Chapter 9 Commodity chemicals and Energy production

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Chapter 9

Commodity Chemicals and Energy Production

Introduction

In 1982, the U.S. chemical industry produced about 158 billion pounds (lb) of organic chemicals (36). About 30 commodity chemicals-defined in this report as chemicals that sell for less than \$1 per lb" —constitute the majority of this market (see table 39).

•Chemicals with higher value such as vitamins, food additives, and amino acids, form the subject of *Chapter 7: Specialty Chemicals* and *Food Additives* The difference between "commodity" and "specialty" chemicals is somewhat fluidly determined by price versus quantities produced Some of the compounds described in chapter 7 are considered by some analysts to be commodity chemicals. These include vegetable oils and their derivatives, single cell protein, and fructose. Because of their predominant use as food additives, however, these compounds are considered in the earlier chapter. Practically all commodity chemicals are currently made from petroleum and natural gas resources and are used as precursors for a variety of materials such as polymers and solvents. The United States, which now imports about 30 percent of its petroleum (34), uses about 7 to 8 percent of its total petroleum and natural **gas** supply for the production of commodity chemicals (10,18,22); the remainder of this supply is used as an energy source.

The chemical industry's reliance on petroleum feedstocks raises a number of problems. Two problems are the fluctuating cost and uncertain

| | Production in 1982 | | Mata |
|---------------------|--------------------|------|-----------------------------------------------|
| Chemical | (billion pounds) | (Mb) | Major uses |
| Ethylene | 24.7 | 25.5 | Polyethylene derivatives |
| Toluene | 15.3 | 26.7 | Benzene, gas additive, solvents, polyfoams |
| Propylene | 12.3 | 24.0 | Polypropylene, isopropanol |
| Ethylene dichloride | 10.0 | 13.7 | Vinyl chloride |
| Benzene | 7.9 | 21.1 | Styrene, phenol, cyclohexane |
| Methanol ., | 7.3 | 10.8 | Formaldehyde |
| Ethylbenzene | | 30.0 | Styrene |
| Vinyl chloride | 6.5 | 22.0 | Polyvinyl chloride, resins |
| Styrene | | 37.5 | Pol yst yrenes |
| Xylene | 5.3 | 18,9 | p- and o-xylene, gas additive, solvent |
| Terephthalic acid | 5.0 | N.A. | Polyester fibers |
| Ethylene oxide | | 45.0 | Ethylene glycol |
| Formaldehyde | 4.7 | 24.4 | Resins |
| Ethylene glycol | 4.0 | 33.0 | Antifreeze, polyesters |
| p-xylene | | 31.0 | Synthetic fibers |
| Acetic acid | 2.8 | 26.5 | Vinyl and celtulosic acetate |
| Cumene | 2.7 | 24.0 | Phenol |
| Phenol | 2.1 | 36.0 | |
| Acrylonitrile | 2.0 | 44.5 | Polymers |
| Vinyl acetate | . 1.9 | 37.5 | Polyvinyl acetates, alcohols |
| Butadiene. | 1.8 | 40.0 | Rubber |
| Acetone | 1.8 | 31.0 | |
| Propylene oxide | . 1.5 | 40.5 | Propylene glycol, urethanes |
| Isopropanol | | 32.9 | Acetone, solvents |
| Cyclohexane | | 25.3 | Nylon, caprolactum |
| Adipic acid | | 57.0 | Nylon |
| Acetic anhydride. | | 41.0 | Cellulose esters |
| Ethanol | . 1.1 | 25.8 | Detergent, solubilizer, cosmetics, solvent, f |

Table 39.—Annual Production and Selling Price of the Major Organic Commodity Chemicals in the United States

SOURCE Office of Technology Assessment, adapted from D Webber, "Basic Chemical Output Fell Third Year in a Row," Ctrern. Eng. News, May 2, 1983, pp. 10-13; T C O'Brien, "Feedstock Trends for the Organic Chemical Industry," Planning Report 15, U.S. Department of Commerce, National Bureau of Standards, April 1983, and Ctrermical Marketing Reporter, "Weekly Price Report, " May 31, 1982, pp. 35-39. supplies of petroleum. Commodity chemical prices are especially sensitive to the cost of petroleum because feedstock costs typically represent 50 to 75 percent of commodity chemical manufacturing costs (6). Other problems of the commodity chemical industry include a current overcapacity of production by the capitalintensive petrochemical companies, the high costs of energy associated with "cracking" petroleum into chemical feedstocks, and environmental, safety, and ideological concerns surrounding the use of nonrenewable, fossil resources (6).

