Botanochemicals: Supplements to Petrochemicals'

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The development of alternative sources for energy and chemicals, particularly the use of plant biomass as a renewable resource for fuel or chemical feedstocks has received much recent attention. This report reviews the chemical utilization of plant materials for liquid fuels or organic chemicals, and presents the possibility of producing hydrocarbon and related chemical products, directly or indirectly, from extant plants rather than from fossil sources such as petroleum or coal.

There is little question today that petroleum can no longer be relied upon as a stable, economical raw material to satisfy this country's tremendous demand for energy and industrial chemicals.

The shortage and depletion of petroleum have led us to consider and adopt alternative sources for fuels and chemicals. In consequence, shifting our resource needs (fuels and chemicals) to a coal base away from the petroleum is strongly suggested by many. The transition from petroleum to coal on the proposed scale is technically sound and economically feasible. Nevertheless, it is not safe environmentally to use coal indefinitely on an expanding scale. There are constraints on the increased use of coal on the scale proposed. Indefinite use of coal will produce considerable amounts of carcinogens and will also cause a carbon dioxide problem (Calvin, 1979b). Thus, supplemental sources for energy and chemicals are needed. It is suggested that utilizing sun power is the most obvious alternative (Calvin, 1974).

According to Calvin (1977) the best solar-converting machine available today is the green plant. Plants yield complex organic substances that contain many compounds which may be used as feedstocks for some liquid fuels or for a wide variety of chemical products. A number of botanochemicals have been used industrially for ages, but they suffered competitive pressures from the petrochemical industry during the recent decades. Today, interest in the utilization of plants for energy and chemicals has resurged. The conversion of wood, agriculture products or other types of biomass materials into fuels or chemicals as a supplemental source for energy has become conceptually feasible (Bagby et al., 1979; Buchanan and Otey, 1979; Calvin, 1979a, 1979b; Goldstein, 1976; Huibers and Jones, 1979; Johnston, 1979; Lipinsky, 1978; Whitworth, 1976). It seems certain that industrial utilization of plants for energy and chemicals will become increasingly more important in the future.

The intent of this report is to give an overview of the chemical utilization of plant materials for liquid fuels or organic chemicals and to present the possibility

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of producing hydrocarbons and related chemicals, directly or indirectly, from extant plants rather than from fossil sources such as petroleum or coal. No attempt is made in the report to show the economics of the production of botan-ochemical products.

OVERVIEW OF PETROLEUM USE

It is well known that crude petroleum oil is the most important single source for fuel and chemical feedstocks, yet a brief overview of current use of petroleum is presented to help the exploration of potential substitutes for petroleum prodnets.

The current petroleum products in the United States include: 1) gasoline, diesel, heating and aircraft fuels with 44.2, 21.4, 11.5 and 6.6% by volume, respectively, 2) asphalt, lubricants, waxes and miscellaneous with a total of 12.2% by volume, and 3) petrochemicals for organic raw materials, 4.1% by volume (White, 1979). It is obvious that a great quantity of petroleum is used to produce fuels for transportation and heating. The major types of products derived from petrochemicals are polymers and plastics (Princen, 1977). Today, the primary petrochemicals used for organic feedstocks are lower olefins and aromatics (White, 1979). Ethylene and propylene are the starting point raw materials used to build up most! synthetic polymers and plastics. Butylene is converted into butadiene which is then used for manufacturing synthetic rubber. Currently, aromatic toluene and benzene are widely used in the United States as an octane booster in unleaded gasoline and for the manufacture of chemical products. Approximately 20% of the petrochemical benzene produced in the United States is used to manufacture phenol; and 50% of phenol produced is used to make phenolic resin (White, 1979). The general utilization of crude petroleum is summarized as follows:

- 1) condensate ethane-heating
- 2) LPG propane and butane-heating
- 3) petroleum etner-solvent
- 4) gasoline-transportation
- 5) butylene → butadiene-synthetic rubber
- 6) aromatics: benzene → phenol—phenolic resins toluene → benzene—ethyl benzene styrene—polystyrene, etc.
- 7) naphtha → steam reforming → ethane—ethyl benzene → ethylene, polyethylene → etc.
- 8) kerosene-heating
- 9) diesel—transportation
- (10) jet fuel-transportation
- 11) heavy oil -> oxidation -> ethylene
 - → propylene—polypropylene
 - -- benzene
 - etc.
 - steam generation—heating

CHEMICAL USE OF LIGNOCELLULOSIC MATERIAL

The raw material is composed of a lignin-hemicellulose-cellulose complex. Pretreatment to separate the hemicellulose and lignin from cellulose is often required for the chemical utilization of lignocellulosic material (Brown and Jurasek, 1979). Chemical uses of lignocellulosic material are discussed individually under items 1, 2, and 3.

1. Cellulose

Cellulose is the most abundant organic material on earth. It, being a naturally-occurring high polymer, can be modified to produce cellulose derivatives without substantial alteration of the cellulose structure. Cellulose-based plastics have a number of valuable properties but generally have been more costly than petrochemically based plastics. However, such economic conditions may be changed as the price of petroleum continues to climb.

