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Lignochemicals

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Introduction

Only 6–8% of the petroleum produced worldwide serves, at present, as raw material for the production of basic chemicals. But since petrochemicals supply 98% of the basic feedstocks used by the chemical industry, its dependence is obvious[2]. Economical production of chemicals from natural oil and gas has been possible because of their relative purity and their continued availability at low cost. Highly developed technologies have evolved based on the well known and specific hydrocarbon composition of petroleum and natural gas. Changing from these sources to biomass, would require the development and adaptation of new process technologies. Wishart[3] envisions 3 phases necessary to convert today's petroleum-based chemical industry to one based on biomass. During phase 1, chemicals will still be based on oil and gas resources, but they will be produced at a higher yield with improved processes and technologies. Phase 2 will be characterized by increased production of synthesis gas from heavy oil and coal to produce bulk chemical feedstocks such as ethylene and methanol. Production of chemicals from biomass will take place in phase 3 which is beginning to be developed now and which will be operative economically and with commercial significance later in the 21st century. A renewed interest in converting biomass components into organic chemical feedstocks is expressed by the increasing number of publications dealing with the subject[4–12]. I would like to discuss here some aspects of physico-chemical pretreatment and microbial conversion for the production of aromatic synthesis chemicals from wood.

Development of microbial processes

The conversion of lignin monomers to catechol with microbial communities under anaerobic conditions is outlined in the preceding article (Kaiser and Hanselmann). According to Wishart's plan, the microbial conversion processes which are being studied and improved today will not have an immediate applicability. Therefore, the decision for, or against, their development should not turn solely on how economical the processes are at present. A proper evaluation should be based on a consideration of the changing raw material resources and the time required to develop industrially interesting microbial fermentation processes, as well as an appreciation of microbial abilities to convert biomass efficiently. Although the production of chemical feedstocks via microbial processes is at present not economically competitive with the production of petrochemicals, the development of these processes should no longer be postponed. We know little about many of the potentially interesting biochemical pathways in microbes and even less about their suitability to be employed in biotechnology. The spectacular hopes invested in genetic engineering can only become reality if we gain enough knowledge about the physiological basis of the metabolic sequences that look useful for biomass conversion.

Wood as a biomass resource

Wood represents a stored form of renewable solar energy and materials (fig. 1). It is the most abundant

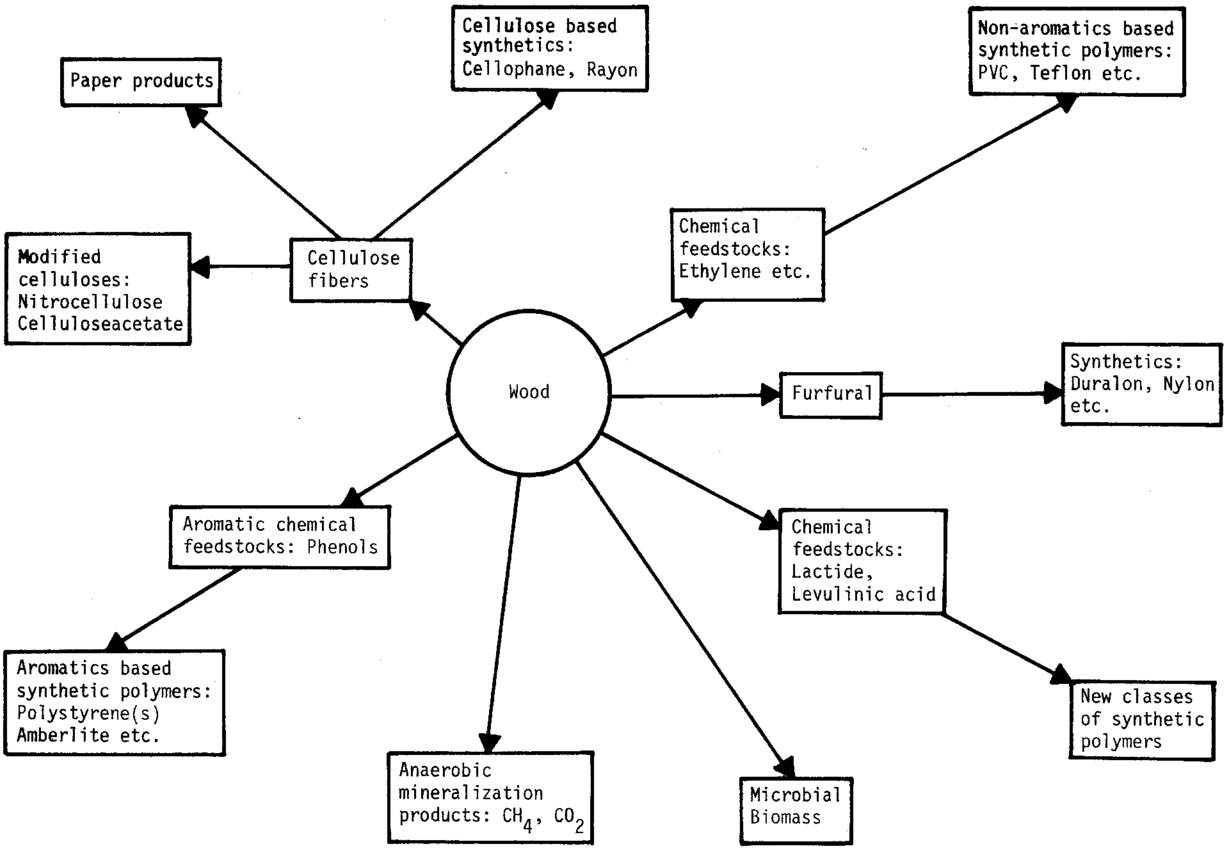


Figure 1. Integrated use of wood for the production of chemicals and paper. Through proper combination of physical, chemical or enzymatic pretreatment of wood and its components with microbial conversion processes, it is possible to obtain wood derived replacements for petrochemical based products.

product of terrestrial plants synthesized as an extremely stable, easily handled crop with a relatively high energy- and mass density (see Schwarzenbach and Hegetschweiler, this issue). Lignocelluloses form extremely stable structures which are very resistant to microbial attack under many environmental conditions. These chemical and physical properties have made wood a desirable building material and energy source for thousands of years. Only during the last few decades have coal, followed by natural gas and oil, begun to fulfill functions originally assigned to wood.

Before addressing the question of how wood might reassume its role as the basic raw material for conversion into fuels and chemicals, we should remind ourselves that nature supplies us with a raw material which, in itself, is many-sided. Wood polymers can often be utilized as - or even more - effectively in the natural form, without prior hydrolysis and degradation, to yield products for resynthesis into materials which will serve the same purpose. Appreciation of the beautiful structural characteristics of wood and its great versatility could also promote economy in the use of energy and materials. Turning to wood as a resource for chemicals will, therefore, be economically more interesting if some use can be made of the synthetic work performed by the plant during photosynthetic CO_2-fixation. Wood serves best if the molecules derived from it are those with the more complex structures: Cellulose, pentoses, hexoses and phenolic compounds. A process in which plant polymers are degraded to yield small molecules which serve as starting material for the synthesis of more complex ones is certainly less energy-efficient. It can be justified only if it produces feedstocks appropriate for existing chemical technologies. Wood can, for example, be converted to carbon monoxide and hydrogen through gasification at elevated temperatures and pressures[13]. The resulting gas mixture has a high H_2/CO ratio and is practically free of sulfur contaminants as opposed to gas originating from coal. This synthesis gas can serve as raw material for the chemical production of methanol, or possibly, for the production of acetate by *Butyribacterium methylotrophicum* (J.G. Zeikus, personal communication). Production and use of synthesis gas is hampered, economically, by the costs of the large amount of process energy required and, technologically, by the state of development of synthesis processes based on it[13].

