Chemicals from Biomass: Petrochemical Substitution Options

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Summary. As a source of chemicals, biomass has several intrinsic advantages over fossil mass: it is renewable, flexible through crop switching, and adaptable through genetic manipulation. Inflexibility of the fossil mass resource is compensated for by highly effective technology for production of olefins and aromatics, economies of scale, and a highly developed system of conversion products with large markets. Direct and indirect strategies to substitute for petrochemicals are based on ecological succession concepts. A proliferation of lignocellulosic fractionation processes is arising from the need for inexpensive, homogeneous, chemically useful biomass feedstocks.

More than 7 percent of U.S. petroleum and natural gas liquids are consumed in the manufacture of over 54 million metric tons of primary chemicals, which are the foundation of the existing U.S. chemical industry (*1*). This industry plays a major role in maintenance of our present standard of living and has a positive foreign trade balance (*2*). These achievements have been based on the low price, ready availability, and high purity of a handful of key intermediates, especially ethylene, propylene, methanol, benzene, toluene, and the xylenes. The era of low price and bountiful availability of these chemicals is drawing to a close. The impending chemical feedstock crisis has been triggered by changes in the relations between petroleum producing and consuming countries.

Although the same fossil mass (petroleum, natural gas, coal, and oil shale) resources are employed to make fuels and chemical feedstocks, the problems of obtaining fuels and chemicals are not closely related. For example, the chemical industry places great emphasis on the purity of chemicals and constancy of composition. In contrast, fuel oils and gasoline derived from petroleum, coal, or shale are mixtures of hundreds or thousands of chemical compounds. They are quite useful as fuels but have limited utility as chemicals.

The impact of inflation on fuel prices and on the prices of chemical feedstocks and the intermediates derived from them is complex. In principle, the chemical industry can bid higher for its raw materials than the fuel sector can. However, the increased costs can have quite adverse effects in end-use markets. For example, 10 years ago ethylene cost about half as much per pound as did cornstarch; now it costs twice as much. This fourfold increase provides the economic basis for the shift in ethanol production from hydration of ethylene to fermentation of glucose derived from starch. Similarly, the petrochemical route to ethylene glycol via ethylene and ethylene oxide is being threatened by a synthesis gas route (*3*), which could be based on coal or biomass.

Development of biomass resources as fuel feedstocks has been impeded by a mismatch between the scale of production of biomass and fossil fuel production rates. Fuel consumption in the United States is so huge (about 84×10^{18} joules per year) that obtaining 7 million tons of biomass (about 10^{17} joules per year) is negligible. This much biomass resource would have a highly salutary effect on chemical feedstocks. The relatively low energy contents, seasonality, and diffuse geographic dispersion of biomass resources also are greater barriers to fuel production than to chemical production. The possibility that biomass resources could compete more effectively with fossil mass resources for production of feedstocks for the chemical industry than for the fuel industry is examined in this article. Success or failure will depend on both strategic and tactical considerations.

Some distinctions and relations between resources, feedstocks, primary chemicals, and key intermediates are shown in Fig. 1. A resource is a raw material as it enters the economy. A feedstock, derived from the resource by physical and/or chemical means, is a mixture of materials, whose composition is controlled to make specific primary chemicals or fuels. A primary chemical usually is a single chemical entity (such as ethylene) or a mixture of closely related chemicals (such as tallow fatty acids) and is the first chemically homogeneous product derived from the feedstock. An intermediate is derived from primary chemicals and is the source of many end products. Examples include styrene from benzene and ethylene and ethylene glycol from ethylene. The resource and the technology determine which category applies to a specific product (for instance, glycerin is a primary chemical from oilseed biomass but it is also an intermediate made from gas- or petroleum-derived propylene).

Where Does Biomass Fit?

Fossil resources include quite a diversity of compositions, ranging from natural gas to coal. Biomass also has a wide range of compositions; for example, corn grain is approximately 70 percent starch, the peanut is 50 percent triglyceride oil, and cotton fiber is more than 90 percent cellulose. The major differences between fossil mass and biomass pertain to the inflexibility of fossil mass composition, which depends on geological phenomena beyond human control. In contrast, biomass resources can be grown to satisfy changing end-use demands on both a quantitative and qualitative basis (*4*). Land can be shifted from corn grain to sunflowers if triglyceride demand makes the oilseed crop more profitable than the starch crop. The shift back to corn or on to another crop also is feasible. However, a coal mine cannot become an oil well or gas well reversibly, even though in situ gasification could make the transition on an irreversible basis. Selection of species and optimization of composition through breeding and other genetic methods can adjust the composition and availability of biomass to meet demand. For example, corn grain is normally about 4 percent triglycerides. The corn oil content can be increased to 18 per-

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cent or reduced to 0.5 percent (*5*). Thus, the competition between biomass and fossil mass is not just a matter of renewable versus nonrenewable resources; biomass also is flexible and adaptable.

