are also more varied depending on the species. Hardwoods have about twice the parenchyma and ray content of softwoods, but the amounts are highly variable, with some species having up to 30% rays by volume.

2.1.4 Cell Wall Structure of Wood

Because there are definite similarities among the various cell types discussed, the cell wall structure of mature, normal softwood fibers will be given as an example. Figure 2-1 shows a comparison between the fine structures of hardwoods and softwoods. Figure 2-2 shows the distribution of the polymeric constituents (cellulose, hemicelluloses, and lignin) in the cell wall of Douglas fir.

The intercellular substance separating two cells is termed the true middle lamella and is composed entirely of lignin. The first actual cell wall layer is the primary wall; when the cell was formed at the cambium, the primary wall isolated the protoplasm of that living cell. Originally the primary wall was essentially pectin, but in the mature wood it also contains about 10% cellulose in poorly oriented microfibrils, probably some hemicelluloses, and considerable lignin. Because of their small cross-section, small contribution to the total amount of the wood, and difficulty to separate, the true middle lamella and the two primary cell walls of adjacent cells are more commonly combined into one entity, the compound middle lamella.

Most of the woody substance in mature cells is present in the secondary wall, which is composed of layers of secondary thickening formed inside the primary wall. The secondary wall, formed during maturation of the fiber, is not homogeneous but subdivided into the outer secondary wall or S_1 layer, the main or dominant secondary wall, the S_2 layer, and the inner secondary wall, the S_3 layer. These secondary wall layers are differentiated on the basis of microfibril orientation. Microfibrils are cellulose strands averaging 35Å in diameter and containing about 40 cellulose macromolecules in cross section. In the S_1 layer the orientation is 50°–70° from the cell axis, and it may show some cross-hatched pattern with one direction predominant. In the S_2 layer the orientation is

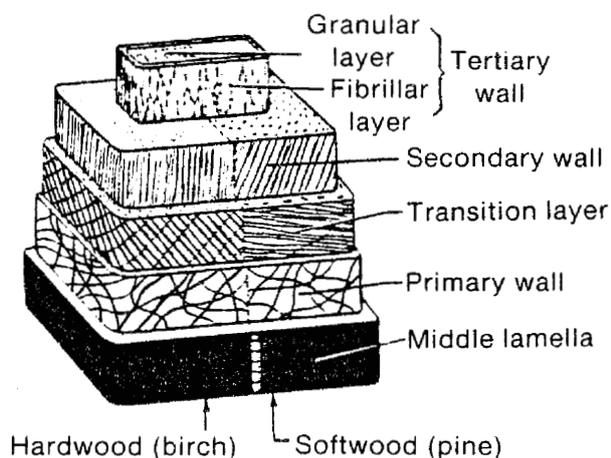


Figure 2-1. Model of the Fine Structure of Hardwood (left half) and Softwood (right half) Fibers

its thickness is fairly constant. The S_1 layer averages 16% with 4-6 laminar layers of microfibrils. The S_2 layer is highly variable in thickness; it has up to 150 laminar layers of microfibrils but averages 75% of the total. The S_3 layer averages 8%, or about half the size of the S_1 layer.

2.1.5 Other Than Normal Wood

Some wood differs anatomically from normal, mature wood in the tree trunk, but may be present as a regular constituent. This category includes juvenile wood, branch wood, and reaction wood.

Juvenile wood forms in a cylindrical column about the pith or center of the stem as the result of prolonged influence of an active crown upon wood formation by the cambium. The duration of the juvenile period is quite variable and somewhat species-dependent, usually lasting 5 to 20 years. In fast-growing plantation trees with a short crop-rotation time, juvenile wood may be an appreciable amount of the wood harvested. Juvenile wood has a shorter fiber length and a greater microfibril angle in the S_2 layer than normal wood. There is less pronounced latewood formation and in general the fibers have thinner cell walls and a smaller total diameter.

Branch wood may contain some reaction wood, especially near the trunk, but even when omitting this material, it is different. Knots are composed of branch wood and therefore this material is present in the trunk of the tree also. The growth rings in knots are narrower with shorter fibers having a smaller diameter. Because of the smaller diameter of the fibers, the appearance is one of branch wood being predominantly latewood.

10° - 30° from the cell axis with one predominant direction for the microfibril helices. The S_3 layer has a less precise microfibril orientation, with a predominantly flat helix that lies at an angle of 60° - 90° to the cell axis. Adjacent to the cell lumen there is often a warty layer, which is probably protoplasmic residue. At the boundaries between the primary wall and the S_1 layer, and between the various secondary wall layers where the microfibril helix orientation changes abruptly, there are zones of structural weakness. In some treatments the cell wall layers can be unravelled to varying degrees along these zones of weakness.

The S_2 layer of the cell wall of fibers shows the greatest variations in amount. It is predominantly this layer that changes in thickness between earlywood and latewood. The S_2 layer can account for more than 90% of the woody substance in the latewood fibers of some species. Relative amounts of cell wall components have been approximated and are summarized. The compound middle lamella is only 2%-5% of the total and

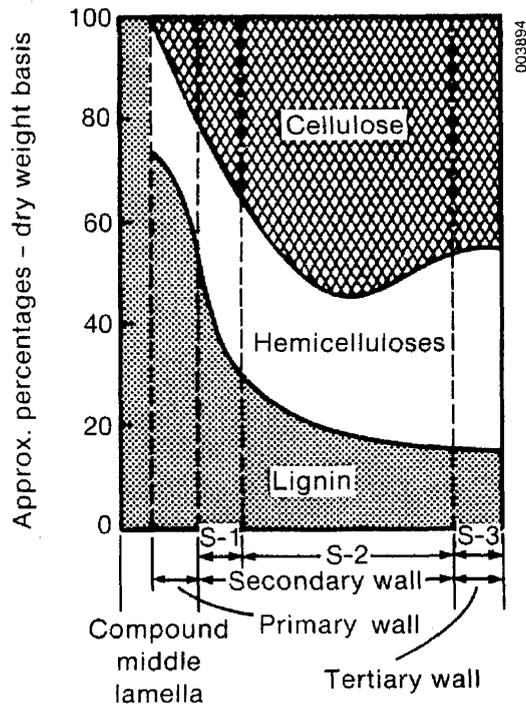


Figure 2-2. Approximate Distribution of Polymeric Constituents in the Cell Wall of Douglas Fir

Reaction wood occurs when outside stress is reflected in growth characteristics. The outstanding example would be a severely leaning tree. Other occurrences of reaction wood are in limbs, especially near the trunk, and in trunks of trees subjected to abnormal stress, such as trees at shoreline or timberline. The amount of reaction wood formed is variable, and there is a gradation from apparent normal wood to extreme reaction wood.

Reaction wood is characterized by individual fibers, and it seems that normal wood fibers and reaction wood fibers can exist adjacent to one another. The reaction of trees to stress is species-variable, especially among hardwoods, with some species being reluctant to form reaction wood.

The reaction wood of conifers is known as compression wood and forms on the lower side of the leaning stem, giving eccentric growth rings with abnormally large proportions of latewood on that side of the stem. The microscopic characteristics are rounded tracheids in the predominant latewood. The tracheids are shorter in length and have spaces between them because the tracheids are round. The cell wall is altered by the absence of an S_3 layer, and the S_1 and S_2 layers are thicker. The microfibrillar orientation in the S_2 layer approaches 45° from the cell axis with helical cavities in the S_2 layer oriented to the microfibrillar angle.

In hardwoods the reaction wood is known as tension wood and causes eccentric ring growth on the upper side of a leaning stem due to faster growth. Some species indicate little if any tension wood formation. In tension wood more fibers are present with fewer and smaller vessels. The microscopic characteristic used for diagnosis of tension wood is a gelatinous or G layer present between the cell cavity and the cell wall. The G layer is almost pure cellulose and there is no apparent lignification. The secondary cell wall normally has all three layers, but it may be missing one or two layers beginning at the cell cavity in tension wood.

2.1.6 Wood Density

In the field of wood science and technology, the density of wood is normally expressed as oven dry weight divided by green volume. This value is assumed unless otherwise specified. In the forest products industry, pounds per cubic feet is usually used, but our discussion will use specific gravity.

The specific gravity of the cell wall is approximately 1.5; i.e., the solid woody substance has about that specific gravity. Pure crystalline cellulose has a value closer to 1.6 and lignin about 1.35. The specific gravity of domestic species varies from a low value of about 0.25 to slightly above 1.0. Generally softwoods are lighter than hardwoods, with most softwoods being between 0.35 and 0.50. Southern yellow pines are considered heavy for softwoods and average between 0.45 and 0.55. Among the hardwoods, a light wood such as aspen would have a specific gravity around 0.40. Many hardwoods, such as oak, ash, maple, and hickory, have specific gravities between 0.50 and 0.65.

Since the cell wall itself has a fairly constant specific gravity, the specific gravity of wood as a whole really indicates the amount of void volume in the material. In wood having pronounced earlywood and latewood bands, as in southern yellow pines, the earlywood may have specific gravities varying from 0.25 to 0.40, averaging about 0.30, while the latewood may have values from 0.65 to 0.85 and even higher, averaging about 0.70. If a southern yellow pine had an earlywood band of a specific gravity of 0.25, a latewood band of 0.75, and roughly equal volumes of both, then as a whole the wood would have a specific gravity of 0.50, but 75% of the material would be in the latewood band. A higher specific gravity indicates a thicker cell wall, specifically a thicker S_2 layer in the cell wall. An exception to this would be in high extractive content wood samples, where the extractives contribute significantly to the density of the material.

In any chemical utilization process, specific gravity or density is very important because it determines digester capacity—the amount of material that can be processed with given equipment or given capital investment.

Specific heat of wood is important in most chemical utilization practices where elevated temperature or steaming are required. The specific heat of wood on an oven-dry basis, in units of kcal/g °C, is 0.266 at 0°C, 0.382 at 100°C, and increases with temperature as indicated by the equation:

$$C_p = 0.266 + 0.00116t,$$

where

$$C_p = \text{specific heat (kcal/g } ^\circ\text{C)}$$
$$t = \text{temperature (} ^\circ\text{C)}.$$

Specific heat is independent of the density of the wood, since it is actually a value for wood substance or the cell wall itself.

2.1.7 Wood/Liquid Relations

Although wood is porous and hygroscopic, many process problems are related to wood-liquid, specifically wood-aqueous solution, interactions.

The flow of liquids in wood is determined by the passageways available for movement of the liquid. In the sapwood of living trees this movement is essentially longitudinal; in softwoods movement involves tracheid lumens and pits between adjacent cells, while in hardwoods it is primarily through vessels. In chemical wood utilization these passageways may lose some of their importance.

In the heartwood of softwoods the pits may be occluded with extractions, and if the wood has been dried both sap- and heartwood pits may be aspirated. In pit aspiration the opening allowing free liquid flow is closed. In the heartwood of certain hardwoods the vessels may be filled by tylose membranes, which effectively block any liquid flow. An example of the effect of tylose formations upon liquid penetration is given by comparing red oak with white oak. Red oak can only be used for slack cooperage because of the lack of tyloses, whereas white oak is used for tight cooperage because it is impervious to liquids. In hardwoods the pit structure of libriform fibers always contains a membrane and is never open to liquid flow as the pits in softwoods can be when not aspirated. Almost without exception sapwood is more permeable than heartwood, and for never dried wood this difference may be considerable. Steaming of dried wood can eliminate some pit aspiration and remove some of the encrusting extractives, thereby increasing permeability.

Liquids that are polar, especially those that can form an H-bond, can diffuse through the cell wall. Diffusion involves the making and breaking of H-bonds on a continuous basis in the polymolecular layer of water in swollen wood. The diffusion, if it is an aqueous solution, would be bound water diffusion under a hygroscopic gradient. Where there is no hygroscopic gradient, as can occur in completely swollen wood (wood above the fiber saturation point), solutes would diffuse under a concentration gradient. In softwoods, where the pit is aspirated, and in hardwoods, where the libriform pit has a membrane, diffusion is the only means of moving liquid or solute into the lumen of the cell. Diffusion occurs both through the pit structure and the cell wall. Although the surface area of the wall is much greater than that of the pit structure transversed by diffusion, both are important because the membrane being crossed in the pit is much thinner than the cell wall.

Where reactions occur in the cell wall, such as delignification, diffusion plays an important role and may be more important than the actual rate of reaction. The thicker the cell wall, the more important rate of diffusion becomes. In woods such as the southern yellow pines that have a heavy latewood band, the overall pulping rate is determined by degree of delignification of the latewood band; consequently the earlywood is overdelignified, which causes undue degradation of the carbohydrates. When a reaction such as delignification of the cell wall occurs, the pore structure opens up, and accessibility and the molecular exclusion limit increase from the lumen outward. This process has numerous effects on overall, apparent rate of reaction. In delignification the molecular size of solubilized lignin fragments increases with reaction time.

In the pulping industry certain heavy wood species such as the live oaks with specific gravities above 0.90 are excluded because the rate of diffusion becomes limiting, with unduly long reaction times for adequate delignification. Denser wood, such as reaction wood, compression wood, and branch wood, also presents diffusion problems. Knots tend not to be adequately delignified in pulping and consequently are rejected in pulp screening. The reason wood is chipped prior to pulping is to minimize, if not alleviate, problems associated with diffusion of the reagents into the wood. Chipping, however, does not eliminate diffusion problems due to a thick cell wall.

2.1.8 Agricultural Residues

Agricultural residues, usually grasses or related raw materials, for chemical utilization will be compared to wood. The most obvious differences from wood are the inability of grasses to significantly increase the diameter of the stem through additional growth and the lack of distinct, separate locations within the stem for the xylem and phloem. Con-

sequently these stems have no concentric organization comparable to that of trees. In some grasses there is a hollow core, such as in the stem of cereal grains or straws; in others the stem is solid, such as in cornstalks and bagasse. In general, the stem consists of pith or fundamental parenchymous material much like the small pith present in trees. However, in these stems isolated vascular bundles pass longitudinally through the pith material. A cutinized epidermal layer covers the outside of the stem, and in many grasses a tissue consisting of several layers of thick-walled sclerenchyma fibers forms a cylinder just beneath the epidermis. The vascular bundles in the pith tissue have both xylem vessels and phloem or bast fibers and are often sheathed by sclerenchyma fibers. This results in four categories of cells, in the following approximate proportions for wheat straw: fibers, both bast and sclerenchyma 50%, parenchyma 30%, epidermis 15%, and vessels 5%. In most of these materials parenchyma cells constitute a large proportion of the total, especially in those with a solid stem. Cornstalks and bagasse contain about equal proportions of fibers and parenchyma cells. For comparison refer to Table 2-1.

The fine structure of grass fibers is similar to that of wood fibers, with a primary wall and three distinct secondary wall layers. The microfibrillar structure of these layers is also similar to wood. Generally, the fiber fraction of the grasses is similar to that of hardwoods. The quantity of nonfiber cells is usually much higher, however, which decreases the value of these materials for papermaking.

2.2 CHEMICAL CHARACTERIZATION

2.2.1 Summary of Chemical Characterization

Biomass, and especially wood, is essentially composed of compounds containing only carbon, hydrogen, and oxygen. Normally there is little ash or mineral content in wood, usually less than 1%. Woody substances are composed predominantly of carbohydrates, the holocellulose fraction, and an aromatic component—lignin. The carbohydrates are all polymers or polysaccharides and are the most highly oxygenated constituents of wood. Lignin is also macromolecular but much less oxygenated. However, lignin is easily oxidized—a property that is often exploited in delignification of wood.

Cellulose is the most plentiful constituent in biomass. In wood the amount present is fairly constant at about 43%, with hardwoods generally having slightly more than softwoods. Cellulose is unique in that it is only found in microfibrils and never as individual molecules. The microfibrils are about 35 Å in diameter and contain about 40 cellulose chains in cross section. The microfibrils have both crystalline and amorphous regions, the nature of which is still conjecture. In wood the crystalline cellulose accounts for approximately two-thirds of the total cellulose and may exist in regions 100 anhydroglucose units in length or longer. The degree of polymerization of cellulose molecules apparently depends on its location in the cell wall, with the cellulose in the middle layer of the secondary wall having the highest degree of polymerization. On the average cellulose in situ contains 10,000 anhydroglucose units, but this value is greatly reduced during isolation procedures. Accessibility of cellulose to reagents is perhaps a more important feature than crystallinity, and the value obtained depends on the reagent used, but always is lower than crystallinity.

Pectin is present only in small amounts and is often ignored because of the ease with which it can be lost, especially during delignification reactions. The other carbohydrate fraction is hemicellulose and consists of two separate entities: a mannose-containing

polysaccharide and a xylose-containing one. The hemicelluloses of softwoods, hardwoods, and grasses (agricultural residues) are related but not identical. Together hemicelluloses account for about 30% of the woody substance, with hardwoods generally having slightly more hemicelluloses than softwoods. In softwoods the hemicellulose that contains mannose is the dominant one; it also contains glucose, galactose, and acetyl groups. Softwood xylan has uronic acid and arabinose side groups. In hardwoods the mannose-containing hemicellulose is present in small amounts. Hardwood xylan is by far the most important hemicellulose. It contains uronic acid side groups and is acetylated. In grasses there are only xylan hemicelluloses, but several types may occur, even in the same plant. Of the two types of hemicelluloses the xylans are easier to remove from biomass.

Lignin is the noncarbohydrate component of woody substances. The basic carbon skeletal structure of the monomeric unit is that of phenylpropane. Lignin is a three-dimensional macromolecule formed by end-wise free radical polymerization; therefore it has no consistent repeating linkage between the monomeric units. Lignin does contain methoxyls, and the amount of this functional group determines many of the properties of lignin. Softwood lignin in normal wood is identical regardless of source. Hardwood lignin differs by species, but in general it has a greater methoxyl content than softwood lignin; consequently, it has a lower degree of polymerization, less condensation, and more free phenolic hydroxyls. Hardwoods are easier to delignify than softwoods, and grasses are easier to delignify than hardwoods.

Softwoods contain about 28% lignin, hardwoods 22%, and grasses even less. Most of the lignin in wood is in the secondary wall because of its size, rather than in the compound middle lamella. About 20% of the secondary wall is lignin; softwoods have slightly more and hardwoods slightly less. The cellulose microfibrils are embedded in a matrix of lignin and hemicelluloses. This arrangement presents a major accessibility problem for large, proteinaceous, cellulase enzymes. One reason for pretreatment of woody biomass is to modify this association of the chemical constituents in the secondary walls, making the cellulose microfibrils more accessible.

