Renewable Resources for the Production of Fuels and Chemicals

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In the future, mankind will make greater demands on renewable resources to satisfy needs for energy and carbon-based chemicals. This situation was envisaged as early as 1949 by Glesinger in his well-known book *The Coming of Age of Wood* (*1*). It can be readily demonstrated that the renewable biomass on our planet is quantitatively sufficient to supply the needs of the current world population. It can also be shown that we possess the needed chemical technology for the production from biomass of many of the commodities that we now produce from fossil fuels, such as fuel oil, gasoline, and synthetic polymers.

The scenario of total depletion of fossil fuel resources is an intriguing concept but not a useful one at the present time. However, there is a need for reducing the annual consumption of oil and natural gas, and eventually that of coal. This reduction may be accomplished in a number of ways; the substitution of renewable resources for oil and natural gas as a source of energy and chemicals is one.

Table 1 is a comparison of the use of our dominant renewable resource, wood, with that of fossil fuels (oil, natural gas, and coal). The energy generation from wood includes that recovered from the waste of pulp mills. In terms of thermal units, it amounts to 1.1 quads (1 quad = 10^{15} Btu) (*2*). Compared with the total energy consumption in the United States, 68 quads in 1970, this is a rather small figure, but it exceeds that for nuclear energy (0.7 quad in 1974).

The total volume of wood products, 237 million metric tons, exceeds that of all synthetic polymers by 13-fold. Wood is the most extensively utilized raw material in the United States, also surpassing in volume all metals combined or the production of concrete. The energy requirements for its processing are low. It has been estimated (*3*) that the energy required to produce 1 ton of lumber in a conventional sawmill is 430 kwh, which may be compared with 2700 kwh for 1 ton of steel and 17,000 kwh for 1 ton of aluminum. The conversion of wood to paper products currently requires energy generated by fossil fuels. In the case of paperboard this amounts to 0.75 pound (1 pound = 0.45 kilogram) of fuel oil per pound of product. This compares favorably with the approximately 2 pounds of fuel required to produce 1 pound of synthetic polymer. Furthermore, current developments in the pulp industry suggest that the pulping and pulp bleaching operations can be made independent of outside energy sources by improving the conservation of energy in the process (*4*) and by better recovery of energy from the waste products.

It is thus obvious that extensive use is already being made of renewable resources, and the processing, in general, is not energy-intensive. It is consequently of great interest to investigate whether the utilization of renewable materials could be further expanded in order to conserve petroleum and natural gas. This could be done either by increasing the generation of energy from renewable resources or by the production, using renewable materials as feedstocks, of synthetic polymers. The potential of the second alternative is somewhat limited. Even complete replacement of synthetic polymers would save only 6 percent of the total consumption of oil and natural gas. Furthermore, two-thirds of this amount consists of processing energy that is replaceable by energy generated from coal. The realizable saving in feedstocks is thus limited to only 2 percent of the total volume of petroleum and natural gas.

Sources of Renewable Resources for Energy Generation

Vegetation biomass, including wood, has certain advantageous properties as fuel. The sulfur content is negligible (< 0.1 percent) in comparison with that of coal. Likewise, the ash content is reasonably low, and the recovered ash may be used as fertilizer. On a dry weight basis, the Btu values of wood range from 8000 to 9000 in comparison with 18,000 for No. 6 fuel oil, 13,500 for bituminous coal, and 18,500 for natural gas. However, in contrast to fossil fuels, freshly cut wood has a high moisture content (40 to 150 percent on a dry weight basis), which reduces the heat value by as much as 20 percent. Thus, the net heat value of freshly cut wood is usually of the order 2500 to 3500 Btu per pound. Similar heat values are valid for agricultural residues as well.

Szego and Kemp (*5*) have proposed the establishment of special energy plantations to grow wood for the sole purpose of fueling large power plants. They estimated that it may be possible to convert, on perpetual basis, sufficient biomass from 370 square miles (1 mile = 1.6 kilometers) to fuel a 100-megawatt steam-electric plant. It has been pointed out (*2*) that, with the present growth rates, 2000 square miles would be a more realistic estimate for the required forest area. Apart from economic considerations, energy plantations would require enormous areas of land for any significant addition to energy supplies.