Biomass will not win markets from fossil mass simply because it is more adaptable, however. What fossil resources lack in flexibility has been compensated for by technology to convert the resources into extremely pure primary chemicals. For example, cracking converts high molecular weight, complex mixtures into simple olefins for reprocessing to desirable end products. Unit costs are further reduced by achieving great economies of scale and increasing the number of end uses for key chemicals through the development of families of derivatives, frequently with higher profit margins than the commodity primary chemical on which they are based. Frequently, patents and technical service also play important roles (*6*).

Biologists have long used the concept of ecological communities to explain the behavior of organisms in terms of interaction with their environment and with each other. The term niche is used to designate the position of an organism in a community—for instance, what it eats, what eats it, and how it responds to changes in the environment (*7*). The concept merits application to chemical systems, with the proviso that there are limits beyond which this metaphor should not be taken.

When a forest fire removes the tree canopy and provides potash and other fertilizer materials in the form of ash, space becomes available in which many species attempt to gain a foothold. The initial invaders may be grasses and weedy species that devote most of their energy to seed production and can attain maturity rapidly. Gradually perennials appear, and finally trees establish themselves and shade out the smaller competitors, restoring the forest to its original state. This progression of species, from opportunism to long-term vigor and ability to withstand hard times, is known as ecological succession (*7*).

A disturbed chemical system may also undergo succession. For example, when environmental regulations required gradual cessation of the use of tetraethyl lead as an octane booster in gasoline (*8*), a chemical market of hundreds of millions of dollars per year was opened for invasion by other chemical species. Among the front-runners have been methyl *tert*-butyl ether, ethanol, methanol, toluene, benzene, and propylene dimer. The market is likely to be fragmented initially but, as with ecological succession, certain octane boosters are likely to gain ascendancy over others. In certain farm states with high tax incentives for using ethanol, ethanol may be the dominant species; propylene dimer may dominate in other areas where propylene is plentiful.

Biological systems evolve from mutations, with survival of the fittest playing a significant role. In chemical systems the "mutations" involve the output of research and development in the form of new processes and new chemical compositions, which are based on human ingenuity and heavy financial investment by industry and government agencies. As with biological systems, most of the mutations are either aborted or fail to survive competition with the well-entrenched elements of the community. When the environment suffers a considerable change, a biological or a chemical system may evolve rapidly because the elements that were previously best adapted may be unable to adjust to the new conditions. Alternatives become available in the form of species (biological or chemical) that previously were not but now are well adapted. The rapid rise in price of petroleum and natural gas may be exactly the type of abrupt change in environmental conditions that stimulates evolution in the chemical industry. The combination of price changes for conventional chemical feedstocks and raw materials with intensified regulation of chemical products and resources could cause sweeping changes.

Niches can be identified for the competing resources and feedstocks (Fig. 2). For example, natural gas is a mixture primarily of methane and the natural gas liquids that can be obtained by condensing the ethane, propane, and butanes in this resource. Natural gas liquids can be converted readily into ethylene and propylene (*9*). These feedstocks and primary chemicals occupy strong niches. Petroleum also can become a source of ethylene and propylene through cracking technology and can compete with natural gas. However, these olefins are not in a natural petroleum niche; the position has been acquired by advances in cracking technology, the unavailability of natural gas liquids in many countries, and the relations between production of these olefins and production of liquid fuels from petroleum (*10*).

