

CHEMICAL CONVERSION PRODUCTS FROM WOOD

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CHEMICAL CONVERSION PRODUCTS FROM WOOD¹

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The chemical utilization of wood has had a long history--a history that shows a few notable successes but is liberally documented with disappointments.

The fact that wood is about two-thirds carbohydrate, which can be converted to sugars, intrigued the earliest organic chemists. But it was this obvious fact that contributed heavily to the economic failure of many past ventures in the chemical conversion of wood. Too much emphasis was placed on the production of a single chemical from a complex, photosynthetic product of nature.

The outlook for the chemical utilization of wood is much brighter today for several reasons. Among them are: (1) increased knowledge of both the fundamental chemistry and engineering kinetics of wood conversion, (2) the trend toward integrated forest products operations rather than single-product plants, (3) rapidly increasing need for industrial chemicals in the world economy, and (4) recognition of the fact that the probability for success of a large-scale chemical operation based on wood depends in large measure on utilizing all three primary constituents of wood, not just one.

A successful industry based on chemicals from wood would be a tremendous tool for forest managers. Residues from logging operations and otherwise little-used tree species could then be harvested and utilized at a profit, with obvious benefits both in immediate forest harvest and thinning operations and in planning long-range species requirements for specific forest lands.

The forest products industries would also benefit from chemical operations based on wood. If mill residues and pulping liquors could

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show even a small profit rather than a disposal expense, the overall programming for woods-run logs through an integrated plant might be affected profoundly. Solid wood products would also be more competitive, because they would no longer have to bear the entire cost of growing, harvesting, and processing the tree.

Raw Material Available

No chemical industry, or any other industry for that matter, can long survive without established markets backed up by a continuous, sufficient supply of raw material. Here in the United States, there are some 480 million acres of commercial timberland, more acreage than is devoted to the production of farm crops. The net growth each year is about 22 billion cubic feet of wood on a base stock of 860 billion cubic feet, and this base is increasing.

The volume of wood being removed from our forests now is roughly half the annual growth. The "other half" of this growth increment is available, to a large extent, for chemical conversion because much of the growing stock is of a quality that does not meet the requirements for lumber or veneer. The economical utilization of this undesirable part of the growth increment would be a boon to forest managers.

The remainder of the raw material supply for wood chemicals would be derived from the physical processing of wood harvested for lumber, veneer, pulp and other wood products. The magnitude of the supply of wood residues from such processing can best be illustrated by a general material balance. The input, or total wood substance harvested, excluding bark, approaches 204 million tons annually. Inclusion of bark in the total would add another 20 million tons.

On the output side appear two principal products--lumber and pulp-wood. They account for 52 million and 39 million tons, respectively. Another 56 million tons represent fuelwood and mill residues used for fuel. Subtracting some 6 million tons for other products leaves 51 million tons of unused logging and mill residues available as raw material for chemical conversion. Another 31 million tons of wood used at a low level may be added for its replacement cost as fuel. This total figure of 82 million tons of available wood compares favorably with the United States output of 115 million tons of steel in 1956, for instance.

Another point to be considered is that the above figures do not take into account the cull timber that should properly be removed from the forest during logging. Although accurate figures are not available, a reasonable estimate would be that about 10 percent of a timber stand is in cull trees, on the average.

On the negative side of the scale, it must be remembered that, as a result of the rapidly increasing use of mechanical and hydraulic barkers for sawlogs, more of the residue from primary log breakdown is bark-free, and is being chipped and sold to pulp mills or particle board plants, rather than burned. Over 40 percent of the raw material for pulp mills in the Pacific Northwest area of the United States consists of chips made from slabs, edgings, trim, and veneer clippings. From the production of every 1,000 board feet of lumber, about 0.4 ton of these chippable residues will result, plus about 0.6 ton of sawdust and shavings, which, except for chemical use, could only be burned for fuel.