The concept of harvesting forest for the sole purpose of energy generation on a continuing basis may not be a realistic one in the United States, but it is worth exploring in the tropical countries where biomass production is more rapid and unused forest areas are still available. On a temporary basis, the principle could be applied for the rehabilitation of commercially unimportant hardwood forests to productive softwoods. Such areas exist both in northeastern and southern parts of the United States. Very recently, the energy potential of aquacultures based on kelps and other algae has been brought into consideration. No competing uses exist for these areas which are located in the continental shelf regions, and the harvesting costs are reasonable. After extraction of commercially important components, such as alginic acid or carrageenan, the remaining biomass could be used for the production of methane by anaerobic fermentation.

Of more immediate interest from the point of view of energy generation are the currently available organic waste products. The potential of obtaining energy from these wastes has been the subject of lively discussion, particularly by Reed (*6*). The estimated amounts are shown in Table 2. It should be stressed that the magnitudes given in this table represent coarse estimates only. Some of the values refer to total amounts produced; others to amounts considered to be collectible in practice. The latter is the case for logging residues. The actual amount of biomass consisting of branches, foliage, and stumps must be much larger than 50 million metric tons—

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Table 1. Comparison between renewable resources and fossil fuels in the production of energy and chemicals.

Production	Amounts used or produced (million metric tons)	
	Wood	Fossil fuels
Consumption for energy (*2*)	63	1800
Synthetic polymers and chemicals	2	18
Lumber and plywood production	~175	
Paper products	60	

perhaps as much as 180 million metric tons.

The total amount of available residues may be 1 billion tons (*7*), equivalent in fuel value to approximately 15 percent of the total energy needs in the United States. Prime consideration should be given to residues that are already collected, such as urban waste, manufacturing residues from wood, and cattle manure. Currently, these residues require disposal, an operation that usually costs approximately $5 per dry ton. The elimination of the disposal cost represents an economic advantage for the energy generation from these fuels. It is consequently understandable that the energy potential of urban waste has generated a great deal of interest and research (*8*). The logging residues are usually disposed of by burning (slash burning), while the agricultural residues are plowed under in the fields. Both of these disposal operations add to the fertilizer pool of the land. The realization of energy generation from these residues would require collection and transportation, a costly operation, especially in the case of logging residues (> $20 per dry ton). Grantham (*2*) has consequently suggested that the collection of forest residues for energy can only be economically justified if sufficient amounts of high-value raw material for the forest products industry can be salvaged from this waste. As far as agricultural residues are concerned, collection and transportation costs have not been estimated, but are likely to be a great deal less than in the case of forest residues. In view of the large mass of these wastes, more than 350 million metric tons annually, the energy potential of agricultural residues would look particularly attractive except for the problems caused by seasonal availability. It is not known how feasible and how costly it would be to store these residues. Under any circumstances, it appears that the use of agricultural residues should be integrated with that of continuously available fuels.

Forms of Energy Generation from Renewable Resources

After the suggestion by Reed (*6*), renewable materials can be divided into dry biomass, with moisture content of 50 percent or less, and wet biomass, in which the difficulty of removing excess water makes its use as solid fuel impracticable. Sewage and cattle manure belong to the latter category.

The options for generating energy from dry biomass are outlined schematically in Fig. 1. Conversion of waste materials to solid fuels is generally possible by relatively simple means; the intrinsic calorific value is recovered in combustion, reduced only by the amount required for the evaporation of water, ash is utilizable as fertilizer, and the gaseous emissions are essentially free of sulfur dioxide and other pollutants such as mercury. On the other hand, this form of energy generation requires costly boiler installations, and particulate emissions are sometimes a problem. Conversion of biowastes to gaseous or liquid fuels improves their versatility, storage, and transportation, but there is a net loss of intrinsic energy value associated with the conversion. This energy loss is particularly high in the conversion of wood waste to fuel oil (*9*), resulting in the retainment of only one-third of the original calorific value in the product.

Should renewable resources be converted to liquid fuels, such as fuel oil or methanol? The decision of the city of Seattle, Washington, to build a methanol plant based on municipal waste (*8*) has often been cited as a pioneering example in this direction. What is not realized is that the decision was based on two circumstances of strictly local nature: (i) lack of market for solid fuel and (ii) lack of market for low Btu gas. Thus, it can be concluded that, while the production of methanol from municipal waste appears to be economical, direct combustion or gasification are more attractive alternatives for the moment. The massive need for synthetic natural gaseous (SNG) and liquid fuels will probably be satisfied from coal in the future (*10*).