These well-publicized problems, which increase in urgency with the passing of time, have intensified the search for nonpetroleum feedstocks for chemical and energy production. The options being pursued at present include the liquification and gasification of coal, the development of synthetic fuel from natural gas, and the conversion of biomass* * to fuels and a wide variety of organic chemicals.

The substitution of natural gas, coal, and other nonrenewable resources for petroleum are issues that have been discussed in several previous OTA reports (28)29,31). Despite the drawbacks outlined in those reports, coal is favored as an alternative resource by U.S. petroleum companies, which control 20 percent of U.S. coal production and 25 percent of US. coal reserves (3,27). Processed coal feedstocks fit readily into most petroleum feedstock schemes for the production of commodity chemicals and thus do not require large capital investments for new chemical plants. Nevertheless, at least one analyst thinks that petroleum will continue to be used as a feedstock for commodity chemicals for some time and that coal will not make a significant impact on the production of chemicals until the 21st century (22).

It appears that countries with substantial inexpensive supplies of petroleum, such as Mexico and Saudi Arabia, are turning to the production of commodity chemicals as a way of adding value to their resources, Thus, countries with petroleum may begin to control the price of these chemicals. Because such countries may be able to produce commodity chemicals at a lower price. companies in the United States, Europe, and Japan may have to develop new ways of using commodity chemicals to produce compounds of greater value or to move directly to the manufacture of higher value-added chemicals from biomass. In any case, a rapid or dramatic shift in feedstock use is unlikely; it is much more probable that there will be a slow transition to the use of biomass as a feedstock in particular instances.

Although nonrenewable resources such as coal will probably be adopted earlier, biomass-including crop and forest product wastes and municipal and agricultural wastes-may provide solutions to some of the long-term problems associated with chemical and energy production from petroleum. It is technologically possible to produce essentially all commodity chemicals from biomass feedstocks such as starch or cellulose, and most commodity chemicals can be synthesized biologically (10,24). A viable biomass feedstock for the production of commodity chemicals may be starch. Less than I percent of the U.S. corn crop would be required to obtain the cornstarch needed to produce a typical commodity chemical at the rate of I billion lb per year (18). Although a few high-volume chemicals that could be produced from biomass, such as ethanol, can be used for fuel, the volume of biomass needed to produce a nation's energy would be substantially greater than that needed to produce its commodity chemicals. Starch probably could not be used for energy production without putting a strain on food and feed uses. Thus, if biomass is to be used extensively for energy production, the biomass source will most likely be lignocellulose.

Biomass as an alternative to petroleum for U.S. energy production was described in OTA'S July 1980 report *Energy From Biological Processes* (30). As emphasized in that report, substantial societal change, i.e., more public support and a higher priority for research on biomass use in the U.S. Departments of Agriculture and Energy programs, will be necessary if biomass is to become a viable alternative to petroleum as a source of energy in the near future. At present, the level of U.S. public support for biomass research is not high. Furthermore, Federal support of applied research and development (R&D) programs for al-

[•] Biomass is all organic matter that grows by the photosynthetic cent'ersion of solar energy.

ternative fuel sources has been plummeting in the recent climate of intense fiscal scrutiny.

A shift from petrochemical processes to bioprocesses for the production of commodity chemicals will be difficult because of the existing infrastructure of chemical and energy production. This infrastructure allows a barrel of oil to be converted to products in a highly integrated system in which the byproduct of one reaction may form the substrate for another reaction. Most chemicals derived from biomass cannot yet compete economically with chemicals made from oil in this infrastructure.