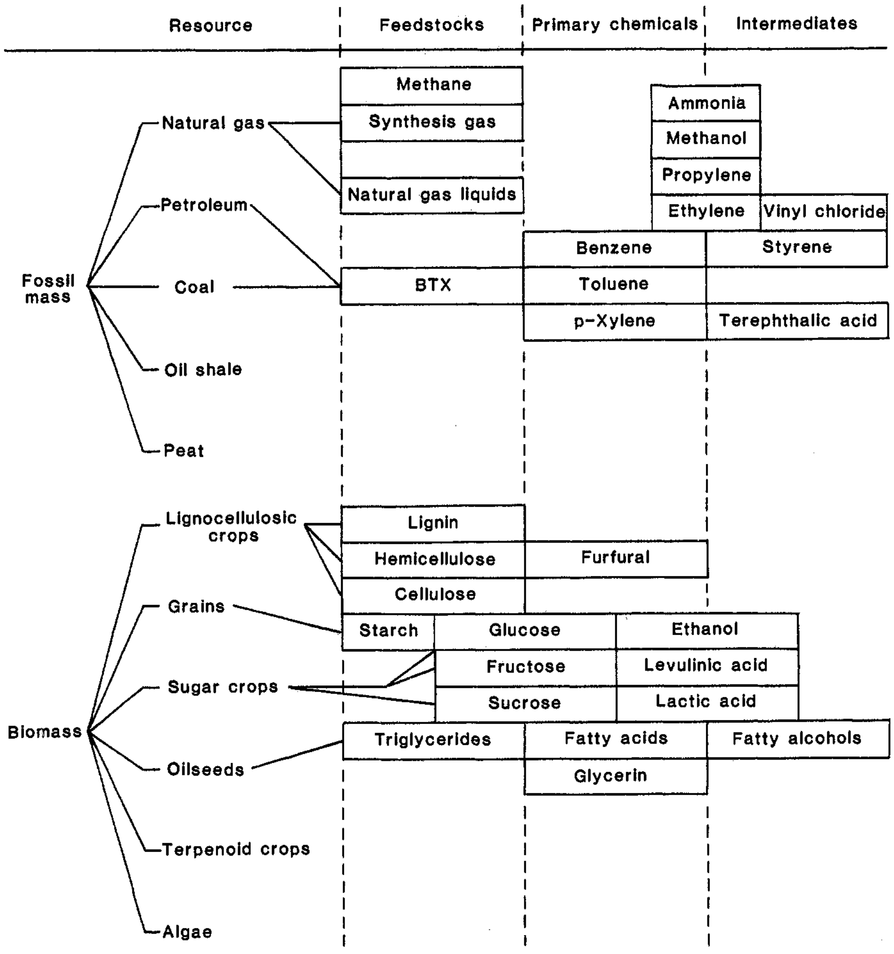

Fig. 1. Relations between resources, feedstocks, and intermediates.

Attempts by starchy biomass to compete for ethylene markets involve conversion of starch to glucose, glucose to ethanol, and finally ethanol to ethylene. Approximately 3 pounds of starch are consumed for every pound of ethylene produced, the reactions would be conducted in relatively small facilities lacking economies of scale, and each reaction is more complex than cracking natural gas liquids (*11*). Thus, ethylene and propylene are likely to remain in the natural gas or petroleum niche when worldwide markets are considered. A local niche for biomass-based ethylene could arise in a country poor in natural gas and petroleum but rich in biomass.

Glycerin lies in the biomass fats and oils niche because it can be obtained from triglycerides by hydrolysis or transesterification. The strength of the U.S. petrochemical industry can be measured by the fact that more petrochemical glycerin is derived by multistage processing of propylene than is made from hydrolysis of triglycerides (*10*, p. 78). This paradoxical phenomenon has arisen because the demand for glycerin exceeds the quantity that is made as a by-product of soap and other chemical operations, taking into account that glycerin is only about 10 percent of the triglyceride.

Petroleum and coal are sources of benzene, toluene, and xylenes (BTX) and it appears difficult for other resources to make identical or closely related aromatic hydrocarbons at attractive costs. Coal synthetic fuel plants may make possible a comeback for coal aromatics, if the gasification or liquefaction process is designed to make these products available.

Whether glucose will come from carbohydrate crops or lignocellulose crops depends in part on the outcome of lignocellulose fractionation research and on how much glucose is needed. Less than 1 percent of the corn crop would be required to provide the feedstock for a typical commodity chemical produced at the rate of 0.5 million metric ton per year. Approximately half the crop would be required to provide 100 percent of the ethylene used in the United States. Probably corn grain would be cheaper as a source of glucose at the 0.5 million metric ton level, and lignocellulose would be cheaper at the 10 million metric ton level.

This discussion has concerned a few key chemicals that "belong" in the stronghold of one or two resources only. Many chemicals that are separated from the initial feedstock by a few reactions could be "captured" by virtually any of the resources, depending on future relative price levels and the ingenuity of the commercial developers. Examples include methanol, acetic acid, ethylene glycol, ethanol, and acetaldehyde. Synthesis gas (carbon monoxide and hydrogen in specified ratios) is a unique family of feedstocks in that it can be made from the various intermediate-energy gases derived from the carbonaceous resources. Economies of scale for coal-based synthesis gas production render it the front-runner, but Johnson (*12*) has described the barriers facing coal synthesis gas systems. Biomass appeared to be less attractive than coal because of scale problems, but recent advances in catalyzed gasification and direct methanol production (*13*) are encouraging. Acetaldehyde might be made again from acetylene derived from coal or by oxidation of ethanol. Although fermentation ethanol appears to be winning over petrochemical ethanol, a synthesis gas process starting from methanol and carbon monoxide may prove cheaper (*14*).