Structurally more complex molecules might have to be isolated and purified from a mixture of very similar molecular species present in wood. Low yields

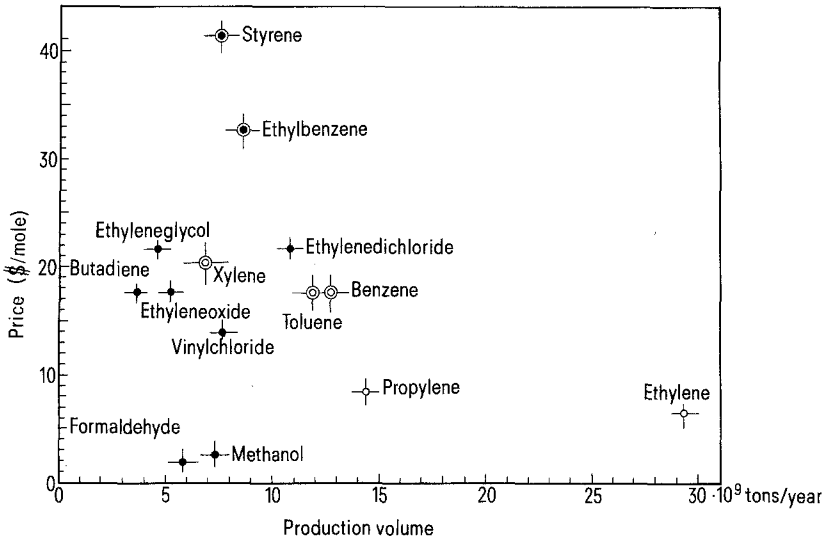


Figure 2. Unit prices and production volume of petrochemicals produced in the U.S. in 1979[34]. Vinylchloride, ethylenedichloride, ethyleneoxide, butadiene and ethyleneglycol are synthesized fromethylene. Ethylbenzene and styrene are based on benzene and ethylene. The high prices for the BTXes make lignin derived aromatics commercially interesting substitution products.

and processing difficulties might make the biomass approach less desirable. If the complex mixture of substrates can be converted microbiologically or enzymatically into a few smaller molecules (preferably belonging to one chemical substance class), however, the yield will increase and separation will become a minor problem (see Kaiser and Hanselmann, this issue).

Synthesis chemicals from wood

The synthetics industry has the largest demand for basic petrochemicals. In Western Europe, for example, 77% of the petrochemicals are used to synthesize polymers: 63% for plastics, 8% for fibers and 6% for elastomers. Solvents (13%), detergents (3%) and various other products (7%) account for approximately one fourth of the market volume[14]. Petroleum-based chemicals with the largest production volume in the U.S. are listed in figure 2. Table 1 shows possible means for deriving them - or replacement products - from biomass. Olefins can be obtained through fermentation of carbohydrates to ethanol and isopropanol and subsequent dehydration to ethylene and propylene. Many of the other primary chemical intermediates can be obtained through chemical modifica-

Table 1. Current primary chemical feedstocks and possible routes to plant chemical replacements

Rank*	Primary chemicals and intermediates	Current source**	Route to plant chemical replacement
1	Ethylene	P (cracking), NG	Dehydration of ethanol derived from anaerobic fermentation of carbohydrates
2	Propylene	P (cracking), NG; byproduct of ethylene production	Dehydration of isopropanol derived from anaerobic fermentation of carbohydrates
3	Benzene	P, C	?
4	Toluene	P, C	?
5	Ethylenedichloride	Synthesis from ethylene	Synthesis from ethanol
6	Ethylbenzene	Synthesis from ethylene and benzene	Synthesis from ethanol and ?
7	Vinylchloride	Synthesis from ethylene	Synthesis from ethanol
8	Styrene	Synthesis from ethylene and benzene	Synthesis from ethanol and ?
9	Methanol	NG, C	Byproduct of hemicellulose fermentation; microbial oxidation of methane
10	Terephthalic acid	P, C	?
11	Xylene	P, C	?
12	Formaldehyde	NG, P	Reduction of formate derived from anaerobic fermentation of carbohydrates
13	Ethyleneoxide	Synthesis from ethylene	Synthesis from ethanol
14	Ethyleneglycol	Synthesis from ethylene	Synthesis from ethanol
15	Butadiene	Synthesis from ethylene	Dehydration of butanediol derived from anaerobic fermentation or synthesis from ethanol

* Listed according to rank of 1979 U.S. production volume[34].
** P = petroleum, C = coal, NG = natural gas liquids (ethane, propane, butane).
? = biomass source and microbial processes are not known.

tion and synthesis based on a few fermentation products (fig. 3). For the moment, there are no satisfactory chemical or biological technologies available to supply aromatic hydrocarbons from biomass to replace the BTXs (benzene, toluene, xylene), although aromatic structures are present in abundance in lignin and other plant constituents.

The production from biomass of two entities would be of particular commercial interest: ethylene because of its large production volume and its importance as a basic chemical, and the aromatics because of their high market value (fig. 2). The development of chemical and microbiological techniques affording access to the valuable aromatics in the lignin polymer is hampered, however, by problems in separating monomers from a complex mixture of lignin hydrolysis products. The toxic effect of phenolic monomers on microbes and the recalcitrance of the lignin polymer to microbial hydrolysis under anaerobic conditions present further challenges.

Besides producing feed stock chemicals for synthetic purposes, one might search more intensively for enzymes capable of catalyzing conversion reactions at higher rates with better yields under less energy consuming conditions. Enzymatic conversion of propylene to propyleneoxide, for example, has been suggested by S.L. Neidleman (cited by Eveleigh[15]) with 3 enzymes (a pyranose-2-oxidase, a chloroperoxidase and a chlorohydrin epoxidase) derived from *Ondemansiella mucida, Caldariomyces fumago* and a *Flavobacterium sp.* respectively.

Qualitative availability of biomass

A great number of low molecular weight substances and polymeric products have been extracted from wood and bark (table 2). These are mostly specialty compounds with small production volumes but they demonstrate the great variety of plant chemicals that are available for particular purposes[16–18]. While purity and source-dependent constancy in composition are characteristic for petroleum resources, compositional flexibility and economic adaptability are properties attributed to plant biomass. Species with a high content of defined components can be grown according to needs for food, chemical feedstocks, synthesis chemicals, pharmaceuticals or fibers (fig. 4). Strains with the desired biomass composition (e.g. sunflowers with high seed oil content, grains with high content of amylose and very little amylopectin) can be bred or species carrying valuable traits can be selected from a large gene pool of the wild plants.