Cellulose, a linear polymer of anhydroglucose units, can also be hydolyzed to glucose by a number of routes. However, the hydrolysis is not as facile as that of starch. Hydrolysis to glucose can be catalyzed by either acids or enzymes. Acid hydrolysis by dilute acid at high temperatures causes decomposition of some of the glucose formed to hydroxymethylfurfural (Harris, 1975) limiting net sugar yield to about 50%. Strong acid hydrolysis at lower temperatures can provide about the same yields of glucose (Kusama, 1960). Shafizadeh (1978) has shown that dry distillation of cellulose at 400–500°C gives about 80% of a tar which contains mainly levoglucosan and may be converted to glucose in 50% yield based on cellulose.

The conversion of cellulose to glucose is the first step in the potential large scale chemical utilization of cellulose. Of greatest potential importance is the fermentation of glucose to ethanol by commercially proven processes with high yields. Ethanol is an important industrial chemical used as a solvent or as a starting point raw material for preparation and synthesis of many organic chemcals and it also has great potential to be used as a liquid fuel and as a petrochemical substitute (Johnston, 1979; Whitworth, 1976, 1977; Whitworth and Harwood, 1977). Ethanol is now produced by hydration of ethylene—a petrochemical derived from crude oil. The dehydration of ethanol to ethylene, the reverse reaction to present ethanol formation from ethylene, also proceeds in high yield. Similarly, butadiene can be readily obtained from ethanol. Both ethylene and butadiene are important petrochemicals and have wide applications. In a chemical economy based on plant resources instead of petroleum, the ethanol could produce ethylene in 96% yield and could also be converted to butadiene in 70% yield by processes which have been proven commercially (Faith et al., 1965). Sugars, produced from the hydrolysis of cellulose, can also serve as the raw materials for the anaerobic production of hydrogen (Andersen et al., 1979). Hydrogen is a clean and recyclable fuel and the use of hydrogen in energy systems has attracted some attention (Gregory and Pangborn, 1976). Ethanol also has a potential use as octane booster in the fuel for internal combustion engines (Holzman, 1979) A summary of chemical utilization of cellulose is presented in Fig. 1.

Currently, the major technical problem in cellulose conversion to chemical

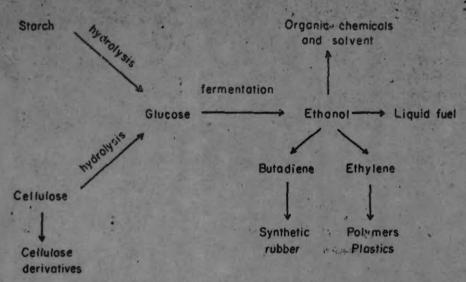


Fig. 1. Potential flow of starch and cellulose for chemical use.

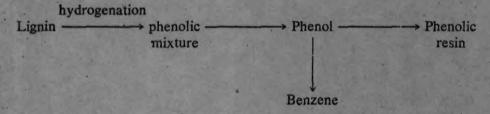
feedstocks lies in the improvement of cellulose hydrolysis to overcome problems of rate of reaction and decomposition of sugars resulting from the relative chemical inaccessibility of cellulose. Some recent improvements have substantially increased the sugar yield on the experimental basis, such as removing the hemicellulose in a previous step or weakening the cellulose structure by pretreatment, allowing acid hydrolysis yield to approach 90% (Bungay, 1979).

2. Hemicelluloses

Hemicelluloses are polysaccharides which are short or branched polymers of 5-carbon sugars, such as xylose, or 6-carbon sugars other than glucose. They are more readily hydrolyzed by acid than cellulose and, consequently, are easily converted into simple sugars under mild conditions. In general, the hemicellulose of softwoods, upon hydrolysis, gives products that contain about equal parts of fermentable and nonfermentable sugars, while that of hardwoods gives sugars that are about 25% fermentable (Pigman and Wolfrom, 1949). The xylans which are more abundant in deciduous trees, yield principally xylose, while the glucomannans, found in larger quantities in conifers, yield mannose. Mannose and other bexoses can be combined with glucose for fermentation to ethanol. Xylose and other pentoses can be converted to furfural, or alternatively, xylose could be reduced to xylitol. Furfural once served as the raw material for nylon until displaced by butadiene, a chemical currently derived from petroleum. However, an abundance of furfural at a reasonable cost should stimulate its uses. Hydrolyzed hemicelluloses, pentoses and hexoses are also present in the waste streams produced during chemical pulping; e.g., sulfite waste lignins contain approximately 2 mill tons/yr of free sugars, principally hexoses, which could be used for the fermentation of ethanol (National Research Council, 1976). Sugars from hemicelluloses, such as xylose, can also be used to produce hydrogen (Andersen et al., 1979).