As the costs of bioprocesses are reduced through R&D, however, a transition to biomass resources may become a more realistic proposition. This chapter examines ways in which biotechnology might improve the efficiency of biomass conversion, thus facilitating the transition to the use of biomass resources. The advances biotechnology could provide for the improved growth of plants used for biomass conversion are discussed in *Chapter 6: Agriculture.*

Since commodity chemicals represent only a small portion of today's U.S. petroleum consumption, a transition to biomass-based commodity chemical production without a *concurrent* transition to biomass-based energy production will not substantially reduce the country's dependence on petrochemical resources. For moving the United States toward the goal of reduced reliance on imported, nonrenewable resources, a unified approach to chemical and fuel production will be necessary.

Biomass resources

The United States has abundant biomass resources. The largest potential amount of cellulosic biomass is from cropland residues such as corn stover and cereal straw, * although the potential amount of cellulosic biomass from forest resources is also quite large. About 550 million dry tons of hgnocelhdose are easily collected and available for conversion to chemicals each year. In addition, some percentage of the 190 million dry tons of corn produced yearly could be converted to starch and used for chemical production (21).

Parameters used to determine the optimal kind of biomass used in microbial systems include availability of the biomass, its energy content per dry weight, the amount of energy that must be expended to achieve the desired products, the environmental impact of the process, and the amenability of the material to conversion by existing microbial systems. Ultimately, biomass resources that minimize usurpation of food sources are sought (e.g., nonfeed crops grown on extant arable land). This chapter emphasizes the use of the two most abundant feedstocks from biomass: starch and cellulose. Starch and cellulose are both polymers of glucose units [6-carbon simple sugars) which, when hydrolyzed, yield glucose molecules (see fig. 24). These glucose sugars provide the starting point for biological chemical production, for example, the transformation of glucose to ethanol. Other derivatives of biomass, such as vegetable oils, are used in bioprocesses, and those resources are considered in *Chapter 7: Specialty Chemicals and Food Additives*.

One drawback to the use of biomass as a feedstock for commodity chemical and energy production is its relatively low energy content per unit dry weight. Dry cellulose biomass, for example, yields roughly 16 million Btu per ton and cornstarch yields 15 million Btu per ton, whereas petroleum yields 40 to 50 million Btu per ton. Thus, the energy yield per unit of weight is lower for biomass than for petroleum. Furthermore, the costs of transporting biomass to a factory **may** bean important economic consideration. Raw material and transportation costs are particularly important in the production of commodity chemicals, because of the low value added to the feedstock in the synthesis of final products.

[&]quot;Agricultural residues left On the soil aid in the sustainability of soil. The environmental impact of the removal of these residues must be studied more thoroughly in order to determine whether agricultural wastes are, in fart, true **wastes**,

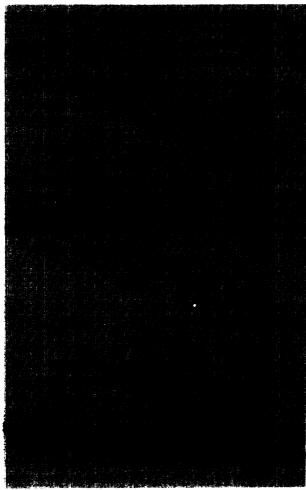


Figure 24.—Polysaccharides of Biomass: Starch and Cellulose

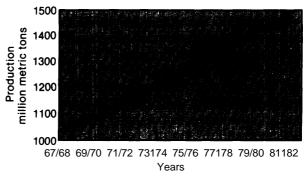
SOURCE Office of Technology Assessment.

Starch

Starch, a molecule composed of many hundreds of glucose units bound together in branched or unbranched chains, is the principal carbohydrate storage product of higher plants and is readily available from such crops as corn and potatoes. In 1979, the United States produced about 666 billion lb of grain from six major cereal crops, and this grain contained 470 billion lb of starch. The major grain produced, corn, contained 316 billion lb of starch (10), which could provide 285 billion lb of glucose.