2.2.2 Chemical Composition of Wood

Wood is essentially composed of carbon, hydrogen, and oxygen, with very small amounts of organic nitrogen and traces of volatile sulfur. Wood is high in oxygen due to the carbohydrates present and consequently is only 50% carbon. The ash content of temperate-zone woods is low--0.2%-1.0%, with hardwoods generally higher in ash than softwoods.

Wood can be divided into cell wall constituents or structural components and extractives. The extractives can be classified by apparent function, with some providing food reserves and others protection against either injury or biological deterioration. Oleoresin in those species having resin canals protects against injury. Protection against decay is due to phenolic compounds and related substances. These phenolic substances are responsible for the darker heartwood and the durability of many species. Sapwood contains little phenolic extractives and consequently is not decay resistant. The sapwood contains water and ether solubles, which are primarily food reserves--carbohydrates and fatty substances--in amounts of 2%-5% or less. The heartwood of extractive-rich species may contain between 10% and 25% extractable material. The excess of extractives is due to phenolics, primarily tannins. These phenolic substances can interfere in utilization involving microorganisms.

The cell wall constituents are carbohydrates, all of which are polysaccharides, and lignin, a polyphenolic polymer. The carbohydrate fraction is known as holocellulose and is composed of cellulose and the hemicelluloses, but without pectin. There are two types of hemicelluloses: one containing mannose and the other containing xylose. Pectin, which is often not considered, is present in minor increments (1%-4%). Pectin is a complex carbohydrate in the primary wall, is intimately associated with lignin, and is easily lost during delignification reactions. Because parenchyma cells are thin-walled and have little secondary wall, their pectin content is higher than that of the fibers. Hardwoods have more parenchyma cells and more pectin than softwoods, and presumably agricultural residues and grasses have even more pectin.

2.2.3 Cellulose

Cellulose is the major cell wall constituent in wood, and its amount in normal wood is relatively constant. Wood has an average of 43% cellulose, with softwoods generally having 2%-3% less cellulose than hardwoods. Often in the literature the value for α -cellulose is substituted for cellulose. α -cellulose is defined as that portion of delignified material insoluble in 17.5% NaOH under specified conditions near ambient temperature. Besides true cellulose, α -cellulose from wood contains a few percent of hemicellulose, a small amount of lignin, and some of the minerals in the original wood. α -cellulose values for wood are usually 2%-5% higher than the true cellulose content.

Cellulose is defined as a linear polymer of anhydroglucose units with all glycosidic linkages between the monomer units being β (1-4). All hydroxyls including those involved in the glycosidic linkage are equatorial, and therefore the polymer is stretched with a 180° spiral orientation.

The degree of polymerization (DP) of cellulose varies depending on the source. Chemical pulps generally contain cellulose with a DP of 1,200-1,500, with dissolving pulps having a DP of about 1,000. The cellulose in holocellulose from cautiously delignified wood may have a DP of 3,000 to 4,000. The average DP value in sound wood in situ is considered to be approximately 10,000. Apparently the DP of cellulose in the cell wall depends on its location. In the primary wall the average DP is only 1,500, in the S_1 and S_3 layers it is 5,500, and in the S_2 layer, where most of the cellulose is, it is 11,500. The maximum DP for cellulose in situ has been determined to be 15,300. Cellulose is the largest naturally occurring polymer; in the S_2 layer it is 6 μm long and has a molecular weight approaching two million.

Cellulose is unique because it is never found in nature as a single molecule. It is only found in microfibrils that have an average diameter of about 35 \AA and contain 40 cellulose chains in cross-section. Some observers have suggested that these microfibrils are made up of smaller subunits, as small as 10 \AA . The microfibrils tend to aggregate once wood has been delignified, and consequently in the older literature microfibril dimensions greater than 35 \AA are given. Values high as 250 \AA are reported in the literature. In situ these microfibrils are embedded in a matrix of amorphous hemicelluloses and lignin in the cell wall.

Another unique aspect of cellulose is that it occurs in both crystalline and amorphous forms in regions of the microfibrils. The degree of crystallinity apparently depends on origin of the material, procedures used, and interpretation employed in the evaluation. In general the cellulose in wood is considered to be about two-thirds crystalline. There is some evidence that in the S_2 layer, where most of the cellulose occurs and where the

cellulose DP is the highest, the cellulose is better ordered and has a higher degree of crystallinity than in the other cell wall layers. The length of the crystalline regions in situ appears to be 500-600 Å, and the cellulose has a DP of 100 or slightly more. When microcrystalline cellulose is prepared by selective hydrolysis of the amorphous regions, a DP value approaching 200 is obtained. Apparently, once there is chain scission in the amorphous region, the residual anhydroglucose units are free to realign themselves and extend the crystalline region.

The nature of the crystalline and amorphous regions of the cellulose microfibril is very important to chemical utilization of the material. This is especially true in pretreatments for enzymatic hydrolysis. Unfortunately, there is still a considerable amount of controversy concerning the structure of microfibrils. The more prevalent views will be critically discussed because of the importance of the subject.

Crystalline cellulose as originally formed is the same regardless of the source and is known as Cellulose I or native cellulose. The crystalline lattice forces are H-bonds, and all available H-bonding capacity is involved; however, some H-bonding is intramolecular. Based on the original X-ray diffraction pattern, a unit cell was proposed where the adjacent cellulose molecules in the microfibril were aligned in opposite directions. In recent years evidence has indicated a parallel arrangement of the cellulose chains in the microfibril. Chains that are parallel would fit with the concept of biogenesis of microfibrils. When native cellulose is treated with sufficiently strong caustic, a rearrangement of the crystalline structure occurs, giving rise to mercerized cellulose or Cellulose II. Other modifications of crystalline cellulose are also possible.

The continuous theory of microfibril composition has a band of crystalline cellulose surrounded or fringed by amorphous cellulose. In another related theory, the fringed micellar theory, the microfibrils are composed of statistically distributed crystalline and amorphous regions formed by the transition of the cellulose chains from an orderly arrangement in the microfibrils in the crystalline regions to a less ordered orientation in the amorphous area. One variant of this theory has both crystalline and amorphous areas in any one cross section of the microfibril, while another has discrete crystalline and amorphous segments within the microfibril.

One of the most unusual models proposes that the cellulose microfibrils consist of a folded-chain structure. The molecule chain forms a pleated ribbon 35 Å wide, the ribbon is then wound in a tight helix, and the straight segments of the molecule chain become parallel to the helical, fibril axis. One of the notable features of the folded-chain formation is that it readily explains the antiparallel arrangement of cellulose that was originally proposed for crystalline cellulose. Considerable evidence is accumulating against this concept.

Another model proposes that there are no true amorphous areas, only chain-end dislocations, or imperfections that cause the observed diffuse X-ray diffraction pattern. Still another proposed model has no true amorphous areas, but only areas of slight disorder due to strain-distorted tilted and twisted regions across the microfibril. These last two models are based on chemical accessibility studies. The last model has some similarity with an earlier one where there are discrete amorphous zones across the entire microfibril. Accessibility studies always give a greater crystallinity percentage than do X-ray studies, and perhaps these two models are similar except for the relative amount of cellulose involved. To date no one model can completely account for all the observed properties and characteristics of the microfibrils.

One problem is accommodating the amount of amorphous cellulose calculated from X-ray studies with observed accessibility. For a microfibril 35 Å in diameter and containing 40 cellulose molecules, 28% of the available H-bonding capacity is on the surface of the microfibril, even in the crystalline regions. The extent to which these hydroxyls are available to chemical reagents depends on the size of the reactant molecule and the packing of the surrounding hemicellulose lignin matrix. The amorphous regions of the microfibrils are almost completely available to water for H-bonding, since calculations using one-third of the amorphous cellulose compare favorably with water absorption at the fiber saturation point. Water is a very small molecule, and even an analysis by reaction with formic acid will give a higher crystallinity value than X-ray studies because less of the cellulose is available for reaction. The number of available hydroxyls determined by X-ray studies should be considered the ultimate amount possible, and the number determined by accessibility studies is only available to a given reagent under the conditions employed. Accessibility is the problem where the pretreatment is intended to modify the cellulose itself prior to enzymatic hydrolysis.

Kinetic studies of selective hydrolysis of cellulose with a mild reagent, such as formic acid, will indicate three separate rates. One is rather rapid hydrolysis of only a few glycosidic linkages, usually 1% or less of the total available before moderate hydrolysis of glycosidic linkages in the amorphous regions. The slowest hydrolysis occurs when only crystalline material remains. The rapid hydrolysis is not an artifact, but is due to bonds more susceptible to hydrolysis. There are two explanations for these weak linkages; either glycosidic bonds are not at optimum length and angle and therefore have a lower bond energy because of distortion of the cellulose molecules in the microfibril, or the bonds are weaker because of a chemical effect, such as adjacent carbonyls in the anhydroglucose monomeric unit. Cellulose is slowly oxidized, even in situ, and contains carbonyl and carboxyl groups in minute quantities. A carbonyl adjacent to a glycosidic linkage activates that bond to either acid or alkaline hydrolysis. Usually glycosidic linkages are stable to alkali, but the DP of cellulose is reduced in alkali due to the presence of carbonyls.

Cellulose is well protected from attack by both chemical and biological agents. The molecules are only in microfibrils, the microfibrils are surrounded with a matrix of other reactive material, and two-thirds of the cellulose is crystalline. Most of the cellulose is in the S₂ layer of the cell wall and not exposed. Making the cellulose in the crystalline regions more accessible and thereby reactive is a major problem.

2.2.4 Hemicelluloses

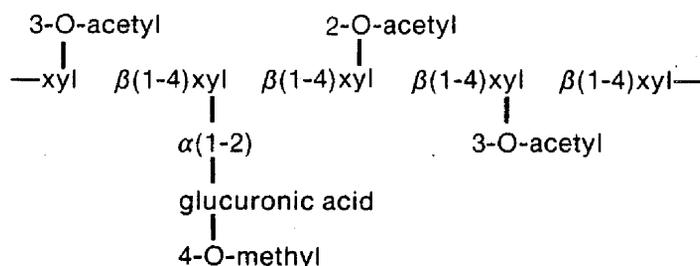
The hemicelluloses are relatively low-molecular-weight, noncellulosic, structural polysaccharides that occur in the plant cell walls with lignin and cellulose. Pectin is normally excluded as a hemicellulose, probably because of its ease of removal during delignification and small quantity involved in woody plants. Arabinogalactan, a water soluble extractive present in a small amount in the lumen of softwoods (except in larch where it is plentiful), is sometimes erroneously classified as a hemicellulose for convenience of discussion.

In spite of the implication of the name, the hemicelluloses have no relationship to cellulose per se. There are two hemicelluloses in both hardwoods and softwoods and although they show some similarity, hemicelluloses in hardwoods are different from those in softwoods. Generally, hardwoods contain slightly more than 30% hemicelluloses and softwoods slightly less than 30%, calculated on an extractive-free basis. Hardwoods

average 2%-3% more hemicelluloses than softwoods. One hemicellulose contains xylose and the other contains mannose; with the rare exception of a few extractive glycosides, the hemicelluloses are the only place where these sugars occur in wood. The xylose containing hemicellulose is commonly referred to as xylan and is somewhat erroneously referred to as the pentosan content of wood. There is no mannan as such present in wood, and the mannose containing hemicelluloses are actually glucomannans.

In hardwoods the dominant hemicellulose is xylan, which accounts for 20%-30% of the total cell wall; birch is an exception and has up to 40% xylan. Hardwood xylan competes with lignin for being the second most plentiful cell wall constituent after cellulose. Hardwood xylan is the only hemicellulose directly isolated from wood without prior delignification as the deacetylated material by a strong caustic solution.

The structural features of hardwood xylan include a backbone of $\beta(1-4)$ -linked xylose units having a DP of about 200 and apparent slight branching. There are two types of side-groups. There is one 4-O-methylglucuronic acid side-group linked $\alpha(1-2)$ to the xylose backbone for approximately every ten xylose backbone units. This means an α -glycosidic bond from the uronic acid to the 2 carbon of the xylose unit. There are also seven acetyl groups for every ten xylose backbone units bonded through an ester linkage to the 2 and 3 carbon positions of the xylose. The "shorthand" formula could be written as follows:



The hardwood xylan hemicellulose is the most easily isolated of all hemicelluloses. It is also the most quantitatively isolated of all hemicelluloses, with exhaustive alkaline extraction of hardwood holocellulose yielding up to 90% of that originally available. Dimethyl sulfoxide (DMSO) extraction of holocellulose will yield up to a maximum of 50% of the available acetylated hemicellulose, which is water soluble when isolated. As indicated, this hemicellulose is readily soluble in alkali because the uronic acid forms a soluble salt. KOH solutions seem more effective than NaOH solutions, and the deacetylated material is not readily water soluble.

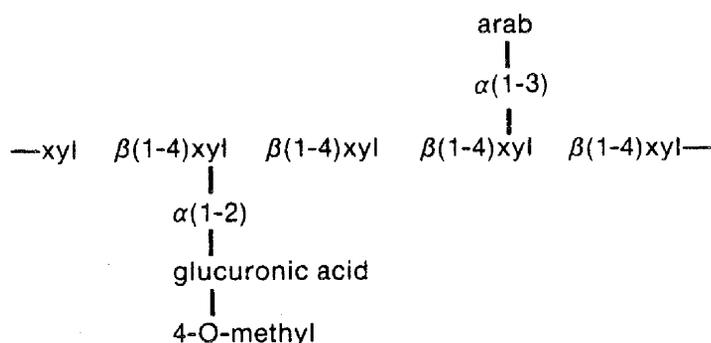
A simple glucomannan is the other hardwood hemicellulose; it is present in only 3%-5% of the total extractive-free wood. The linear polymer of $\beta(1-4)$ linked glucose and mannose units has no side-groups, no branching, and a DP of approximately 100. The typical ratio of glucose to mannose is 1 to 1.5-2.0; birch is an exception because it has slightly more glucose units in the backbone. There is an apparent random arrangement of glucose and mannose units with no repeating pattern in the backbone. The "shorthand" formula would be:



Hardwood glucomannan is the most difficult hemicellulose to isolate and the least abundant of all hemicelluloses. It can be dissolved with difficulty in strong alkaline solutions, and boric acid must be added to obtain an adequate yield through formation of

a soluble complex—actually a borate ester. Because of solubility difficulties hardwood α -cellulose retains one-half to one-third of the original glucomannan present.

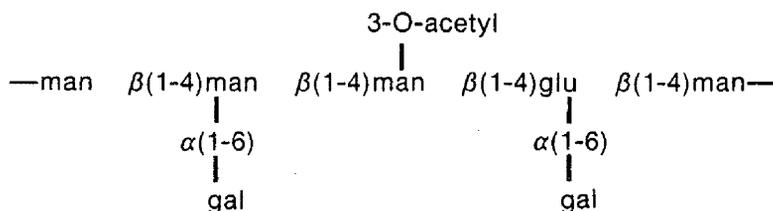
The xylan in softwoods is the minor hemicellulose present in the wood, although it appears in appreciable quantities of 8%-14% in the extractive-free wood. The backbone of the polymer is identical with that of hardwood xylan having β (1-4)-linked xylose units, a DP of about 200, and slight branching. As in hardwood xylan, there are two types of side-groups present. Identical to hardwood xylan there are 4-O-methylglucuronic acid groups with α (1-2) linkage to the xylose in the backbone, only there are two uronic acids for every ten xylose units. The other side-group is arabinose with α (1-3) linkage to the xylose in the backbone. The arabinose units are extremely acid labile and can be removed under mild acid conditions in which the xylose chain remains intact. In situ there are probably 1.5 arabinose for every 10 xylose. The "shorthand" formula for softwood xylan would be:



As with hardwood xylan, this hemicellulose is easily isolated from holocellulose using alkali, especially KOH solutions, because the uronic acids present will form soluble salts. The arabinose content of isolated material is highly variable, especially if the holocellulose is prepared by the acid-chlorite method.

Softwood glucomannan is the major hemicellulose present in wood, accounting for 16%-22% of the cell wall. The only similarity it has with hardwood glucomannan is that the DP is about 100, and it has glucose and mannose units in the backbone with β (1-4) linkage and an apparent random arrangement of the units. The differences are that softwood glucomannan has two types of side-groups and more mannose in the backbone. In the backbone the ratio of glucose to mannose is 1 to 3-3.5. Acetyls comprise one of the side-groups, and one acetyl is present for every four backbone sugar units, ester linked to the 2-carbon position and the 3-carbon position of the sugar.

The other side-group is galactose with α (1-6) linkage to the backbone units; consequently this hemicellulose is actually a galactoglucomannan. The amount of galactose present is highly variable; evidently softwoods contain a whole family of related galactoglucomannans that differ mainly in their galactose content. No softwood glucomannans have been isolated that are completely devoid of galactose. In the other extreme some have been isolated with almost two galactose units per glucose, but there is always the possibility that some compression galactan may also be present. Softwood (galacto) glucomannans are often divided into two groups based on solubility of the alkaline-extracted (deacetylated) polymers. A water-insoluble but alkaline-soluble component, commonly called glucomannan, contains only 2%-5% galactose, or approximately one galactose unit for every 40 backbone units, and accounts for about two-thirds of the total hemicellulose. The water soluble component, commonly called galactoglucomannan, contains about 5 to 10 times as much galactose and accounts for the remaining one-third. The "shorthand" formula for softwood (galacto) glucomannan would be:



The acetylated softwood glucomannan is much more difficult to isolate and purify than the acetylated hardwood xylan. The galactose side-groups are easily removed by acid hydrolysis but are not as sensitive as the arabinose in softwood xylan.

In reaction wood the structure of the normal wood hemicelluloses is not changed, but the amount present is changed drastically. Reaction wood contains an additional, new hemicellulose, a galactan, which is different in hardwoods and softwoods. In softwoods the reaction wood is known as compression wood, and the galactan as compression galactan. It is a linear polymer of $\beta(1-4)$ -linked galactose units with a DP of 300-400; the amount present in reaction wood is variable, sometimes as high as 8%-16% of the total cell wall. The tension galactan found in hardwood reaction wood is not as well characterized but is probably a polymer with a $\beta(1-4)$ -linked galactose backbone containing $\beta(1-6)$ -linked galactose side-groups. The amount of galactan in tension wood is not as great as compression galactan in the softwoods, and apparently some species have none since they form no tension wood.