3. Lignin

Lignin is a 3-dimensional random polymer formed from phenylpropane units. The principal by-product of wood saccharification is an insoluble lignin residue. The lignin becomes soluble on heating in alkali or certain organic substances (Pigman and Wolfrom, 1949). It constitutes a potential source of aromatic chemicals such as benzene and phenol which are considered to be very important petrochemicals. The conversion of lignin to simple compounds requires some drastic hydrogenation and hydrogenolysis processes similar to those contemplated for coal. The production of phenolic products from the lignin by various hydrogenolysis techniques has been demonstrated, but no commercial production has been attempted. Complex mixtures of phenols in yields of up to 50% have been-reported (Goheen, 1971; Goldstein, 1975; Schweers, 1978); and projected yields of 35% pure phenol have been suggested (Hellwig et al., 1969). Benzene has been isolated as a component from lignin hydrocracking, and could be obtained in 25% yield on lignin by dehydroxylation of phenol (Goldstein, 1978). Other applications of lignin, that are in need of considerable research investment, are those that use this material in as high a polymeric state as possible (e.g., as a rigid plastic), as a filler, as adhesive or additive, or in lieu of carbon black for strengthening rubber. According to a recent report (Crawford, 1980), production of useful chemicals from lignin by microbiological conversion is also possible and research in this field is being conducted. A scheme of potential utilization of lignin as a chemical feedstock is given as follows:



CHEMICAL USE OF STARCH

Starch is considered to be the most abundant reserve polysaccharide available to man; its synthesis takes place vigorously in the grains of cereal plants. Starch, like cellulose, is a high polymer composed of D-glucose units. The molecules of these polymers differ only in the manner in which the glucose units are joined together. Normally, starch contains about 20% of a water-soluble fraction called amylose, and 80% of a water-insoluble fraction called amylopectin (Morrison and Boyd, 1973). Starch has considerable potential as industrial raw material. The industrial applications of starch in the United States during 1974 had reached 3,550 mill lb (Otey, 1977). Starch may become increasingly available, as an agriculture residue, from grain processors upgrading the protein content of certain cereal products by removing part of the starch. Expanding use of starch for industrial applications is highly possible in the future. Upon treatment with acid or under the influence of enzymes, the components of starch are readily hydrolyzed progressively to dextrin, maltose, and finally glucose. Normally, hydrolysis of starch gives a good yield of glucose. As mentioned previously, glucose is the fermentable chemical used to produce ethanol which can further be converted to

ethylene and butadiene. Hence, a number of researchers believe that starch holds considerable promise as a feedstock for some products currently made from petroleum. Starch can also be used directly to produce hydrogen which is currently being considered as a clean and recyclable fuel (Andersen et al., 1979). In addition, the chemical industry is also considering the use of starch to produce biodegradable and flame-resistant plastics and polymers (Otey, 1977). Some of the more promising uses for starch, as a petroleum substitute or chemical feedstock, are listed in Fig. 1.

CHEMICAL USE OF EXUDATES AND EXTRACTIVES

1. Plant latex

· Plant latex is a milky or, less frequently, pale, cloudy, yellow or red fluid in specialized cells or tube-like structures known as laticifers in many species of plants of diverse families (Metcalfe, 1967). It is a liquid matrix or serum containing minute organic particles in dispersion or suspension. This liquid may be in any or all parts of the plant and is considered by some as merely a by-product of chemical processes involved in photosynthetic conversion of sunlight to energy and organic molecules (Shukla and Crishna-Murti, 1971). Latex contains an assortment of substances including water, salts, hydrocarbons and various other organic compounds. Water and hydrocarbons have been found to be the principal components of latex in many plants (Schery, 1972; Shukla and Crishna-Murti, 1971). Normally, the hydrocarbons found in plant latex are polymers of isoprene (C₅H₈) ranging from relatively large molecules, such as natural rubber (molecular weight: 500,000-2,000,000), to the relatively small molecules, such as some petroleum-like materials (molecular weight: 50,000 or less). Natural rubber, commonly harvested by tapping Heyea trees, has been used as an important industrial material for a century (Imle, 1978). More recently, a great deal of interest and speculation has risen concerning the use of plant latex as a substitute for petroleum (Calvin, 1979a, 1979b; Dehgan and Wang, 1979; Maugh, 1979; Nie'son et al., 1977). Euphorbia latex has received increasing attention because it contains a mixture of light hydrocarbons which have a molecular weight on the order of 20,000 instead of 2 million. Hence, after the water is removed from the latex the resulting material is a liquid oil. The hydrocarbons from Euphorbia are primarily a blend of C₁₅, C₂₀, or C₃₀ compounds (Nielson et al., 1979; Nielson et al., 1977) that, when subjected to catalytic cracking, yield various products virtually identical to those obtained by cracking naphtha (Maugh, 1979), a high quality petroeum fraction that is one of the principal raw materials used in the chemical industry.

Euphorbia tirucalli L. was planted by a Japanese firm on Okinawa with great success. The Japanese company has calculated that, with plants on 4-ft centers and at the present rate of growth, they could expect to produce between 5 and 10 barrels of oil per acre per year (Calvin, 1979b). Currently, several species of Euphorbia are being investigated by scientists at the University of California (Calvin, 1979a). A potential production of 10 barrels of oil per acre in about 9 mo from E. lathyris L. was also calculated by the California scientists (Calvin, 1979a). The dry plant of E. lathyris contains 4-5% heptane extractives which collectively

have a heat value of 18,000 Btu/lb and these reduced photosynthetic materials consist almost entirely of polycyclic triterpenoids (Nemethy et al., 1979).