Combustion of wood and other renewable resources for energy can probably be improved a great deal by the application of modern engineering principles. To an even greater degree, the same thing holds true for the large-scale production of low Btu gas from wood and other renewable resources (*11*), which is still in its infancy. Initial results look promising. The heating values of wood gas are similar to those of coal producer gas—150 to 200 Btu per cubic foot (1 foot = 0.3 meter) with air and 270 to 330 Btu per cubic foot with oxygen. Wood gasification requires no steam and less oxygen than coal gasification. The gas is practically free of sulfur and has a higher ratio of H_2 to CO than that of coal gas (*7*). On the other hand, the efficiency of gasification of wood is some 7 percent less than that for coal when expressed as heating value of gas divided by that of the fuel used.

Table 2. Estimated annual volumes of urban, agricultural, and wood waste.

Waste	Million metric dry tons per year
Urban (*6*)	
Municipal waste	160
Sewage	60
Agricultural (*7*)	
Cereal straws	132
Other plant residues	220
Cow manure	210
Wood (*2*)	
Logging residues	50
Manufacturing residues	15
Total	844

After removal of excess moisture, solids, and condensibles, low Btu gas, whatever the source, consists of hydrogen, carbon monoxide, carbon dioxide, and some methane and other hydrocarbons. Combustion of this gas may often be an advantageous alternative to incineration of the original fuel, which requires large-scale scrubbers to remove particulates from the stack gas. It can also be applied to the energetically favorable gas turbine steam plant combination. Gasification deserves to be evaluated as a means of gleaning energy from wood and bark waste at pulp mills and forest products manufacturing plants.

Pyrolysis gas from renewable materials would appropriate feedstock for the production of SNG (largely methane), except for the fact that the differences of the sources preclude the production of sufficiently large quantities in one location. An alternative and more promising method of producing methane from renewable resources is bioconversion by means of anaerobic fermentation. Despite the customary recovery of methane from municipal sewage plants in Europe, detailed engineering evaluations about the feasibility of this type of energy generation from different types of waste are not available. An alternative to methane generation from wet waste products is liquid combustion (Zimmerman process) (*12*). The clarification of the relative merits of the two approaches in future engineering studies is of outstanding importance.

Chemicals and Polymers from Renewable Resources

The ready availability and low price of petrochemical feedstocks provided a tremendous competitive edge for chemicals and synthetic materials manufactured from these sources during the period after World War II. The price differential was large enough to virtually stagnate the development of new chemicals from wood and coal and to eliminate the wood distillation industry and the manufacture of many organic solvents by fermentation of carbohydrates. The question arises as to what degree the continuously decreasing availability and higher prices of petroleum and natural gas feedstocks will reverse the previous trend and increase the use of renewable resources as feedstocks for chemicals and polymers.

It is obvious that the reversal is most likely to occur in areas where a renewable product with low demands for energy in its manufacturing has remained competitive until now with petrochemical synthetics (*13*). An example of this is cotton, which until now has held about 50 percent of the world textile market, compared to 29 percent supplied by synthetic fibers. Another example is natural rubber, which now satisfies 40 percent of the world market. It is to be expected that the current situation will also stimulate the development of improved production methods for cotton and natural rubber, thus further strengthening their competitive position.

The reversal is not as likely in cases where the conversion of renewable resource to product requires energy. This is the case with paper and board products competing with synthetic films in the packaging market. The paper industry in the United States now consumes an average of 27 million Btu's of purchased energy per ton of paper produced; the total amount corresponds to about 2 percent of the energy consumption in the United States. On the other hand, there are clear indications, especially if comparisons are made with the manufacturing practice in northern Europe (*4*), that it will be possible to reduce the amount of purchased energy to a fraction of its current amount by improved technology and better recovery of energy from the waste products.

The situation is not as favorable in the case of cellulose derivatives such as rayon and cellulose acetate that are used as plastics, films, and textiles (*7*). The current production volume of these materials is 2 million metric tons per annum in the United States. The manufacture of these products consists of two processes: (i) conversion of wood to chemical cellulose (dissolving pulp) and (ii) conversion of chemical cellulose to derivatives. The former process produces low yields (28 to 33 percent of wood) and consumes significant amounts of energy (0.3 to 0.6 pound of oil per pound of cellulose). The second conversion requires capital-intensive mills, which are currently experiencing severe pollution problems. The question arises of whether or not better methods of manufacturing cellulose derivatives could be evolved from intensified research and development work. There ought to be more direct ways of converting wood and other lignocellulosic materials to cellulose derivatives than the traditional processes.