The information presented on hemicellulose structure is also presented in Table 2-2 in a more simplified form. Some general comments are also appropriate here. The most prevalent hemicellulose in both hardwoods and softwoods is acetylated. The acetyl content of hardwoods is higher—3%-5%, compared to softwoods at 1%-2%—because hardwood xylan has 2.5 times the acetyl content of softwood glucomannan. This is one reason for hardwoods being preferred for destructive distillation: the yield of wood vinegar is higher. The uronic acid content of wood is relatively constant at 3%-5%, with some due to pectin. However, the xylan of softwoods contains twice the number of uronic acid side-groups as does the xylan of hardwoods, but the amount of softwood xylan present is roughly half that of hardwood xylan. The $\alpha(1-2)$ linkage between the uronic acid and the xylose in the backbone is the most resistant glycosidic linkage to acid hydrolysis. Although DP is probably somewhat species dependent, in general the xylans of both hardwoods and softwoods have twice the DP of the respective glucomannans. The amount of the various side-group units is apparently also species dependent and the values given are averages. Also, both DP values and side-group amounts are affected by the isolation and purification procedure used to obtain the hemicelluloses. The neutral sugar side groups of the two softwood hemicelluloses are easily removed by acid hydrolysis.

Table 2-2. Summarizing Data for Wood Hemicelluloses

Hemicellulose	Amount	Sugar Unit	Ratio of Parts	Linkages	
Hardwood xylan	20%-30% DP 200	xylose (backbone)	10	β (1-4)	
		4-O-methyl-glucuronic acid	1	α (1-2)	
		O-acetyl	7	C ₂ & C ₃	
Hardwood glucomannan	3%-5% DP 100	glucose (backbone)	1	β (1-4)	
		mannose (backbone)	1.5-2.0	β (1-4)	
Softwood xylan	8%-14% DP 200	xylose (backbone)	10	β (1-4)	
		4-O-methyl-glucuronic acid	2	α (1-2)	
		arabinose	1.5	α (1-3)	
Softwood glucomannan	16%-22% DP 100	glucose (backbone)	1	β (1-4)	
		mannose (backbone)	3-3.5	β (1-4)	
		galactose (low)	0.1-0.2	1	α (1-6)
		O-acetyl	1	C ₂ & C ₃	

Often the pentosan content of wood is assumed to represent the xylan content of the wood. In wood analysis any substance which yields or analyzes as furfural is reported as pentosan. The acetyl side-groups of hardwood xylan are not involved, and only about one-third of the uronic acids are involved after decarboxylation. Pectin gives a positive value under pentosan analysis conditions. Primarily as a result of compensating errors, the pentosan content of wood probably gives the xylose sugar content within a few percent.

2.2.5 Lignin

The noncarbohydrate constituent of the cell wall is lignin, a polymer whose monomeric unit has a phenylpropane nine-carbon skeletal structure. A recent definition based on formation describes lignin as a three-dimensional polymer whose basic structure is the result of free-radical polymerization of p-hydroxy cinnamyl alcohol units with varying methoxyl content. Older definitions of lignin based on chemical behavior give some insight regarding reactivity and possible utilization.

Lignin condenses in acid, especially in strong mineral acids, whereas the carbohydrate fraction of wood is hydrolyzed into soluble sugars. The acid-insoluble lignin residue is more condensed than the original lignin; i.e., it has an increase in carbon-carbon bonding among the monomeric units, which is highly undesirable for most uses. Lignin is soluble in hot alkali and bisulfite-sulfite solutions, which is the basis for delignification in chemical pulping. Lignin is not as oxygenated as the carbohydrate portion of wood, giving it a higher fuel value. Lignin, however, is the readily oxidized component of wood, and this property is utilized in holocellulose preparations and in pulp bleaching.

The three monomers that polymerize in varying proportions to produce a lignin macromolecule are p-coumaryl alcohol, containing no methoxyls; coniferyl alcohol, containing one methoxyl; and sinapyl alcohol, containing two methoxyls. Because the polymerization is of the free-radical type, the eventual lignin polymer formed is not the result of enzymatic control. The properties of lignin are determined instead by the proportion of the different monomers involved, which is genetically controlled. Because the polymerization is free radical, the bonding among the various monomeric units is not of one type that is repeated, as would be the case where enzymatic control is involved. This situation has caused most of the difficulties in completely characterizing the lignin macromolecule. In addition, it appears that most lignin, with the possible exception of softwood lignin, also has varying amounts of related acids, specifically ferulic, p-coumaric, and p-hydroxy benzoic acid, esterified to the macromolecular core.

Softwoods have between 24%-33% lignin (the average is 28%) and seem to have only one type of lignin with no difference among species and even families. The lignin is 80% coniferyl alcohol derived units, with the remainder containing twice as many p-coumaryl as sinapyl derived units. As a consequence the lignin contains slightly less than one methoxyl for each phenyl propane (C_9) unit. Softwood lignin is also referred to as guaiacyl lignin, indicating that the aromatic ring has predominantly one methoxyl. Although it is difficult to determine the degree of polymerization (DP), especially in situ, values given indicate a broad range from a low of 3 to 200 or even higher, with an average value around 50-80.

Besides the methoxyl, other functional groups in the monomeric moiety are present on the propyl side-chain. The lignin macromolecule has few free phenolic hydroxyls, perhaps less than 3%, with most involved in ether bonding between monomeric units. In lignin few olefinic bonds remain (6%); aliphatic hydroxyls are dominant with some involved in ether bonding between monomeric units. Lignin also has a few carbonyl groups but no carboxyls. Virtually every aliphatic carbon has some type of oxygenated function if the monomeric moiety has no olefinic bond.

The bonds that join the individual monomeric units are varied because of the nature of free radical polymerization, but certain ones are quite common. Virtually all phenolic hydroxyls are involved in ether linkages, predominantly with the middle carbon on the propyl side-chain of another monomeric unit, but also with the benzyl carbon to some extent and with the terminal carbon to a lesser extent. It is these phenolic (aryl) ether bonds that are disrupted in any delignification, resulting in considerable depolymerization to the extent that solubilized lignin can diffuse through the cell wall structure. Softwood lignin also contains considerable carbon-carbon bonding between monomeric units, and these bonds are essentially inert. Most of this bonding involves either the unoccupied aromatic carbon adjacent to the phenolic group or the benzyl carbon, although others may also be involved.

Compression wood contains up to 40% more lignin than does normal wood, and the composition of the lignin is somewhat different. Compression wood lignin contains more p-coumaryl derived units and consequently a lower methoxyl content, but apparently it has more carbon-carbon bonding between the monomeric units as a result. The lignin in the compound middle lamella is also apparently more highly condensed, but this is probably a result of less interference to polymerization because fewer other cell wall constituents are present.

In contrast to softwood lignins, hardwood lignins vary with the species. There is also less lignin present, ranging usually from 16% to 24% (the average is 22%). Hardwoods contain

considerably more sinapyl derived units, and the difference among the species is primarily due to the ratio of coniferyl to sinapyl derived units. The amount of sinapyl derived units in hardwood lignin can vary from a high of 60% in one species to a low of 25% in another. This difference is reflected in the methoxyl content, which can vary from 17% to 22% depending on the species. Often for simplicity hardwood lignin is considered to be about 50% sinapyl derived and 50% coniferyl derived. There are probably also some p-coumaryl derived units, but, again, for the sake of simplicity they are often ignored. Hardwood lignin is also referred to as syringyl lignin, indicating that the majority of monomeric units are related to the aromatic compound having two methoxyls (which may not be completely correct).

By increasing the sinapyl derived content of lignin, major changes occur in the macromolecular structure. Because both methoxyls are adjacent to the phenolic hydroxyl, they interfere spacially with reactions of this group and result in less ether formation. The second methoxyl on the aromatic ring adjacent to the phenolic hydroxyl also considerably reduces carbon-carbon bonding. The result of these two effects is considerable reduction in DP and much less condensation. This is one reason hardwoods are easier to delignify than softwoods. The other reasons are less initial lignin and less lignin in the secondary wall of hardwoods compared to softwoods. In chemical pulping hardwoods generally retain half the residual lignin of softwoods. Also, the value of hardwoods as a nutrient for ruminant animals varies greatly, whereas softwoods essentially have no nutrient value.

Hardwoods also tend to have related acids esterified to the lignin macromolecular core. An outstanding example is aspen, which has up to 10% p-hydroxy benzoic acid esterified to the lignin core. Therefore, aspen is among the easiest of woods to delignify since removal of the esterified acids opens up the pore structure of the cell wall. Aspen also has considerable value as a nutrient for ruminant animals without pretreatment; that value ranges from 25% to 40%, depending on the source of information.

Hardwoods also exhibit a difference in lignin within the anatomical structure. Vessels are primarily of the guaiacyl type lignin, the fiber compound middle lamella is apparently intermediate guaiacyl-syringyl type lignin, and the fiber secondary wall is primarily syringyl type lignin. It has not been shown that the species differences in amount of sinapyl and coniferyl derived lignin, as indicated by the syringyl and guaiacyl lignins present, is really due to the relative amount of vessels and fibers.

In evaluating lignin as a possible by-product from any chemical utilization process, several problems are evident. In any delignification scheme considerable free phenolic hydroxyls are produced, but substitution on the aromatic ring at positions ortho and para to the free phenolic hydroxyl is not reduced but often increased due to acid or alkaline condensation reactions. This generally is detrimental to any use requiring phenolic directed substitution reactions. Hardwood lignins are less condensed than those of softwoods and should show more potential. A major goal should be to remove methoxyl and carbon bonding on the aromatic ring without introducing a functional group at that position. Because of its relatively high fuel value compared to wood carbohydrates, by-product lignin is perhaps most commonly used to supply energy required for biochemical conversion processes.

2.2.6 Cell Wall Distribution

For chemical utilization, it might simplify matters if the chemical constituents were uniformly distributed throughout the cell wall. Unfortunately this is not the case, and we mentioned earlier that the compound middle lamella is predominantly lignin. However, because of the relative size of the compound middle lamella compared to the secondary wall of fibers, it is not possible for most of the lignin in wood to be present in the compound middle lamella. Most lignin in wood is present in the secondary wall of fibers. Since the compound middle lamella has rather constant dimensions regardless of cell type or whether it is associated with early- or latewood, the percentage of total lignin present in the secondary wall will vary with the thickness of the secondary wall, specifically with the thickness of the S_2 layer. Parenchyma cells, which are quite thin-walled, have about 40% lignin, considerably more than wood as a whole. As might be expected, the thinner earlywood fibers have slightly more lignin and consequently less cellulose than the thicker latewood fibers.

Since the compound middle lamella has essentially constant dimensions, the difference in lignin content between hardwoods and softwoods appears in the secondary wall of fibers. The secondary wall of hardwood fibers is 19% lignin by volume and when averaging early- and latewood accounts for 60% of the total lignin in wood. In softwood, the secondary wall of tracheids (fibers) is 22% lignin by volume, and for the wood as a whole 75% of the total lignin occurs in the secondary wall. In a cross-sectional view of the cell wall, the contribution of lignin to the total substance available varies continuously. The true middle lamella is essentially pure lignin. The primary wall apparently has more lignin than any other chemical constituents, but the amount present is considerably reduced from the outer primary wall, adjacent to the true middle lamella, toward the inner primary wall, adjacent to the S_1 layer. In the secondary wall there is a more gradual reduction in lignin contribution in the S_1 layer, with a minimum contribution in the S_2 layer and possibly a sharp increase in the S_3 layer at the lumen. The sharp increase in relative lignin amount in the S_3 layer may be due either to the presence of the warty layer or extractives at the lumen surface.

The contribution of cellulose to the total substance in the cell wall shows a pattern directly opposite that of lignin. Cellulose contributes the most to the cell wall in the S_2 layer, where it is about 50% of the total substance. Also in this cell wall layer cellulose has the highest DP and probably the highest degree of crystallinity. In contrast to lignin, latewood has slightly more cellulose than earlywood because of the greater size of the S_2 layer in latewood. In softwoods the glucomannans appear to follow the pattern set by cellulose, and the xylan follows that of lignin in the secondary wall. In hardwoods the xylan appears to follow the pattern established for cellulose. Note that the major acetylated hemicellulose appears to be associated with cellulose. In softwoods it has been suggested that the glucomannans form a sheath surrounding the cellulose microfibril, but there is no evidence to substantiate this assumption. In hardwoods there would not be sufficient glucomannan to sheath the cellulose microfibrils.

In reaction wood the distribution of the chemical constituents in the cell wall is modified. Compression wood seems to have a heavily lignified layer between the S_1 and S_2 layers of the secondary wall. In tension wood an almost pure cellulose layer, the gelatinous or G layer, exists between the secondary wall and the cell lumen. These locations apparently contain the "extra" lignin and cellulose in compression wood and tension wood, respectively.

The degree of association between lignin and wood carbohydrates, especially the hemicelluloses, has been the subject of much conjecture over the years and has recently received renewed interest. Most researchers believe that there is covalent bonding between the lignin and the hemicelluloses, and there is plenty of indirect evidence that this may be the case. The possible types of lignin-carbohydrate bonding are numerous, but almost all of them have some drawbacks. From studies of lignin biosynthesis with free radical polymerization, it appears that ether linkages between carbohydrate hydroxyls and lignin should be established. Because of the stability of many ether bonds, selected degradation reactions should yield a low-molecular-weight lignin fragment, such as a monomer or dimer, with a hemicellulosic-derived sugar unit. This has not been accomplished unequivocally. Even the stability of a lignin-carbohydrate bond is open to disagreement, with some researchers insisting that it must be labile under both acidic and alkaline conditions. The possibility of no covalent bonding but instead only H-bonding between the oxygenated functions of lignin, especially the aliphatic hydroxyls, and the carbohydrate hydroxyls has not been completely eliminated.

2.2.7 Agricultural Residues

Members of the grass family, including most agricultural residues, generally are more similar to the hardwoods than softwoods, but there are notable differences. Grasses exhibit as much variation among species as hardwoods do. Grasses have a much higher ash content than wood, which is often due to a large extent to silica in the outer epidermal cells. For most straws ash will vary from 2% to 10% by weight, but for cornstalks it is only 1%-2%. Because much of the ash, especially silica, is highly insoluble, it tends to be present in lignin during lignin analysis and also in the holocellulose and α -cellulose fractions.

When α -cellulose is corrected for ash and pentosans, the true cellulose content is generally 36%-37%. However, the actual value is likely to be higher since some cellulose from the thin walled parenchyma cells will end up in the fines and pass through the filter during analysis. A more comprehensive analysis gave a cellulose content of about 42% for cornstalks and wheat straw.

The hemicellulose fraction from grasses yields no mannose upon hydrolysis and is apparently composed of xylans, which may be separated into an acidic (containing uronic acids) and a more neutral xylan component in some grasses. In straws the pentosan content is about 25%-29%, and the uronic acid and acetyl contents are 1% and 2%, respectively. This gives a total hemicellulose content of straws similar to that of wood. Cornstalks have about the same pentosan value as straws but considerably higher uronic acid and acetyl values (about 5% each). Three types of side-groups may exist in xylan, all of which may not occur together on individual xylan molecules. Grasses may have both 4-O-methyl and nonmethylated glucuronic acid side-groups attached with α (1-2) linkage to the xylose backbone as in wood. Also, grasses have acetyl side-groups as in hardwood xylan and arabinose side-groups as in softwood xylan.

The lignin content of most grasses is only 15%-18% when corrected for ash. The lignin figures are probably low because of some solubility and therefore loss of material during lignin analysis. When appropriate corrections are made for soluble lignin, values comparable to that of hardwood lignin content are obtained. The lignin of grasses is generally similar to that of hardwoods except that more related acids, particularly 3%-12% p-coumaric acid, and 1%-3% ferulic acid, are esterified to the lignin macromolecular core. This accounts for the greater fraction of soluble lignin. The total lignin amount in

cornstalks is exceptionally low at 14%. The lignin analysis of grasses, especially when herbaceous, can be considerably in error, even when soluble lignin and ash content are taken into account. Proteinaceous material and residual waxes, specifically cutin, can interfere with the analysis and give high values. Often lignin in grasses is determined by difference after neutral permanganate oxidation.

A considerable portion of most grasses (12%-13%) is soluble in hot water, mainly hemicelluloses and some lignin. It is apparent that the cell wall structure is more open (i.e., it has a larger exclusion limit), in grasses than in wood; consequently the individual cell wall constituents are more accessible. For this reason grasses can serve as a nutrient for ruminant animals, but wood only serves as roughage, with the notable exception of aspen, which has some nutrient value. Both aspen and grasses have appreciable acids esterified to a lignin macromolecular core. A comparison to the cell wall constituents for various biomass is shown in Table 2-3.

2.3 INFLUENCES OF BIOMASS ON CHEMICAL UTILIZATION

Biomass slated for conversion to chemicals and energy should be grouped into three categories: hardwoods, softwoods, and grasses or agricultural residues. A case will be presented for considering hardwoods as the preeminent raw material for most bioconversion to chemicals and energy. However, we do not imply that residues from agriculture and softwood utilization should be ignored, especially when they are readily available in quantity because of another utilization activity.

Softwoods have considerable value as construction lumber and pulpwood; thus use of this raw material for biomass conversion probably is not economically feasible. Conversion processes that use logging and manufacturing residues should be designed to take the following factors into account. Branches and tops constitute most of the logging residues. Because of the higher density of branch wood, liquor diffusion into the cell wall may present a problem. The probable presence of compression wood in branches also is a problem. The higher and more condensed lignin content of compression wood together with a thicker cell wall makes any adequate delignification difficult. Compression wood has a lower total carbohydrate content (especially cellulose), making it less desirable as a raw material. The tops of trees have many branches and may have considerable juvenile wood in the main stem. Because juvenile wood has a low density and thin cell walls, it would be overreacted before the branch wood could be adequately treated. In utilizing precommercial thinnings, the large amount of juvenile wood, with its low density, would have an undesirable effect on digester capacity. Logging residues probably are best used as a fuel source.

