12 September 1975, Volume 189, Number 4206 SCIENCE

Potential for Converting Wood into Plastics

Chemicals from wood may regain importance as the cost of petroleum continues to rise.

Irving S. Goldstein

Recent increases in the price of petroleum and concern about its availability at all have stimulated interest in using renewable resources in its place. This study attempts in a preliminary way to consider the use of wood including wood residues as a raw materials base for synthetic polymers. Wood is our most abundant renewable resource and has the additional advantage over annual vegetation that most of the biomass resulting from the conversion of solar energy is stored in the tree, often for scores of years, until it is harvested.

Chemicals from wood is not a new concept. The destructive distillation of wood to charcoal is an ancient art, and until recently the controlled thermal degradation of wood by pyrolysis and distillation was used as a source of chemicals. However, during this century fossil materials such as coal, oil, and natural gas have become more convenient sources of chemicals. Current economics favors petroleum, although we may eventually return to our renewable resource—wood—as the raw material of choice.

Despite the fact that most of the synthetic organic chemicals produced for use as solvents, polymers, plastics, and chemical intermediates are petroleum based, chemicals from wood, or silvichemicals as they are sometimes called, are still derived in large quantity. Table 1 lists those which are in commercial use.

Most important in this compilation is our most widely used polymer, cellulose, which is for the most part used in its natural fibrous state after extraction from the wood. However, chemically modified derivatives of cellulose such as cellulose acetate and rayon also amount to billions of pounds.

A considerable research effort has been directed for many years toward the production of greater quantities of chemicals and polymers from wood (*1, 2*). However, with the exception of periods of national emergency in several countries there have been no full-scale commercial plants operated outside of the U.S.S.R. Industrial chemicals from wood *have* found a place in the controlled economy of the U.S.S.R.

In the rest of the world the trends during the past decade until 1973 have been much stronger in the opposite direction, with the cost of petrochemicals continuing to decline while the cost of wood continued to rise. These trends led to such effects as the virtual discontinuance of research on chemical utilization of wood in the United States and the development of petrochemical based polymers for synthetic pulp, which, although useful for their inherent properties by themselves, were being talked about as replacements for cellulose on a lower cost basis.

It has now become apparent that this price trend was temporary, and that ultimately the true cost of a limited exhaustible material will become greater than that of a renewable resource. We can continue to enjoy inexpensive petroleum at a price based only on low extraction costs plus an arbitrary profit margin only as long as the supply lasts or other countries are willing to sell it to us. Eventually we will have to rely on another source of carbon for our organic materials because petroleum will have become either exhausted or so scarce that it will be too expensive.

Of the alternative carbon sources coal and wood, coal is also a finite resource and will ultimately be consumed leaving only wood as a renewable resource in perpetuity. Extraction costs and transportation costs for coal are higher than for petroleum and costs to repair and prevent environmental damage are also considerable. Just as the cost of oil has not reflected the depletion of the resource, the cost of coal has not reflected environmental damage. Chemicals from wood appear to have a better competitive chance against coal-derived chemicals than against the artificially priced petrochemicals. Research on coal chemicals has also been neglected.

The objective of this article is to provide a perspective on the suitability of wood as a chemical raw material for plastics and for production of polymers. For this purpose sufficient wood must be available, suitable processes for conversion must be on hand or developed, and the costs must not be unreasonable.

Availability of Wood

In 1974 the total U.S. production of plastics noncellulosic synthetic fibers and synthetic rubber amounted to almost 37 billion pounds or over 18 million tons. These materials are broken down by categories in Table 2, which also shows the amount of lignocellulose raw material from wood needed to produce the various synthetic polymers estimated from optimistic approximate yields of the monomers obtainable from the wood. About 95 percent of the total polymers produced are conceptually derivable from wood, although the multiple process steps required for some would militate against the exploitation of this source. The amount of lignocellulose required would be just under 60 million tons. Interestingly enough the ratio of the two major wood components, cellulose and lignin, which would be

---

The author is Professor and Head of Wood and Paper Science, School of Forest Resources, North Carolina State University, Raleigh 27607. This article was first presented at the 169th national meeting of the American Chemical Society, Philadelphia, Pennsylvania, 7 April 1975.

needed is about 2 : 1, which is the same as their natural abundance in the wood.

In 1974 the estimated total wood pulp production in the United States was just under 50 million tons; this amount required about 100 million tons of wood at 50 percent yield. The wood needed for chemical conversion to polymers, therefore, would amount to 60 percent of that now being used for pulp.