Thus the quality and quantity of biomass production can partially be controlled and be grown according to

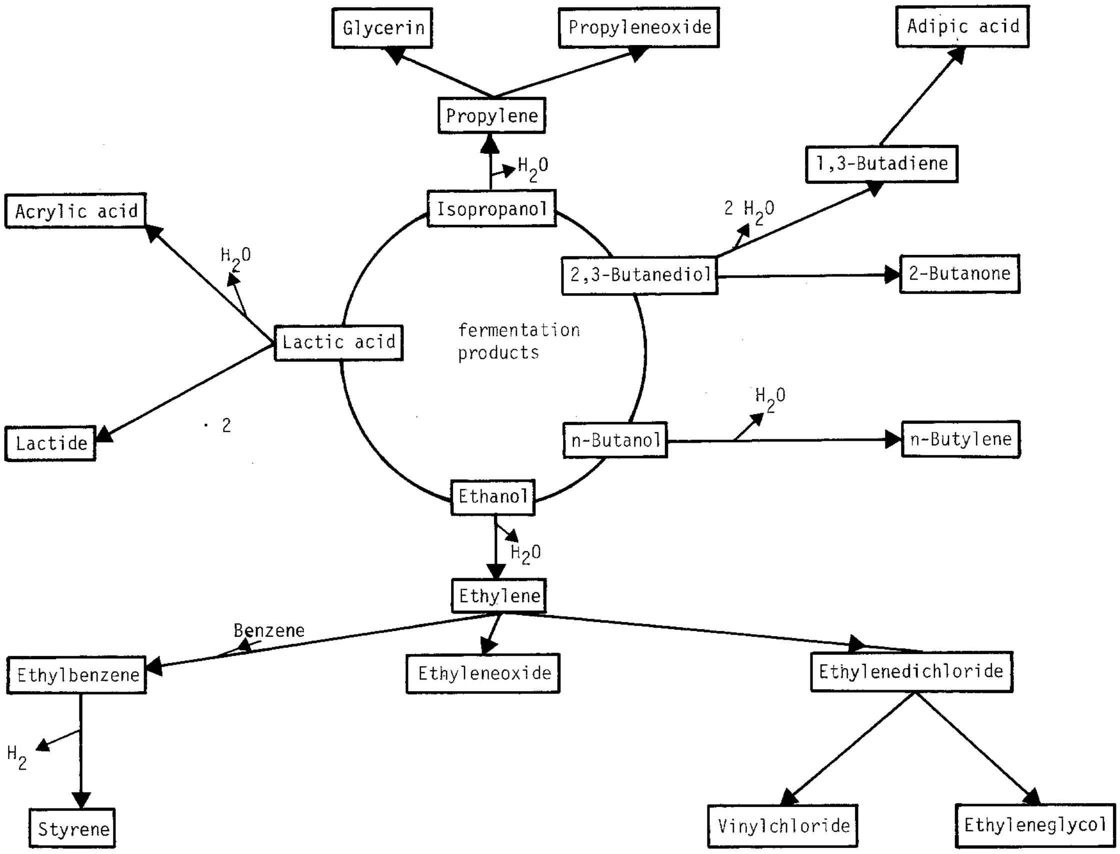


Figure 3. Fermentation products as feedstocks for synthesis chemicals. With the exception of the aromatics the most frequently used petrochemicals could be derived from a few products obtainable through anaerobic microbial fermentations and dehydration.

Table 2. Non-fibrous chemicals presently obtained from wood and wood components (pure chemicals, mixtures and complex components)

- Ethylalcohol
- Dimethylsulfide (DMS)
- Dimethylsulfone ($DMSO_2$)
- Dimethylsulfoxide (DMSO)
- Methylmercaptan
- Acetic acid
- Formic acid
- Levulinic acid
- Furfural
- Hydroxymethylfurfural
- Glycerin
- Ethyleneglycol
- Polyols (mannitol, xylitol)
- Phytosterols (Sitosterol)
- Guaiacol
- Catechol
- Protocatechuic acid
- Vanillin
- Vanillic acid

- Lignosulfonates
- Tall oil fatty acids (oleic, linoleic)
- Arabinogalactan
- Hemicellulose extract
- Wood sugars
- Lignans
- Tannins
- Levoglucosan
- Sugar acids

- Gum rosin
- Gum turpentine
- Pine oil, tall oil
- Sulfate turpentine
- Wax

- Charcoal
- Activated carbon

- Yeast biomass

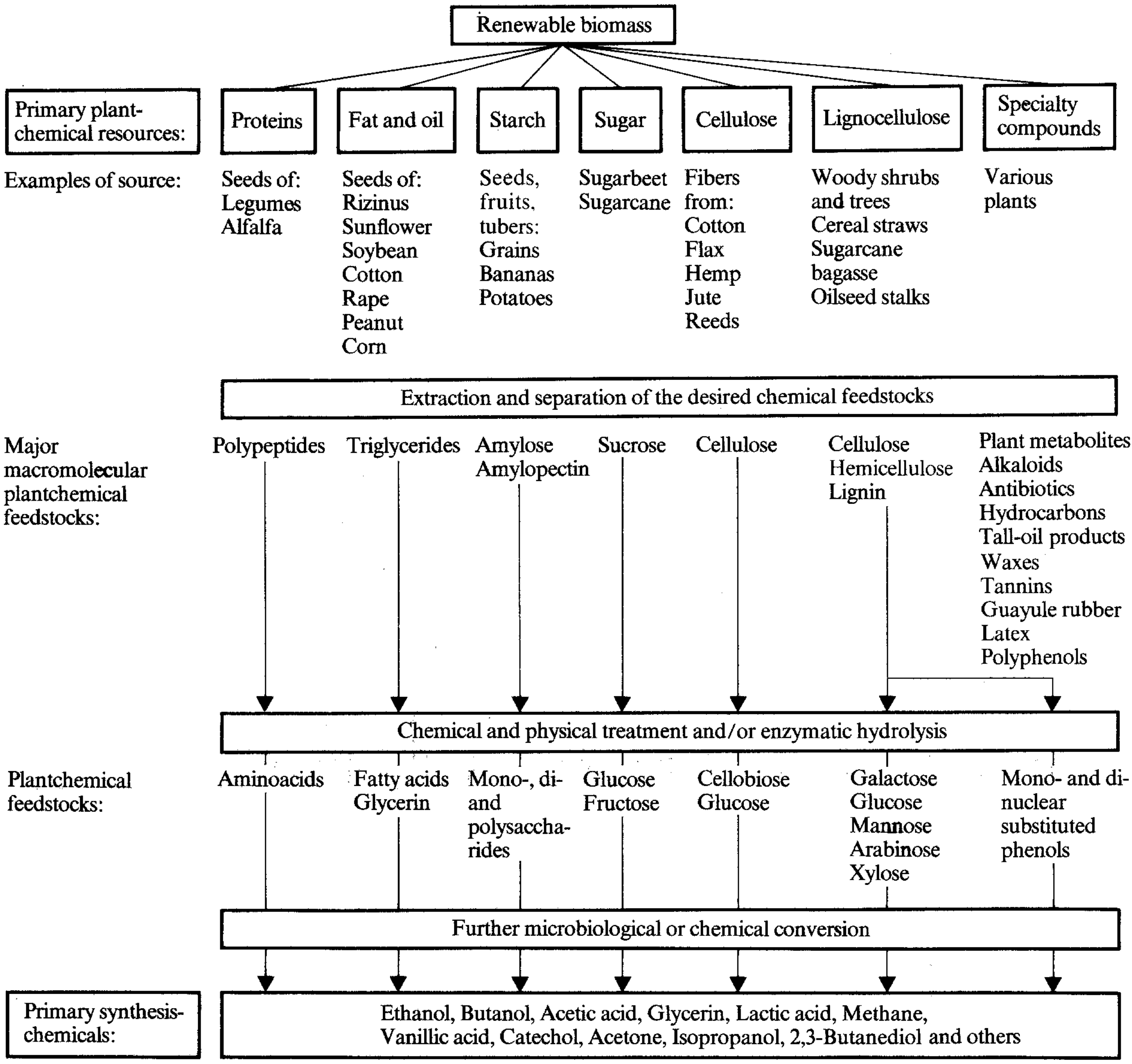


Figure 4. Conversion of primary plantchemical resources into primary synthesis chemicals. The great diversity of plant constituents combined with one of the many microbial fermentation pathways leads to high flexibility in the production of various synthesis chemicals.