The primary manufacturing residues are debarking residues, sawdust, and sanderdust. Bark, especially from thick-barked softwood species, is not readily adaptable to nor desirable for wood carbohydrate utilization. However, it should be noted that the need for suitable uses of bark is great and its utilization will probably be of a chemical nature when it is developed. In certain regions, much more sawdust is produced than can be consumed in the pulping industry; often sanderdust is also available. The primary impediment to their use is the type of lignin present in softwoods. Not only is delignification more difficult than with hardwoods, but opening the cell wall structure and providing access to the cellulose is more difficult. On the average, softwoods have less total carbohydrates and slightly less cellulose than the hardwoods. The hemicellulose fraction is also more complex, with less pentosans available for possible conversion to furfural.

Table 2-3. Cell Wall Constituents of Biomass (%)

Normal Wood	Softwoods	Hardwoods	Grasses	Comments
Cellulose	41-43	43-45	35-39 ^a	^a May be higher
Lignin (average)	28	22 ^b	16 ^b	^b Some soluble lignin
range	24-33	16-24	15-18	
Xylan	8-14	20-30	27-34	
(Pentosans)	(5-10)	(12-24)	(25-29)	
Glucomannan	16-22 ^c	3-5	None	^c Contains variable galactose amounts

Reaction Wood	Compression (Softwood)	Tension (Hardwood)	Comments
Cellulose	32	56 ^d	^d Excess in G layer
Lignin	40	14	
Xylan	variable	low	
Glucomannan	low	low	
Galactan ^e	8-16	0-8	^e New hemicellulose

The principal problem with agricultural residues is that the quantity available is only a small fraction of that available from hardwoods. Also harvesting of agricultural residues usually takes place within a short time span once a year. Storage space must be provided for an annual supply. Agricultural residues are quite susceptible to microbiological degradation, particularly when wet, which can destroy their bioconversion potential in a matter of days. Most agricultural residues are best stored under shelter, thereby adding to the cost and complexity of storage. Agricultural residues tend to be bulky because of their low density, thus complicating transportation, handling, and storage, and generally resulting in higher costs than for the same operation using wood. Digester capacity is greatly reduced and the liquor-to-residue ratio substantially increased due to low bulk density. In the actual processing, the high silica content of most agricultural residues may cause substantial abrasion and may necessitate more frequent changing of cutting edges and operating down time due to equipment problems.

Agricultural residues have an advantage resulting from their chemical composition. Because of the amount and nature of the lignin present, grasses are easily delignified and the carbohydrates are made readily accessible. Since the hemicellulosic fraction is closely related to xylans with no glucomannans present, this also simplifies chemical conversion. Xylans are much more susceptible to acid hydrolysis and alkaline extraction than cellulose and can be readily removed if necessary. The technology is available for converting xylans to furfural, an industrial chemical used in adhesives and resins and as a plasticizer. Corn stover (cornstalks) is unique and occupies a similar position among agricultural residues as aspen does among the hardwoods. It has a lignin content of only 14% rich in esterified acid groups, and has a xylan rich in both acetyl and uronic acids. Very mild treatment will make the cellulose accessible. The availability of cornstalks for bioconversion, however, is limited because of their competing use as silage.

Hardwoods should be considered the primary raw material for bioconversion because of their availability and desirable properties. Although some hardwoods are valuable and

much in demand, many are considered a silvicultural problem because of their abundance and low utilization potential. Often the trees are of small diameter and without a usable trunk, with the result that the trees are usually chained down to make space available for plantations, usually softwood plantations.

The advantages of using hardwood material for bioconversion include the high density of many species; relative ease of delignification and accessibility of the wood carbohydrates; and practically only one hemicellulose, xylan, which can be easily removed. Also, reaction wood in hardwoods has additional cellulose that is readily available, and tension wood lignin does not present problems in delignification. Other advantages include low ash content, particularly silica, and slightly higher total carbohydrate and cellulose content. Also, the possibility of by-product utilization is great, especially when compared to softwoods. Hardwoods have a higher acetyl content than softwoods and most grasses and would yield more acetic acid. Xylan conversion to furfural would produce a product with a potential market (Parker et al. 1983). The small amount of glucomannan hemicellulose could probably be converted together with cellulose, especially if fermentation is considered.

Lignin utilization still presents the greatest challenge. Most prior lignin research aimed at utilization involved softwood lignin, but hardwood lignin may have some advantages. Hardwood lignin is less condensed, meaning it has a lower DP and less carbon-carbon bonding. Hardwood lignin also has less tendency to condense under acid or alkaline conditions. Hardwood lignin has a greater methoxyl content, which in destructive distillation of wood resulted in more methyl alcohol (wood alcohol), thereby making hardwoods preferred over softwoods. It may be possible to obtain methyl alcohol from hardwood lignin without pyrolysis. Hardwood lignin becomes plastic at a lower temperature than softwood lignin, which is the basis for using hardwoods in wood bending. Perhaps this property could also be exploited. The immediate use for lignin produced by bioconversion would be as a fuel because it has a much higher energy value than wood. This by-product lignin should be evaluated for use as a raw material for synthesis gas formation. For higher quality utilization of lignin, some chemical modification, e.g., removal of aromatic ring substitution groups, such as methoxyls, without introducing another functional group would probably be necessary. Potential markets for lignin utilization have been reviewed by Chum et al. (1985).

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SECTION 3.0

PRETREATMENT OPTIONS

3.1 INTRODUCTION

In this section a few biomass pretreatment options are examined. Process designs and economic summaries are presented where enough data were available to justify their preparation. In some cases, only a preliminary flowsheet has been developed, because the pretreatment was tested only on a small scale. Further, there is no supporting data on auxiliary operations, such as product separation and purification or recycling of solvents and liquors.

The pretreatments for which a detailed process design was developed are organosolv, wet oxidation, and steam explosion. The base case organosolv evaluation was prepared by TRW (Anastasi and Motley 1982). The wet original oxidation evaluation was also performed by TRW (Anastasi and Motley 1981). All other analyses were performed by SERI researchers based on the referenced reports and studies.

The process and economic evaluations were based on a consistent set of assumptions. All costs are based on third quarter 1982 dollars and are inflated according to the Marshall and Swift equipment cost index. (The Marshall & Swift index rose 4.3% between the third quarter of 1982 and that of 1984, which is a small increase compared to the $\pm 30\%$ accuracy of the estimates.) The total equipment cost for each process is multiplied by 2.7 to yield the installed cost for the portion of the plant inside battery limits (ISBL). This factor covers installation, piping, engineering, construction overhead, contingencies, contractors' fees, and special charges. The cost of equipment outside battery limits (OSBL) or off site is estimated at 30% of ISBL costs and includes capital for the boiler (plus the fuel storage and handling system), steam and water distribution, buildings, site development, utilities, and pollution control. The total represents the total fixed investment (TFI) allocated to pretreatment as part of a cellulose-to-ethanol plant. Working capital requirements are specified as four months' production costs less depreciation.

The cost of production for each process was determined from the total annual requirements for raw materials and utilities as calculated from the process material and energy balances. Also included are annual estimates for operation, maintenance, and overhead. The production cost, expressed in cents per pound of cellulose produced, represents the total cost of the cellulose. The dollars per gallon figure represents the contribution of raw materials handling and pretreatment to the ethanol production cost in an integrated cellulose-to-ethanol plant. Based on a present worth calculation, a discounted cash flow selling price is determined for the cellulose product. This price (and the associated contribution to ethanol price) includes depreciation, property taxes, insurance, interest paid on capital investment, and return on investment. Financial assumptions are presented in Table 3-1. A parametric analysis was performed for the processes mentioned above. All processes were examined for their responses to variations in the wood feedstock or steam costs, which constitute the largest components of production cost in all cases. Other parameters not applicable to all processes are discussed more fully in the following sections.

Table 3-1. Financial Assumptions

Base year for constant \$	1982
Year for investment outlay	1985
Year for cost information	1982
Year of first commercial operation	1987
Book life	10 years
Tax life for depreciation	10 years
Taxes and insurance, fraction of capital investment	15%
Income tax rate	50%
Investment tax credit	10%
Debt/total capitalization	1
Common stock/total capitalization	0
Preferred stock/total capitalization	0
Rate of return on debt (before taxes)	30%
Rate of return on common stock	0
Rate of return on preferred stock	0
General inflation	0
Capital cost escalation rate	0
Operation and maintenance escalation rate	0

3.2 ORGANOSOLV

Delignification of lignocellulosic materials has been known to occur in a large number of organic or aqueous-organic solvent systems with or without added catalysts at temperatures of 150°-200°C. The review by Sarkanen (1980) contains a comprehensive overview of the literature and should be consulted. Among the solvents tested, those with low boiling points (methanol and ethanol) have been used as well as a variety of alcohols with higher boiling points (ethylene glycol, tetrahydrofurfuryl alcohol) and other classes of organic compounds (e.g., dimethylsulfoxide, ethers, and phenols). Examples of the acid catalysts employed are mineral acids (approximately 0.05% hydrochloric acid or 0.2% sulfuric acid) and organic acids such as oxalic, salicylic, and acetylsalicylic. Acid salts such as sodium hydrogen sulfate or sulfite as well as sulfur dioxide have been employed. In addition, aluminum salts (chloride and sulfate) have been tested as catalysts. The addition of the acid catalysts permits the use of lower hydrolysis temperatures relative to the uncatalyzed systems. The use of base catalyzed systems with ammonia, ammonium sulfide, or ethanol amine leads to a high degree of selectivity in the delignification reactions but involves the use of large quantities of base. Therefore, a costly base recovery scheme is necessary.

The delignification is accompanied by solvolysis and dissolution of the lignin and hemicellulosic fractions depending on the process conditions (solvent system, temperature, type of wood, reactor design [batch versus continuous process]) as well as by solvolysis of the cellulosic fraction (to a smaller extent). Optimal conditions must be found for each type of wood, with hardwoods and agricultural residues being pulped much more easily than softwoods. The end products from the delignification are the following:

- Cellulosic fibers, which contain the original cellulose component and varying amounts of hemicellulose and residual lignin.

- Solid lignin, obtained after the removal of the volatile solvent from the organosolv liquor by distillation. It may contain lipophilic extractives from the original lignocellulosic feedstock.
- An aqueous solution of the hemicellulose sugars, which consists mainly of xylose in the case of hardwoods or agricultural residues. This solution is the filtrate of the previous solvent-evaporated liquor in which the lignin fraction was precipitated.

The main chemical processes associated with the organosolv processes are as follows:

- Hydrolyses of the internal bonds in lignins (mainly α -O-4 ether linkages and to a much smaller extent β -O-4 ether bonds) as well as lignin-hemicellulose bonds (ether and 4-O-methylglucuronic acid ester bonds to the α -carbons of the lignin units [Erikson and Lindgren 1977])
- Hydrolysis of the glycosidic bonds in hemicelluloses and to a smaller extent in cellulose depending on the process conditions
- Acid-catalyzed degradation of the monosaccharides into furfural and 5-hydroxymethyl furfural followed by condensation reactions between lignin and these reactive aldehydes.

More detailed account of the reactions during this process can be found in the reviews by Sarkanen (1980 and 1982).

Many variables have been investigated by Sarkanen et al. under subcontract to SERI: solvent system (proportion of organic solvent to water), amount and type of catalyst, temperature, and type of lignocellulosic material in batch reactions. Hardwoods were the major feedstocks investigated; cottonwoods (Populus trichocarpa) and specific selected poplar hybrids (P. trichocarpa and P. deltoides) were compared in order to assess the potential of genetic upgrading of the raw material for ease of delignification and high cellulose yields (Sarkanen 1983). The use of methanol/water solvent allows the delignification reaction to occur at lower temperatures than the corresponding ethanol/water system, probably because of the higher solubility of low-molecular-weight lignins in the methanol/water solvent. A systematic investigation was performed on methanol and catalyst concentrations in the delignification of black cottonwood in a batch reactor at 170°C for 1 hour. Increasing the catalyst concentration fivefold (from 0.01 to 0.05 M sulfuric acid) decreased the degree of polymerization (DP) of the resulting cellulose from 1000-1400 to 150-200. Further increase in catalyst concentration did not have a positive effect. At the same time, the hemicellulosic components were nearly completely hydrolyzed at the higher acid concentrations. It was shown that it is possible to lower the concentration of methanol from 70% to 30% by volume without impairing the separation of individual fibers. However, at the lower methanol concentrations, increased concentrations of residual lignins remain in the cellulosic fibers (from 0.3% to 14% when methanol is reduced from 70% to 30%). Lower degrees of polymerization of the cellulosic fraction should lead to a material much more susceptible to enzymatic hydrolysis, comparable to material produced in steam explosion treatments. Whether the organic solvent concentration can be lowered to 30% methanol v/v and produce a cellulose susceptible of hydrolysis by enzymes remains to be determined. Enzymatic hydrolyzability of cellulosic substrates produced with catalysts such as NaHSO₄, H₂SO₄, and H₃PO₄ have been achieved (Baker et al. forthcoming).

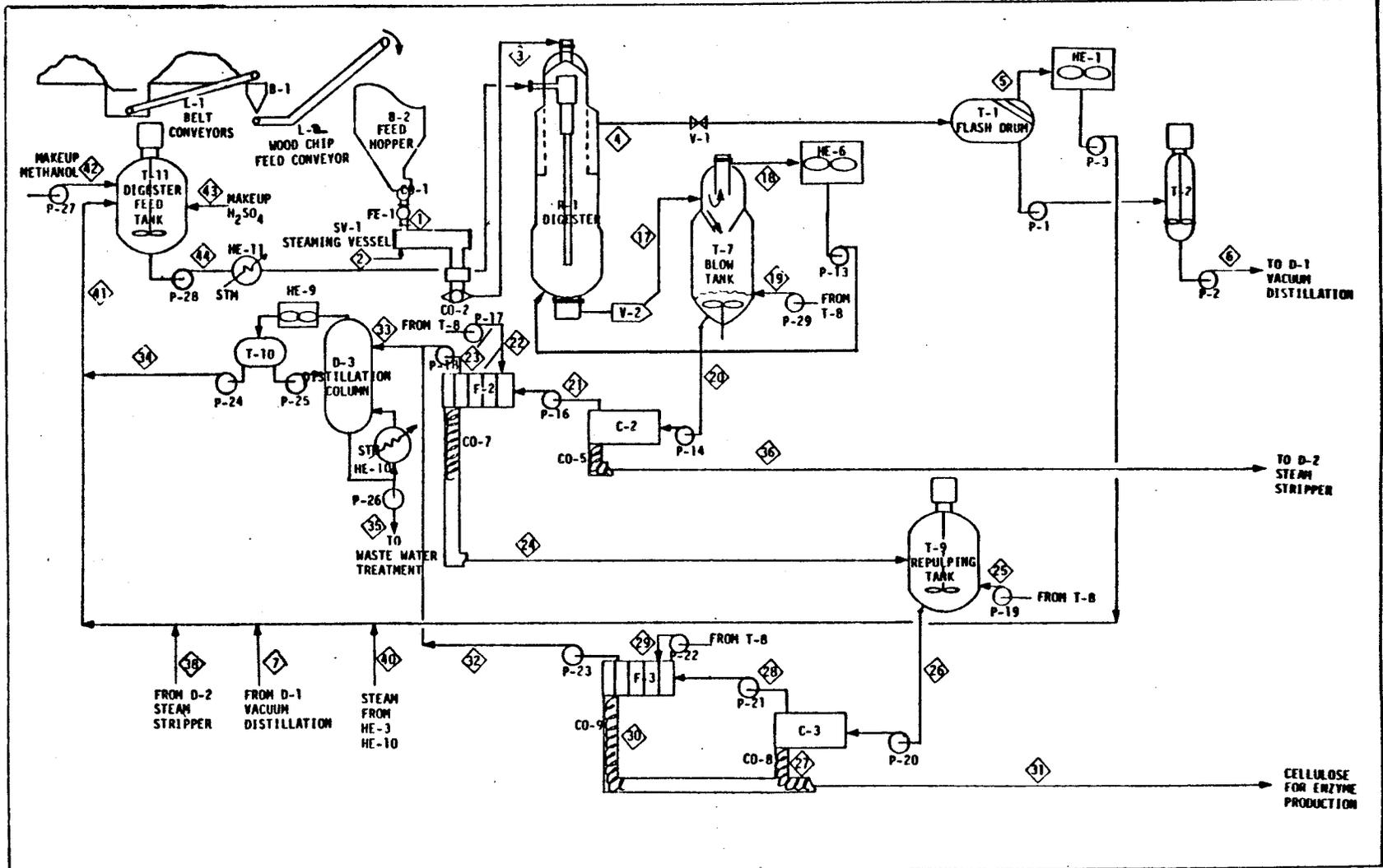
A very important recent development was the confirmation of Kleinert's (1967) findings that organosolv delignification of aspen wood is three times faster in a flow-through reactor than in a batch system. McCarthy and Pla (1983) repeated kinetic experiments of Sarkanen et al. using a flow-through reactor and found delignification rates higher by a factor of 4 in the continuous system compared to the data obtained in the batch reactor. The flow-through reactor is described by Dolk et al. (1983), who also present data on the delignification of western hemlock. These results indicate that in the batch reactor the lignin released in solution undergoes additional reactions that allow part of the lignin to reabsorb on the cellulosic fibers. In the flow-through reactor the shorter residence times decrease these side reactions. The reabsorption in the batch process causes an apparent lowering of the rate of delignification.

3.2.1 Process Description

The complete acid-catalyzed organosolv process is shown in Figures 3-1 and 3-2. Debarked wood chips are steamed for 15 min to remove entrained air and to swell the fibers, then they are transferred by a screw feeder to the digesters. Operated at 200 psia (1.38 MPa) and 284°F (140°C), the digesters are similar to those used in the paper industry, where the organosolv process was originally developed. In the base case the cooking liquor consists of 70 wt % methanol in water with a 0.01 M sulfuric acid catalyst; the liquor-to-wood ratio in the digester is 4:1. Design is based on an annual capacity of 660 million lb (3×10^5 metric tons*) of cellulose, or 38×10^6 gal (1.1×10^5 mt) of ethanol with an assumed conversion of 80% in the hydrolysis step and 95% in the fermentation step. Four digesters, 15 ft (4.5 m) in diameter by 64 ft (19.5 m) high, are required to process 174 tph (158 mt/h) of wood chips (50% moisture) and 230,000 gph (6×10^4 L/h) of cooking liquor. After the 60-min digestion the pulp is fractionated to recover products and solvent. Ninety-eight percent of the methanol is recovered, primarily by vacuum distillation (at 380 mm Hg or 50.7 kPa) of the digester liquid. The cellulose product (35 wt %) is recovered from the pulp by centrifugation followed by steam stripping. The small amount of cellulose in the supernatant is concentrated to 40% and used to culture the cellulase enzyme for the later hydrolysis. Lignin and hemicellulose are removed in the bottoms product of the vacuum still and isolated by centrifugation and filtration.