Although wood for pulping must meet certain requirements such as species suitability for pulping, fiber length, and fiber morphology, wood destined for chemical utilization need not. Consequently, large quantities of wood unsuitable for pulping or conversion into solid wood products would be suitable for chemical processing. The demand for wood for chemicals would be modest compared to other wood uses and could be filled from sources not suitable for other uses.

In 1970 wood residues at primary manufacturing plants amounted to 15 million tons and logging residues to about 50 million tons (*3, 4*). Supplies of hardwood timber are increasing although material suitable for high quality uses is limited. Fortunately, chemical conversion can utilize the small tree sizes and the species for which other markets are limited. In 1970 there was an excess of 70 million tons of net annual growth over removal of hardwoods (*4*).

A further source of wood for the production of chemicals could result from the clearing of cutover land now containing only cull trees in connection with reforestation with the supertrees now being developed by genetic improvement. Considering only poor sites now containing hardwoods which would be more productive in pine, a conservative estimate for the Southern states alone would be 1250 million tons obtainable as a by-product of improved land management. Furthermore, the potential utilization of this "green junk" as it is alluded to by many foresters, could be the deciding factor in bringing about the use of the land for productive, managed forests that would meet our increasing needs for high-quality wood for lumber, plywood, and pulp.

An analogous situation applies in the Southwest where woody shrubs such as mesquite have invaded almost 100 million acres and compete with grass for scarce moisture. Removal of the mesquite, helped by a credit for its chemical utilization, would increase grazing capacity and have a positive effect on meat supplies.

It is obvious from these considerations that the wood needed for meeting our polymer needs should not seriously disrupt other demands on the forest resource for lumber, plywood, woodpulp, and the like; it could even increase the availability of these other products by supplying capital to hasten improved forest management.

Table 1. Silvichemicals of commerce (*18*).

Cellulose
Cellulose esters
Cellulose ethers
Rayons
Wood rosin
Turpentine
Pine oil
Tall oil
Tall oil rosin
Tall oil fatty acids
Dimethyl sulfide
Dimethyl sulfoxide
Kraft lignin
Lignin sulfonates
Ethyl alcohol
Vanillin
Yeast
Charcoal
Bark products
Hemicellulose extracts

Technical Feasibility

A common problem in elementary organic chemistry courses begins as follows: "Starting with coal, air and water synthesize the following. . . ." In a qualitative sense, therefore, wood as a source of carbon can be used to synthesize any organic material known to man. The technical processes discussed in this section are principally restricted, however, to those that retain to some degree the synthetic work already performed by the tree in converting carbon dioxide to more complicated molecules. Reversion of the wood to carbon monoxide or carbon dioxide would offer no advantage over the use of coal.

Wood is a mixture of three natural polymers—cellulose, lignin, and hemicelluloses—in an approximate abundance of 50 : 25 : 25, depending on species and other biological variation such as genetic differences within species and growing conditions. Cellulose and hemicelluloses are carbohydrate polymers that are built up from molecules of simple sugars. Cellulose is a long-chain polymer of glucose and differs from starch, which is also a glucose polymer, only in the way the glucose molecules are arranged. Hemicelluloses are shorter or branched polymers of five-carbon sugars (pentoses), such as xylose, or six-carbon sugars (hexoses) other than glucose. Lignin is a three-dimensional polymer formed from phenylpropane units which have grown into a complicated random large molecule with many different kinds of linkages between the building blocks.

In the production of wood pulp, the lignin, which acts as a cement between the cellulose fibers and as a stiffening agent within the fibers, is dissolved away by various chemical processes leaving the cellulose together with some remaining hemicelluloses behind in fibrous form. Some hemicelluloses are lost in the process because of their lower molecular weight and greater solubility.

Conversion to Gas or Liquid Feedstocks

Wood can be converted in very high yield to synthesis gas (carbon monoxide + hydrogen) by heating at temperatures up to 1000°C (*5*). This product can be readily converted to methanol. Small quantities of by-products useful in polymer synthesis are also generated. For example, from 3300 tons of wood per day the following are obtainable: ethylene, 172 tons; acetylene, 25 tons; propylene, 17 tons; benzene, 60 tons; and toluene, 9 tons. At these low yields about 150 million tons of wood would be needed each year to meet our ethylene needs for polymers alone.

Somewhat higher yields of unsaturated hydrocarbons in wood gasification have been reported when an electric arc at a temperature of 2000° to 2500°C is used. Acetylene has been obtained in yields of up to 15 percent (*6*), which would still require an excessively large wood supply.

Recent research at the U.S. Bureau of Mines (*7*) has successfully converted wood into oil that can be used as a liquid boiler fuel. Wood or other organic materials are reacted with carbon monoxide and water at 350° to 400°C at a pressure of 4000 pounds per square inch in the presence of various catalysts. Oil yields of 40 to 50 percent have been obtained. A pilot plant is under construction at Albany, Oregon.