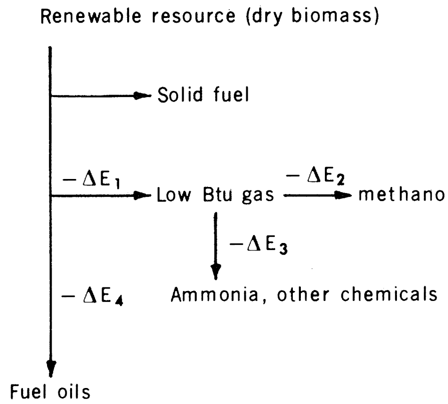

Fig. 1. Options for generating energy from "dry" renewable sources. ΔE signifies energy conversion.

Starch is a relative newcomer in the polymeric materials field, and its annual consumption in this area amounts only to 25 thousand tons. Since it is isolatable from corn in 60 percent yield by a simple process, its use in chemical industry has the potential of rapid expansion, possibly to the level of 1 million metric tons annually. It can be used for the production of polymethane-type plastics and foams, polyelectrolytes, and the like.

Chemical and By-product Potential of Renewable Resources

In the chemical pulping of wood, 42 to 52 percent is usually recovered as the fibrous product, incorporating the cellulose component, a part of the original hemicelluloses, and some residual lignin. Thus, more than half of the original organic material is not recovered as a product, but rather is used as fuel to provide process energy. These materials, obtained in an amount of over 20 million metric tons annually, could be feedstocks for the production of chemicals but remain in a noncompetitive position during the period of cheap petrochemicals. Notable exceptions are tall oil, a mixture of fat and resin acids, and turpentine, a mixture of monoterpenes. Both are extractive products isolated from kraft pulping. Together with similar products isolated from pine trees and stumps (oleoresin and gum turpentine), the annual production volume amounts to 0.5 million metric tons. In addition, lignin products in the form of lignin sulfonates have found gradually increasing applications as dispersants, particularly as oil well drilling additives, as emulsifiers, and as complexing agents (*14*).

The competitive position of by-products from pulping has substantially improved and will continue to do so. New potential products include those derived from hemicelluloses and from lignin.

In the conventional acid sulfite pulping process, the majority of hemicelluloses are hydrolyzed monosaccharides. Conversion of these sugars by microorganisms such as *Candida utilis* to proteins edible for both humans and animals has been known for a long time but practiced on a very limited scale. Similarly, the fermentation of hexose sugars to ethyl alcohol in sulfite waste liquors has been quite limited. However, expansion of protein and ethanol production from sulfite waste liquors is limited because less than 10 percent of the chemical pulp produced in the United States is manufactured by the sulfite process and the production is currently declining.

There are many alternative sources for monosaccharides. In the widely used kraft pulping process, they are converted to saccharinic acids but could be partially recovered by steam hydrolysis of wood prior to pulping. They can be obtained by acid-catalyzed hydrolysis of practically all vegetative biomaterials, including wood and agricultural residues, and by enzymatic hydrolysis of those with low lignin content. These include grain, starch, waste paper, and algal biomass. While monosaccharides undoubtedly could be produced on a massive scale, it is not yet clear what sources would be the most advantageous ones.

Both hexose and pentose sugars are appropriate feedstocks for the production of protein. Pentose sugars are readily converted to furfural, a raw material for a number of resins and adhesives and a potential intermediate in the manufacture of nylon. Agricultural residues and hardwoods, both rich in xylans, are appropriate starting materials. Limited quantities of furfural are now produced from corncobs, and the integration of furfural production with kraft pulping of hardwoods has been demonstrated.

Fermentation techniques for making use of hexose sugars show promise as low-energy production methods. In addition to production of ethanol by fermentation, similar methods are known to produce acetic, butyric, and lactic acids as well as glycerol. Many other products are undoubtedly possible, as is bioconversion to specific polysaccharides. A virtually unexplored area is the conversion of hexoses to anhydro sugars such as levoglucosan (glucose 1,6-anhydride), which could serve as intermediates for many products (*15*). Anhydro sugars may also be obtained from plant materials by controlled pyrolysis. Levulinic acid, $CH_3COCH_2CH_2COOH$, a product obtainable by high-temperature hydrolysis of hexoses or plant materials in general (*16*), deserves reevaluation as a chemical intermediate. The carbohydrate acids that are formed in massive quantities (approximately 14 million metric tons per annum) in the kraft pulping process should also be studied in terms of intermediate potential.