The exudate from copaiba tree (Copaifera langsdorffii Desf.) is also interesting and has attracted attention because its sap, which can be harvested by tapping, is an oil that can be used directly from the tree as a fuel for diesel engines (Maugh, 1979). Results of a complete chemical analysis of the oil obtained from copaiba tree indicate that the oil is composed entirely of hydrocarbons and has a molecular-weight distribution very much like that of diesel oil (Amer. Chem. Soc., 1979). Copaiba trees grow wild in most of Brazil—from the tropical Amazon basin to as far south as Rio de Janeiro, a latitude comparable to Florida. It was estimated that an acre of 100 mature copaiba trees might be able to produce 25 barrels of fuel per year, and Brazilians are just beginning to plant copaiba trees, on an experimental basis, to study its potential.

2. Plant resins

Plant resins include a number of terpene compounds and their derivatives. The parent hydrocarbons, on which the various derivatives are based, have carbon structure which may be regarded as being built up of isoprene units (C_5H_8) . They are classed, according to their molecular size, as monoterpenes $(C_{10}H_{18})$, sesquiterpenes $(C_{15}H_{24})$, diterpenes $(C_{20}H_{32})$ and triterpenes $(C_{30}H_{48})$. Derivatives of these, containing hydroxyl, carboxyl, and other substitutent groups also occur (Farmer, 1967).

Resin is usually found in special cells and canals in a wide variety of plants and plant parts. The most important commercial resins come from the Pinaceae. Some Far Eastern resins (damars) from the Dipterocarpaceae and several highly aromatic resins (balsams) from the Leguminosae and Burseraceae are also being used commercially.

Of all the plant resins that are produced in this country, those products from pines known as naval stores have the largest aggregate volume and value. Normally, pine resins are present in trees as volatile oils (turpentine) and nonvolatile resins (rosin) and currently collected or produced from oleoresin (gum naval stores), resinous wood (wood naval stores), or sulfate pulping by-products (sulfate naval stores). Chemicals in turpentine include α -pinene, β -pinene, camphene and some other terpenes. Turpentine has been used as a solvent and a chemical raw material. Rosins from pine trees consist primarily of diterpene resin acids of the abietic type and pimaric type. Crude southern tall oil, a sulfate naval stores product, contains 40-60% resin acids, 40-50% fatty acids and 5-10% neutral constituents. Rosins and tall oil fatty acids are primarily used as chemical intermediates and coatings. It is believed that naval stores could become a source of isoprene and a substitute for styrene which are by-products of petroleum and key chemicals in making synthetic rubber and other polymers; therefore, interest in utilizing such chemicals for industrial feedstocks has increased during the past few years. Since turpentine is a highly combustible chemical, consideration has also been given to the incorporation of turpentine into automobile fuel formulations (Collier, 1977; Zinkel, 1975). A comparison of heats of combustion of various fuels is presented in Table 1 to show the energy potential of turpentine-the

TABLE 1. COMPARISON OF HEATS OF COMBUSTION OF BIOMASS CONSTITUENTS, FUELS FROM BIOMASS, AND FOSSIL FUELS. VALUES FOR HEAT OF COMBUSTION ARE APPROXIMATE.

Heat of combustion (gigajoules/ metric ton)	Eiomass constituents	Fuels from biomass	Fossil fuels
50		Methane	Natural gas
40	Turpentine	Butanol	Gasoline
35	Triglyceride oils ~ steroids ~ lignin		Fuel oil > bituminous coals
30		Acetone > ethanol	
20		Furfural > methanol	
15	Wood > starch ~ cellu- lose > sucrose > glucose		
10		Acetic acid	40 30

^{*} Lipinsky, 1978.

heat content of turpentine is equivalent to that normally found for gasoline. It is believed that a mixture of turpentine with gasoline could be as promising as gasohol in some areas.

A market growth for chemical products from naval stores can be expected as they hold great potential for partially replacing many of the petroleum-based raw materials in industrial manufacturing processes (Bungay and Ward, 1977; National Research Council, 1976). Today, potential new sources, such as lightwood from paraquat-treated pine (Bungay and Ward, 1977; Robert, 1973) and foliage biomass (Barton, 1978) are being examined, and the availability of naval stores chemicals will increase gradually. Projected use of turpentine, rosin and tall oil fatty acid in the United States for the year 2000 could reach to 5,090, 15,270 and 550 mill lb respectively (National Research Council, 1976).

3. Essential oils

Essential oils are widely distributed through the plant kingdom, unusually abundant in several unrelated plant families such as the Labiatae, Rutaceae, Geraniaceae, Umbelliferae, Compositae, Lauraceae, Myrtaceae, Gramineae, and Leguminosae. Essential oils consist chemically of a variety of organic substances, including benzene derivatives, terpenes, and various other hydrocarbons and straight-chain compounds. They usually occur as mixtures of more than one oil. In comparison with other oils, essential oils have smaller molecules, ordinarily fewer than 20 carbon atoms. They are typically liquid and possess an aromatic fragrance, owing to their volatilization upon contact with air. They may be readily extracted from plant tissues by steam distillation, expression, or solvent extraction. Uses of essential oils are varied. Although the chief uses of essential oils are for perfumery and flavoring, these chemicals also have many additional uses