This wood-to-oil process has implications for polymer synthesis in that the oil produced might be further converted to monomers in the same way that petroleum is processed. Since the oil still contains as much as 8 percent residual oxygen, conventional hydrocracking processes might not be effective because of the poisoning of catalysts by the water generated.

Conversion to Monomers for Conventional Polymers or Plastics

Of the 18 million tons of synthetic polymers listed in Table 2, 95 percent are derivable from ethylene (47 percent), butadiene (12 percent), and phenol (36 percent). These building blocks are all obtainable from wood. Ethylene and butadiene can be made from ethanol, which in turn can be made by fermentation of glucose, the hydrolysis product of cellulose.

$$\text{Cellulose} \xrightarrow{\text{hydrolysis}} \text{glucose} \xrightarrow{\text{fermentation}} \text{ethanol} \longrightarrow \text{butadiene or ethylene}$$

Phenol and related compounds are obtainable from the hydrogenation or hydrogenolysis of lignin.

Lignin ⟶ phenols ⟶ phenolic resins, polyesters, and other aromatics

Wood hydrolysis, the conversion of the carbohydrate polymers in wood to simple sugars by chemical reaction with water in the presence of acid catalysts, has been known for 150 years and has been practiced on a commercial scale in this country during World War I, in Germany during World War II, and is still in use in the U.S.S.R. The simple hydrolytic cleavage to sugars is complicated in the case of cellulose by its crystalline organization, which restricts the accessibility of the dilute acid to the bonds to be hydrolyzed. This resistance to hydrolysis requires the use of temperatures and acid concentrations which cause decomposition of the resulting sugars. Processes must balance rate of hydrolysis against rate of decomposition of the desired products (*1, 8, 9*). Glucose yields of approximately 50 percent of the weight of the cellulose have been attained.

Increasing this yield by rendering the cellulose more accessible to the hydrolyzing reagent would provide great economic benefits and warrants a high level of technical activity. The nature of the lignin residue is affected by the catalyst used and by the operating temperatures in the hydrolysis. It would be desirable to end up with the most reactive lignin possible to allow its facile conversion to other useful products. The Udic-Rheinau process (*8*) utilizing strong hydrochloric acid as the catalyst does provide such a reactive lignin.

Conversion of cellulose to glucose by enzymatic hydrolysis using an enzyme from *Trichoderma viride* has received much attention at the U.S. Army Natick Laboratory. However, lignocellulose is resistant to the enzymes unless very finely ground or partially delignified. Other microbiological conversions of wood to useful chemicals are entirely possible, but have not advanced beyond the preliminary research stage.

Fermentation of the glucose solutions to ethanol is readily accomplished in yields of 85 to 95 percent by means of commercially proven techniques. The further conversion of ethanol to ethylene in 96 percent yield and to butadiene in 70 percent yield is also straightforward and was practiced on a commercial scale in the United States during World War II in plants that require much lower capital costs than those based on hydrocarbon conversion (*10*).

Phenolic products have been obtained from the lignin component of wood by various hydrogenation and hydrogenolysis techniques. Yields of 25 to 35 percent of monomeric phenols have been reported (*11, 12*) in pilot plant experiments, but verification on a commercial scale has not been attempted because of hitherto unfavorable economic comparisons with phenol production from petroleum.

Polymers and Plastics from Macromolecules Present in Wood

The components of wood are already high polymers and can be utilized in that form without degradation to simple compounds and repolymerization. Most notable is the use of cellulose to the extent of almost 50 million tons per year, a quantity greater than the total of all synthetic polymers combined.

Cellulose derivatives such as rayon and cellophane (both regenerated celluloses), cellulose acetate, carboxymethylcellulose, and cellulose butyrate are important materials and could become even more important compared to completely synthetic materials as economic conditions change. Polymeric materials are marketed on the basis of cost and performance. The properties of cellulose derivatives may be modified and new derivatives developed—for example, by graft polymerization—to meet performance criteria at competitive costs. These shifts would probably occur in response to normal market influences.

The lignin component of wood may also be modified, esterified, etherified and condensed to change its physical properties. Furthermore, a relatively neglected major component of bark, polyphenolic acids, may be extracted in high yields and can be used in the preparation of resins, adhesives, and binders. Meeting adhesive and resin needs from this source would reduce the requirements for phenol.