Several modifications to the original TWR design were required. These fall into two categories: process modifications and equipment modifications. The first process modification involves recycling of solvent-rich liquor (stream 18) to the bottom of the digester. From this point it contacts the feed countercurrently, thus improving the efficiency of delignification. The second process modification, by-product utilization, will be considered for all the processes examined. The by-product lignin and hemicellulose (and in the case of steam explosion, furfural as well) can either be burned to produce process steam, or they can be recovered at greater capital and operating expense. If the latter option is chosen, the by-products must be sufficiently dry and pure to have commercial value. The level of purity is taken as 99% solids for the lignin and 50% solids for the hemicellulose product. Combustion must be preceded by an evaporation step to raise the solids content to 55%. Stream 6 on Figure 3-2 would be taken to an evaporator, and the resulting solids would be combustible.

*Abbreviated as mt throughout this report.



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Figure 3-1. Organosolv Delignification Pretreatment Process Flow Diagram - Part 1

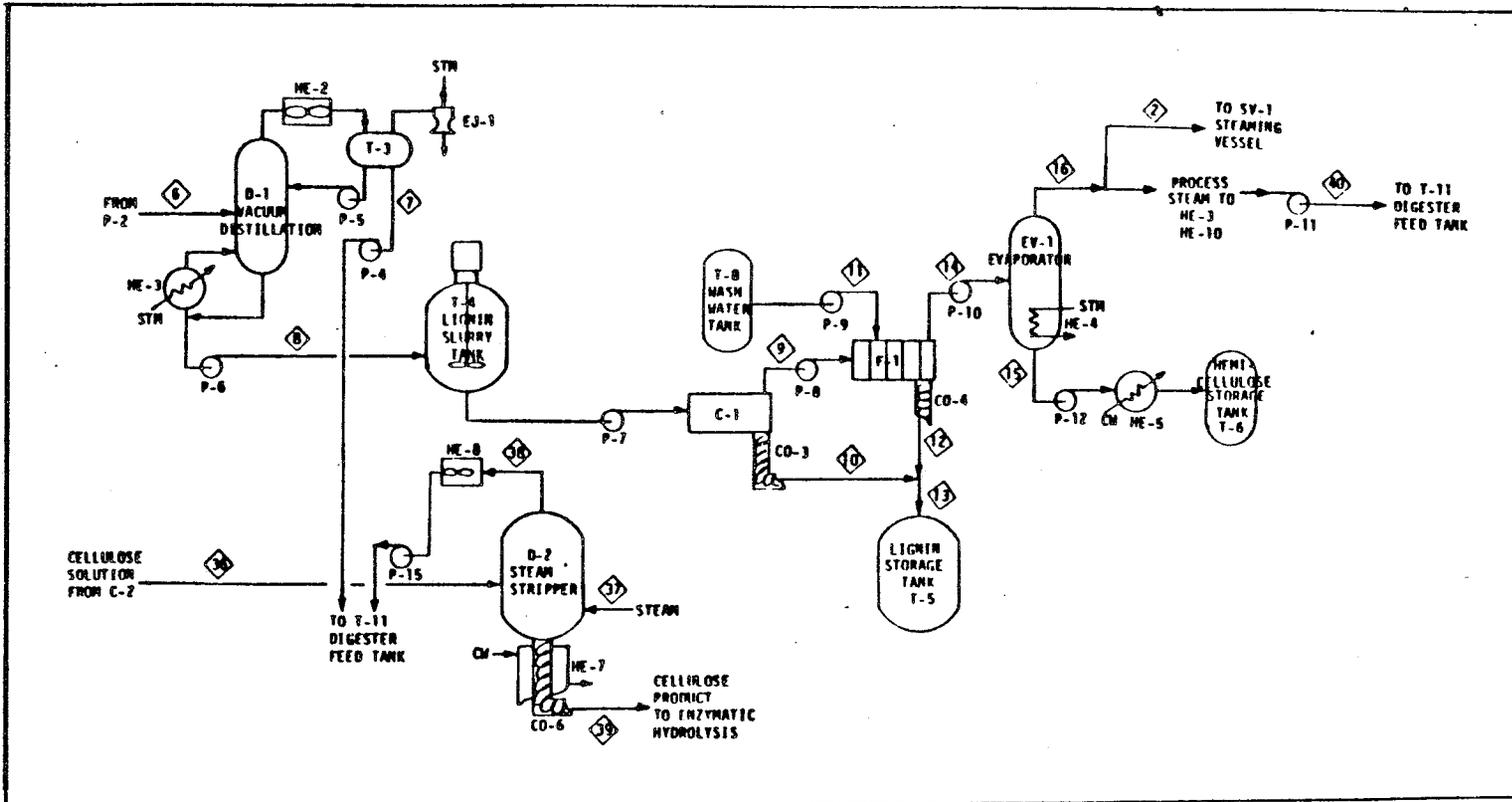


Figure 3-2. Organosolv Delignification Pretreatment Process Flow Diagram - Part 2

Capital and operating costs were affected by replacing certain pieces of equipment with others that were more appropriate. The major equipment modification was the replacement of air-cooled heat exchangers (e.g., HE-1) with water-cooled ones. There are two reasons for this: the heat gained by the cooling water can be recovered by further integration, which cannot be accomplished with the air; and cooling water costs will generally be lower than the power costs associated with air-cooling. Capital costs for the two are essentially the same. Additional equipment modifications might be necessary for the centrifuge-filter combinations. Drum washers or diffusion washers as used industrially might be more effective for the high solids recovery efficiencies required. More testing and operating experience will determine the best equipment for this use.

3.2.2 Cost of Production

Capital and operating costs for the base-case organosolv process, which includes combustion of by-products, are summarized in Table 3-2. Costs for the other alternative, recovery and sale of by-products, are shown in Table 3-3. The background of by-product credits and some additional comparisons will be presented later in this section. There is one difference in the accounting techniques used for the two options: since either option will be followed by hydrolysis, fermentation, and distillation to produce fuel-grade ethanol, a coal-fired boiler is required to satisfy the plant's steam demand. For the by-product combustion, it is assumed that a second boiler would be required to burn the by-products, but the additional steam could be distributed through the existing steam distribution network. It is also feasible to use a multifuel boiler, but the whole plant's demand would have to be examined in much more detail. This method is more useful in distinguishing between combustion of coal only and combustion of coal plus by-products. For the by-product recovery option, all steam would be produced from the coal-fired boiler, so no additional capital is required; however, an operating cost of \$4.00/1000 lb of steam reflects the additional fuel costs required to satisfy the steam demand.

Recovery of by-products increases capital costs by 14% and operating costs by 49% (primarily steam); these increases are more than offset by the by-product credits, as Table 3-3 shows. Since heat ethanol currently sells for \$1.50-\$1.75/gal, the combustion option is probably too expensive. Before we analyzed the effects of feedstock and utilities on costs (for all the processes), we looked at effects of particular parameters important to the organosolv process. The parameters that warranted more detailed investigation were the nature of solvent and the liquor-to-wood ratio.

3.2.3 Effect of Solvent Choice

Instead of 70% methanol, organosolv has been studied using 50% ethanol as the solvent. Advantages of ethanol are the use of a less concentrated solution, which is cheaper, and less toxicity toward fermentative organisms downstream than methanol. Since ethanol is also the final product of the conversion of cellulose to fuels and chemicals, it would be available at below-market price, and in dilute recycle streams around the plant, thus offsetting any increases in energy costs. The economic summary of ethanol-based organosolv presented in Table 3-4 also shows that even though less alcohol is used, the actual cost is higher since a gallon of ethanol costs almost twice as much as a gallon of methanol. Overall, the production cost of \$35.8 million/yr is about 9% higher for the ethanol process, with ethanol accounting for 27%. Total fixed investment is independent of the solvent since the two processes are essentially identical.

**Table 3-2. Estimated Cost of Production for Organosolv Pretreatment—
By-Product Combustion Option**
(Liquid-to-wood ratio is 4:1 using 70% methanol.)

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 660 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	25.22
Offsites	7.56
Total fixed investment	32.78
Working capital	10.98

Production Cost Summary

	Units/yr	Price (\$/unit)	Annual Cost (10 ³ \$)	¢/lb	\$/gal
<u>Raw Materials</u>					
Wood chips-feedstock, ton (dry)	694,924	30.00	20,848		
Sulfuric acid, ton	2,728	80.00	218		
Methanol, gal	11,232,000	0.60	6,739		
Total Raw Materials Costs			27,805	4.2	0.73
<u>Utilities</u>					
Power (kWh)	11,524,210	0.05	576		
Cooling water (10 ³ gal)	6,777,350	0.06	407		
Process water (10 ³ gal)	144,960	0.60	87		
Steam, 600 psi (10 ³ lb)	0	4.00	0		
Steam, 135 psi (10 ³ lb)	0	4.00	0		
Total Utilities Costs			1,070	0.2	0.03
<u>Operating Costs and Expenses</u>					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,513		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,361		
Total Operating Costs/Expenses			3,715	0.6	0.10
TOTAL COST OF PRODUCTION			32,590	4.9	0.86
<u>By-product credits</u>					
Lignin, ton	0	(150.00)	(0)		
Hemicellulose, ton	0	(50.00)	(0)		
Furfural, ton	0	(160.00)	(0)		
Total By-Product Credits			(0)		
NET COST OF PRODUCTION			32,590	4.9	0.86
ANNUALIZED PRODUCT PRICE^a			44,777	6.8	1.18

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

**Table 3-3. Estimated Cost of Production for Organosolv Pretreatment—
By-Product Recovery Option**
(Liquid-to-wood ratio is 4:1 using 70% methanol.)

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 660 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	29.63
Offsites	8.89
Total fixed investment	38.51
Working capital	6.06

Production Cost Summary

	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³ \$)</u>	<u>¢/lb</u>	<u>\$/gal</u>
<u>Raw Materials</u>					
Wood chips-feedstock, ton (dry)	694,924	30.00	20,848		
Sulfuric acid, ton	2,728	80.00	218		
Methanol, gal	11,232,000	0.60	6,739		
Total Raw Materials Costs			27,805	4.2	0.73
<u>Utilities</u>					
Power (kWh)	14,144,160	0.05	707		
Cooling water (10 ³ gal)	12,164,400	0.06	730		
Process water (10 ³ gal)	150,720	0.60	90		
Steam, 600 psi (10 ³ lb)	0	4.00	0		
Steam, 135 psi (10 ³ lb)	4,030,790	4.00	16,123		
Total Utilities Costs			17,650	2.7	0.46
<u>Operating Costs and Expenses</u>					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,730		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,502		
Total Operating Costs/Expenses			4,073	0.6	0.11
TOTAL COST OF PRODUCTION			49,529	7.5	1.30
<u>By-product credits</u>					
Lignin, ton	166,350	(150.00)	(24,953)		
Hemicellulose, ton	128,100	(50.00)	(6,405)		
Furfural, ton	0	(160.00)	(0)		
Total By-Product Credits			(31,358)	(4.8)	(0.83)
NET COST OF PRODUCTION			18,171	2.8	0.48
ANNUALIZED PRODUCT PRICE^a			31,340	4.7	0.82

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

**Table 3-4. Estimated Cost of Production for Organosolv Pretreatment—
By-Product Combustion Option**
(Liquid-to-wood ratio is 4:1 using 50% ethanol.)

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 660 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	25.22
Offsites	7.56
Total fixed investment	32.78
Working capital	10.98

Production Cost Summary

	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³ \$)</u>	<u>¢/lb</u>	<u>\$/gal</u>
<u>Raw Materials</u>					
Wood chips-feedstock, ton (dry)	694,924	30.00	20,848		
Sulfuric acid, ton	2,728	80.00	218		
Ethanol, gal	8,023,000	1.20	9,628		
Total Raw Materials Costs			30,694	4.7	0.81
<u>Utilities</u>					
Power (kWh)	11,524,210	0.05	576		
Cooling water (10 ³ gal)	6,777,350	0.06	407		
Process water (10 ³ gal)	144,960	0.60	87		
Steam, 600 psi (10 ³ lb)	0	4.00	0		
Steam, 135 psi (10 ³ lb)	0	4.00	0		
Total Utilities Costs			1,070	0.2	0.03
<u>Operating Costs and Expenses</u>					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,513		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,361		
Total Operating Costs/Expenses			3,715	0.6	0.10
TOTAL COST OF PRODUCTION			35,469	5.4	0.93
<u>By-product credits</u>					
Lignin, ton	0	(150.00)	(0)		
Hemicellulose, ton	0	(50.00)	(0)		
Furfural, ton	0	(160.00)	(0)		
Total By-Product Credits			(0)		
NET COST OF PRODUCTION			35,469	5.4	0.93
ANNUALIZED PRODUCT PRICE^a			47,832	7.2	1.26

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

**Table 3-5. Estimated Cost of Production for Organosolv Pretreatment—
By-Product Recovery Option**
(Liquid-to-wood ratio is 4:1 using 50% ethanol.)

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 660 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	29.63
Offsites	8.89
Total fixed investment	38.51
Working capital	7.02

Production Cost Summary

	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³ \$)</u>	<u>¢/lb</u>	<u>\$/gal</u>
<u>Raw Materials</u>					
Wood chips-feedstock, ton (dry)	694,924	30.00	20,848		
Sulfuric acid, ton	2,728	80.00	218		
Ethanol, gal	8,023,000	0.60	9,628		
Total Raw Materials Costs			30,694	4.7	0.81
<u>Utilities</u>					
Power (kWh)	14,144,160	0.05	707		
Cooling water (10 ³ gal)	12,164,400	0.06	730		
Process water (10 ³ gal)	150,720	0.60	90		
Steam, 600 psi (10 ³ lb)	0	4.00	0		
Steam, 135 psi (10 ³ lb)	4,030,790	4.00	16,123		
Total Utilities Costs			17,650	2.7	0.46
<u>Operating Costs and Expenses</u>					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,730		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,502		
Total Operating Costs/Expenses			4,073	0.6	0.11
TOTAL COST OF PRODUCTION			52,418	7.9	1.38
<u>By-product credits</u>					
Lignin, ton	166,350	(150.00)	(24,953)		
Hemicellulose, ton	128,100	(50.00)	(6,405)		
Furfural, ton	0	(160.00)	(0)		
Total By-Product Credits			(31,358)	(4.8)	(0.83)
NET COST OF PRODUCTION			21,060	3.2	0.55
ANNUALIZED PRODUCT PRICE^a			34,395	5.2	0.91

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.



3.2.4 Effect of the Liquor-to-Wood Ratio

TRW's original organosolv analysis was based on bench-scale data from a system with a liquor-to-wood ratio of 10:1 (Sarkanen 1983). For this process to become a commercial success, lower liquor-to-wood ratios, in the range of 4 or 5:1 as in the forest products industry, must be used. The major effect of decreasing the liquor-to-wood ratio is to reduce the amounts of water and solvent in the system, which reduces capital costs substantially, since smaller tanks and pumps are required for the same quantities of feedstock (Table 3-5). Similarly, operating costs are reduced, especially energy for pumping and solvent recovery. However, there are some potentially negative effects as well: separation equipment, especially filters and centrifuges, must work more efficiently, since inlet and outlet solid concentrations are much higher. Another problem may be the consistency of the lignin product at a very low liquor-to-wood ratios (below 4:1): The practical limit of the liquor-to-wood is roughly 3.5:1, based on the initial moisture content of the feedstock and the concentration of the organic solvent. The analyses presented here were based on liquor-to-wood ratios of 4:1 but maintained consistency with TRW's methodology as much as possible. Additional research on these lower LW ratios will be required in continuous systems. Results of aspen organosolv pulping using a 4:1 liquor-to-wood ratio have been reported (Chum et al. 1985a).

3.2.5 Effect of Solvent Cost

Of the three major cost components, the solvent cost will be examined first for its effect on production cost. (The effects of steam and feedstock costs will be discussed later for all the pretreatments.) The effects of solvent cost and recovery are shown in Table 3-6a, using the by-product combustion option. Two prices were considered for each solvent: a "high" price and a "low" price. Both methanol and ethanol are subject to price fluctuations based on a number of market factors beyond the scope of this report. The high price for methanol of \$0.60/gal represents the current list price at the time of the original TRW analysis; the low price of \$0.45/gal represents the depths to which the price of methanol has plummeted as a result of increasing overcapacity. The "high" ethanol price of \$1.20/gal is lower than the current list price of \$1.82/gal (\$0.48/L), but a spot price of about \$1.50, coupled with current tax incentives and the availability of "waste" ethanol in the plant, makes \$1.20 a reasonable "high" price. The \$1.00/gal (\$0.32/L) "low" price might represent the target price for ethanol from the fully developed cellulose-to-ethanol plant under consideration here.

As discussed in Section 3.2.3, the methanol-based process has slightly lower costs of production than the ethanol process, based mainly on the solvent cost itself.

This section has outlined some of the methods for minimizing organosolv production costs. Decreases in L:W ratio and increases in solvent recovery can result in production costs below 7¢/lb of cellulose, i.e., below \$1.20/gal ethanol contributed. The effect of steam and feedstock costs as well as additional by-product credits will be considered Section 3.5.

Recent research results suggest that the methanol concentration in the organosolv could be decreased by increasing the acid catalyst concentration. If the cellulosic substrates produced under these conditions have good enzyme susceptibility, it is likely that the organosolv costs could be decreased even further.

Table 3-6b shows the effect of recovering various amounts of solvent on the total pretreatment costs. A decrease from the base case value of 98% to 96% requires twice as much make-up solvent, while 99% recovery requires only half as much solvent. The increases are more pronounced with ethanol, which is the more expensive of the two solvents.