needs. However, seasonal growth differences in temperate regions, limited species selection for different climatic zones, slow growth (particulary of certain desirable wood species), the vulnerability of plant monocultures to infectious diseases and insect pests, the relatively low ratio of biomass per unit area, the lack of appropriate and economic conversion facilities and technologies, and the competition with alternative uses, are disadvantages for a biomass-based chemical producing industry. To date, little effort has been expended on breeding woody plants to improve cellulose and lignin content. But some use can be made of the ecological diversity in the plant kingdom. The natural abundance of different species adapted to various environments offers a large pool of possibly desirable lignocellulose producers[19]. Sjöström[20] has compiled data on the composition of 20 tree species (table 3). Lignocellulose content varies between 60% and 76% of the dry weight. Softwood species have a higher lignin to cellulose ratio than hardwoods. The major aromatic building blocks of softwood lignin are the coumaryl-, coniferyl- and sinapyl precursors. However, the differences between carbohydrate and lignin content and the kind of aromatic monomers become less important if an integrated use of the whole biomass is considered.

Integrated use of wood for the production of chemicals

The great variety of anaerobic metabolic routes taken by different microorganisms allow utilization of any of the many forms of biomass (figs 3 and 4). This leads to great versatility in the kind of substrates that can be processed[21] and a flexible adaptability to products that are in great demand (e.g. fig.2). Polymers with non-aromatic and aromatic building blocks could be synthesized, for example, if the microbial conversion processes suggested in the flow diagrams (fig.5, a-e) proved to be technologically applicable and economically feasible.

Table 3. Lignocellulose content of some wood species*

	Ligno-cellulose (% of dry wood weight)	Lignin: cellulose ratio	Species
Softwoods (average of 9 species)	67.3	42:58	
1	69.1	40:60	*Picea abies*
2	68.2	39:61	*Larix sibirica*
3	68.2	45:55	*Tsuga canadensis*
4	68.1	43:57	*Pseudotsuga menziesii*
5	67.9	43:57	*Abies balsamea*
6	67.7	41:59	*Pinus silvestris*
7	67.0	41:59	*Picea glauca*
8	65.1	49:51	*Juniperus communis*
9	64.6	42:58	*Pinus radiata*
Hardwoods (average of 11 species)	67.3	36:64	
1	76.3	41:59	*Eucalyptus camaldulensis*
2	73.4	36:64	*Gmelina arborea*
3	73.2	30:70	*Eucalyptus globulus*
4	69.2	31:69	*Ochroma lagopus*
5	67.4	38:62	*Acer rubrum*
6	65.9	38:62	*Acer saccharum*
7	64.2	39:61	*Fagus silvatica*
8	63.7	33:67	*Acacia mollissima*
9	63.1	39:61	*Alnus incana*
10	63.0	35:65	*Betula verrucosa*
11	60.8	35:65	*Betula papyrifera*

* Calculated from data given by Sjöström[20].

After the 2nd World War, wood distilleries which produced many organic solvents through cellulose fermentation and other processes were closed because competition from inexpensive petroleum based chemicals could not be met. As a consequence, no research priority was given to the development of new manufacturing techniques for chemicals from alternative raw materials. Reversal of this trend is opportune today and should be fostered.

Many processes that use wood today do not use the lignin as raw material but as fuel. If the 'waste' produced in cellulose production is burned, for example, it supplies some of the process energy; if it has to be disposed of, it constitutes a burden to the environment. Cellulose production would become uneconomical if the full costs of disposal had to be included in manufacturing costs. But it can remain economical if lignin is converted into high priced chemicals. Thus the development of technologies that achieve better use of all the components present in a biomass resource should be encouraged.

Convertibility of biomass

Plants store photosynthesis products in special cellular organelles and in other structural components as polymers with large molecular weights or as hydrophobic aggregates[22]. Reactivity and osmotic activity of the monomers are decreased through polymerization, making stored plant reserves chemically inert substances. Our ability to harvest and store plant reserves is based on these characteristics. With the exception of lignin and cellulose in lignified tissues most plant polymers can be hydrolyzed easily with the aid of enzymes. The hydrolysis of wood-cellulose into fermentable sugars, however, represents a rate limiting step in the cellulose to ethanol conversion process. Thus large research efforts have been directed toward improving microbial productivity of cellulases. The lignin polymer with its non-reactive intermonomer C-C and C-O linkages is very slowly degraded by some fungi and bacteria under aerobic conditions (see Higuchi, this issue). In anaerobic environments lignin is recalcitrant[35]. Lignin incrustations make cellulose in vascular and supportive tissues inaccessible to the cellulases of many organisms. For practical purposes, therefore, mechanical or chemical dissolution of the lignocellulose complex has to be employed. Today, steam explosion of wood is regarded as the most efficient separation process[11]. This process yields cellulose digestable to microorganisms, partially hydrolyzed hemicellulose, and low molecular weight lignin oligomers consisting of 3-10 aromatic units. Further hydrolysis yields a mixture of phenolic compounds whose composition and yield depend on the cracking procedure employed and the source of the lignin. Alkaline oxidation at elevated pressures and temperatures in the presence of a catalyst, for example, yields

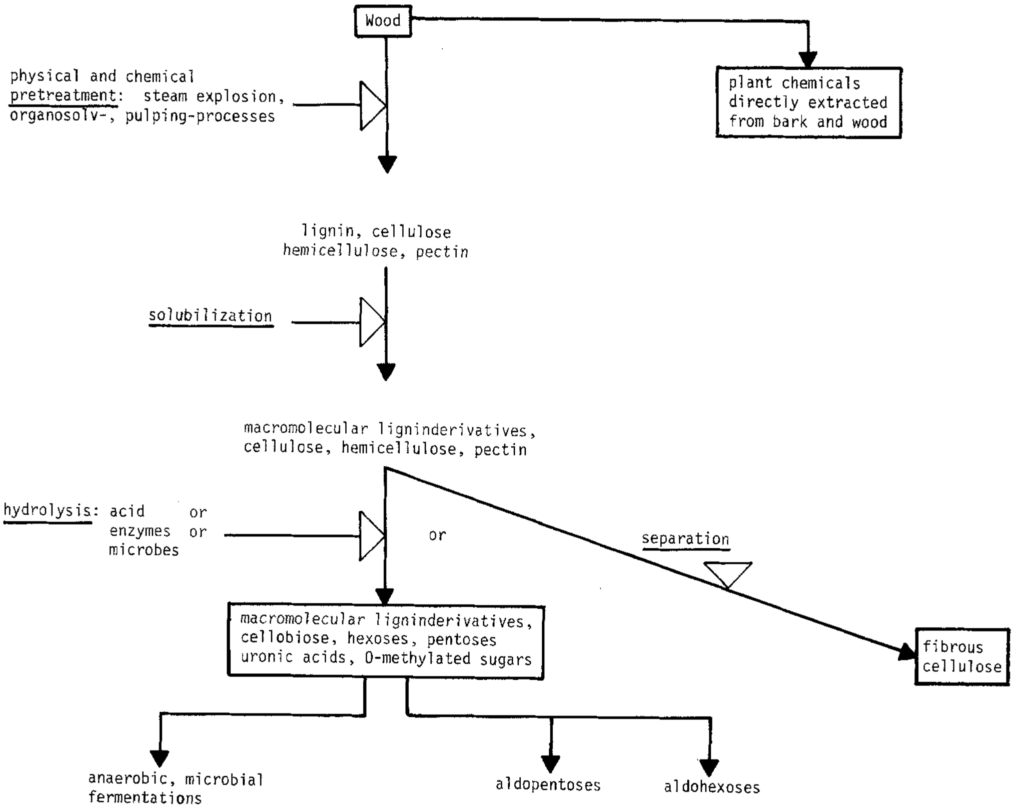


Figure 5. *a* Extraction, partial solubilization and separation of some wood components.