New wood-based intermediates. The hemicellulose component of wood is much more readily hydrolyzed to simple sugars (pentoses) than the cellulose is to glucose. Prehydrolysis of the wood with a dilute acidic solution provides an aqueous xylose solution which can be further converted to furfural in 75 percent yield (*13*). Furfural can serve as a raw material for resins and adhesives and as an intermediate for the production of chemicals useful in making condensation polymers such as nylon. Furfural is now produced

Table 2. 1974 production of plastics, synthetic fibers, and rubber (*19*) and estimated lignocellulose raw material base required.

Material	Production (10^3 tons)	Lignocellulose required* (10^3 tons)
Plastics		
Thermosetting resins		
Epoxies	125	355 (L)
Polyesters	455	1,220 (L)
Urea	420	
Melamine	80	
Phenolic and other tar-acid resins	670	1,915 (L)
Thermoplastic resins		
Polyamide	100	285 (L)
Polyethylene		
Low density	2,985	11,940 (C)
High density	1,420	5,680 (C)
Polypropylene and copolymers	1,125	4,500 (C)
Styrene and copolymers	2,505	7,445 (L)
Polyvinyl chloride	2,425	4,225 (C)
Other vinyl resins	175	440 (C)
Total plastics	12,485	
Synthetic fibers		
Cellulosic		
Rayon	410	
Acetate	190	
Synthetic fibers (cont'd.)		
Noncellulosic		
Nylon	1,065	3,045 (L)
Acrylic	320	640 (C)
Polyester	1,500	4,020 (L)
Olefin	230	920 (C)
Total noncellulosic fibers	3,115	
Synthetic rubber		
Styrene-butadiene	1,615	5,700 (C), 1,920 (L)
Butyl	180	1,060 (C)
Nitrile	95	190 (C)
Polybutadiene	360	2,120 (C)
Polyisoprene	100	
Ethylene-propylene	140	825 (C)
Neoprene and others	280	
Total synthetic rubber	2,770	
Total plastics, noncellulosic fibers, and rubber	18,370	
Obtainable from lignocellulose	17,490	58,445
Cellulose derived (C)		38,240 (C)
Lignin derived (L)		20,205 (L)

*Estimated from optimistic approximate yields of monomers obtainable. (C) Cellulose derived; (L) lignin derived.

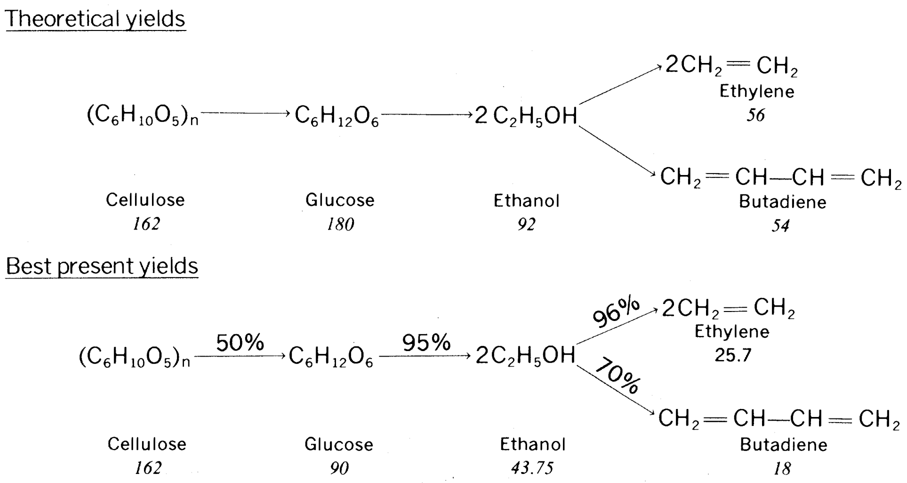

Fig. 1. Conversion of cellulose to ethanol, ethylene, and butadiene. The numbers in italics refer to molecular weights in the case of theoretical yields, and actual weights for best present yields. The same applies to Fig. 2.

from corncobs and bagasse, but would be available in much greater yield from an integrated large-scale wood hydrolysis plant.

The glucose obtained from hydrolysis of cellulose instead of being fermented into ethanol can be converted into 5-hydroxy-2-furaldehyde which in turn is readily converted to levulinic acid (*14*). This material could well serve as an intermediate for a new family of polymers. Levulinic acid primarily for processing into diphenolic acid was produced commercially for a time in the 1960's, but the loss of the diphenolic acid outlet caused the venture to be abandoned.

New lignin-based intermediates. More complex molecules than simple phenols may be obtained from lignin by less drastic treatments than hydrogenation. For example, hydrolysis of alkali lignins under neutral conditions gives yields of up to 25 percent of material with catechol (dihydroxyphenol) reactivity (*15*). These compounds could find useful applications in various resins. Other treatments of lignin might provide fragments with reactivity which would use even more of the lignin molecule.