in medicinals and as an industrial raw material. To some extent essential oils can be converted into certain fine products by simple chemical techniques. It was reported that the convers on can be very attractive commercially, since the market value of the converted derivative is often worth many times that of the original precursor (Barton, 1978). An example is citronellol, which may be produced from either α - or β -pinene (major constituents of many essential oils) in a 4-step synthesis involving hydrogenation, heating, acidification and alkaline hydrolysis (Keays and Barton, 1977). Another example is napol, a primary alcohol obtained from the reaction of β -pinene and formaldehyde (Keays and Barton, 1977). Some essential oils can be obtained inexpensively as by-products of other industries. For example, a number of industrial oils are obtained from citrus residues after juice extraction from oranges, grapefruits, and other Citrus species of the Rutaceae. Citrus stripper oil is currently obtained as a by-product from the processing of the peels of oranges and grapefruits for molasses. This citrus oil contains 95% D-limonene, a monocyclic terpene used as a raw material in making of fine organic chemicals. Increasing use of limonene for industrial materials is expected (National Research Council, 1976). Like tyrpentine, essential oils are highly combustible. A recent research project conducted in Japan was aimed at using eucalyptus oil as an alternative to gasoline. The Japanese have carried out comparative tests of gasoline, eucalyptus oil, and a 70/30 eucalyptus oil/gasoline blend. According to the USDA report on energy activities (1979), eucalyptus oil had fairly good performance as an engine fuel, and they believe that blends with gasoline are seen to be most promising.

4. Vegetable oils and waxes

Oils and waxes are common in many plant species. Oils are found abundant in seeds, and waxes are normally rich on the surface of leaves or stems. Chemically, oils and waxes are very similar and consist of fatty acids and their derivatives. Vegetable oils are an important class of extractives from the standpoint of volumes and values. Most of the vegetable oils used today are produced by agricultural means. The production of plant oils is frequently on the order of thousands and even millions of tons annually (Pryde, 1977), and these plant oils are necessary in one way or another for a variety of industries. Industrial usage of vegetable oils, like many other natural products, has suffered competitive pressure from cheap petroleum-based synthetics. However, vegetable oils still retain some industrial markets for such uses as coatings, plasticizers, surface active agents, lubricants, and as raw materials for some chemical industries. The use of vegetable waxes, on the other hand, has been largely limited to a few special types by the competition from cheaper synthetic and petroleum waxes (paraffin). The most important vegetable wax is obtained from the carnauba palm (Copernicia cerifera Mart.) grown in the northeastern states of Brazil. The utilization of vegetable oils and waxes for energy and chemicals has been the subject of much discussion during recent years (Buchanan et al., 1978a; Buchanan et al., 1978b; Laver, 1978; National Research Council, 1976; Pryde, 1977). Systematic screening programs for oil-producing crops and research to obtain good vegetable waxes from diverse plant materials have been undertaken and some promising candidates for new crops with seed oils of various fatty acids have been reported

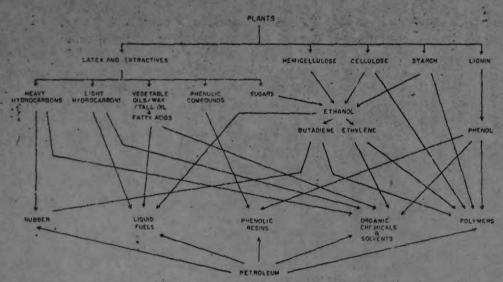


Fig. 2. Botanochemical products versus petroleum products.

(Princen, 1977). Expanding and new uses of vegetable oils are expected because some of them can be used inexpensively (National Research Council, 1976; Pryde, 1977) as alternatives to petrochemicals, and as sources for long-chain aliphatic compounds. Vegetable oils also have great potential to be used as liquid fuel or as a source for hydrocarbons. Vegetable oils are combustible and some of them will combust in diesel engines. Normally, considerable amounts of heat can be produced from the combustion of these oils (Table 1). The average heat value of common triglyceride oils is equivalent to that normally obtained from fuel oil. Since the conversion of carboxylic acid to hydrocarbon, decarboxylation, is technically possible in a number of ways, it is believed that some hydrocarbons can also be produced from the plant oils.

5. Tannins and phenolic compounds

Many plants contain considerable amounts of tannins and phenolics which are collectively termed polyphenols or polyflavonoids. These substances are soluble in water, alcohol or acetone. Normally, the hydrolyzable tannins are esters of a sugar with one or more polyphenolic acids: gallic, digallic, or ellagic acid. The condensed tannins, on the other hand, are complex molecules, the basic unit of which is, in many cases, catechin (Farmer, 1967). Although the complete chemical structures of the condensed tannins and other types of polyflavonoids from plants are not well established, certain features have been described. These substances consist, at least in part, of epicatechin and catechin units linked from the C-4 position of one to an undetermined position of another (Hemingway and McGraw, 1976, 1977; Karchesy et al., 1976; Sears and Casebier, 1970). Traditionally, they have found wide use in tanning leather, in oil-well drilling, and in many other areas. The polyphenols or polyflavonoids, because of their functional phenolic hydroxyl groups which offer strong nucleophilic centers as anions for attack by the formaldehyde, have attracted much attention aimed at making adhesive compositions since early 1950s (Van Beckum and Cook, 1951). Stephan (1954) pro-