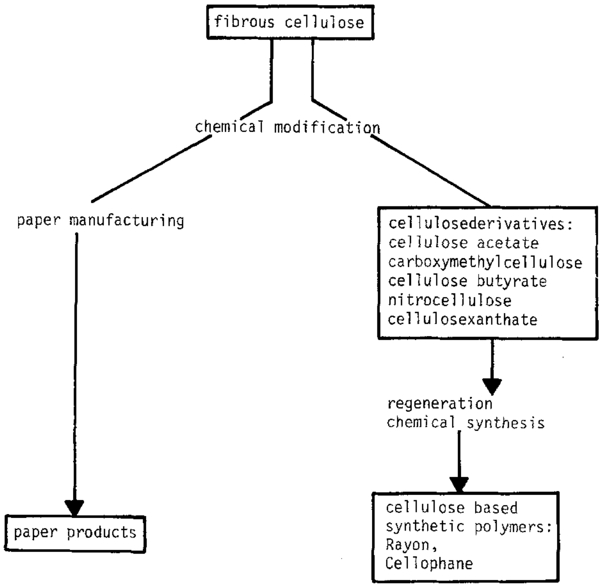
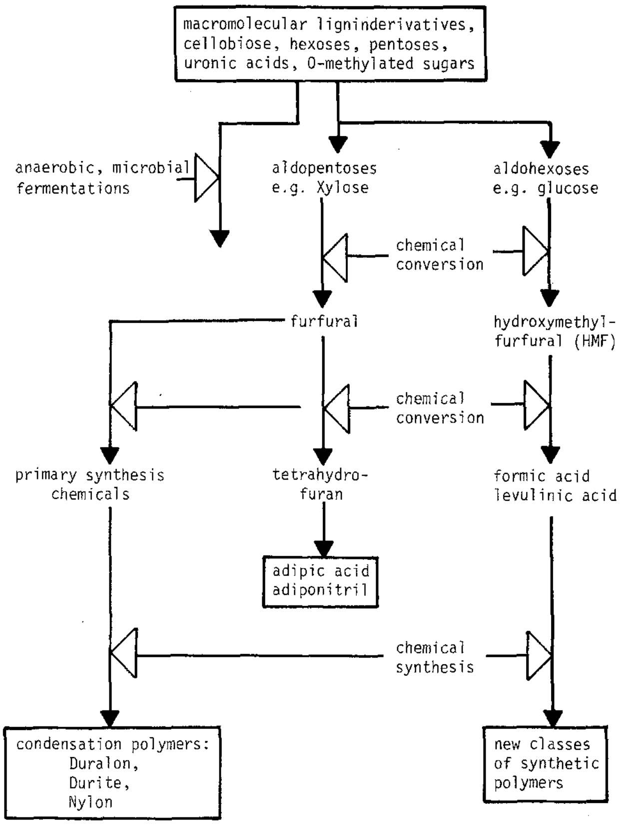


Figure 5. *b* Synthetic polymers based on fibrous cellulose.

Figure 5. *c* Synthetic polymers based on hemicellulose- and pectin components.



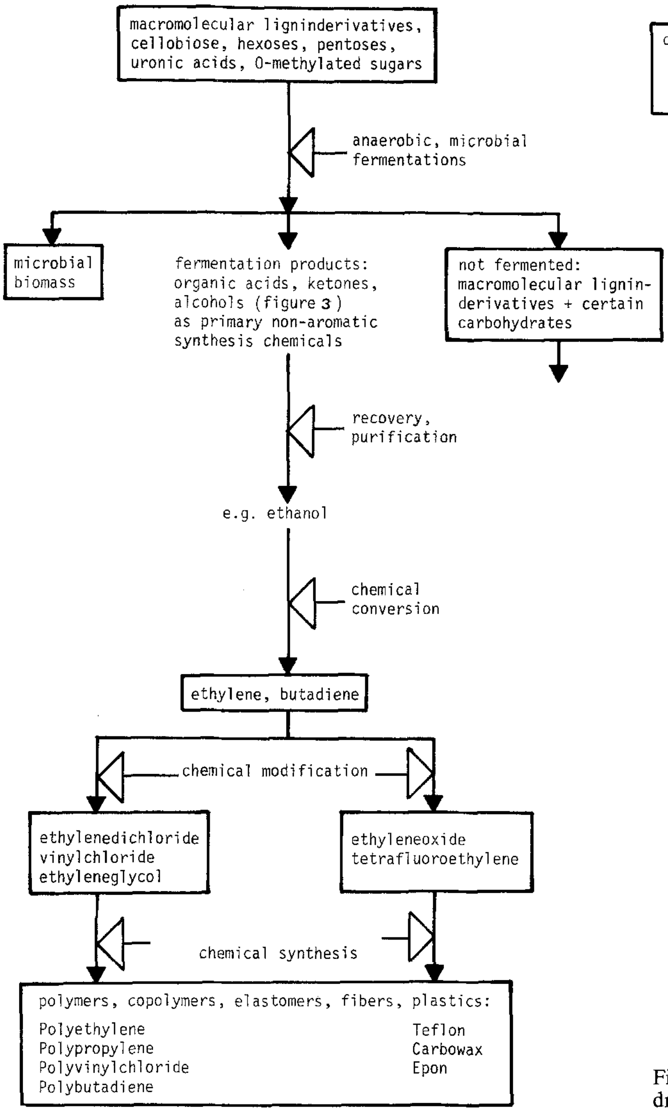


Figure 5. *d* Synthesis chemicals and synthetics based on carbohydrate to ethanol fermentation.