3.3 WET OXIDATION

Wet oxidation is the process of treating lignocellulosic materials with water and air or oxygen at temperatures above 120°C. Schlaeger and Brink (1978) observed that the rate of cellulose acid hydrolysis is increased after wet oxidation by using an air pressure of 50 psi (345 kPa). The reactions in this process are mostly the formation of acids both from hydrolytic processes as well as oxidative reactions. All three constituent biopolymers are affected in this process. The hemicelluloses are extensively cleaved to carboxylic acids; the lignins undergo substantial cleavage and oxidation; and the cellulose is degraded to a form highly susceptible to hydrolysis by enzymes (Schultz et al. 1984).

McGinnis et al. (1983a) reported wet oxidation results employing higher oxygen pressures (240-480 psi or 1.66-3.31 MPa) and temperatures varying from 120°-240°C for loblolly pine, black oak, and a mixture of low-grade hardwoods. The process is effective in separating the cellulosic fraction from modified lignin and hemicellulosic fractions. Acid

Table 3-6a. Effect of Solvent Cost on Organosolv Cost (By-Product Combustion)

Solvent	Cost (\$/gal)	\$/lb	
		Cellulose	Ethanol
Methanol	0.60	6.8	1.18
	0.45	6.6	1.15
Ethanol	1.20	7.2	1.26
	1.00	7.0	1.21

Table 3-6b. Effect of Solvent Recovery on Pretreatment Cost (Organosolv)

Percentage Recovered	Methanol		Ethanol	
	¢/lb Cellulose	\$/gal Ethanol	¢/lb Cellulose	\$/gal Ethanol
94	8.9	1.55	10.3	1.79
96	7.9	1.37	8.8	1.53
98	6.8	1.18	7.2	1.26
99	6.2	1.08	6.5	1.12



hydrolysis rates of the cellulosic materials were enhanced by this pretreatment. Whereas most of the cellulosic fraction can be converted to ethanol, the hemicelluloses are converted mainly into mixtures of carboxylic acids such as formic, acetic, glycolic, lactic, glyceric, succinic, erythronic, and threonic acids. Carbon dioxide, insoluble products, and traces of methanol are also formed. The nature of the accumulated acids will depend on the autooxidation conditions. Whereas milder conditions favor hydroxyacid formation, higher temperatures favor formic and acetic acid formation. McGinnis et al. (1983b) report the yields of the various acids as a function of reactor conditions and of addition of metal ion catalysts. In the case of mixed hardwoods at 240°C and 240 psi (1.66 MPa) of oxygen, ~23% and ~10% of the original wood weight is converted into acetic and formic acids, respectively.

The separation of the acids for commercial application may be costly. Whereas the steam explosion and organosolv pretreatments lead to hemicellulosic feedstocks that could be fermented into ethanol or sold as a sugar syrup, the wet oxidation produces a mixture of acids as by-products.

3.3.1 Process Description

The wet oxidation pretreatment shown in Figure 3-3 is a pressurized batch process that cooks the wood chips at 338°F (170°C) and 240 psia (1.65 MPa) for 30 min with a ferric sulfate catalyst. The process and equipment are similar to a kraft pulping operation. The process shown was designed to use a mixed feedstock of 60% hardwood and 40% loblolly pine that yields turpentine as a by-product. Both feedstocks contain 43% cellulose. Hemicellulose levels are 32% in the hardwood and 25% in the pine, while corresponding lignin levels are 25% and 32%. Several additional pieces of material handling equipment (used for sizing, metal detection, and reclaiming) plus the turpentine recovery sections were deleted from the original TRW analysis since they are not relevant to a direct comparison of the processes.

For a 38-million gal/yr ethanol plant, 190 tph (170 mt/h) of wood (with 40% moisture content) are required. This amount is based on loss of 10% of the cellulose in the digester, 80% conversion in hydrolysis, and 95% conversion in fermentation. Although a successful enzymatic hydrolysis should have a 90% or higher conversion rate, the only available data for this analysis were based on acid hydrolysis data provided to TRW by Dr. Gary McGinnis of Mississippi State University. For that study each of the eight digesters was 56 ft (17.1 m) high with a diameter of 15 ft (4.6 m), constructed of carbon steel with stainless steel lining. The shell thickness was 2.75 in. (70 mm) because of the 400 psia (2.7 MPa) pressure. With domed top and conical bottom, this vessel resembled the conventional kraft batch digester as well as the organosolv digester.

The additional equipment shown in Figure 3-4 takes the liquid stream from wet oxidation (111) and concentrates it by multiple effect evaporation to 55% solids. This by-product, composed of over 90% of the initial lignin and hemicelluloses, has more than enough fuel value to satisfy the steam requirements of the pretreatment. Alternatively, the by-product could be sold for credit, although isolation of the lignin from the carboxylic acids might be necessary. Figure 3-4 shows the combustion option.

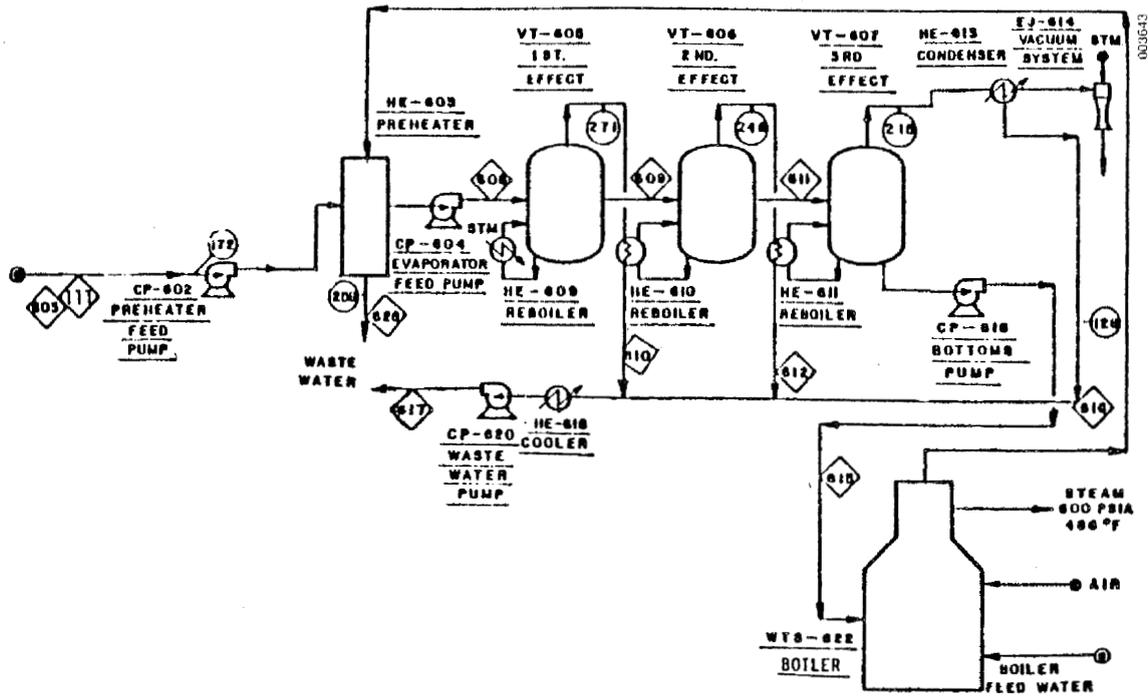


Figure 3-4. Wet Oxidation Pretreatment Flow Diagram-Part 2
(By-product combustion option shown)

3.3.2 Cost of Production

The installed equipment cost converted to third quarter 1982 dollars for the wet oxidation pretreatment is estimated at \$32.41 million (see Table 3-7). With an additional 30% for off-site facilities such as the cooling water system and miscellaneous buildings, the total fixed investment becomes \$42.13 million. For consistency the boiler and the oxygen plant are also included in the off-sites, even though both are shown on the flow diagrams. Annual production cost is estimated at \$1.27/gal (\$0.33/L) contributed to ethanol costs; 57% of that amount is the cost of the wood feedstock.

The \$48.5 million annual production cost is somewhat higher than the organosolv cost, but the cost per pound of cellulose and the allocated cost per gallon of ethanol are competitive. If the estimated lignin recovery efficiency can be achieved, then the by-product recovery option (Table 3-8) also looks very attractive, even though the hemicellulose-derived carboxylates are not recovered.

3.4 STEAM EXPLOSION

Steam treatment (at 170°-185°C) of wood to remove the hemicellulosic fraction is used in the commercial prehydrolysis kraft process. The acid, mainly acetic, is generated in situ in the wood by hydrolysis of the acetylated hemicelluloses. Chua and Wayman (1979) have investigated the autohydrolysis of aspen (*Populus tremuloides*) as a function of temperature and residence time. The longer reaction times favor higher yields of a modified lignin fraction, which is heavily condensed (because of self-condensation and reaction with furfural). At shorter residence times, acid hydrolytic reactions prevail. This method is also employed for increasing digestibility and nutrient value of aspen and a

variety of grass straws. Allen et al. (1980) reviewed this subject, and Schultz et al. (1984) compared steam explosion with other heat/steam wood pretreatments.

In the steam explosion, the autohydrolysis is combined with a mechanical process to help disrupt the wood structure. This process was first developed by Mason (1926) for the production of hardwood boards for the Masonite Corp. Babcock (1932) proposed the use of this type of pretreatment for ethanol production from pine, and interest in this process is reviving. Although disruption and hydrolysis are not as pronounced for softwoods as for hardwoods, recent work on steam explosion of *Pinus radiata* has shown increased amount of free phenolic structures in the softwood lignins (Hemmingson 1983).

In the batch mode this process consists of feeding chips to a reactor, heating them by steam injection (at pressures between 500 and 600 psi [3.5 and 4.1 MPa]) for a short residence time (such as 1 min to temperature and less than 1 min at temperature). The pressure is then suddenly released, thus quenching the autohydrolytic and degradation process that may occur during steaming. For poplars, this technique renders the hemicelluloses almost completely soluble in hot water. Almost 90% of the lignin fraction can be solubilized in an ethanol/water solution. The cellulose has low molecular weight and very short fibers and is still very crystalline (Marchessault and St. Pierre 1979). Iotech Corp. of Canada has been involved in the application of this process to produce cellulosic substrates that are readily converted into glucose by enzymes. The lignin fraction has a low molecular weight (the weight-average is approximately 2,000) and a high free phenolic content because of the hydrolytic processes. In this process, which is similar to the autohydrolysis process at short residence times, some recondensation with furfural (and 5-hydroxymethyl furfural) occurs, mainly at long residence times. Glasser et al. (1983), Himmel et al. (1983), Marchessault et al. (1982), Chum et al. (1984), and Chum et al. (1985a) have partially characterized some of these materials and compared them with those obtained in the organosolv process.

The chemical reactions that occur in the steam explosion process are similar to those described in the organosolv process (see Section 3.2). This method separates the biomass components under relatively mild conditions, by cleaving the linkages between the hemicelluloses and the lignin (mostly α -ether bonds and 4-O-methylglucuronic acid ester bonds to the α -carbons of the lignin units), and therefore releasing the lignin from the cell wall matrix. Hydrolysis of α -O-4 and, to a lesser extent, β -O-4 ether bonds in the lignins occurs, leading to a lignin of high free phenolic content. This lignin is similar to that from organosolv pretreatments. The cellulosic fraction, contrary to some conditions of organosolv pretreatment, is not in fiber form suitable for papermaking.

3.4.1 Process Description

The steam explosion pretreatment (Figure 3-5) data were developed by Iotech Corporation Limited of Canada. High-pressure steam is injected into the steaming vessel (the "gun"), penetrating the lignocellulose structure. After the prescribed cooking time, the feed is forced through a small (1-9/16 in. or 40 mm) nozzle, to a cyclone at essentially atmospheric pressure. The effect of this explosive decompression is a violent disengagement of the fibers that produces a dark brown powder. The product is fractionated into the three main constituents through consecutive aqueous and base extraction procedures. Iotech's investigations into process optimization revealed the need for a dilute acid presoak of 0.65% H_2SO_4 for 2 h at 35°C. Lower temperatures require longer soak times, while higher temperatures result in premature hemicellulose destruction. Optimum conditions for the explosion were found to be 500-600 psia

**Table 3-7. Estimated Cost of Production for Wet Oxidation Pretreatment—
By-Product Combustion Option**

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 670 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)					
Battery limits			32.41		
Offsites			9.72		
Total fixed investment			42.13		
Working capital			11.07		
Production Cost Summary					
	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³) \$</u>	<u>¢/lb</u>	<u>\$/gal</u>
Raw Materials					
Wood chips-feedstock, ton (dry)	900,000	30.00	27,000		
Ferric Sulfate, ton	3,050	129.80	393		
Oxygen, ton	6,280	80.00	503		
Total Raw Materials Costs			27,896	4.2	0.73
Utilities					
Power (kWh)	4,165,700	0.05	208		
Cooling water (10 ³ gal)	7,680,000	0.06	461		
Process water (10 ³ gal)	360,920	0.60	217		
Steam, 600 psi (10 ³ lb)	0	4.00	0		
Steam, 135 psi (10 ³ lb)	0	4.00	0		
Total Utilities Costs			880	0.2	0.02
Operating Costs and Expenses					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,945		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,641		
Total Operating Costs/Expenses			4,427	0.7	0.12
TOTAL COST OF PRODUCTION			33,203	5.0	0.87
By-product credits					
Lignin, ton	0	(150.00)	(0)		
Hemicellulose, ton	0	(50.00)	(0)		
Furfural, ton	0	(160.00)	(0)		
Total By-Product Credits			(0)		
NET COST OF PRODUCTION			33,203	5.0	0.87
ANNUALIZED PRODUCT PRICE^a			48,459	7.2	1.27

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

**Table 3-8. Estimated Cost of Production for Wet Oxidation Pretreatment—
By-Product Recovery Option**

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 670 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	33.11
Offsites	9.93
Total fixed investment	43.04
Working capital	4.66

Production Cost Summary

	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³ \$)</u>	<u>¢/lb</u>	<u>\$/gal</u>
Raw Materials					
Wood chips-feedstock, ton (dry)	900,000	30.00	27,000		
Ferric Sulfate, ton	3,050	129.80	393		
Oxygen, ton	6,280	80.00	503		
Total Raw Materials Costs			27,896	4.2	0.73
Utilities					
Power (kWh)	6,021,760	0.05	301		
Cooling water (10 ³ gal)	1,968,960	0.06	118		
Process water (10 ³ gal)	360,920	0.60	217		
Steam, 600 psi (10 ³ lb)	0	4.00	0		
Steam, 135 psi (10 ³ lb)	2,621,600	4.00	10,486		
Total Utilities Costs			11,122	1.7	0.29
Operating Costs and Expenses					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,987		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,669		
Total Operating Costs/Expenses			4,497	0.7	0.12
TOTAL COST OF PRODUCTION			43,515	6.5	1.15
By-product credits					
Lignin, ton	196,850	(150.00)	(29,528)		
Hemicellulose, ton	0	(50.00)	(0)		
Furfural, ton	0	(160.00)	(0)		
Total By-Product Credits			(29,528)	(4.4)	(0.78)
NET COST OF PRODUCTION			13,987	2.1	0.37
ANNUALIZED PRODUCT PRICE^a			28,340	4.2	0.75

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

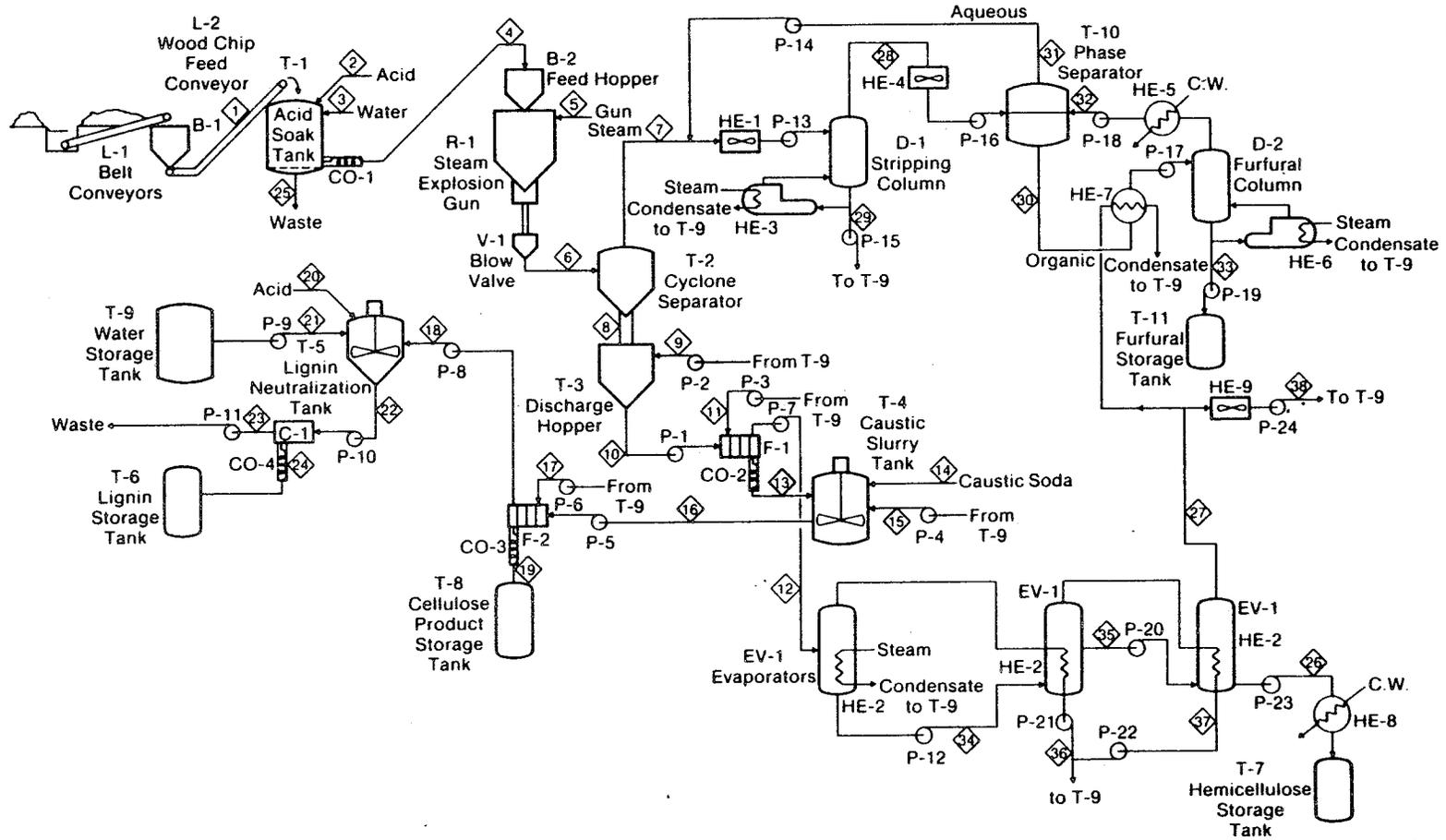


Figure 3-5. Steam Explosion Pretreatment Process Flow Diagram



(3.4-4.1 MPa) steam in a 60-s or less cooking process (3 min turnaround for the gun). The quantities of water and furfural flashed out of the cyclone were not directly measured, but were estimated by a material balance based on the lost hemicelluloses. About 90% of the lignin fraction and 60% of the hemicelluloses are recovered in salable form. The cheapest way to accomplish the combustion alternative is to run the enzymatic hydrolysis without removing lignin and hemicellulose; i.e., separate them from the resulting glucose stream. At this point, however, there is insufficient data on the feasibility of that strategy. In this analysis, the by-products are separated and isolated before hydrolysis, resulting in by-product combustion being slightly more expensive than by-product recovery. The measured lignin content actually increases because of the condensation of furfural and 5-hydroxymethyl furfural with the lignin. A water wash precedes the filtration, thus removing modified hemicelluloses and low-molecular-weight soluble lignins in the filtrate. The remaining solids are then treated with sodium hydroxide to dissolve most of the lignin. The cellulose pulp (with a small amount of residual lignin) removed after this second step is suitable for enzymatic hydrolysis. When the filtrate from the second step is neutralized with sulfuric acid, the lignin flocculates and can be recovered.