There are very realistic possibilities of expanding the current use of lignin products to such areas as synthetic polymers or the production of low-molecular-weight phenols (*17*). It is known that kraft lignin can be applied as an additive (up to 20 percent) to phenolic resins, but it cannot be used as a replacement for phenol in these polymers. It can also be used as a component in polyurethanes. Suitable chemical modifications may improve its properties in these applications. Kraft lignin is a potential substitute for carbon black in automobile tires (*14*).

The hydrogenolysis of kraft and other lignins has been shown to yield low-molecular-weight phenols in yields up to 55 to 65 percent (*17*). This process has now become economically feasible. Extensive studies are needed to compare the response of different types of lignin toward hydrogenolysis, for example, those of softwood, hardwood, and grass lignins.

The question may be asked whether chemical feedstocks from renewable resources should be recovered as by-products of the pulping industry or whether separate chemical plants should be set up to produce, in an integrated manner, a number of chemicals from renewable resources. Since large amounts of lignin and hemicellulose materials are already available in large quantities from pulping processes, the former alternative would seem to possess more immediate feasibility. "Integrated chemical plants" based on renewable resources should nevertheless be contemplated; one such proposition was made in a recent article by Goldstein (*18*). According to his proposal, polysaccharides in wood would be converted to ethylene by complete hydrolysis to sugars, fermentation to ethanol, and dehydration, while the remaining lignin would be converted to phenol and other aromatics by hydrogenolysis. Ethylene and aromatics could be used as feedstocks for the manufacture of conventional synthetic polymers. However, fermentation ethanol (from grain) is currently not competitive with that produced by the hydration of ethylene as an industrial solvent. It has been estimated that competitiveness will be reached when crude oil prices have reached $20 per barrel (*13*). On this basis, it seems probable that the production of ethylene by dehydration of ethanol will become economically feasible after approximate doubling of current crude oil prices.

Production of Chemicals by Gasification

It was emphasized above that pyrolysis gasification of organic waste products could be used advantageously in the production of energy. The same gas can also serve as synthesis gas to produce such chemicals as methanol, ammonia, methane, and other hydrocarbons by well-known technology. The gas produced from lignocellulosic materials has the advantages of a higher ratio of H_2 to CO and lower desulfurization costs in comparison with coal gas. Prahacs *et al.* (*19*) has evaluated the processes of converting wood waste to methanol or ammonia and arrived at favorable conclusions concerning the feasibility of such processes. There are only a few locations, however, where sufficient amounts of renewable materials can be supplied on a continuing basis. Industrial plants producing methanol or ammonia from renewable resources would be limited in size to small production units. It would seem more logical, therefore, to investigate the feasibility of large plants that could be operated with both fossil fuels (oil and coal) and wood or agricultural waste. For example, ammonia fertilizer plants in agricultural regions could rely on the plentifully available agricultural residues during harvesting seasons and shift to the use of fossil fuels when these residues are not available.

Conclusions

Of the renewable resources available in the United States, organic waste products with an approximate volume of 1 billion tons annually represent significant potential in conservation of fossil fuels. The largest impact could be accomplished in the generation of energy, while less significant savings of fossil fuels are possible in using renewable resources as feedstocks for chemicals. In view of the limited and diffuse availability of renewable resources, they should generally be regarded as auxiliary fuels and chemical feedstocks rather than as direct substitutes for fossil fuels.

The clarification of the exact potential of renewable resources requires a substantial research effort. The area should be looked at as a whole, rather than having separate groups of parochial researchers concentrate on forest residues, waste products from the pulping industry, agricultural residues, or marine resources. This calls for a broader interdisciplinary endeavor than is possible in the framework of existing government agencies. The prime targets for research ought to be the relative economic feasibility of collection and storage of residues, improved technology of direct combustion, of gasification, and of bioconversion to methane, as well as hydrolytic and pyrolytic conversions to chemical feedstocks. Specific information is needed concerning lesser known materials such as cow manure or algal biomass.

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