posed a plywood adhesive formulation from alkaline extraction of redwood bark and many similar attempts immediately followed (Anderson and Runckel, 1961; Hall et al., 1960; Herrick and Bock, 1958; Herrick and Conca, 1960; Plomley, 1966; Plomley et al., 1964). This type of use appears particularly attractive because of the present concern over future restriction on the supply and price of petrochemical phenol. Today, 50% of this petrochemical is used to produce resin for adhesives (White, 1979). Much effort has been and presently is being made to use these vegetable phenolics as replacements for petroleum-derived phenol or resorcinol in adhesive formulations (Hemingway, 1977). Anderson et al. (1974a, 1974b, 1974c) have conducted a series of studies on particleboard adhesives and prepared particleboard resins from some tannin-rich species by extraction of the bark with sodium carbonate and curing the extract with paraformaldehyde. Several tannin adhesives were also prepared from the wattle bark extract by Saaymon and Oatley (1976) in South Africa. Use of southern pine bark polyflavonoids in exterior wood adhesive formulations has been evaluated by Hemingway and McGraw (1977) and investigations are being continued. Saaymon and Brown (1977) studied the fortification of starch corregating adhesives with tanninformaldehyde resins and this approach seemed to work well with wattle tannins. Currently, tannins are commercially used for wood adhesives in South Africa as well as in Australia.

SUMMARY AND CONCLUSIONS

Technically, the utilization of plant materials as a supplemental source for liquid fuels and chemical feedstock is possible and this approach appears promising as a means of minimizing our dependence on fossil energy. The general use of petroleum and the potential flow of plant materials for chemical use are summarized in Fig. 2.

Application of these plant-derived chemicals as a supplementary source for energy and chemicals would become increasingly attractive and important as the price of petroleum continues to go up. Development of these renewable resources will present many new challenges to chemists, biologists and engineers.

LITERATURE CITED

- Amer. Chem. Soc. 1979. Brazil's biomass program is one of most extensive. Chem. Engin. News 57: 35.
- Andersen, K., H. Spiller, S. Eisenmeier, and K. Shanmugam. 1979. Biological production of H₂ for energy use. Proc. Alternative Energy Sources for Florida. pp. 74-77. Univ. Fl.
- Anderson, A. B., and W. J. Runckel. 1961. Bonding particleboards with bark extracts. Forest Prod. J. 11: 226-227.
- A. Wong, and K. Wu. 1974a. Utilization of white fir bark and its extract in particleboard. Forest Prod. J. 24: 40-45.
- _____, and _____. 1974b. Utilization of white fir bark in particleboard. Forest Prod. J. 24:
- ———, K. Wu, and A. Wong. 1974c. Utilization of ponderosa pine bark and its extract in particle-board. Forest Prod. J. 24: 48-53.
- Bagby, M. O., R. A. Buchanan, and F. H. Otey. 1979. Multi-use crops and botane-chemical production. Preprint. USDA, Northern Regional Research Center. Peoria, IL.
- Barton, G. M. 1978. Chemicals from trees, outlook for the future. Special Paper, 8th World Forestry Congress.

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- Brown, R. D., and L. Jurasek. 1979. Hydrolysis of cellulose: mechanisms of enzymatic and acid catalysis. Advances in Chemistry, series 181. Amer. Chem. Soc. Washington, DC.
- Buchanan, R. A., I. M. Cull, F. H. Otey, and C. R. Russell. 1978a. Hydrocarbon- and rubber-producing crops. Econ. Bot. 32: 131-145.
- ——, and F. H. Otey. 1979. Multi-use oil- and hydrogen-producing crops in adaptive systems for food, material, and energy production. Biosources Dig. 1: 176-202.
- ——, C. R. Russell, and I. M. Cull. 1978b. Whole-plant oils, potential new industrial raw materials. J. Amer. Oil Chem. Soc. 55: 657-662.
- Bungay, H. R. 1979. Overview of cellulose hydrolysis. Biomass Refining Newslett. 1: 32-36.
- , and R. W. Ward. 1977. Silvichemicals and fuels from paraquat-treated pine trees. Proc. Annual Meeting of Lightwood Research Coordinating Council.
- Calvin, M. 1974. Solar energy by photosynthesis. Science 184: 375.
- ----. 1977. Hydrocarbons via photosynthesis. Energy Res. 1: 299.
- ——. 1979a. Petroleum plantations. In Solar Energy: Chemical Conversion and Storage. R. R. Hantala, R. B. King and C. Kutal, ed. pp. 1-30. Humana Press Clifton, NJ.
- ----. 1979b. Petroleum plantations for fuel and materials. BioScience 29: 533-538.
- Collier, T. J. 1977. Feasibility of petrochemical substitution by oleoresin. Proc. Annual Meeting of Lightwood Research Coordinating Council.
- Crawford, D. L. 1980. Bioconversion of plant residues into chemicals: production of chemicals from lignin. Biosources Dig. 2: 52-63.
- Dehgan, B., and S. Wang. 1979. Hydrocarbons from plants—latex. Proc. Alternative Energy Sources for Florida. pp. 31-48. Univ. Florida.
- Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd ed. Wiley, New York.
- Farmer, R. H. 1967. Chemistry in the utilization of wood. Pergamon Press, Long Island, NY.
- Gregory, D. P., and J. B. Pangborn. 1976. Hydrogen energy. Annual Rev. Energy 1: 279-310.
- Goheen, D. W. 1971. Low molecular weight chemicals. In Lignins. K. V. Sarkanen and C. H. Ludwig, ed. pp. 797-831. Wiley, New York.
- Goldstein, I. S. 1975. Perspectives on production of phenols and phenolic acids from lignin and bark. Applied Polymer Symp. No. 28. pp. 259-267.
- ——. 1978. Chemicals from wood: outlook for the future. Special Paper, 8th World Forestry Congress.
- Hall, R. B., J. H. Leonard, and G. A. Nicholls. 1960. Bonding particle boards with bark extracts. Forest Prod. J. 10: 263-272.
- Harris, J. F. 1975. Acid hydrolysis and dehydration reactions for utilizing plant carbohydrates. Applied Polymer Symp. No. 28. pp. 131-144.
- Hellwig, K. C., S. B. Alpert, C. A. Johnson, and S. C. Schuman. 1969. Production of phenols from lignin. Paper presented in Tech. Asso. Pulp Paper Industry Meeting, New York.
- Hemingway, R. W. 1977. Bark, a renewable source of specialty chemicals. Special paper presented to W. R. Grace and Co. Symp. on Chem. from Renewable Resources.
- , and G. W. McGraw. 1976. Progress in the chemistry of shortleaf and loblolly pine bark
- flavonoids. Applied Polymer Symp. No. 28. pp. 1349-1364.