When the overall utilization of our timber resource is considered, it becomes increasingly clear that a chemical plant based on residue wood will more likely be successful as a component part of an integrated forest products complex. There will always be a demand for high-quality wood for lumber, veneer, poles, and other products made of wood in its natural form. Requirements for pulpwood will be less critical, but chippable residues will continue to find profitable uses in pulp and various reconstituted board products. There is already a definite trend for plywood plants to add sawmills and particle board operations, and for pulp mills to add sawmills and other operations, for instance, so that their timber resources can be managed to produce a variety of products more efficiently than only one. A chemical plant will fit into such an integrated operation because, no matter how efficiently a timber stand is managed, a large percentage of the timber stand improvement cuttings will be valuable only for the chemicals it contains. This situation is particularly true in such areas as the south and southeastern parts of the United States, where much of the new growth is now in low-grade hardwoods, rather than in the more desirable softwoods.

Chemical Nature of Wood

At the beginning of this paper, it was emphasized that the successful chemical utilization of wood, at least on a large scale, will probably require profitable uses for all three of its primary constituents. These are the hemicellulose, cellulose, and lignin fractions. The hemicellulose is the carbohydrate fraction that can be easily hydrolyzed from the more resistant cellulose. The lignin fraction is the highly complex, aromatic polymer residue remaining after the hemicellulose and cellulose have been isolated.

Although there are some differences between hardwoods and softwoods, species within these groups have about the same composition. An average hardwood consists of 25 percent hemicellulose, 45 percent cellulose, and 23 percent lignin, plus some 7 percent of acetyl

groups. A representative softwood also contains 25 percent hemicellulose, but 42 percent cellulose and 30 percent lignin, with about 3 percent of acetyl groups.

Although the above percentages show some variations, the most important difference between hardwoods and softwoods, chemically, is in the sugars that comprise the hemicellulose fraction. When further hydrolyzed, hardwood hemicellulose gives mostly the 5-carbon sugar, xylose. Hydrolyzed softwood hemicellulose, on the other hand, contains very little xylose, but is about 50 percent mannose, a 6-carbon sugar. Cellulose is hydrolyzed with much difficulty to give glucose, another 6-carbon sugar. If cellulose could be hydrolyzed with the ease of hemicellulose, wood saccharification would now be a widespread industrial process.

A great variety of other chemicals usually found in small amounts (3 to 5 percent) are loosely classed as extractives. These compounds are responsible for odor, resistance to decay, and other such properties that give many woods their special characteristics.

Status of the Chemical Industry

At the present time, there are a variety of examples of successful chemical operations based on wood. The most notable of these is the production of rayon, both viscose and acetate, from dissolving pulp. Wood, primarily softwood although some hardwoods have been used, is pulped by either the acid sulfite or prehydrolysis sulfate process to a low yield of high-purity cellulose. It is essential that lignin and hydrolyzed sugars be completely removed. In the production of viscose rayon, the cellulose is dissolved in carbon disulfide, precipitated in sulfuric acid, and spun from the acid medium into fiber. Rayon is still the primary fiber used in tire cords, and is a familiar fiber in the wearing apparel of our wardrobe.

The cellulose from dissolving pulp also has other important uses. Some is nitrated, for example, and becomes a component of one of the current propulsion systems for solid-fuel rockets. Although this use is now small, it could have a spectacular future if research can solve certain problems, including thermal and dimensional stability. Methyl and ethyl cellulose, cellulose acetate, nitrate, butyrate, and many others find application in such a diverse range of products as photographic films, cosmetics, sponges, and plastic items such as toys and the familiar, clear yellow, seemingly indestructible tool handles.

Dissolving pulp accounts for a bit less than 5 percent of the total pulp production in the United States. Only the cellulose fraction

of the wood is now being utilized, but, especially in the prehydrolysis sulfate process, hydrolyzed sugars are available for further utilization.

In the southern part of the United States, the naval stores and tall oil industries return a profit from the resinous extractives in some of the southern pines. Naval stores is the term applied to the turpentine and rosin that result from the cleaning and steam distillation of the pine gum collected from grooves cut in the bark of the living trees. If the trees are worked properly, their value for lumber is not impaired. Fatty acids and resin acids are recovered from the pulping liquor when southern pines are pulped by the Kraft process. The crude chemicals, which are skimmed from the surface of the liquors, are called tall oil. A small fraction of the residual lignin in Kraft pulping liquor is also being utilized to produce an industrial chemical, dimethyl sulfide, in at least one plant.