3.4.2 Cost of Production

A capital cost estimate for a steam explosion pretreatment plant was prepared for the process in Figure 3-5. Based on a quantitative cellulose recovery from the gun, 80% hydrolysis yield (as measured by Iotech), and 95% fermentation yield, the plant could supply a 38 million gal/yr ethanol plant. The annual cellulose capacity is 660 million lb (3.5×10^5 mt). The 175 tph (160 mt/h) feed flow rate is the same as organosolv but lower than for wet oxidation. Converted to the third quarter 1982 dollars, the purchased equipment cost yields an ISBL installed cost of \$23.0 million. Total fixed investment is \$29.8 million, which compares favorably with the organosolv processes.

Table 3-9 presents the economic summary for steam explosion pretreatment with combustion of by-products. The annual production cost is \$33.3 million or 6.8 ¢/lb (15.0 ¢/kg) of cellulose. Contribution to ethanol production cost is \$1.09/gal (\$0.29/L). Feedstock cost represents two thirds of the annualized product price. The caustic soda required for removing the lignin costs \$150/ton (16.5 ¢/kg) and contributes 12% to the production cost. The use of liquid (i.e., 50%) caustic soda is preferred over the pure solid for ease of handling and mixing; the price is not significantly higher and the extra water is necessary for the system anyway. Another noteworthy feature of the process is the incidental production of furfural. During steam explosion 2%-3% of the original dry feedstock or about 10% of original hemicelluloses is converted to furfural. Higher furfural yields can be achieved by lengthening the gun residence time, but significant cellulose losses would also occur. More importantly, when the gun product is flashed to atmospheric pressure in the cyclone, uncondensed furfural is essentially the only volatile constituent besides steam. 5-Hydroxymethyl furfural (HMF) in particular has a much lower vapor pressure so it remains with the solids. Furfural recovery is straightforward and relatively inexpensive. Installed costs of \$2.5 million represent about 11% of the total battery limits; the allocated annual production cost of \$2.4 million represents 0.3 ¢/lb (0.6 ¢/kg) of cellulose, or about 5.5 ¢/lb (12.1 ¢/kg) of furfural. The steam explosion process produces 37.6×10^6 lb (1.7×10^4 mt) per year of furfural. Further discussion of furfural will be presented in Section 3.5.

The by-product recovery option for steam explosion is summarized in Table 3-10. Since the hemicelluloses are separated from the lignin and cellulose by hot water extraction,

**Table 3-9. Estimated Cost of Production for Steam Explosion Pretreatment—
By-Product Combustion Option**

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 660 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	22.95
Offsites	6.89
Total fixed investment	29.84
Working capital	10.11

Production Cost Summary

	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³ \$)</u>	<u>¢/lb</u>	<u>\$/gal</u>
Raw Materials					
Wood chips-feedstock, ton (dry)	700,000	30.00	21,000		
Sulfuric acid, ton	21,100	80.00	1,688		
Caustic soda, ton (50%)	34,130	150.00	5,120		
Total Raw Materials Costs			27,808	4.2	0.73
Utilities					
Power (kWh)	13,801,080	0.05	690		
Cooling water (10 ³ gal)	42,030	0.06	3		
Process water (10 ³ gal)	0	0.60	0		
Steam, 600 psi (10 ³ lb)	336,000	4.00	1,343		
Steam, 135 psi (10 ³ lb)	0	4.00	0		
Total Utilities Costs			2,037	0.3	0.05
Operating Costs and Expenses					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,377		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,272		
Total Operating Costs/Expenses			3,490	0.5	0.09
TOTAL COST OF PRODUCTION			33,335	5.0	0.88
By-product credits					
Lignin, ton	0	(150.00)	(0)		
Hemicellulose, ton	0	(50.00)	(0)		
Furfural, ton	18,800	(160.00)	(3,008)		
Total By-Product Credits			(3,008)	(0.5)	(0.08)
NET COST OF PRODUCTION			30,327	4.6	0.80
ANNUALIZED PRODUCT PRICE^a			40,412	6.3	1.09

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

Table 3-10. Estimated Cost of Production for Steam Explosion Pretreatment By-Product Recovery Option

Basis: U.S. Midwest, 3rd quarter 1982
 Capacity: 660 million lb/yr cellulose
 Operating: 8,000 h/yr for 38 million gal/yr ethanol

Capital Cost Summary (10⁶ \$)

Battery limits	22.99
Offsites	6.90
Total fixed investment	29.89
Working capital	1.46

Production Cost Summary

	<u>Units/yr</u>	<u>Price (\$/unit)</u>	<u>Annual Cost (10³ \$)</u>	<u>¢/lb</u>	<u>\$/gal</u>
Raw Materials					
Wood chips-feedstock, ton (dry)	700,000	30.00	21,000		
Sulfuric acid, ton	21,100	80.00	1,688		
Caustic soda, ton (50%)	34,130	150.00	5,120		
Total Raw Materials Costs			27,808	4.2	0.73
Utilities					
Power (kWh)	13,600,920	0.05	680		
Cooling water (10 ³ gal)	622,830	0.06	37		
Process water (10 ³ gal)	0	0.60	0		
Steam, 600 psi (10 ³ lb)	1,878,300	4.00	7,515		
Steam, 135 psi (10 ³ lb)	1,059,980	4.00	4,240		
Total Utilities Costs			12,472	1.9	0.33
Operating Costs and Expenses					
Operators at \$23,000 (7/shift)			483		
Supervision (20% of labor)			97		
Maintenance material and labor (6% of ISBL)			1,344		
Direct overhead (45% labor + supervision)			261		
General plant overhead (65% operating costs)			1,251		
Total Operating Costs/Expenses			3,436	0.5	0.09
TOTAL COST OF PRODUCTION			43,716	6.6	1.15
By-product credits					
Lignin, ton	180,950	(150.00)	(27,143)		
Hemicellulose, ton	183,700	(50.00)	(9,185)		
Furfural, ton	18,800	(160.00)	(3,008)		
Total By-Product Credits			(39,336)	(5.9)	(1.03)
NET COST OF PRODUCTION			4,380	0.7	0.12
ANNUALIZED PRODUCT PRICE^a			14,039	2.1	0.37

^aIncludes all taxes, insurance, depreciation, interest, and return on investment.

the lignin has to be essentially completely recovered before it could be burned in the combustion option. Therefore, the equipment modifications required for recovery are a smaller evaporator section (to recover only hemicelluloses), the deletion of the second boiler, and the addition of product storage tanks. The result is that capital costs for the recovery option are actually slightly lower than for the combustion option. Operating costs are higher due to higher steam requirements, but credits for the three by-products more than compensate for the higher operating costs. Annualized product price for steam explosion is 2¢/lb of cellulose, with a net contribution of \$0.34 per gallon of ethanol produced from this material.

3.5 PARAMETRIC ANALYSIS OF PRETREATMENTS

3.5.1 Production Costs

Figure 3-6 shows production costs for each of the processes discussed earlier (again, excluding by-product credits). Each vertical bar corresponds to one of the economic summaries (Tables 3-2 to 3-9). Base-case steam and feedstock costs are used. The cost components shown are the same as in the tables: total raw materials, total utilities, operation/maintenance/overhead (i.e., the sum of total operating costs and total overhead expenses), and depreciation, which is 10% of TFI for each process. Based on the above criteria, steam explosion has the lowest annualized product price. However, all other pretreatments have annualized prices that are very close to that of the steam explosion. Within the error of the estimation of these costs ($\pm 30\%$), the four processes have comparable costs.

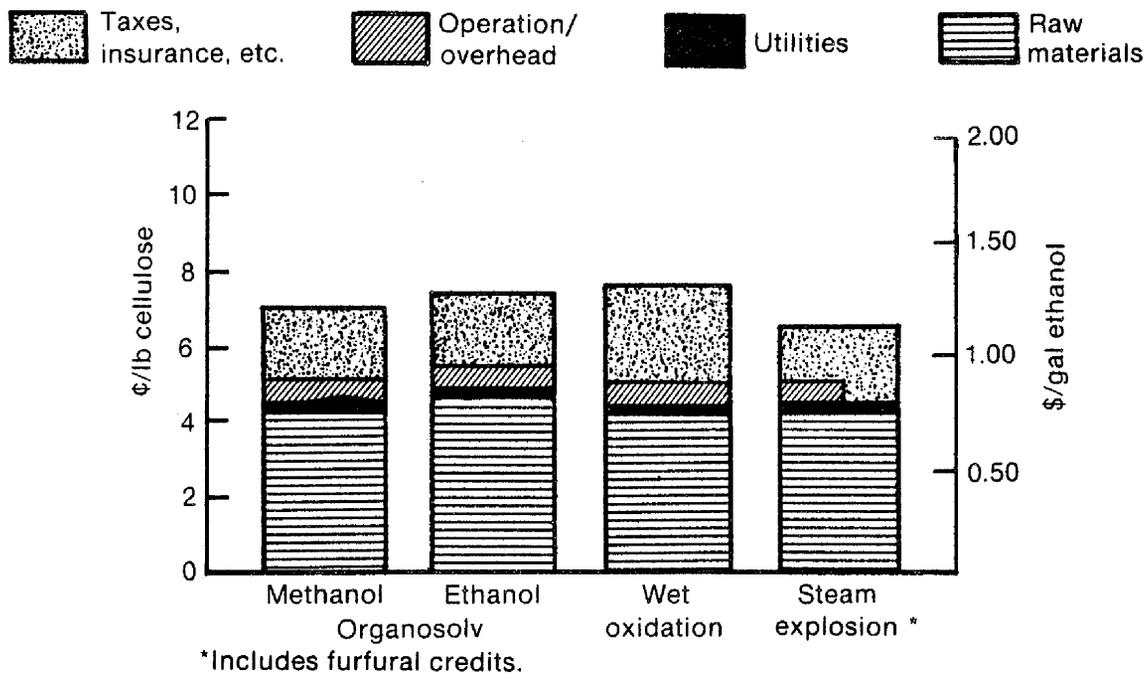


Figure 3-6. Comparison of Annual Product Prices for Pretreatments—By-Product Combustion Options

3.5.2 Effect of Feedstock Cost

The base-case feedstock cost of \$30/odt (\$27.3/mt) represents a nation-wide average cost of wood. The actual delivered cost varies with location: it might decrease in forested regions where harvesting is familiar and transport distances are short, and increase sharply in regions where delivery distances make transportation costs prohibitive. The feedstock costs were varied from \$30 to \$50/odt (\$27.3 to \$45.5/mt). The annualized costs are shown in Table 3-11.

Wet oxidation has slightly higher feedstock requirements per gallon of ethanol, so the process is the most sensitive to increased feedstock cost. Steam explosion and organosolv remain the same relative to each other.

3.5.3 Effect of Steam Cost

The base steam cost in all the analyses was \$4.00/thousand lb (\$8.80/mt) of steam. This represents the estimated operating costs and is assumed independent of boiler design system capacity, but indirectly dependent on pressure. Since higher pressure steam has a lower latent heat of vaporization, its cost per Btu is higher than that of lower pressure steam. Steam at 550 psia (3.8 MPa), for example, would cost \$5.38/10⁶ Btu (\$5.10/GJ) while 135 psia (0.9 MPa) steam costs \$4.60/10⁶ Btu (\$4.36/GJ). These are reasonable values for steam produced from coal at \$1.00-\$2.00/10⁶ Btu (i.e., \$25-50/t).

Table 3-12 shows the effects of increasing steam cost from \$4 to \$8/thousand lb. The cases considered are those in which the by-products are recovered rather than burned, since these cases do not rely on by-product-derived ("free") steam. Steam explosion has the lowest production cost over the entire range. The higher sensitivity of organosolv compared with the other processes is due to higher steam consumption. Wet oxidation and steam explosion have lower sensitivities than the organosolv processes.

3.5.4 By-Products and Credits

The following paragraphs present a brief discussion of the potential values of the by-products from the various pretreatment processes. This section is included as background and to strengthen the arguments already presented in support of the economics. First, the quantities of cellulose and the various by-products are summarized

Table 3-11. Effect of Feedstock Cost (By-Product Combustion)

	\$30/ton		\$50/ton	
	¢/lb Cellulose	\$/gal Ethanol	¢/lb Cellulose	\$/gal Ethanol
Organosolv (methanol)	6.8	1.18	9.0	1.57
Organosolv (ethanol)	7.2	1.26	9.5	1.65
Wet oxidation	7.2	1.27	10.0	1.77
Steam explosion	6.3	1.09	8.5	1.48

Table 3-12. Effect of Steam Cost (By-Product Recovery)^a

	\$4/10 ⁶ Btu		\$6/10 ⁶ Btu		\$8/10 ⁶ Btu	
	¢/lb Cellulose	\$/gal Ethanol	¢/lb Cellulose	\$/gal Ethanol	¢/lb Cellulose	\$/gal Ethanol
Organosolv (methanol)	4.7	0.82	6.0	1.05	7.3	1.27
Organosolv (ethanol)	5.2	0.91	6.5	1.13	7.8	1.35
Wet oxidation	4.2	0.75	5.1	0.89	5.9	1.04
Steam explosion	2.1	0.37	3.1	0.53	4.0	0.70

^aCredits:

Lignin:	7.5¢/lb
Hemicellulose:	2.5¢/lb (except wet oxidation)
Furfural:	8.0¢/lb (steam explosion only)

in Table 3-13. Furfural is produced only by the steam explosion process. In the wet oxidation process, most if not all of the hemicelluloses are degraded to carboxylic acids, and their recovery was not considered here. The hemicelluloses from the other two processes could be suitable for use as food or feed, depending on the toxicity effects of any lignins present. The value chosen for the hemicellulose credit, 2.5 ¢/lb, represents a conservative estimate of the price of such sugar syrups. The substantial discrepancy in hemicellulose content between organosolv and steam explosion is due to the reaction conditions and methods of recovery. Hot water extraction recovers the hemicelluloses cleanly from the remaining components in the steam explosion process, while in the organosolv process, lignin and hemicelluloses are both in solution, so that more than one-fourth of the hemicelluloses remain with the lignin product. Given the large amounts of revenue generated from by-products, solutions to this problem are critical.

The lignin products from organosolv and steam explosion are essentially similar. They contain many highly reactive phenolic hydroxy groups of fairly uniform molecular weight distribution. A study done cooperatively by Virginia Polytechnic Institute and SERI (Chum et al. 1985) indicated that while the lesser quality lignins could compete as

**Table 3-13. Production Summary for Pretreatments
(10⁶ lb/yr)**

Product	Organosolv	Wet Oxidation	Steam Explosion
Cellulose	660.0	670.0	660.0
Lignin	332.7	393.7	361.9
Hemicellulose	256.2	—	367.4
Furfural	—	—	37.6

sources of asphalt at about 7.5¢/lb, some of the higher-quality lignins might be suitable for conversion to specialty resins and could thus have a value up to 20¢/lb. On this basis, two values of by-product lignin were considered. First was the 7.5¢/lb value, which lignins from all three of the processes could command. The second value was based on the 20¢/lb value and on the assumption that no more than half the lignin from these processes would be of this quality. With half the lignin selling for 7.5¢ and half for 20¢/lb the average lignin by-product credit could be as high as 13.75¢/lb. Less is known about the wet oxidation lignins but it is expected that they could perform well in some of these applications.

The effects of by-product credit are shown in Table 3-14. By showing the combustion cases as well, this table essentially summarizes the entire situation for the three pretreatments. For all the cases where the higher lignin credit could be realized, it contributed substantially to further cost savings. In the case of steam explosion, in fact, the increased revenue was sufficient to offset all operating costs, plus all capital charges (such as interest and depreciation). The cellulose product can be literally given away, thereby reducing the ultimate cost of the ethanol produced.

In regard to furfural, much of what could be presented here has been more thoroughly covered by Parker et al. (1983). The results of that study indicate significant potential for low-cost (8-29¢/lb) furfural to displace petroleum as a feedstock for certain commodity chemicals, subject to further research and development. For the analysis presented here, the furfural credit chosen was 8¢/lb, the lowest value at which it could compete with petroleum.

The potential of by-products to improve the economics of both of these processes is quite apparent. Again, these credits are the minimum that are available; as higher-value uses of these substances are demonstrated, the process economics will become even more promising.