Economic Opportunity

The preceding discussion on technical feasibility has indicated several areas where it would be highly profitable to devote further technical effort. The following seem especially important:

1) Conversion of viscous oxygen-containing oils from wood liquefaction into useful monomers.

2) Increasing the accessibility of crystalline cellulose to hydrolytic reagents to allow higher yields in wood hydrolysis.

3) Developing processes for the conversion of reactive lignins from wood hydrolysis to low-molecular-weight phenolic materials useful for polymer synthesis.

Chemical utilization of wood has progressed conceptually to a remarkable degree considering the relatively small research effort which has been devoted to it in comparison with the effort expended on petrochemicals during the past 50 years. An increase in the scale of wood research could be expected to provide commensurate further progress.

It is not possible with the data now available to provide a permanent and complete economic analysis of the relative costs of producing synthetic polymers from a wood and a petroleum base. Such calculations are also made difficult by the current flux in the costs of petroleum, other fuels, wood, plants, and capital. There is also the problem of internal accounting in which the internal transfer price of feedstocks affects petrochemical prices, and this is greatly influenced by the demand for and supply of gasoline and heating oil as well as by crude oil costs.

The published cost data cited below are now obsolete, but they are presented as points of reference to which escalation factors can be applied. Data for raw material costs alone are provided for ethylene, ethanol, butadiene, and furfural.

Wood costs. Exact figures for wood costs are difficult to assign. The cost of wood at the mill can vary from a negative cost for unusable residues which must be disposed of to as much as $40 per ton for quality hardwood sawlogs. Chipped wood can vary from $15 per dry ton from a total tree chipping operation to $25 per dry ton for bark-free pulp chips. For the purpose of this study a value of $20 per dry ton is assumed for wood suitable as a raw material for chemical conversion. With petroleum at $12 per barrel, wood has an equivalent value as fuel of about $20 per ton or 1 cent per pound compared to 3.8 cents per pound for the petroleum.

The cost of wood for producing a specific chemical also depends on the yield obtainable. Given the raw material at 1 cent per pound, a hydrolysis plant producing only glucose in 50 percent yield on cellulose would have a wood cost of 4 cents per pound of glucose (50 percent cellulose × 50 percent yield). However, if the plant were integrated to utilize the lignin and hemicellulose components as well, the wood cost per pound of glucose would be only 2 cents a pound. It is obvious that such integrated plants would be mandatory for a successful chemicals from wood scheme.

Gasification and liquefaction processes. Preliminary calculations provided in the 1971 report (*5*) concluded that the production of synthesis gas with some attendant yield of chemicals from lignocellulosic residues would require a raw material supply at a cost of only $2 to $5 per ton. The low yield of chemicals from this process plus the low likelihood of availability of the large tonnages of waste wood at such a low cost make it appear unpromising. The authors also estimated that acetylene production from wood (*6*) would not be economical because of the high temperatures and high voltage electrical energy required.

Perhaps the most complete cost figures obtainable for a wood conversion process are those developed for the Bureau of Mines liquefaction process (*7*). The operating costs for a 3000 ton per day wood waste plant with a capital investment of $51,000,000 (1973) would be $7.24 per barrel of liquid fuel produced at 50 percent yield. If the wood waste were free, this would be the entire cost of the product. If the wood cost were $20 per ton, the cost per barrel would increase to $15.64 [$8.40 wood cost for a 420-pound barrel (42 gallons at a density of 1.20) at 50 percent yield]. This range of $7 to $15 per barrel is certainly comparable to the present $11 to $12 price for some imported petroleum. The conversion of this liquid oil from wood to chemicals useful for synthetic polymers has not been studied, but at $15.64 a barrel or 3.9 cents per pound this synthetic oil with a density of 1.20 would cost the same for a raw material as crude oil with a density of 0.88 at $12 a barrel. High chemical yields (about 40 percent) would be needed to avoid excessive wood demands.

Ethanol, ethylene, and butadiene. Figure 1 summarizes the process steps and yields in these transformations. The first step in the production of ethanol from wood is the hydrolysis of cellulose to glucose. Hydration of the cellulose yields 180 pounds of glucose for each 162 pounds of cellulose hydrolyzed. If the glucose yield is 50 percent and the cellulose component of the wood costs 1 cent a pound, assuming utilization of the lignin and hemicellulose wood components, the material cost for glucose production would be 1.8 cents a pound. If the wood cellulose could be completely hydrolyzed to glucose in 100 percent yield, the material cost would be 0.9 cent a pound. Gross production costs for hydrolysis of waste to sugars were estimated in 1971 (*16*) at 1.65 to 2.08 cents a pound giving a total glucose cost of 2.55 to 4 cents a pound, depending on yield.