As shown in figure 25, world grain production has increased steadily over the past several years,



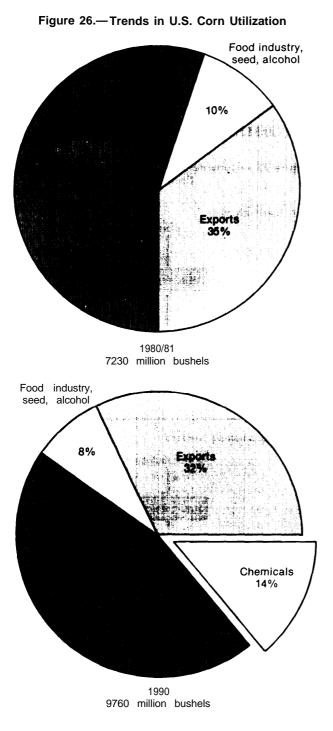


SOURCE: Off Ice of Technology Assessment, adapted from CPC, Int., 1983.

and this trend is expected to continue through the end of the century as the result of yield improvement and an expansion of acreage planted (19). Furthermore, the price of corn has remained relatively constant over the past decade, especially when compared to the nearly tenfold increase in the price of oil over the same period of time.

The utilization of U.S. corn has changed over the past 10 years. A decrease in U.S. meat consumption caused a concurrent decrease in the amount of corn used for animal feed, while at the same time, technological advances increased corn yields. Consequently, the export market for U.S. corn has risen from 15 percent of the crop to 35 percent. Since U.S. corn production is expected to increase and meat consumption is expected to decrease, U.S. farmers will need new markets for their corn. Commodity chemical production from a starch feedstock could provide a market for U.S. corn. The potential for industrial use of starch from corn alone is large, and an increase in the industrial use of corn would probably aid in supporting farm prices. Currently, only about 7 percent of the corn produced in the United States is processed into cornstarch (7,19). Figure 26 suggests that 14 percent of the 1990 corn crop could go to chemical production, and enough corn would still be available for other uses.

Because of its high volubility in water and ease of hydrolysis into individual glucose units, starch is highly amenable to bioprocessing and may be an ideal feedstock for chemical production. The use of starch for both chemical and fuel production, however, might be at the expense of its use



in food production. Starch may not be produced in large enough quantities to be used both as a source of food and a source of energy. *

Lignocellulose

Lignocellulose is composed of cellulose, an unbranched chain of glucose units, lignin, a linked mixture of aromatic molecules, and hemicellulose, a polymer composed mainly of 5-carbon sugars. This structure provides the rigidity necessary for cellulose's primary function, the support of plants. Because of its wide availability, lignocellulose has the potential to be the most important of all the raw materials for use in bioprocessing. Currently, however, several problems impede the use of lignocellulose on a large scale. Lignocellulose is highly insoluble in water and its rigid structure makes cellulose much more difficult than starch to hydrolyze to individual sugars. Furthermore, most microaganisms cannot utilize lignocellulose directly without its having been pretreated either chemically or physically. Despite the considerable advances made in both chemical and enzymatic hydrolysis techniques, the cost of glucose derived from cellulose is still much higher than that derived from starch.

The inherently diffuse nature of lignocellulose resources means that very high collection costs, especially in energy and manpower, will be encountered in any attempt at large-scale utilization, These considerations have given rise to the concept that the utilization of lignocellulose for energy will be feasible only through a widespread network of smaller manufacturing facilities that draw on local resources and supply local needs. Indeed, this pattern has already been established for farm-scale alcohol production from corn. An alternative to multiple small-scale production units

^{*}As detailed in OTA'S July 1980 report *Energy From Biological Processes* (30), starch could be used to produce approximately 1 billion to 2 billion gal of ethanol in the United States each year (about 1 to 2 percent of U.S. gasoline consumption) before food prices might begin to rise.

is the concept of centralized, intensive lignocellulose production on so+-died "energy plantations." The potential ecological problems and highly questionable economics have detracted from prospects for success, but the development with biotechnology of more effective biological agents for lignocellulose utilization could radically change this picture.