Table 3-14. Effect of By-Product Utilization

Pretreatment	Combustion		7.5¢/lb Lignin Credit		13.75¢/lb Lignin Credit	
	¢/lb	\$/gal	¢/lb	\$/gal	¢/lb	\$/gal
	Cellulose	Ethanol	Cellulose	Ethanol	Cellulose	Ethanol
Organosolv (methanol) ^a	6.8	1.18	4.7	0.82	1.4	0.24
Organosolv (ethanol) ^a	7.2	1.26	5.2	0.91	1.9	0.33
Wet oxidation	7.2	1.27	4.2	0.75	—	—
Steam explosion ^{a,b}	6.3	1.09	2.1	0.37	-1.5	-0.26

^aAlso includes 2.5¢/lb hemicellulose credit.

^bAlso includes 8¢/lb furfural credit (in all cases).

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SECTION 4.0

CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

This report has evaluated three pretreatment processes of lignocellulosic material. Where the preliminary available data were sufficient, process flowsheets were constructed and heat and material balances calculated. The processes have been treated like pulping systems for the purposes of this evaluation; i.e., the processes were evaluated for their cost to produce cellulose. This was the most consistent basis for the evaluation because of the variability of the data available. This approach is not the most efficient in terms of process cost and energy, but it provides a method for comparing processes and allows a direct comparison to conventional kraft pulping.

The data in the Table 4-1 summarize the costs for each process to produce the cellulose fibers and gives the pretreatment contribution to the selling price of ethanol produced from these fibers. As mentioned earlier, these economics were determined based on pulping processes and are not optimized in an integrated process to produce ethanol. The production costs include the cost of the feedstock, the amortization of the equipment, and the steam and chemical costs. Elements of the Chem Systems Inc. model were used to complete the economic analysis and include standard features such as labor costs and depreciation of capital equipment. Throughout the table by-product credits are taken for lignin (7.5¢/lb), hemicellulose (2.5¢/lb, except wet oxidation), and furfural (8¢/lb, steam explosion only).

The data in the table offer insight into the value of continued research to develop improved pretreatment processes to reduce the process costs and increase the conversion efficiency of the hydrolysis step. Finding or developing lower cost feedstocks is also a good research target, as shown by the effect of feedstock costs on the selling price of the products. The data in the table show that all of these processes produce cellulose fibers at a lower cost than conventional kraft pulping. Steam explosion produced cellulose at the lowest cost within our knowledge of this and the other systems. Continued R&D in the various pretreatments may reduce their cost. This is particularly important in the case of the organosolv process, for which not enough data were available to allow a better analysis of the system. These processes, therefore, should be of value to the pulping industry and also should improve the economics of ethanol from cellulose via enzymatic hydrolysis.

4.1.1 Steam Explosion

Steam explosion is by far the most extensively studied and documented among the pretreatments reviewed. Iotech Corporation Ltd. of Canada has produced data on the effect of the processing parameters on the enzymatic susceptibility of the cellulose fibers produced in the process and has tested their results in a bench-scale process and at the 1-ton/day facility at the Gulf plant at Jayhawk, Kans. Materials from their process have been evaluated at numerous laboratories in the United States and Canada and were found to have excellent properties. The cellulose was easy to hydrolyze enzymatically, and the lignin has been used by Iotech to make wafer board with good mechanical properties, when substituted for up to 75% of conventional phenol formaldehyde resin.

Table 4-1. Comparative Economics of Pretreatments

	¢/lb Cellulose ^a		\$/gal Ethanol ^b	
	Feedstock Cost		Hydrolysis Yield ^c	
	\$30/ton	\$50/ton	80%	95%
By-Product Combustion				
Organosolv (methanol) ^d	6.8	9.0	1.18	0.99
Organosolv (ethanol) ^d	7.2	9.5	1.26	1.06
Wet oxidation	7.2	10.0	1.27	1.07
Steam explosion	6.3	8.5	1.09	0.92
By-Product Recovery^e				
Organosolv (methanol) ^d	4.7	6.7	0.82	0.69
Organosolv (ethanol) ^d	5.2	7.3	0.91	0.77
Wet oxidation	4.2	7.0	0.75	0.63
Steam explosion	2.1	4.2	0.37	0.31

^aCompare with conventional kraft pulping (unbleached) at 17.3¢/lb cellulose (from Paper Trade Journal, May 1985, 2nd quarter 1985 contract price).

^bContribution of pretreatment to ethanol production cost with feedstock at \$30/ton.

^cFermentation yield 95%.

^dBased on 99% solvent recovery.

^eCredits:

Lignin:	7.5¢/lb
Hemicellulose:	2.5¢/lb (except wet oxidation)
Furfural:	8.0¢/lb (steam explosion only)

Additional assumptions include a steam cost of \$4/thousand lb, and U.S. dollars from the third quarter of 1982. For details of assumptions and calculations, see Section 3.0.

In more recent experiments, the substrate has been soaked in a dilute acid solution prior to the steam explosion treatment, thereby reducing both the steam requirements and the loss of the hemicellulosic fraction. This treatment permits use of over 85% of the carbohydrates from the original substrate. Steam explosion has been tested on a variety of substrates and has been found to be most useful on hardwoods and crop residues. The most favorable substrate seems to be Populus trees because this species has a high cellulose content and responds very well to this process. Crop residues respond well to this process but appear less desirable as a substrate because of an unfavorable energy balance due to the low cellulose content.

Steam explosion is the basic pretreatment of lignocellulosic substrates because the process is so well documented, was tested at several levels and at various institutions, and satisfies all the requirements of the process. The energy costs are moderate and the general process has been demonstrated on a commercial scale at the Masonite plants. The lignin alkaline extraction procedure discussed here may dissolve more of the cellulosic cake than an alcohol extraction procedure. These effects were not considered in this report.



4.1.2 Organosolv

The organosolv pretreatment process covers a broad range of organic solvents, such as methanol, ethanol, butanol, and phenol. The process involves mixing an organic liquid and water together in various portions and adding them to the wood. This mixture is heated to dissolve the lignin and some of the hemicellulose and leave a reactive cellulose cake. In addition, a catalyst is sometimes added to either reduce the operating temperature or enhance the delignification process. Most of these processes produce similar results and for that reason are grouped here as a single class.

The base case process uses a 4:1 L:W ratio, and for this report we used ethanol and methanol as the organic liquids. For the ethanol base case a 50% solution was used and for methanol a 70% solution was used, because most experimental data were developed in this range. Parametric studies were performed to evaluate the solvent recovery needs. At 99% solvent recovery, no appreciable difference exists between the organosolv (methanol) and steam explosion processes. The pulping industry uses the same L:W ratios as a standard procedure, and they were therefore assumed to be a reasonable target. These processes have demonstrated their ability to delignify wood and crop residues with a great deal of selectivity and produce a lignin fraction having relatively low number-average molecular weights (in the range of 500-700). Enzymatic susceptibility of the cellulose pulp has been shown to be comparable to that of steam exploded pulps when appropriate reaction conditions are used (see Section 3.2).

The organosolv process has the potential to compete with steam explosion as an economic pretreatment. The fractionation properties are particularly suited to producing clean by-product streams for downstream processing to alternate chemicals and fuels. Before this approach can be developed into a feasible process alternative, an integrated program of research and process engineering needs to be completed and the results evaluated in an integrated process. Three key issues need attention:

- Development of a continuous process (reactor)
- Verification of the feasibility of using the lower L:W ratios
- Development of systems requiring reduced amounts of the organic liquid.

4.1.3 Wet Oxidation

Of the processes studied wet oxidation is the simplest in terms of energy, equipment, and chemicals required for operation. Using the current configuration of the process, fractionation of feedstock is limited to two streams: one is a cellulose pulp and the other a liquid stream containing solubilized lignin fractions and degradation products from the hemicellulosic fraction (mainly carboxylic acids). The cellulose cake is susceptible to enzymatic hydrolysis. The second stream of liquid products is a complex mixture of compounds that could be used as a boiler feed or recovered.

4.2 RECOMMENDATIONS

A clearer picture has emerged from the review of the data leading to the evaluation of the candidate pretreatment processes presented in this report. These data indicate that more basic research and process engineering are needed. Further research is needed on specific processes as well as general areas.

4.2.1 Process-Specific Research

Of the processes studied, steam explosion requires the least continued work and should be tested in an integrated experiment to validate the laboratory results on a scale of sufficient size to establish the technical and economic feasibility of the process. The lignin from this process should be studied in greater detail to determine its market value.

Several areas of the organosolv process need further research. Experiments need to be performed to determine the processing factors that affect the enzymatic susceptibility of the cellulose pulp. The experiments to date have stressed selective delignification as the principal goal, while recent results suggest that partial delignification coupled with removal (partial or substantial) of the hemicellulose is a more effective treatment for producing an active cellulose. This effect needs to be validated and quantified as part of a broad research effort to understand the mechanism of this process.

Other issues requiring attention are improved solvent recycle and recovery; tests of lower L:W ratios; development of a continuous reactor process; development of systems with less of the organic phase; and evaluation of the lignins produced in these and other processes for potential market value.

4.2.2 General Research Needs

The following general areas require additional research:

- Obtain results from integrated experiments that include coupling of pretreatments and enzymatic hydrolysis to complete the assessment of the processes and their economic feasibility.
- Evaluate the effect of the size of the feedstock on the processes in terms of both processing efficiency and economic impact.
- Initiate a basic research program to develop fundamental knowledge of the physical and chemical interaction at the cell wall level to explain the mechanisms of pretreatment at the molecular level. This program should benefit from all the previous knowledge in this field concerning conventional pulping processes.
- Identify and initiate research on innovative pretreatment process suggested by the fundamental studies.
- Develop a better correlation between rumen digestibility and cellulase activity to use the large data base available for rumen digestion to aid in identifying processes that are applicable to cellulose.
- Initiate work to establish a data base or an annotated bibliography of pretreatments for wood and agricultural residues.
- Work with the research community both in the United States and abroad to set up a workshop on the pretreatment of lignocellulosic biomass.

APPENDIX A

PARTIAL MASS BALANCES

FOR PRETREATMENT PROCESSES

Table A-1. Partial Mass Balance for Organosolv Process (lb/h)

	Wood to Digester 3	Liquids to Digester 44	Liquids from Digester 4	Cellulose from Digester 17	To Distill. 6	Distill. Overhead 7	Distill. Bottoms 8	Cellulose Product 39	Lignin Product 13	Hemicell. Product 15
Water	197,903	9,997	133,718	81,306	120,287	33,346	86,941	151,402	86,411	28,130
Cellulose	86,865	—	—	86,865	—	—	—	82,522	—	—
Hemicellulose	43,433	—	—	—	—	—	—	—	—	—
Lignin	43,433	—	41,696	1,737	41,696	—	41,696	619	41,592	104
Methanol	1,424	485,572	345,009	189,714	232,459	223,161	8,938	1,012	3,599	—
Acetic acid	—	—	417	417	471	—	417	6	167	250
Xylose	—	—	36,275	11,512	36,275	—	36,275	538	14,514	21,761
Glucose	—	—	3,753	156	3,753	—	3,753	55	1,501	2,252
Furfural	—	130	11,251	52	—	—	—	17	484	727
Sulfuric acid	—	682	573	313	—	—	—	112	228	342
Total	373,058	496,381	562,697	361,672	434,887	256,507	178,020	236,283	144,018	56,260

Note: Additional details available from authors.

Table A-2. Partial Mass Balance for Wet Oxidation Process (lb/h)

	Wood Feed 101	Steam 103	Solids to Hydrolysis 112	By- Products ^a 111	Solids to Heat Generation 615
Water	151,000	223,836	139,993	456,725	98,836
Cellulose	97,395	—	83,760	2,204	2,204
Hemicellulose	66,138	—	—	—	—
Lignin	62,967	—	13,635	49,332	359
Dissolved products	—	—	6,062	69,263	118,236
Ferric sulfate	—	—	38	729	—
Total	377,500	223,836	243,488	578,253	219,635

^aTo combustion or recovery.

Note: Additional details available from authors.

Table A-3. Partial Mass Balance for Steam Explosion Process (lb/h)

	Gun Feed 4	Gun Steam 5	Gun Product 6	Flash Vapors 7	Cyclone Bottoms 8	Filter Solids 19	Lignin Product 24	Hemicellulose Product 26	Furfural Product 33
Water	212,515	234,942	450,958	52,593	398,365	154,454	61,208	98,165	—
Cellulose	87,535	—	87,535	—	87,535	83,213	2,080	2,189	—
Hemicellulose	43,330	—	26,141	—	26,141	3	3	25,880	—
Lignin	43,768	—	45,064	—	45,064	39	38,627	5,475	—
Glucose	—	—	1,560	—	1,560	—	—	1,545	—
Xylose	—	—	3,899	—	3,899	—	—	3,860	—
Furfural	—	—	4,983	4,704	279	—	—	277	4,704
Sulfuric acid	925	—	925	—	925	—	42	915	—
Sodium hydroxide	—	—	—	—	—	43	43	—	—
HMF	—	—	1,950	—	1,950	—	—	1,930	—
Total	388,073	234,942	623,015	57,297	565,719	237,751	93,603	131,695	4,704

Note: Additional details available from authors.

APPENDIX B

DESIGN OF PRETREATMENT SECTION OF AN ENZYMATIC HYDROLYSIS PLANT

(Source: Anastasi and Motley 1982 [see Section 3.7])

This appendix presents the detailed design basis for the TRW organosolv evaluation. All other process evaluations were designed to be fully consistent with this design.

The process design was developed for the pretreatment section of an enzymatic hydrolysis plant producing 50 million gallons of ethanol per year from debarked hardwood chips. The plant is located in the upper midwestern United States and is assumed to have unlimited access to debarked poplar chips from either natural stands or energy plantations.

B.1 WOOD CHIP FEEDSTOCK

Wood feedstock composition - debarked poplar chips

- Cellulose, 50%
- Hemicellulose, 25%
- Lignin, 25%

The 174 tph of chips needed by the plant are delivered at a rate of 880 tph, 8 hours per day, 5 days per week, 10 months per year. Storage for 2-1/2 months of chips is provided.

B.2 STEAMING VESSEL

The wood chip steaming vessel was designed to the following specifications:

- Type horizontal, screw conveyed
- Temperature 212°F (100°C)
- Pressure near atmospheric
- Feed debarked wood chips
- Residence time 15 minutes

B.3 ORGANOSOLV REACTOR

The following parameters were used to design the organosolv reactor:

- Temperature 284°F (140°C)
- Pressure 200 psia
- Liquid-to-wood ratio 10:1
- Solvent 7:3 methanol to water
- Acid concentration 0.01 M H₂SO₄ in liquid phase

- Residence time 60 minutes
- Type continuous counterflow digester
- Conversion 100% of hemicellulose

Assumptions:

- The hemicellulose completely hydrolyzes to produce the following:

	Weight %
xylose	87
glucose	9
furfural	3
acetic acid	1

- The cellulose is completely recovered in the reactor bottoms along with 4% of the lignin and hemicellulose.
- Although these assumptions are optimistic, they are loosely based on organosolv delignification data received from Dr. Sarkanen at the University of Washington.
- The liquids-to-solids ratio of the reactor liquor (and therefore of the reactor bottoms) is about 3:1.
- The reactor overhead contains 96% of the dissolved hemicellulose sugars and lignin.

B.4 CELLULOSE RECOVERY

- It was assumed that only a single washing of the cellulose pulp was necessary to precede enzymatic hydrolysis.
- 5% of the cellulose pulp is subjected to additional washing steps to purify the media for growing enzymes for enzymatic hydrolysis.

Blow Tank T-7

- Type closed steel vessel
- Temperature 162°F (72°C)
- Pressure near atmospheric
- Liquid-to-wood entering 3:1
- Residence time 15 minutes
- Overhead composition 79 mol % methanol
21 mol % H₂O

Centrifuges C-2 and C-3

- Type solid bowl decanting

Filters F-2 and F-3

- Type wet leaf

Assumptions:

- Centrifuge and filter bottoms are 40 wt % solids; additional equipment, such as press rolls, may be necessary to achieve this high solids level.
- Centrifuges and filters recover 95% of input solids as bottoms.

- Filter wash efficiency of 97.5% for two wash volumes.

Steam Stripper D-2

- Type closed steel vessel
- Temperature 162°F (72°C)
- Pressure near atmospheric
- Overhead composition 79 mol % methanol
21 mol % H₂O
- Bottoms 35 wt % cellulose
- Methanol recovery 99%
- The stripper is fed a combination of steam and water to maintain an overhead temperature of 162°F.

Distillation D-3

- Temperature 162°F (72°C)
- Pressure near atmospheric
- Number of trays 12
- Overhead composition 79 mol % methanol
21 mol % H₂O
- Reflux ratio 0.664
- Methanol recovery 98%
- Condenser duty 91.4×10^6 Btu/h
- Reboiler duty 99.3×10^6 Btu/h
- The liquid bottoms are sent to wastewater treatment.

B.5 METHANOL RECOVERY

Flash Tank T-1

- Type closed steel vessel
- Temperature 162°F (72°C)
- Pressure near atmospheric
- Residence time 5 minutes
- Overhead composition 79 mol % methanol
21 mol % H₂O

Vacuum Distillation D-1

- Temperature 122°F (50°C)
- Pressure 0.5 atm

- Number of trays 10
- Overhead composition 90 mol % methanol
10 mol % H₂O
- Reflux ratio 0.36
- Methanol recovery 98%
- Condenser duty 582×10^6 Btu/h
- Reboiler duty 545×10^6 Btu/h
- Since the evaporation of the methanol is accomplished under reduced pressure, the water-insoluble lignin separates as a solid and is recovered as a fine powder separately from the dissolved hemicellulose sugars.

B.6 LIGNIN AND HEMICELLULOSE SUGARS RECOVERY

- The lignin and hemicellulose sugars are recovered separately.

Centrifuge C-1

- Type solid bowl decanting

Filter F-1

- Type wet leaf

Assumptions:

- Centrifuge and filter bottoms are 40 wt % solids; additional equipment, such as press rolls, may be necessary to achieve this high solids level.
- Centrifuge and filter recover 95% of input solids as bottoms
- Filter wash efficiency of 97.5% for two wash volumes

Evaporator EV-1:

- Capacity 247,500 lb/h
- Pressure near atmospheric
- Temperature 212°F (100°C)
- Methanol recovery 100%
- Water recovery enough to supply the water recycle requirements of the organosolv reactor
- Bottoms concentration 34% dissolved hemicellulose sugars
- Reboiler duty 263×10^6 Btu/h

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