The hydrolyzate sugars in solution may then be converted to ethanol by fermentation. The cost of this fermentation is difficult to estimate since no large fermentation plants have been constructed recently in this country for the production of ethanol. Yields of 95 percent are obtainable. Fermentation costs of 1.35 cents a pound were suggested in 1973 for a 250-ton-a-day plant (*16*), and could be as low as 1 cent a pound in a large installation. The cost of ethanol from glucose (87.5 pounds from 180 pounds at 95 percent yield) would then be 6.25 to 9.25 cents a pound or 41 to 61 cents per gallon. Material costs alone would be 3.7 cents per pound or 25 cents per gallon at 50 percent yield of glucose. The current market price for ethanol from petrochemicals is $1 per gallon for 95 percent (190 proof) alcohol.

The conversion of ethanol to ethylene in 96 percent yield has been performed commercially in this country, but not for the past 20 years. The plants have been dismantled and attempts to locate production cost data from old files have been unsuccessful. Since the process is simple, a production cost of 1 cent per pound might be assumed for the sake of argument. The cost of ethylene from ethanol (27 pounds from 46 pounds at 96 percent yield) would then be 11.7 to 16.8 cents per pound, depending ultimately on yield and production costs for glucose production from cellulose. Material costs alone would be 6.3 cents per pound at 50 percent glucose yield and 4.2 cents per pound at 75 percent glucose yield. The current published market price for ethylene is 9 to 11 cents per pound.

The conversion of ethanol to butadiene in 70 percent yield has also been performed commercially in this country, again not for over 20 years. In this case also, the plants have been dismantled and production costs have not been located. The process is reputed to require lower capital costs than other butadiene syntheses. Here we might assume a production cost of 2 cents per pound since two steps are required. The cost of butadiene from ethanol (37.8 pounds from 92 pounds at 70 percent yield) would then be 18.5 cents to 24.5 cents per pound, depending again on the cost of glucose. Material costs alone would be 9 cents per pound at 50 percent glucose yield and 6 cents per pound at 75 percent glucose yield. The current published market price for butadiene is 18 to 22 cents per pound.

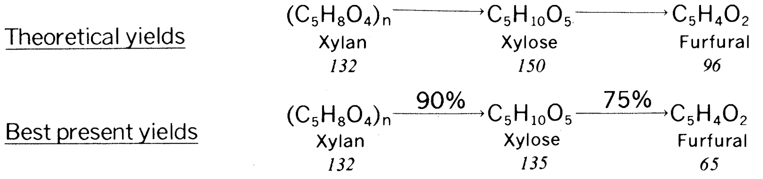

Fig. 2. Conversion of xylan to furfural.

These crude cost estimates indicate that the cost of ethanol, ethylene, and butadiene from wood might come within striking distance of the cost of these materials from petroleum. A more rapid increase in petroleum costs over wood costs might bring about a truly competitive situation or even a change in the raw material of choice.

Recent projections of the cost of ethylene and ethanol (*17*) based on naphtha reaching $124 to $136 per metric ton by 1977 place ethylene at 14 to 16 cents per pound and ethanol at $1.00 to $1.33 per gallon in 1977.

Phenols and furfural. At the time that pilot plant studies were being carried out on the production of phenols by hydrogenation of lignin in 1966 (*11*), cost estimates indicated that a $6,000,000 plant could produce about 100,000,000 pounds of phenolic materials a year at a price of 9 cents a pound for phenol and 6 cents a pound for cresylic acids. Since synthetic phenol was then available at 7 cents a pound, a commercial plant was not built.

Today phenol has become both expensive and scarce. The published price is 27 to 33 cents per pound. Wood costs and plant costs have not risen that rapidly, and thus it appears that now a plant to produce phenols from lignin could be very profitable. Catechols can also be obtained from lignin (*15*) at a much lower cost than by synthetic methods starting with benzene.

When furfural was 11 cents per pound in 1961, a cost estimate for the production of furfural from xylose solutions from the hydrolysis of wood indicated a break-even price of 8.7 cents per pound (*13*). Now that the market price for furfural is 37 cents per pound, the economics for furfural production from wood in an integrated plant would be even more favorable. In the 1961 study the cost of xylose in solution was estimated at 2.3 cents a pound. In an integrated plant in which all the wood was used, the raw material cost per pound of furfural would be only 2 cents per pound.