Biomass Strategies

A key issue confronting those who plan biomass-to-chemicals research, development, and commercialization is whether biomass should compete by direct substitution or by substituting chemicals to perform the same functions as petrochemicals without duplicating their molecular structures. Each approach has its pros and cons.

Even though many programs for deriving fuels from biomass are concerned with production of chemicals (such as ethanol), the strategies for a chemical industry based on biomass differ considerably from those for a fuel industry based on biomass (*15*). Fuels are sold in energy units (dollars per gigajoule); chemicals are usually sold in weight units (dollars per kilogram). Conversion of carbohydrates that are about 50 percent oxygen into ethanol or methane is a desirable fuel process. Most of the energy is conserved, even though half of the resource is lost as carbon dioxide. This weight loss is a considerable burden in the production of chemicals from biomass.

A system is flexible if it can maintain the desired outputs even though its inputs change drastically. As an example, consider antifreeze for automotive engines. At present, the predominant antifreeze is ethylene glycol made from ethylene, which in turn is made from natural gas liquids or petroleum. These raw materials are increasing in price at a high rate. The system could adapt in the following ways, among others:

1) Continue to make ethylene glycol from ethylene, but make the ethylene from biomass or coal.

2) Continue to use ethylene glycol, but obtain it from coal via synthesis gas.

3) Replace ethylene glycol with an entirely different antifreeze that is made from biomass (such as levulinic acid salts or glycerin).

4) Redesign the automobile to eliminate the need for antifreeze (for instance, use air-cooled engines).

Some of these paths would involve direct substitution of the end-use chemical, while others would involve changes earlier in the transformation process or in the end use.

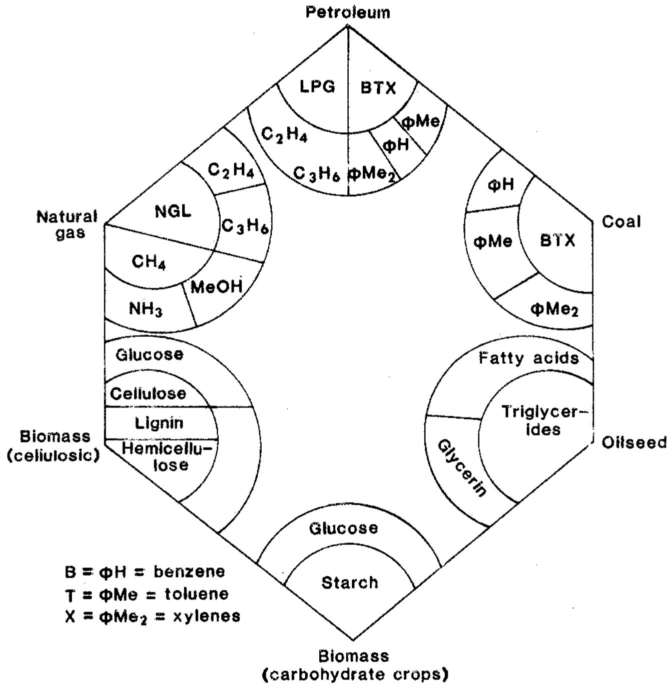

Fig. 2. Feedstock and primary chemical niches for selected resources.

Direct Substitution

Rudd and co-workers have discussed direct substitution of biomass-derived olefins for petrochemical olefins (*16, 17*). They conclude that petrochemical olefins can withstand biomass competition, even at very high prices for petroleum and natural gas liquids, because of the unfavorable stoichiometry of reactions to convert biomass to petrochemicals. The high level of demand for ethylene and propylene also gives a considerable advantage to the system of natural gas liquids (mostly a mixture of ethane and propane) that yields this product mix. However, their analysis appears to be primarily valid for the United States and similar countries with mammoth chemical industries. Less-developed countries (LDC's) that are intent on building chemical industries of a more limited scope, so that they can attain import substitution and use their renewable resources constructively, may prefer to make ethanol, in part for ethylene production. When ethanol is the source of ethylene, very small systems can be built at low capital costs, so that the LDC would have available ethylene oxide and its derivatives and perhaps polyethylene. The experience gained in the downstream processing could give such an LDC quite an edge in human resource development. Brazil is adopting this farsighted (but temporarily expensive) option (*18*).