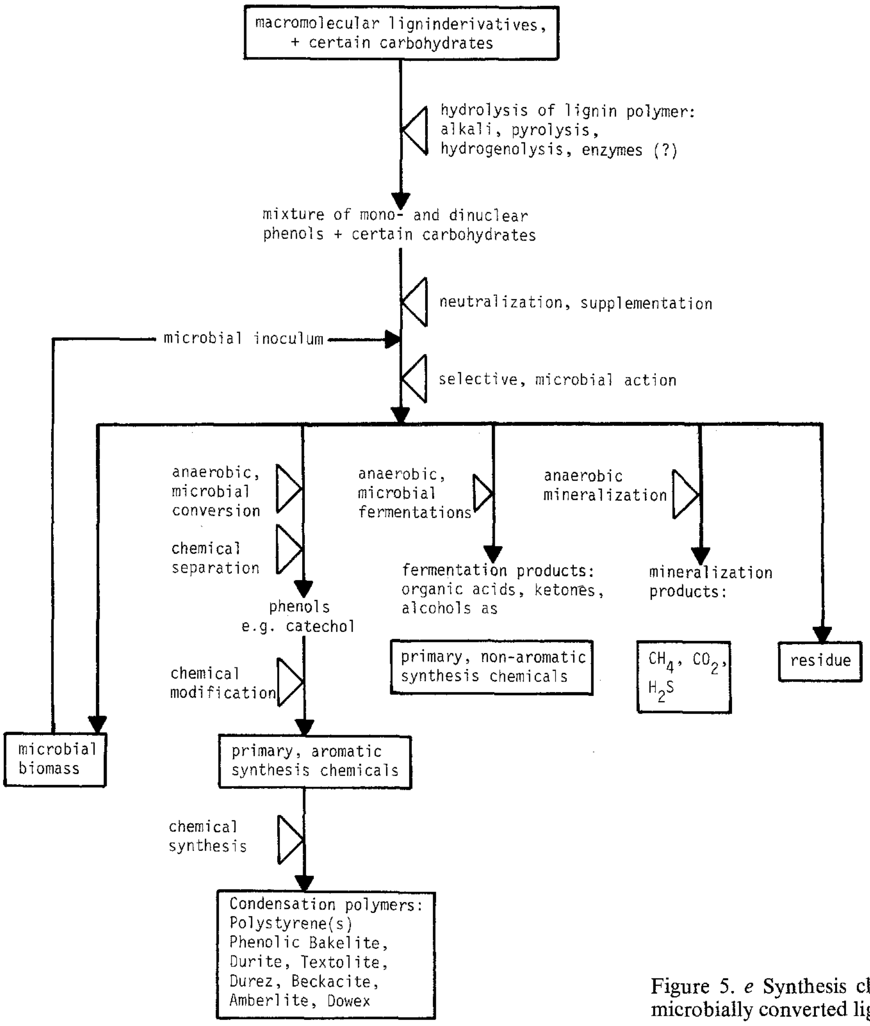


Figure 5. *e* Synthesis chemicals and synthetic polymers based on microbially converted lignin monomers.

a mixture of substituted phenols. Vanillin, vanillic acid, acetovanillone and smaller amounts of p-hydroxybenzaldehyde and syringaldehyde have been obtained from softwood lignin. Hardwood lignins yield higher amounts of syringaldehyde, bamboo-, grass- and canelignin yield more p-hydroxybenzaldehyde[23]. Nakano[24] obtained a mixture of more than 10 phenolic compounds, all in relatively small yields, in an acidic oil fraction from hydrogenation of lignosulfonate.

Although a great number of publications and patents exist in the field of lignin residue utilization, there is still no established procedure for harvesting a chemically and commercially useful phenolic fraction at a high yield. The main difficulties are encountered in fractionating the complex mixture of 10–15 different monomers obtained in the distillable phenol fraction. The yields of phenols published in 56 papers between 1919 and 1973 vary between 3.6 and 61.7% (w/w) depending on the source of the lignin and the hydrolysis procedure employed[25]. The highest value reported is for alkaline-treated lignin but hydrogenation processes seem to give constantly high yields from different kinds of lignins. The average yield of distillable phenols is 35% of the lignin weight. The major compound classes in hydrolyzed lignin preparations are phenols, xylenols, catechols, guaiacols and syringols (table 4). McCarthy et al.[23] improved biodegradability of lignocellulose by hot alkaline treatment[26] at pH 13 and 200 °C for 1 h. Integrated use of lignocellulose requires that cellulose first be solubilized by mild acid treatment and the resulting carbohydrate fraction fermented to ethanol before residual lignin is treated with hot alkali.

Enzymes capable of cleaving ether linkages are produced by white-rod fungi and certain soil bacteria[27]. They liberate from wood mono- and dinuclear phenols. These enzymes might one day become efficient catalysts for converting the polymer into monomeric substrates for further anaerobic conversion processes.

It might sound contradictory to advance microbial processes for the production of chemicals from a natural polymer that shows extreme resistance to biodegradation, particularly in the absence of oxygen. However, the combination of appropriate physicochemical or enzymatic pretreatment of lignocellulose with anaerobic microbial degradation and conversion of the phenolic monomers could make lignin a realistic and attractive source for aromatic chemicals. The conditions that could make an anaerobic microbial process practicable are discussed elsewhere in this issue (Hungate; Kaiser and Hanselmann; Wuhrmann).

Technological feasibility

Fermentation competes with alternative technologies that have been proposed for a more efficient use of wood[28]. Thermal degradation methods (gasification, pyrolysis) demand a high energy input and their main products are small molecules which again require a lot of energy if they are to be used to synthesize more complex molecules. Great effort is also needed to separate valuable chemical byproducts from the complex mixture. The applicability of the gas mixture produced by thermal degradation in synthesis with homogeneous catalytic systems has been summarized by Pruett[13].

A more selective breakdown of wood components is achieved by hydrolysis. Dilute sulfuric acid at an elevated temperature hydrolyzes wood carbohydrates but not the lignin[29]. Pretreated cellulose becomes more susceptible to enzymatic breakdown and can readily be converted to ethanol[29,30]; lignin remains in the residue. During fermentation after hot alkaline treatment, many aromatic monomers are converted to catechol which can be harvested. Others are mineralized to CH_4 and CO_2. Several problems remain to be solved before microbial fermentation combined with chemical pretreatment will become technologically more feasible than the gasification methods. For instance, relatively low concentrations of products must be recovered from the fermentation broth, the system must be product tolerant and substrate conversion must be more efficient and proceed at higher rates.

How can lignin-derived chemicals become useful in synthesis? If it becomes possible to separate and purify phenolic monomers obtained through microbial conversion, these monomers would represent more desirable chemicals for the synthesis of plastics than any high molecular weight fraction of lignin or the small molecules that result from gasification, pyrolysis or fermentation[31]. Aromatic polyamides, polyphenylene oxides and polyesters synthesized from lignin-derived phenolics have thermal properties and processing behaviors comparable to synthetics based on petrochemicals[32]. Polyphenylene oxides can be synthesized from 2,6-dimethoxy phenol, the decarboxylation product of syringic acid, and from other 2,6-disubstituted phenols. Lindberg et al.[32] synthesized aromatic polyesters at melting temperatures between 227 and 277 °C from vanillin (fig. 6). The aldehyde was first oxidized to vanillic acid, esterified to a dibasic acid with dibromoethane, and polymerized by condensation. Alternatively, vanillic acid could be converted to its hydroxyethylether which is coupled to form the aromatic polyester by condensation polymerization (fig. 6). The physical properties of the polymers are not altered drastically by the presence of the methoxy substituent.