Enzymatic processes. An alternative method of producing glucose is the enzymatic hydrolysis with cellulase. Economic analysis of the U.S. Army Natick Laboratory two-step process involving the culture of *Trichoderma viride*, followed by application of an enzyme-containing filtrate to the substrate, indicated a production cost of 5.3 cents per pound (*16*), somewhat higher than the acid hydrolysis cost estimates. Moreover, cellulose with a high lignin content is resistant to enzymatic hydrolysis, so wood would have to be partially delignified or finely ground to undergo hydrolysis by enzymes, adding additional processing costs.

Summary

The conversion of wood into chemicals for the production of most of our synthetic plastics, fibers, and rubbers is technically feasible. With refinements in technology a large integrated plant utilizing all components of the wood for production of ethanol (to be further processed to ethylene and butadiene), phenols and furfural would be approaching economic feasibility as well at current petrochemical prices. If crude oil prices continue to climb at a faster rate than wood costs, the economic feasibility of chemicals for polymers from wood would become certain.

Although technical feasibility has not been established, synthetic oils from liquefaction of wood might serve as feedstocks for cracking to chemicals in the same way that crude oil is presently used.

The fulfillment of all our polymer needs from wood as a raw material should not place an impossible burden on our wood supply, but might actually improve the availability of wood for lumber, plywood and pulp by providing a use for less valuable wood which would allow reforestation and improved forest management.

References and Notes

1. J. A. Hall, J. F. Saeman, J. F. Harris, *Unasylva* **10** (1), 7 (1956); J. F. Harris, J. F. Saeman, E. G. Locke, in *The Chemistry of Wood*, B. L. Browning, Ed. (Interscience, New York, 1963), pp. 535–585.
2. N. I. Nikitin, *The Chemistry of Cellulose and Wood*, J. Schmorak, Tranl. (Israel Program for Scientific Translations, Jerusalem, 1966), pp. 560–567; A. Rieche, *Grundriss der Technischen Organ-*

ischen Chemie (Hirzel Verlag, Leipzig, 1965), pp. 261–301; A. J. Stamm and E. E. Harris, *Chemical Processing of Wood* (Chemical Publishing, New York, 1953), pp. 392–577; H. F. J. Wenzl, *The Chemical Technology of Wood* (Academic Press, New York, 1970), pp. 157–300.

3. J. B. Grantham, E. M. Estep, J. M. Pierovich, H. Tarkow, T. C. Adams, "Energy and raw material potentials of wood residue in the Pacific Coast States," *U.S.D.A. Forest Service General Technical Report PNW-18* (Portland, Ore., 1974).
4. U.S. Department of Agriculture Forest Service, "The outlook for timber in the United States," *Forest Resource Report No. 20* (U.S.D.A. Forest Service, Washington, D.C., 1973).
5. S. Prahacs, H. G. Barclay, S. P. Bhatia, *Pulp Pap. Mag. Can.* **72**, T199 (1971).
6. D. W. Goheen and J. T. Henderson, "Formation of unsaturated hydrocarbons in the pyrolysis of lignocellulose materials," International Wood Chemistry Symposium, Seattle, Wash., September 1969.
7. H. R. Appell, Y. C. Fu, S. Friedman, P. M. Yavorsky, I. Wender, "Converting organic wastes to oil: A replenishable energy source," *Bureau of Mines Report of Investigations 7560* (U.S. Department of the Interior, Washington, D.C., 1971); I. Wender, F. W. Steffgen, P. W. Yavorsky, in *Recycling and Disposal of Solid Wastes*, T. F. Yen, Ed. (Ann Arbor Science Publishers, Ann Arbor, Mich., 1974), pp. 43–99.
8. E. G. Locke and E. Garnum, *For. Prod. J.* **11**, 380 (1961).
9. R. A. Lloyd and J. F. Harris, "Wood hydrolysis for sugar production," *U.S.D.A. Forest Service Research Report No. 2029* (U.S.D.A. Forest Service, Forest Products Lab., Madison, Wis., 1963); A. J. Wiley, J. F. Harris, J. F. Saeman, E. G. Locke, *Ind. Eng. Chem.* **47**, 1397 (1955); M. Oshima, *Wood Chemistry Process Engineering Aspects* (Noyes Development Corp., Pearl River, N.Y., 1965).
10. W. L. Faith, D. B. Keyes, R. L. Clark, *Industrial Chemicals* (Wiley, New York, ed. 3, 1965).
11. D. W. Goheen, in *Lignin Structure and Reactions*, J. Marton, Ed. (American Chemical Society, Washington, D.C., 1966), pp. 205–225.
12. ———, in *Lignins*, K. V. Sarkanen and C. H. Ludwig, Eds. (Wiley, New York, 1971), pp. 797–831; K. C. Hellwig, S. B. Alpert, C. A. Johnson, S. C. Schuman, "Production of phenols from lignin," presented at Technical Association of the Pulp and Paper Industry annual meeting, New York, 1969.
13. J. F. Harris and J. M. Smuk, *For. Prod. J.* **11**, 303 (1961).
14. S. W. McKibbins, J. F. Harris, J. F. Saeman, W. K. Neill, *ibid.* **12**, 17 (1962).
15. J. D. Benigni and I. S. Goldstein, *J. Polym. Sci. Pt. C* **36**, 467 (1971).
16. International Research and Technology Corporation, *U.S. Environmental Protection Agency Report No. EPA 670/2-73-056* (International Research and Technology Corp., Cincinnati, Ohio, 1973), pp. 139, 144–145.
17. Anon., *Chem. Eng. News*, 9 December 1974, pp. 8–9.
18. D. W. Goheen, *American Institute of Chemical Engineers (AICHE) Symp.* **69**, 20 (1972).
19. Anon., *Chem. Eng. News*, 2 June 1975, pp. 31–34.
20. This material was prepared with the support of the National Science Foundation, Research Applied to National Needs program.