In the industrialized countries that also have substantial biomass resources, the best opportunities for direct substitution appear to be offered by petrochemicals made through multiple reactions of petrochemical olefins. Tempting targets include methyl ethyl ketone, glycerin, tetrahydrofuran, and adipic acid. In some instances one can immediately find an attractive biomass-based synthetic route; in other cases, the target is tempting but the route to it is not yet evident. As a few examples of obvious routes that are not yet necessarily economically attractive, consider the following. Simple sugars can be microbiologically transformed into 2,3-butanediol, which can be transformed into methyl ethyl ketone by acid digestion of the fermentation broth (*19*). This technology would replace processes that use four-carbon olefins now. Tetrahydrofuran might be made by decarbonylation and hydrogenation of furfural. Adipic acid and adiponitrile previously were made from tetrahydrofuran derived from furfural. The biomass route was dropped when the market for adipic acid grew rapidly and supplies of biomass at low cost could not keep pace. Then the furfural route was replaced with a butadiene-based route and an acrylonitrile route. Now that butadiene is three to four times as expensive as it was when it displaced furfural and new lignocellulose fractionation processes may make possible low-cost furfural, the adipic acid–adiponitrile supply chain may shift back to a biomass feedstock.

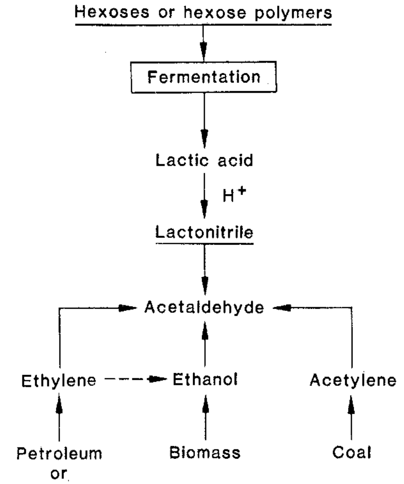

Fig. 3. Some alternative routes to lactic acid.

Linear alcohol and olefin petrochemicals in the detergent (12 to 18 carbon) and plasticizer (6 to 10 carbon) molecular weight ranges were developed to exploit the price advantage that ethylene had over fats and oils derived from coconut, tallow, and other sources. Ziegler ethylene telomerization (*20*) and related technologies made this achievement possible. Now that ethylene costs more than many fats and oils and is likely to escalate in price more rapidly than these biomass materials, production of linear alcohols and olefins from the natural products may increase. However, it will be necessary to improve yields of olefins and develop products in the plasticizer molecular weight range from fatty acid derivatives. This opportunity is linked to the opportunity for biomass-derived glycerin to take over petrochemical glycerin markets, because the first step in the preparation of fatty alcohols or olefins involves conversion of the triglyceride ester to the methyl ester and glycerin.

Indirect Substitution

Direct imitation of petrochemicals has the advantage of instant product acceptance, provided product specifications can be met. This is an enormous near-term marketing advantage, especially if the goal is displacement of primary chemicals or of intermediates with many transformation opportunities. However, this strategy provides the petrochemicals with major advantages that even great price increases do not necessarily erase. A major technological advantage for petrochemicals that impairs direct substitution by biomass is the very large scale of the petrochemical facilities that manufacture the major commodities. This scale effect and the cost reductions achieved through experience make it very difficult for direct substitution to occur.

Today's high-volume petrochemicals are those that are easy to manufacture from simple hydrocarbons and mixtures of hydrocarbons. Such cellulosic polymers as rayon, cellulose acetate, cellulose acetate butyrate, and vulcanized fiber were dominant, but their positions were eroded by nylon, polyurethane, polyester, and polyolefins. However, petrochemical technology uses no optically active starting materials to provide the world with fiber, films, and engineering polymers. Nature builds comparable materials, but uses optically active substances extensively and gains the advantages that hydrogen bonding and controlled crystallinity provide in controlling strength, elasticity, and other properties. The increased understanding of stereochemistry, polymer science, and reaction mechanisms that we now have will make possible the production from biomass of chemicals with a sophistication that transcends the capabilities of petrochemicals. Indirect substitution will permit full use of the chemical superiority of biomass in the form of premade polymers and complex intermediates.

Chemical Intermediates

Lactic acid and levulinic acid illustrate the types of key intermediates that might be made from carbohydrates to substitute indirectly for major monomers and chemical intermediates derived from fossil mass.

Lactic acid is a key biomass intermediate. The two major synthetic routes (Fig. 3) are from acetaldehyde or fermentation of hexoses or hexose polymers. Acetaldehyde can be derived from petrochemical ethylene or from coal via acetylene. If a switch to biomass were to take place, it would most likely be through improved conversion of glucose to lactic acid. The material balance is such that one molecule of glucose yields two molecules of lactic acid with no loss of carbon dioxide or other small molecules. If acetaldehyde is made from fermentation ethanol, one molecule of carbon dioxide is lost per molecule of ethanol formed. Thus, the raw material cost of lactic acid made from acetaldehyde would be substantially higher than that of lactic acid made from glucose by fermentation.