Conversion of biomass to commodity chemicals -

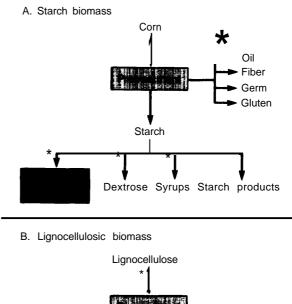
As noted above, there are numerous types of biomass resources, including lignocellulosic products and feed crops such as corn. Because of the varying compositions of these raw materials, different methods are used in rendering them into useful chemicals. Nevertheless, all microbial conversion of biomass to marketable chemicals is a muhistep process that includes:

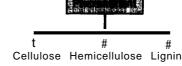
- pretreatment (particularly with lignocellulosic biomass),
- hydrolysis (saccharification) to produce hexose (6-carbon) and pentose (5-carbon) sugars,
- bioprocessing of these sugars by specific micro-organisms to give commodity chemicals,
- subsequent bioprocessing or chemical reactions to produce secondary commodity chemicals, and
- separation and purification of end products.

Figure 27 is a schematic summary of the multistep processes for the conversion of starch and lignocellulosic biomass to commodity chemicals. Although figure 27 emphasizes the microbial steps that could be used for these processes and applications of biotechnology to them, it should be noted that a variety of chemical syntheses can also be used to convert the components of biomass into useful chemicals (9,10,17,18).

Pretreatment

Before either starch or lignocellulosic biomass can be used as feedstocks for bioprocesses, they must be pretreated in preparation for hydrolysis. Starch from corn requires little pretreatment. Lignocellulosic materials such as wood, however, demand extensive pretreatment to make cellulose and hemicellulose available for hydrolysis. Figure 27.—Convers!on of Biomass to Commodity Chemicals







* = Possible microbiological step

SOURCE: Office of Technology Assessment

STARCH

The United States relies primarily on corn for starch feedstocks. About 500 million bushels are processed by corn refiners yearly to produce cornstarch products. In the production of cornstarch, refiners employ a process known as "corn wet milling" in which corn kernels are cleaned, soaked in warm, dilute acid, and ground to yield a slurry composed of starch, protein, and oil. Much of the starch is further converted to sweeteners, such as glucose and high fructose corn syrup (7). Cornstarch is the milling product that could be used to make commodity chemicals.

The pretreatment of starch requires minimum inputs of acid and heat. Energy requirements are low compared with the potential energy gained, and almost all byproducts are marketable. Combined with starch thinning and saccharification costs (see below), corn wet milling is estimated to yield monomeric sugar at a cost of 12¢lb (at \$3.40/bushel of corn) (21).

LIGNOCELLULOSE

Methods used to pretreat lignocellulosic biomass include chemical pretreatment in acids and bases, steam explosion, and mechanical grinding. These methods, described in OTA'S July 1980 biomass report (30), add substantially to the costs involved in using lignocellulosic biomass as a chemical resource.

In the future, biodelignification (the biological degradation of lignin) by micro-organisms may prove useful in the pretreatment of lignocellulosic biomass (8,24). Biodelignification results in removal of lignin, exposing the crystalline cellulose and lowering the costs of mechanical pretreatment. At present, however, biodelignification is an inadequate, expensive means of pretreatment, and it is not used in the pilot projects for use of lignocellulose currently underway. As yet, there are no valuable uses for lignin. Uses must be found for lignin derivatives before these processes will be commercially viable (2).