Historically, ethyl alcohol was produced exclusively by fermentation of sugars. Although most industrial alcohol is now produced synthetically, a West Coast plant is recovering alcohol from the fermentation of residual sugars in spent sulfite liquors. An experimental plant for the production of alcohol from wood was constructed in the United States toward the end of World War II, but never became fully operational because the market dropped before the plant was finished at the end of the war. The technical soundness of the process was proved, however, and much engineering data obtained. Numerous plants for the production of alcohol from wood are reported in Europe, especially in Russia.

Yet another operation based on spent sulfite pulping liquor is the production of nutritional yeast. *Torula* yeast that can assimilate both 5-carbon and 6-carbon sugars is grown on a sugar-containing solution from the spent liquor. The yeast converts the carbohydrate to protein, primarily, plus vitamins and fats, at a rapid rate. Under optimum conditions, the yeast is capable of doubling the protein content in the fermentor every three and one-half to four hours. Here again, price is a limiting factor, as is consumer resistance to the use of yeast grown on waste liquors in food for human consumption.

The lignin fraction in spent sulfite liquors has found a multitude of uses, none of which have been too successful from a profit point of view. An important point that must not be overlooked here, however, is that utilization of pulping residues, even at negligible profit, is important to the extent that it reduces pollution of the flowing water to which the waste effluent is discharged.

After wood is pulped by the sulfite process, the lignin exists as water soluble lignosulfonates. Theoretically, a variety of

aromatic compounds can be produced from these lignosulfonates by alkaline cleavage and other reactions. Actually, vanillin is the only cleavage product presently being marketed to any extent. Today, pure, food-grade vanillin from a small fraction of the available spent liquor supplies almost the entire vanillin flavor market, some one million pounds per year in the United States. Most current uses for lignosulfonates do not involve cleavage to specific compounds. The complex lignosulfonates vary widely in their properties, which contributes to the difficulty in characterizing and utilizing them. Presently, they are used in foundry molds, drilling mud formulations, and as dispersing agents, tanning agents, surface-active agents, and in a variety of other applications where their reactive groupings can be used to advantage.

The destructive distillation of wood is also a source of chemicals. Although much charcoal is now being produced in small kilns with no facilities for byproduct recovery, about six large plants produce roughly half the total annual output. Some of these high-volume plants maintain quite expensive equipment for the recovery and refining of methanol and acetic acid, primarily, from the vapors driven from the wood during carbonization. Actually, charcoal itself is a chemical conversion product, and, in addition to its primary use as recreational fuel, also finds application in metallurgy and in purification operations as activated carbon.

Chemical utilization has been considered as a possible solution to the problem of bark disposal. Most current approaches involve chemical modification rather than conversion, however. Typical among the products are composted bark, which serves as a combination fertilizer--soil conditioner, and sulfonated and caustic extracts of bark dust, which are finding rather extensive use in ore flotation, oil-well drilling muds, and so forth. Fine chemicals such as dihydroquercetin have been produced from bark, however, and an exterior-quality adhesive for plywood consisting of about half polyphenolic hemlock bark extract has been developed.

What the Future Promises

So far, the chemical utilization of wood has not achieved the successes that seem to be within reach. Its future now looks brighter than ever, but the need for more research, both on fundamental chemistry and on engineering application is also becoming increasingly obvious.

Economic studies indicate that, at least in certain locations and under favorable conditions of competition, a chemical operation based on wood carbohydrates, the hemicellulose and cellulose fractions,

could be profitable even if the lignin is only burned for fuel. Such an operation would be in a much more favorable competitive situation, obviously, if the lignin fraction, roughly a fourth of the total raw material, could be utilized at a higher level of return than for its fuel value.

One good approach to the chemical utilization of wood would start with a mild prehydrolysis to remove the hemicellulose fraction. The lignin could then be separated from the cellulose by means of a lignin solvent, or could remain as a residue after total hydrolysis of the cellulose. The alternative actually used may depend on the end use intended for the lignin, because the lignin that remains after complete cellulose hydrolysis will undoubtedly have lost a part of its reactive groupings.