 , and ——. 1977. Southern pine bark polyflavonoids: structure, reactivity, use in wood adhesives. Proc. Tech. Assoc. Pulp Paper Industry Forest Biology/Wood Chem. Symp. pp.
- Herrick, F. W., and L. H. Bock. 1958. Thermosetting exterior plywood type adhesives from bark extracts. Forest Prod. J. 8: 269-274.
- ——, and R. J. Conca. 1960. The use of bark extracts in cold-setting waterproof adhesives. Forest Prod. J. 10: 361-368.
- Holzman, D. 1979. Alcohol fuels-a critical analysis. People and Energy 79: 3-9.
- Huibers, D. T. A., and M. W. Jones. 1979. Fuels and chemical feedstocks from lignocellulosic biomass. Paper presented in Annual Fall Conference, Canadian Soc. Chem. Engin., Sarnia, Ontario, Canada.
- Imle, E. P. 1978. Hevea rubber-past and future. Econ. Bot. 32: 264-277.

261-269

Johnston, F. J. 1979. Ethanol—an alternative to its use as a fuel. Paper presented in Workshop on Fernantation Alcohol in Developing Countries, Vienna, Austria.

Karchesy, J. J., P. M. Loveland, M. L. Laver, D. F. Barofsky, and E. Barofsky. 1976. Condensed tannins from the barks of Alnus rubra and Pseudotsuga menziesli. Phytochemistry 15: 2009– 2110.

Keays, J. L., and G. M. Barton. 1977. Innovations dans l'utilisation du feuillage. Information Report VP-X-137F. Fisheries and Environment Canada and Canadian Forestry Service.

Kusama, J. 1960. Wood saccharification by hydrogen chloride gas process. Annual Report, Noguchi Res. Inst. 9: 11-22.

Laver, M. L. 1978. Chemicals from bark. Special Paper, 8th World Forestry Congress.

Lipinsky, E. S. 1978. Fuels from biomass: integration with food and material systems. Science 199: 644-648.

Maugh II, T. H. 1979. Unlike money, diesel fuel grows on trees. Science 206: 436.

Metcalfe, C. R. 1967. Distribution of latex in the plant kingdom. Econ. Bot. 21: 115-127.

Morrison, R. T., and R. L. Boyd. 1973. Organic chemistry. 3rd ed. Allyn and Bacon, Boston.

National Research Council. 1976. Renewable resources for industrial materials. Report Committee Renewable Resources for Industrial Materials, Washington, DC.

Nemethy, E. K., J. W. Otvos, and M. Calvin. 1979. Analysis of extractables from one, Euphorbia. J. Amer. Oil Chem. Soc. 56: 957-960.

Nielson, P. E., H. Nishimura, Y. Liang, and M. Calvin. 1979. Steroids from Euphorbia and other latex-bearing plants. Phytochemistry 18: 103-104.

, —, J. W. Otvos, and M. Calvin. 1977. Plant crops as a source of fuel and hydrocarbon-like materials. Science 198: 942-944.

Otey, F. J. 1977. New industrial potentials for carbohydrates. In Crop Resources, D. S. Siegler, ed. pp. 47-60. Academic Press, New York.

Pigman, W. L., and M. L. Wolfrom. 1949. Advances in Carbohydrate Chemistry. Vol. 4. Academic Press, New York.