Several groups are working toward obtaining faster biodelignification using mixed cultures of micro-organisms, but microbial reaction rates at present do not approach those needed for economic feasibility. With use of the best candidate, the degradative mold *Chysosporium pruinosum*, **40** percent of lignin remains intact after 30 days of treatment (l). At least 20 strains of bacteria that have lignodegradative abilities have been identiCh. 9—Commodity Chemicals and Energy Production •243

fied, but efforts to use micro-organisms for delignification are hampered by the fact that lignin metabolizes are toxic to these micro-organisms. Thus, more work remains to be done before biodelignification and other methods of biological pretreatment are competitive with the currently used chemical or mechanical pretreatment methods. Were more information available on these micro-organisms, biotechnology could be used to improve their efficiency.

Hydrolysis

STARCH

Enzymes from microbial systems are widely used industrially to catalyze hydrolysis of starch into sugars. * Batch bioprocesses are used for hydrolysis. Three enzymes, alpha -amylase, betaamylase, and glucoamylase, are used to hydrolyze the starch chains to yield complete hydrolysis and the formation of glucose (15). The largest industrial use of enzymes is in the corn wet milling industry.

The major U.S. corn refiners have ongoing active research programs for the improvement of enzymatic degradative processes, and these manufacturers have made major advances in the areas of bioprocessing and enzyme immobilization. These manufacturers have continued their efforts toward improvement of enzymes by using new biotechnology (32).

CELLULOSE

The well-ordered crystalline structure of cellulose necessitates harsher treatments than those used for starch. Whereas hemicellulose is readily hydrolyzed into its 5-carbon sugars under mild conditions, the hydrolysis of cellulose requires strong acids, heat, and pressure. These conditions lead to the formation of byproducts which must be separated and utilized to minimize the overall costs of lignocellulose use. In addition, the acid used for the hydrolysis of cellulose must be neutralized before the mixture is used for bioprocess ing, a requirement that raises the cost of hydrolysis.

^{*}For further discussion of these enzymes, see *Chapter 7: Specialty Chemicals and Food Additives*.

The use of enzymes known as cellulases (and microorganisms that produce cellulases) to hydrolyze cellulose, either alone or in conjunction with chemical treatment, offers an increasingly popular alternative to chemical methods of hydrolysis. Cellulose is the most abundant biological compound on earth, and a myriad of microorganisms employ cellulases to obtain energy for growth from the resulting glucose molecules. Research efforts to improve cellulase activity by mutagenesis and selection of cellulolytic (cellulosedegrading) microa-ganisms have yielded mutant strains of microa-ganisms (particularly fungi) that produce cellulases with higher tolerance to glucose (the product of hydrolysis that inhibits cellulase activity), increased efficiency and reaction rate, and better functioning at the elevated temperatures and high acidities used in industrial bioprocesses (l).

The enzymatic activity of cellulases has been improving over the past several years, and in some cases, the time needed for saccharification and subsequent bioprocessing to produce ethanol from cellulose has been reduced several fold (11). Despite these improvements, however, the activity of cellulases does not begin to compare with the activities of amylases, which are about 1,000 times more catalytically efficient (5).

Although research into the molecular biology of cellulases is in its early stages, biotechnology is being used to improve the cellulase-catalyzed hydrolysis of cellulosic biomass in several ways. Two challenges for biotechnological approaches to cellulase production are increasing the low activity of the cellulase and making sure the entire cellulase gene complex is expressed. Processes that optimize cellulase activity and efficiency are prerequisite to the use of lignocellulosic biomass resources.

Researchers at the National Research Council of Ottawa, Canada, the University of British Columbia, the University of North Carolina, and Cornell are using recombinant DNA (rDNA) techniques to clone cellulase genes from several micro-organisms into bacteria that may be induced to produce cellulase in large quantities (20). Similarly, researchers at the U.S. Department of Agriculture are cloning celhdase genes from the fungus **Penicillium funiculosum (12)**. Another possibility for a biotechnological improvement is to transfer the ability to utilize the 5-carbon sugars from hemicellulose into cellulose utilizing microorganisms. A third possibility is improving the specificity of organisms that can utilize lignocellulose directly, e.g., *Clostridium thermocellum*. The "wild types" of these microorganisms produce a range of products, typically ethanol and several organic acids. This varied synthesis results in low yields for each product and great difficulties in subsequent recovery and purification. Genetic mechanisms could be used to select for high production of any one of the products.