Table 4. Mono- and dinuclear phenols obtainable through hydrolysis of lignin

Phenols
Phenol
2-Methylphenol (o-Cresol)
3-Methylphenol (m-Cresol)
4-Methylphenol (p-Cresol)
2-Ethylphenol
3-Ethylphenol
4-Ethylphenol
4-Propylphenol
3-Methyl-4-ethylphenol
4-Hydroxyphenol (Hydroquinone)
p-Hydroxybenzoicacid
p-Hydroxybenzaldehyde

Xylenols
2,4-Dimethylphenol (2,4-Xylenol)
2,5-Dimethylphenol (2,5-Xylenol)
2,6-Dimethylphenol (2,6-Xylenol)
3,4-Dimethylphenol (3,4-Xylenol)
3,5-Dimethylphenol (3,5-Xylenol)

Catechols
2-Hydroxyphenol (Catechol)
4-Methyl-2-hydroxyphenol (Homocatechol)
4-Ethyl-2-hydroxyphenol
4-Propyl-2-hydroxyphenol

Protocatechuic acid
Protocatechualdehyde
Homoprotocatechualdehyde

Guaiacols
2-Methoxyphenol (Guaiacol)
4-Methyl-2-methoxyphenol
4-Ethyl-2-methoxyphenol
4-Propyl-2-methoxyphenol
4-Propenyl-2-methoxyphenol
(Isoeugenol)
4-Acetyl-2-methoxyphenol
(Acetylguaiacone)
Vanillin
Vanillic acid
Carboxyvanillic acid
Carboxyvanillin

Syringols
2,6-Dimethoxyphenol
4-Methyl-2,6-dimethoxyphenol
4-Ethyl-2,6-dimethoxyphenol
4-Propyl-2,6-dimethoxyphenol

Syringaldehyde
Syringic acid

Dinuclear phenols
4,4′-Dihydroxy-3,3′-dimethoxy-stilbene
Dehydrodivanillin
Dehydrodivanillic acid
4,4′-Dihydroxy-3,3′-dimethoxychalcone
4,4′-Dihydroxy-3,3′-dimethoxybenzophenone

Depolymerization of lignin yields a mixture of phenolic products. Its composition depends on the source of the lignin (gymnosperm, angiosperm) and the hydrolysis conditions employed.

Haraguchi and Hatakeyama[33] have synthesized polystyrenes with building blocks that are structurally related to lignin monomers: Poly(p-hydroxystyrene), poly(3-methoxy-4-hydroxystyrene) and poly(3,5-dimethoxy-4-hydroxystyrene). Under aerobic conditions these substances were biodegradable by mixed microbial cultures enriched from soil. Thus, introduction of functional groups which are characteristically present in lignin monomers change polystyrene into a biodegradable polymer. These few encouraging results on production and application of lignin-derived aromatics support the technological feasibility of using wood as a resource for aromatic synthesis chemicals. Some ingenuity in chemical synthesis may be needed to find ways to use other lignin-derived aromatics.

Economic aspects

Lignochemicals become economically attractive if the costs for the raw material and the production of desired chemicals are competitive with the costs for comparable chemicals obtained from fossil oil. Today the technology and the plants for the refining of oil and gas are available while corresponding facilities for lignochemistry would still have to be developed. This means large investments into an enterprise that will presumably not become commercially interesting within the next few decades[3]. A proper cost-benefit analysis cannot be made for most of the proposed biological processes since many have not even reached the pilot-plant stage.

Although there are countries with large reserves of wood, this alone would not justify the buildup of a lignochemical industry. We will not solve our materials problems for the future, and probably will cause great ecological damage by using the biomass accumulated over several centuries at a faster rate than at which it can be reproduced. For a balanced lignochemical industry, the source for raw materials has to be secured through silviculture. Selection and planting of the species best adapted to a particular climatic region and their growth until harvest, however, takes many years (see Schwarzenbach and Hegetschweiler, this issue).

The schedule to be followed for the next decades, therefore, will demand restricted use of oil and natural gas, reserving them for the production of chemical feedstocks. Meanwhile, the developing

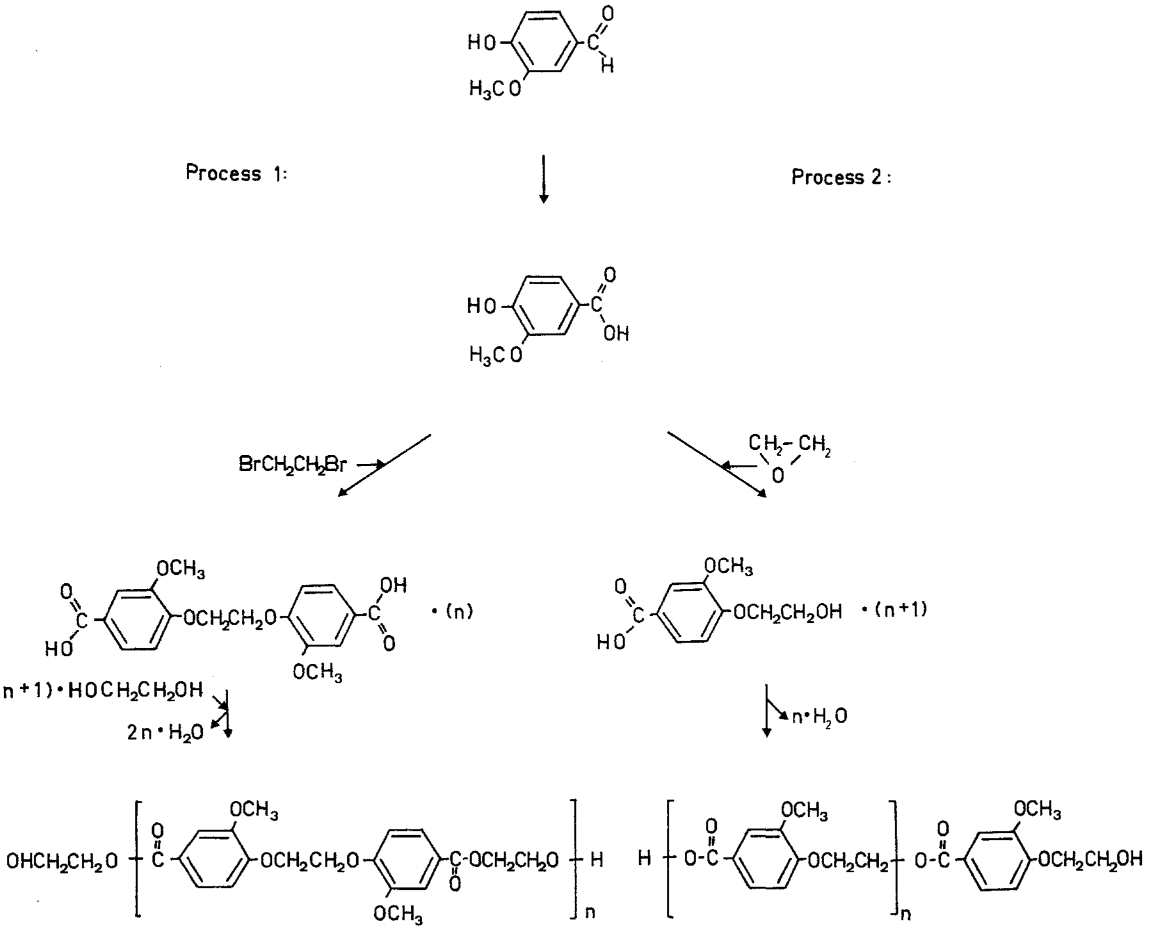


Figure 6. Polymer synthesis with vanillic acid monomer derived from lignin[32].

wood-based chemicals industry should concentrate on specialty products that can be made from lignocellulose. A more efficient use of wood could increase revenues and make existing wood processing plants economically more attractive. An example shall serve as illustration. The production of 1 m^3 of ethanol by the Inventa process requires 5.2–7.7 tons of wood[30]. Assuming an average lignin to cellulose ratio of 2:3 (table 3) one is left with 2–3 tons of lignin per m^3 of ethanol. In the Inventa process the lignin serves as fuel for process energies. If alternative energy sources can be applied, lignin would be available for hydrolysis and microbial conversion to valuable aromatic synthesis chemicals. In this way one could achieve the production of olefins (from ethanol) and aromatic hydrocarbons in the same plant, an option that would appear profitable. Lignin residues produced by paper mills could similarly increase revenue for this group of wood users.