Solar Energy Conversion by Water Photodissociation

Transition metal complexes can provide low-energy cyclic systems for catalytic photodissociation of water.

V. Balzani, L. Moggi, M. F. Manfrin,
F. Bolletta, M. Gleria

There are two fundamental ways for converting solar energy into useful energy: (i) thermal conversion, in which the solar radiation is degradated to heat in the absorbing system, and (ii) quantum conversion, in which the solar radiation is used to cause some kind of photochemical or photoelectric process in the absorbing system. In this article, we discuss some aspects of the photochemical conversion of solar energy by simple, nonbiological systems.

Any endothermic photochemical reaction represents a conversion of light energy into chemical energy. A kinetically stable photoproduct must be considered as a "fuel" since it can be stored, transported, and then converted to other chemical species with evolution of energy. Therefore, direct conversion of solar radiation into chemical energy is, in principle, a very useful conversion mode since it remedies the major defects of solar energy, namely its low density and intermittency.

In looking for a photochemical process to be used as a solar energy conversion system, some obvious restrictions must be taken into consideration: (i) the solar radiation that reaches the surface of the earth has a defined wavelength distribution (see Fig. 1); (ii) the infrared radiation is not useful for generating photochemical reactions since it cannot cause electronic excitation; (iii) the ecological equilibrium of our planet must not be perturbed; and (iv) the system to be used must be as economical as possible. Taking these restrictions into account, we can state eight requirements for systems to be used for the photochemical conversion of solar energy. These requirements, which have been discussed in detail elsewhere (*1*), are as follows:

1) The electronic absorption spectrum of the system must overlap the emission spectrum of the sun.

2) Upon absorption of solar radiation, the system must be able to undergo an endothermic photoreaction.

3) The endothermic photoreaction must be followed by other (thermal or photochemical) reactions which must lead the system to its original state (in other words, the process must be a closed cycle).

4) The quantum yield of the endothermic photoreaction must be as high as possible.

5) At least one of the exothermic reactions involved in the cycle must take place under controlled conditions (useful reaction).

6) The useful reaction should return as large a portion as possible of the solar energy absorbed.

7) The reactants of the useful reaction should be suitable for storage and transportation.

8) The system must be as economical as possible.

Each photochemical system involving the splitting of water and then the recombination of gaseous (g) molecular hydrogen and oxygen

$$H_2(g) + {}^1\!/_2O_2(g) \longrightarrow H_2O(g) + 58\ \text{kcal} \quad (1)$$

satisfies requirements 5, 6, and 7 (*2–4*). However, as we will see later, the direct photodissociation of water cannot take place with solar radiation since water does not satisfy the first requirement.

We will try to show that this basic difficulty can be theoretically overcome by using properly devised systems in which transition metal complexes are used as "catalysts." At the same time, our discussion will provide an example of the type of approach that should be used in dealing with the problem of the photochemical conversion of solar energy by nonbiological systems (*5*).

V. Balzani is professor of photochemistry and L. Moggi, M. F. Manfrin, and F. Bolletta are assistant professors in the "G. Ciamician" Chemical Institute, University of Bologna, Bologna, Italy. M. Gleria is researcher in the Laboratorio di Fotochimica e Radiazioni d'Alta Energia (Bologna) of the National Research Council of Italy. This article is adapted from a talk presented by Dr. Balzani at the workshop "The current state of knowledge concerning photochemical formation of fuel" sponsored by the National Science Foundation, Research Applied to National Needs program, and held in Boston, Massachusetts, on 23 and 24 September 1974.