Although the production of lactic acid by fermentation of hexoses is well known and is practiced commercially, product isolation remains a serious problem, causing this potentially valuable intermediate to be costly—especially if it is needed in pure form. This is an excellent area for the combined efforts of microbiologists, product separation technologists, and engineers.

If lactic acid can be produced in high yield at low cost from biomass, it can provide access to opportunities for direct substitution for petrochemicals (such as acrylic acid and related chemicals) as well as opportunities that utilize its own unique properties. Lactic acid forms lactide through internal esterification, and lactide can form homopolymers and copolymers (*21*) with many hydroxy acids (Fig. 4). These polymers form transparent films and strong fibers and are biodegradable (Table 1). Crystallinity can be controlled so that a wide range of properties can be obtained. The major uses at this time are in medical applications for sutures that do not have to be removed surgically, and a market is developing in controlled release of pesticides.

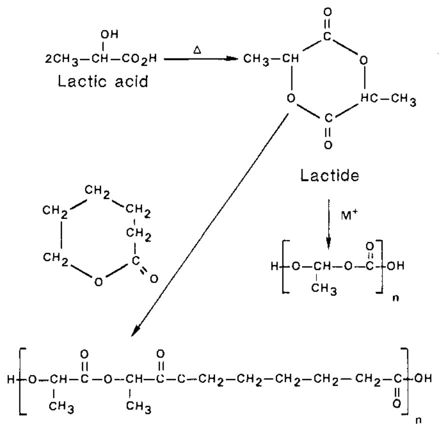

Fig. 4. Lactide polymers and copolymers.

For high-volume markets, lactide polymers would provide a challenge for polymer scientists and technologists. High-speed thermoplastic processing is required to meet the standards of the modern polymer industry and properties must be tailored to meet the applications requirement for specific end uses. Research, development, and commercialization campaigns for lactide polymers would follow very closely those for conventional polymers derived from petroleum. Different properties have been obtained, depending on the stereochemistry of the starting lactic acid. By selection of the appropriate microorganisms, *l*-lactic acid, *d*-lactic acid, or a mixture could be obtained for use as the starting material.

Levulinic acid is a difunctional chemical intermediate that can be made from many biomass feedstocks. It has long been known that acid digestion of hexoses or polymers of hexoses yields levulinic acid as the final product (Fig. 5) (*22*). Many processes that involve acid hydrolysis of cellulose to obtain glucose as a starting material for fermentation attempt to control reaction conditions to prevent the "undesirable" degradation of the glucose. However, levulinic acid is a highly versatile chemical intermediate (*23*). Levulinic acid production and utilization were studied intensively several times in the past, and for a while the product was manufactured commercially from wood (*24*). It would have attractive applications now as a source of lactone solvents (to compete with valerolactone), maleic anhydride, and methyl ethyl ketone. Levulinic acid salts have been proposed as replacements for ethylene glycol in automobile antifreeze systems.

Polymers

The first thermoplastics and synthetic fibers were cellulosics, but their markets were eroded as ingenious petrochemically derived polymers arose and competed. Whether cellulosics can expand from their limited present niche to occupy some of the territory previously won by petrochemicals will depend primarily on two factors: (i) the ability of cellulosic polymer technologists to tailor properties for additional end uses and (ii) the cost of chemical cellulose. The amount of effort expended on tailoring cellulosics will in large measure depend on the anticipated future selling price of chemical cellulose. Therefore, this discussion will center on technology for obtaining

Table 1. Comparison of lactide copolymers with commercial petrochemical polymers (*37*).

Polymer	Polystyrene versus 95/5 copolymer		Flexible PVC versus 85/15 copolymer	
	Polystyrene	95/5 copolymer of L(−)-lactide and ε-caprolactone	85/15 copolymer of L(−)-lactide and ε-caprolactone	Flexible PVC*
Tensile strength (psi)	7,000	6,900	3,200	1,500–3,500
Elongation (%)	2	1.6	6–500	200–450
Initial modulus (psi)	450,000	112,000	84,000	50,000–100,000
Impact strength (ft-lb/in.)	0.25	0.36	No break	0.4–7
Hardness, Shore D test	85	90	87	20–76
Specific gravity	1.08	1.26	1.26	1.16–1.35
Abrasion resistance			Excellent	Excellent
DTA† melting point (°C)	None	145	133	None
Compression molding (°C)	130–200	160–170	125–150	140–175
Ease of molding	Excellent	Good	Excellent	Good
Brittle point (°C)				0–15
Volume resistivity (ohm-cm)	10^{15}	10^{16}	10^{15}	10^{11}–10^{15}
Dielectric constant (10^3 cycles)	2.5	4–5	5–6	4–8
Dissipation factor (10^3 cycles)	0.0002	0.03	0.03	0.07–0.16
Weather resistance	Good	Fair	Fair to poor	Good
Lube oil resistance	Swells	Excellent	Excellent	Excellent
Solvents and nonsolvents	Benzene, $CHCl_3$, MEK‡, alcohol, ether, heptane	Benzene, $CHCl_3$, MEK (swells), alcohol, ether, heptane	Benzene, $CHCl_3$, heptane, alcohol, ether	Benzene, $CHCl_3$, heptane, alcohol, ether
Mineral acid	Resistant	Resistant	Resistant	
Caustic	Resistant	Attacked	Attacked	