Goldstein[31] showed that about 95% of the polymers produced today theoretically could be manufactured from monomers derived from lignocellulose: 47% with ethylene, 12% with butadiene and 36% based on phenolic compounds as building blocks. An average of 2.62 tons of lignocellulose would be required to produce 1 ton of lignin-derived synthetics (table 5). This ratio could be improved if the yields of aromatics obtained from lignin in physico-chemical procedures could be increased in combination with microbial conversion.

It will be difficult to find substitutes for the large quantities of fossil fuels that are used today for transportation and heating[12]. To replace petrochemicals by lignochemicals, today, is not so much a question of quantity as a problem of processes and economics.

Petrochemical products account for approximately one third of the sales turnover and half of the total capital investments of the chemical industries[2]. Worldwide production of petrochemicals is divided presently among Western Europe (30%), North America (25%), Japan (10%), countries with central economic planning (25%) and other countries (10%). Oil producing countries are now developing their own petrochemical industry rapidly in order to decrease their dependence on imported chemical products and to increase their share in the world market for petrochemicals. Oil and natural gas resources are plentiful there and the gas, for example, is presently not at all being used economically. With regard to raw materials, energy and production costs, the OPEC countries are in an enviable situation. The financial

Table 5. Estimate of lignocellulose raw material required for the production of plastics, synthetic fibers and synthetic rubber*

Product	Tons of lignocellulose required per ton of product synthesized	Principal biomass source of monomers
A) Plastics		
Epoxies	2.84	Lignin
Polyesters	2.68	Lignin
Phenolic resins	2.86	Lignin
Polyamides	2.86	Lignin
Styrene and copolymers	2.97	Lignin
Polyethylene	4	Cellulose
Polypropylene and copolymers	4	Cellulose
Polyvinylchloride	1.74	Cellulose
Other vinyl resins	2.51	Cellulose
Average lignin-derived plastics	2.84	
Average cellulose-derived plastics	3.06	
B) Synthetic fibers		
Polyamide fibers (Nylon)	2.86	Lignin
Polyester fibers (Dacron)	2.68	Lignin
Acrylic fibers	2	Cellulose
Olefinic fibers	4	Cellulose
C) Synthetic elastomers (rubbers)		
Butadiene-styrene	3.53 + 1.19	Cellulose + lignin
Isoprene-isobutylene (butylrubber)	5.89	Cellulose
Nitrile	2	Cellulose
Polybutadiene	5.89	Cellulose
Ethylene-propylene	5.89	Cellulose
Average cellulose-derived synthetic elastomers	4.64	
Average lignin-derived synthetics	2.62	
Average cellulose-derived synthetics	3.77	

* Calculated from data given by Goldstein[31], based on 'optimistic approximate yields of the monomers obtainable from wood'.

assets which they have accumulated since the drastic increase of the oil prices allow those countries to finance the transfer of technological know-how and the chemical plants from industrialized nations. The European petrochemical industry will therefore be pressured from two sides: by the dwindling availability and the rising prices of petroleum on one hand and by the market competition for refined petrochemicals and synthetic products on the other. Two of the options the chemical industry might consider are:

1. A partial substitution of fossil hydrocarbons by renewable biomass as the alternative basis of chemical resources and,
2. a reorientiation towards development of advanced chemical and biochemical technologies for the production of more refined basic chemicals for medicinal, agricultural and chemical uses.

Intelligently applied biochemical capabilities of microorganisms could play a decisive role in this transition.

Conclusions and outlook

Would there be enough wood to supply the raw material for chemical feedstock production? Fulfilling the demands of the plastics industry in Switzerland, for example, would require 10 times the amount of wood which is presently processed by the paper industry. Today's silviculture, mostly directed towards paper manufacturing, fire wood production and the lumber industry could not supply the additional quantities needed for lignochemical production. Large forest areas would have to be carefully cultivated, without upsetting their ecological functions, to yield the amount of wood needed by a lignochemical industry. Silviculture with new species, well adapted to local conditions could become a reservoir for renewable lignochemical feedstocks. It is assumed that low grade wood and woody shrubs could be used for the production of chemicals while wood of high quality should be reserved for lumber, plywood and pulp. Also the lignin residues that remain after cellulose extraction in paper mills constitute an unused source for the production of synthesis chemicals.

In the future we will be forced to make more intensive use (and, it is to be hoped, more intelligent use) of the ability of green plants to synthesize a multitude of chemical structures from CO_2 and H_2O. Three routes of development might be persued concurrently:

1. Selection of plants that produce high yields of a desired biomass;
2. search for microbiological processes to convert plant raw materials into 'useful' chemicals; and
3. development of chemical techniques to process new classes of chemicals in synthesis.

The transition from fossil hydrocarbons to renewable biomass requires farsighted decisions and long term investments.

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The formation of methane from biomass - ecology, biochemistry and applications

R.E. Hungate explains why methane as a product and cellulose as a substrate command so much attention today; he then examines the ecology of one natural methane producing system, the rumen. Other natural ecosystems are discussed by K. Wuhrmann.

The known biochemical pathways of methanogenesis are reviewed by R.S. Wolfe. It is astonishing how some of the structural and chemical properties of the cells are uniquely and specifically restricted to the group of methanogens. The practical engineering, operational and economic aspects of the methane production are reviewed by J.T. Pfeffer who discusses substrate properties, process characteristics, residue disposal and costs.

The special case of biogas production from agricultural wastes, especially those from animals, is presented by P.N. Hobson and practicable high- and low-technology systems are compared, particularly in regard to their application in underdeveloped countries.

The article by M. Gandolla and co-workers describes a small experimental landfill which, in producing methane, is a solid state fermentation system. This paper stresses many of the practical problems and considerations associated with such a system (composition of gas, leakage at the landfill, purification, storage, utilization and safety).

Methane formation and cellulose digestion - biochemical ecology and microbiology of the rumen ecosystem

by R. E. Hungate

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In postulates[1] on the Earth's origin, gaseous chemical elements combined with each other during cooling; compounds with the highest boiling points condensed first, followed by those containing lighter elements. Living material, formed gradually by chemical reactions of the lighter elements and traces of the heavy ones, was peculiar in its tendency to revert to non-living material unless chemical work maintained its living state. Abundant non-living compounds of C, H, and O also formed in various proportions. The relatively large energy changes involved in the oxido-reduction of these elements equipped them to be agents for the chemical work.

Because the Earth was initially anaerobic, with insufficient oxygen to combine completely with the available carbon and hydrogen, much of the carbon must have been in an intermediate state of oxidation. In the absence of O_2, energy was not available through the oxidation of carbon to CO_2 and H_2O, but it could be derived by converting C atoms at an intermediate state of oxidation to CO_2 and CH_4. These molecules are in a low energy state anaerobically, incapable of further redox reactions except that CO_2 can be reduced with H_2 to CH_4. Thus methane was, presumably, an important waste product of early metabolism, and methanogenesis was a primitive phenomenon, accomplished by possibly many diverse forms.

The primitive carbon compounds at intermediate states of oxidation do not have an equal potential for chemical work. This is evident from the following comparisons of single-C compounds containing both H and O[2].

$$4\,HCOOH\ (\text{formic acid}) \rightarrow 3\,CO_2 + CH_4 + 2\,H_2O \qquad (I)$$

$$\Delta G_0' = -120\ \text{kJ}$$

184 daltons -0.65 kJ/dalton