Plomley, K. F. 1966. Tannin-formaldehyde adhesives for wood. II. Wattle tannin adhesives. Forest Prod. Tech. Paper No. 39. Commonwealth Scientific Industrial Research Organization, Australia.

— J. W. Gottstein, and W. E. Hillis. 1964. Tannin-formaldehyde adhesives for wood. I. Mangrove tannin adhesives. Australian J. Appl. Sci. 15: 171-182.

Princen, L. H. 1977. Potential wealth in new crops: research and development. In Crop Resources, D. S. Siegler, ed. pp. 1-16. Academic Press, New York.

Pryde, E. H. 1977. Nonfood uses for commercial vegetable oil crops. In Crop Resources, D. S. Siegler, ed. pp. 24-45. Academic Press, New York.

Robert, D. R. 1973. Inducing lightwood in pine trees by paraquat treatment. USDA Forest Service Research Note SE-191.

Saaymon, H. M., and C. H. Brown. 1977. Wattle-base tannin-starch adhesives for corrugated con-

tainers. Forest Prod. J. 27: 21-25.

and J. A. Oatley. 1976. Wood adhesives from wattle bark extract. Forest Prod. J. 26: 27-33.

Schery, R. W. 1972. Plants for Man. 2nd ed. Prentice-Hall, Englewood Cliffs, NJ.
Schweers, W. 1978. Utilization of lignins isolated under mild conditions from wood to wood waste for the production of useful chemicals and other chemical products. Special Paper, 8th World Forestry Congress.

Sears, K. D., and R. L. Casebier. 1970. The reaction of thioglycolic acid with polyflavonoid bark fractions of Tsuga heterophylla. Phytochemistry 9: 1589-1591.

Shafizadeh, F. 1978. Development of pyrolysis as a new method to meet the increasing demands of food, chemicals, and fuel. Special Paper, 8th World Forestry Congress.

Shukla, Q. P., and C. R. Crishna-Murti. 1971. The biochemistry of plant latex. J. Sci. Industr. Res. 30: 640-662.

Stephan, J. T. 1954. Plywood adhesive from redwood bark. U.S. Patent 2,675,336.

USDA Forest Service. 1979. Eucalyptus oil for gasoline. Quads 8: 2.

Van Beckum, W. G., and H. L. Cook. 1951. Plywood adhesive. U.S. Patent 2,574,803.

White, J. T. 1979. Growing dependency of wood products on adhesives and other chemicals. Forest Prod. J. 29: 14-20.

Whitworth, D. A. 1976. Production of liquid transport fuel from cellulose material (wood). I. Economic considerations of acid hydrolysis of wood for subsequent conversion to ethyl alcohol. New Zestand Energy J. 49: 173-177.

- 1977. Production of liquid transport fuel from cellulose material (wood). II. Energy conversion efficiencies of the processes. New Zealand Energy J. 50: 14-17.
- , and V. D. Harwood. 1977. Production of liquid transport fuel from cellulose material (wood). III. Laboratory preparation of wood sugars and fermentation to ethanol and yeast. New Zealand Energy J. 50: 166-169.
- Zinkel, D. F. 1975. Naval stores: silvichemicals from pine. Applied Polymer Symp. No. 28. pp. 309-327.

BOOK REVIEWS

Photographic Manual of Woody Landscape Plants. Michael A. Dirr. 378 pp. illus. Stipes Publishing Company, Champaign, Illinois, 1978. \$14.60 (soft cover).

This book is a companion piece to Dirr's Manual of Woody Landscape Plants, which was reviewed in Economic Botany 33(2). It attempts to fill a "long... evident" need in ornamental horticulture and landscape architecture "for a reference text which encompasses photographs of plant habit and ornamental characteristics." To this end, it presents black-and-white photographs—1.295 of them—of plants, including habit and, where appropriate, leaves, flowers, fruit, and bark; both summer and winter habit shots are included for a number of species. Truly a picture book this, the text is minimal, giving notes on description, soil preference, landscape value, faults, and hardiness zone.

The major criticism I have is that some of the photographs are so pale that they obfuscate rather than elucidate their subject. Aside from this, the book will serve its purpose well. I, for one, will keep it handy next to Dirr's Manual.

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Food and Drugs in America. Eiline Kingsley. 133 pp. illus. Energy Held Publications, Los Angeles, California, 1980. \$6.95.

The author, a teacher of health communication at the University of Southern California, offers in this little book a unique theory on the non-protein nitrogen effect of alkaloids on the citric acid cycle and how our social conceptions of presumably beneficial alkaloid effects have been restricted by paradigms about drugs.

Divided into 10 chapters, the material on the American diet is developed step by step: (1) "Origins of American Consumption," (2) "Sociological Persuasion," (3) "Psychological Invasion," (4) "Physiological Addiction," (5) "Biochemical Transformation," (6) "Pharmaceutical Documentation," (7) "International Consumption," (8) "Alkaloid Commercialization," (9) "Cocaine Importation," and (10) "Medical Recommendations."

The last chapter summarizes the theme of the book, saying "that we need to rethink the ways that we communicate about food and drugs in America" and "that food and drug abuse are different expressions of the same attitude and just because we label a plant a 'drug' does not mean it will have no nutritional effects."

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