*PVC, polyvinyl chloride. †DTA, differential thermal analysis. ‡MEK, methyl ethyl ketone.

chemical cellulose at a reasonable price, compared with alternative petrochemical polymer starting materials. If the price ratio between cellulose and petrochemical monomers is favorable, the prospects for technical success are good.

Cellulose that is suitable for polymer manufacture is expensive. The escalation of the price of chemical cellulose can be traced to increased processing costs for making and purifying cellulose pulp. Small amounts of hemicellulose, lignin, or other noncellulose materials adversely affect the production and performance of such cellulosic polymers as cellulose acetate, cellulose butyrate, and rayon. To remove the last few percent of contaminants, a disproportionate quantity of cellulose must be sacrificed. When these problems were added to pulpwood price increases, the result was a continuing disadvantageous position for chemical cellulose versus petrochemical products.

New methods of chemical cellulose production arose indirectly from research on gasohol. Efforts to manufacture pure glucose for conversion to fuel-grade ethanol were initiated with simple sugars and starch in mind. However, the potential advantages of using lignocellulose as the source of glucose provided the impetus for investigation of lignocellulose fractionation processes (*25*). Simple acid hydrolysis of lignocellulose to obtain the sugars was difficult to control, and enzymatic hydrolysis with cellulases tended to be slow and incomplete (*26*). Emphasis was placed on lignocellulose fractionation in which the lignocellulose complex is broken into its constituents: lignin, cellulose, and hemicellulose. It appears that the cellulose can be obtained in a high state of purity (*27*). Ironically, the discovery of microorganisms that directly convert the entire lignocellulose complex into ethanol may render obsolete the original reason for conducting research on lignocellulose fractionation (*28*). Further, the discovery that the five-carbon sugars from lignocellulose (*29*) can be converted to ethanol in high yield may result in ethanol being made from lignocellulose, but not necessarily from the cellulose fraction. Regardless of the events that led to the discovery, the fact is that there are now multiple approaches to the attainment of high-quality chemical cellulose. Results of experiments to verify whether the quality is indeed high enough for commercial cellulosics (and if not, what the deficiencies are) have not yet been made public.

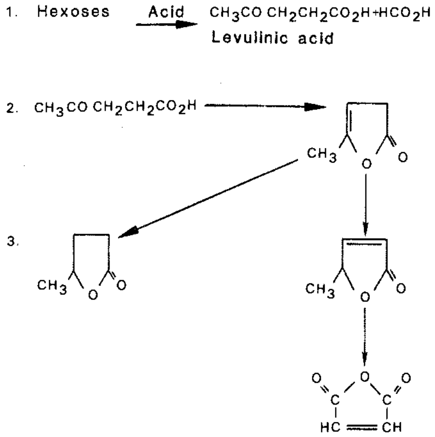

Fig. 5. Levulinic acid and some transformation products.

The two major approaches to chemical cellulose production are variants on old technology: (i) steam explosion and (ii) nonaqueous solvent processing. Both batch (*30*) and continuous (*31*) processing systems are under development for subjecting the lignocellulose complex to steam explosion. The output of steam explosion consists of cellulose, a partial hydrolyzate of hemicellulose, and a low molecular weight material derived from lignin. It appears that a fraction of the cellulose (probably part of the amorphous portion) has been hydrolyzed and is mixed with the hemicellulose hydrolyzate. Depending on conditions, the hemicellulose hydrolyzate may undergo some degradation, reaction with the lignin fraction, or both. The lignin fraction is said to have a greatly reduced molecular weight, indicating that it consists of an oligomeric-type phenolic material with perhaps three to ten aromatic units (*27*). The lignin fraction is soluble in such simple solvents as ethanol and acetone.

Solvents that have been investigated for the organosolv and related processes include ethanol and butanol (*32*). The solvent process requires much longer reaction times—for instance, 1 hour compared to a few minutes for steam explosion processes. The lignin appears to be converted to a material similar to that obtained by steam explosion. Up to now the organosolv process has been developed primarily as a means of obtaining fiber, and hemicellulose hydrolysis has not been a goal. It is likely that the solvent processes can be reoptimized to remove both lignin and hemicellulose, leaving a purified cellulose material.