In this theoretical scheme of utilization, the three major constituents of wood, once isolated, can then be processed to the final conversion products for which they are best suited. To take a very promising example, consider the hemicellulose fraction from hardwoods. The major constituent of the solution from hydrolysis of hardwood hemicellulose is xylose, a 5-carbon sugar. This solution could be processed to molasses or yeast for cattle feed, but would have no advantage over other sugar sources such as blackstrap molasses. Xylose is unique, however, in that it can be converted to furfural, a basic chemical intermediate in the production of nylon. Furfural is currently being produced inexpensively from corncobs, but the bulk density and seasonal nature of the corncob supply are serious disadvantages. If the industrial need for furfural for nylon, solvents, and resins continues its present trend, hardwood hemicellulose will unquestionably become a major starting point in the production of furfural.

Since hemicellulose is hydrolyzed to xylose in acid aqueous solution, it would be most advantageous to make the further conversion to furfural in the same solution. Such a process would be much different from present commercial practice. The kinetics and engineering aspects of this acid-catalyzed conversion of xylose to furfural have been studied extensively at the U. S. Forest Products Laboratory.

The chemical conversion of the cellulose fraction of wood could follow any one of a variety of alternatives. If a course parallel to that for hemicellulose were to be followed, the first step would be acid hydrolysis of the cellulose to its component sugar, glucose. Actually, this hydrolysis step would be necessary in all utilization schemes except those in which the cellulose is used directly, such as in the production of rayon, nitrocellulose, cellulose acetate, and so forth. Once the saccharification step is completed, the glucose is available in acid solution for further processing. A significant

factor here is the availability of large quantities of very pure sugar at low cost from cane sources on the world market. This factor currently dictates further conversion of the glucose rather than purification to sugar for human or animal consumption.

To again parallel the course of action with xylose, the glucose can be further converted in acid solution to hydroxymethylfurfural. A continuation of the reaction results in levulinic acid. Both of these compounds are reactive intermediates that have considerable potential as industrial chemicals. The kinetics of both reactions have been studied at the Forest Products Laboratory because the basic glucose amounts to more than half the weight of many woods. Also, both compounds are inevitable byproducts in the production of wood sugar. In fact, they are the primary impurities. If they can be separated from the sugar economically, it is possible they may pay the cost of upgrading the sugar.

There are at least four other primary ways that have been studied extensively in which the glucose from cellulose can undergo further chemical conversion. First, as has been covered earlier, it can be fermented to ethyl alcohol. There are also two other microbiological conversions where the end product is either nutritional yeast or glycerol. The fourth conversion is hydrogenolysis to glycerol and other polyhydric alcohols.

Consider first the microbiological conversion of wood sugars to food yeast. The yeast most commonly used, Torulopsis utilis, was first selected for this application in Germany. It is particularly well suited for the job since it can convert both 5-carbon and 6-carbon sugars, both of which are found in wood hydrolyzates, to yeast. On a dry basis, the yeast is about 50 percent protein and 5 percent fat; the yield is 45 to 50 percent of the sugars consumed. The process generally used is rapid and continuous; fermentations have been run continuously for months without objectionable contamination.

Countries that are now or soon will be facing critical population problems may find great value in such a process for the rapid production of protein from wood and pulp mill residues, especially if their existing food supply is preponderantly carbohydrate.

The remaining microbiological conversion of wood sugars yields glycerol, primarily, plus other polyhydric alcohols. From 1920 until recently, the bisulfite-steered fermentation was the basic process. The bisulfite removes acetaldehyde from further reduction, so that the reaction can proceed to yield glycerol. This process has a major disadvantage in that the large quantities of bisulfite make normal separation and recovery of the glycerol difficult. Newer methods based on ion exchange and ion exclusion now show promise of greatly

reducing this problem. A continuous fermentation process has been developed that will be economically feasible when the cost of wood sugar ready for fermentation is reduced to a competitive level.

In the past few years, fermentations with osmophylic yeasts have received much attention. These yeasts, of the genus Zygosaccharomyces, require no steering agent, and cultures have been isolated that are more specific in the polyhydric alcohol they produce. One culture, for instance, produces only the desired glycerol, a 3-carbon polyhydric alcohol. The yield may approach 45 percent, much better than in the bisulfite-steered fermentation, and recovery appears to be much less of a problem. Another culture produces only arabitol, a 5-carbon polyhydric alcohol, at a yield of over 50 percent. Erythritol, a 4-carbon alcohol, is produced by a third culture at a 22 percent yield.

Currently, only the glycerol has an established market value. The other polyols may well become valuable if the substantial quantities necessary to supply a commercial plant can be shown to be potentially available at a reasonable and attractive cost. A variety of compounds such as butanol, acetone, isopropyl alcohol, lactic acid, acetic acid, and others have also been fermented from wood sugars. Commercial adaptation is limited mainly by economics.

Hydrogenolysis constitutes the final currently studied method of utilizing wood sugar solutions. Again, the primary product is glycerol. Interest in hydrogenolysis has increased since the idea of an intermediate step of hydrogenating the glucose to its sugar alcohol, sorbitol, was added. Hydrogenolysis of the sorbitol then gives much improved yields of glycerol. As in the fermentation processes, other polyhydric alcohols also result.

A point that should not be overlooked in all these processes for the chemical conversion of glucose is the necessary degree of purity of the glucose solution. Questions that can be answered only by further research include such things as whether other residual sugars may affect a reaction or interfere with product recovery, or whether certain impurities may be toxic to the yeasts in fermentation reactions. Thus, although knowledge of the effect of impurities is needed, the removal of these impurities from the reaction scene may not be necessary.

Now, with the hemicellulose and cellulose fractions dealt with successfully, only the lignin remains. Though the technical literature on the subject has reached almost phenomenal proportions, lignin still remains, to a degree, an enigma. The mystery of lignin remains primarily because its properties depend to a great extent on the conditions under which it is separated from the other components of

wood. Characterization of properties thus is a function of preparation variables, and thousands of analyses must be performed to determine these properties as affected by various combinations of reaction times, temperatures, and so forth.

Because lignin is so complex, there are two mutually exclusive approaches to its utilization. In one, uses are developed to fit the lignin as it is isolated by various means from the other wood constituents. In the other, lignin is broken down into a variety of specific chemicals.

Almost all present uses for lignin fall in the first category, and a characteristic of most of them is that they serve more to get rid of a problem waste than to return a proportionate share of the manufacturer's profits. If lignin is to carry its weight in the chemical utilization of wood, it must be used at a higher economic level.

Present research along the first line of thinking is to design polymeric uses, such as in plastics, rubber, and resins, around the alcohol and aldehyde groups in lignin, which will provide reactive points for polymerization. These reactive points should therefore be protected in a mild separation, where lignin is the material to be conserved, and the effect of the separation on the cellulose may be ignored.

The other approach to lignin utilization involves reduction to specific chemicals, typified by the successful alkaline cleavage to produce vanillin. Since lignin is a virtual storehouse of aromatic materials built with phenyl propane units, it should be an excellent source of phenols and other cyclic compounds, either upon direct chemical breakdown or after hydrogenation. The literature is full of the chemicals that have been isolated from lignin, and they need not be described further here. Progress in the utilization of lignin, more than of any other wood constituent, depends upon much more fundamental research.

Conclusions

Although there are many possible approaches to the chemical utilization of wood, most applied research to date has been in the field of acid hydrolysis. First, an inexpensive reagent fractionates the wood carbohydrates quite effectively, and second, these hydrolyzed carbohydrates can be further converted in solution by the same chemical to such industrially promising chemical intermediates as furfural, hydroxymethylfurfural, and levulinic acid.

Other products, including nutritional yeast, ethyl alcohol, and vanillin, are now being produced commercially from the residues of wood processing--others have been shown to be feasible. Although a profitable operation could now be based on the carbohydrate fractions of wood, a truly sound operation requires that lignin be used at a higher level of return than only for its fuel value.

The benefits of a sound, expanding chemical industry based on wood to forest management would be far-reaching. Intensive management based on improvement cuttings would become self-supporting. Logging residues could be removed from the forest at a profit, with an accompanying reduction in fire hazard; and long-range species requirements could be established through the profitable chemical utilization of little-used or otherwise undesirable tree species.

The forest products industries would also benefit two fold. The waste disposal problem would be practically eliminated, and the cost of growing, harvesting, and transporting the wood to the mill would be carried proportionately by the entire wood fraction, rather than the 50 percent or so of the tree that currently ends up in product form.

Because of the extent of the world's wood resource, and the highly important fact that this resource is rather rapidly renewable, it can be predicted with confidence that wood will someday equal petroleum as a source of industrial chemicals.

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