It is too early to select a winner among these lignocellulose fractionation processes or to discuss others for which details have not been released. The fittest of these processes may provide cellulosic polymer scientists and technologists with the cheap raw material (compared with petrochemical monomers) needed for a successful comeback, not only by traditional cellulosics but also by new ones developed with the advanced knowledge of cellulose morphology that is now available.

As an example of the application of new concepts to old cellulosics, consider vulcanized fiber. Vulcanized fiber was probably the first engineering polymer and it is still noted for its high impact characteristics (*33*). It was made from high-purity cellulose fibers (such as cotton waste from textile factories) by treatment with zinc chloride or other strong acids. Heat and pressure were applied to many layers of this material. Under these reaction conditions, the cellulose was partly degraded to low molecular weight entities, which underwent a retrograde reaction to form a highly cross-linked polymer. The material lacked esthetic quality but was incredibly strong; its applications included inexpensive luggage and containers used in machine shops. The small companies that commercialized this product were not able to marshal the sophisticated instruments and talents required to overcome its drawbacks and optimize its properties. Control of the diffusion of the acid catalyst and development of methods to fabricate more complex shapes are two significant areas for improvement. Perhaps now is the time for a concerted effort to develop vulcanized fiber-type cellulosics.

The low molecular weight lignin by-product appears to have characteristics that may allow direct substitution or development of nonpetrochemical polymers. Direct substitution might involve hydrocracking to phenol and benzene (*34*). Indirect substitution might involve phenolics or epoxies (*35*). A principal advantage is expected to be a relatively low price (because chemical cellulose and the hemicellulose hydrolyzate will cover much of the cost of generation of this material). Unlike the lignins and lignosulfonates now on the market, low molecular weight lignin is soluble in common organic solvents, which makes it easier to transform these molecules. However, this low molecular weight material is by no means a winner just because of low price and solubility. Product development is hampered because too little is known about its specific chemical structure and the way the structure varies with the lignocellulose starting material and processing conditions. Sometimes, the new knowledge of structure and the applications development go hand in hand—as with the application of electrochemistry to low molecular weight lignins (*36*).

Prognosis

It appears that the future augurs well for biomass as a resource for chemical production. In principle, biomass has a significantly better long-term strategic position than does fossil mass for the production of chemicals, but fossil mass has advantages over biomass for fuel production. Biomass resources are renewable, adaptable to changing conditions, and can be designed to meet the requirements of customers. Fossil mass has the strategic advantage of being the entrenched resource to which downstream processes and products are now adjusted. Biomass would make little progress if the price of petroleum and natural gas were not rising rapidly. However, these rising prices also contribute to general inflation, which aids the entrenched resource by discouraging investment in new facilities.

The strategic position of biomass appears stronger for chemical use than for fuel use, when fuel subsidies and incentives are not taken into account. When these tactical factors are taken into account, fuel ethanol and methanol are rendered more attractive than are many chemical products. A viable strategic plan would incorporate this consideration without allowing it to dictate future product mix.

The processing of biomass into chemical feedstocks and primary chemicals is at a primitive level of development, compared with that of petroleum and natural gas. Development of technology to transform lignocellulose into chemical feedstocks will receive high priority. These feedstocks could be ethanol and native lignin produced by the Thermocellum process developed at the Massachusetts Institute of Technology, or chemical cellulose, pentose, and low molecular weight lignin produced by one of numerous lignocellulose fractionation processes that are under development. Although lignocellulose biomass resources are projected to be cheaper in the future than grains, sugar crops, oilseeds, or animal by-products, the latter biomass resources have firmly established inexpensive routes for feedstock production. They are in a position to compete immediately, with profits reinvested in further improvements.

Both direct and indirect substitution strategies will be employed. Direct substitution will concentrate on ethanol and its major transformation products, glycerin, linear aliphatic alcohols, and olefins. A breakthrough in the cost of methanol derived from biomass compared to that derived from fossil mass would open a huge segment of the chemical process industry to biomass systems. The possibility of producing phenol and benzene from lignin is an example of an opportunity to achieve direct substitution in aromatic chemicals. Indirect substitution in the polymer area is likely to involve cellulosic polymers or lactide polymers. Indirect substitution in chemical intermediates also may involve lactic acid or levulinic acid.

Biomass systems present opportunities to continue to provide the chemicals we need at reasonable prices and profits for industry, while conserving fossil resources and satisfying a portion of end-use demand with renewable resources. Now is the time to initiate vigorous, broad-based programs to substitute biomass-derived chemicals for petrochemicals.

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