Microbial production of commodity chemicals

Some commodity chemicals, including ethanol and acetic acid, are now produced in the United States with microbial bioprocesses (9), while other chemicals, such as ethylene and propylene, will probably continue to be made from petroleum feedstocks because of lower production costs. The commodity chemicals that are attractive targets for production from biomass include ethanol, acetone, isopropanol, acetic acid, citric acid, propanoic acid, fumaric acid, butanol, 2,3-butanediol, methyl ethyl ketone, glycerin, tetrahydrofuran, and adipic acid (9.18). Additionally, some chemicals, such as lactic and levulinic acids, could be used as intermediates in the synthesis of polymers that might replace petrochemically derived polymers (18).

Because the chemical composition of biomass differs from that of petroleum and because microorganisms are capable of a wide range of activities, it maybe that the most important commodity chemicals produced from biomass till be, not chemicals that directly substitute for petrochemicals, but other chemicals that together define a new structure for the chemical industry. Microorganisms used to produce organic chemicals could be used with micro-organisms that fix nitrogen to produce nitrogenous chemicals, either higher value-added compounds or ammonia, a high volume commodity chemical. Other microorganisms, such as the methanogens or the microorganisms that metabolize hydrogen sulfide, may be used to produce sulfur-containing chemicals (14).

The aerobic and anaerobic microbial pathways leading to a number of important compounds are shown in figure 28. Some of the micro-organisms

responsible for these reactions are listed in table 40. Knowledge of biochemical pathways for the synthesis of particular chemicals will lead to the

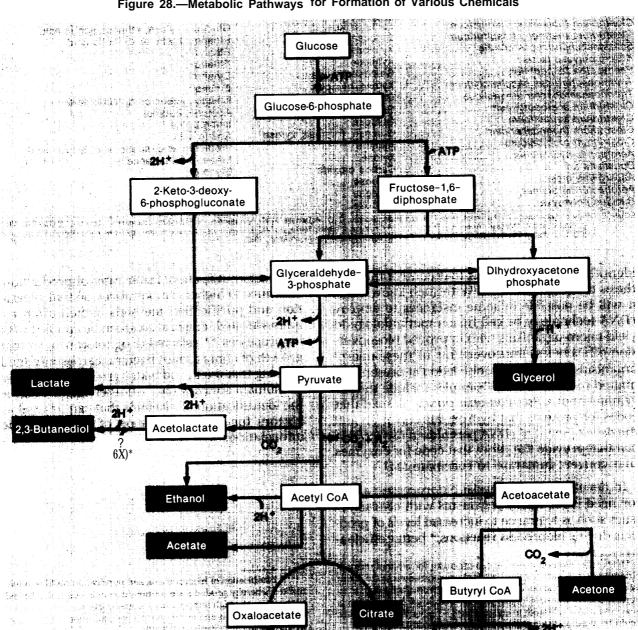


Figure 28.—Metabolic Pathways for Formation of Various Chemicals

SOURCE T K Ng, R M Busche. C C. McDonald, et al "Production of Feedstock Chemicals." Science 219:733.740, 1983

ing and the

1946년 1월 1일 <u>-</u>

Oxaloacetate

Fumarate

211

Citrate

Butyrate

Line of the

i i tradicio

Butanol

| Table 40.—Potentially Important | Bioprocessing Systems | for the Production of | Commodity Chemicals |
|---------------------------------|-----------------------|-----------------------|---------------------|
| | | | |

| Aicro-organism | Carbon source(s) | Major fermentation product(s) |
|----------------------------------|----------------------------|-------------------------------------------|
| Saccharomyces cerevisiae | Glucose | Ethanol |
| Saccharomyces cerevisiae | Glucose | GI ycerol |
| <i>Tymomonas mobilis</i> | Glucose | Ethanol |
| Sostridium thermocellum | | Ethanol, acetic acid |
| /ostridium thermosaccharo/yticum | Lactic acid | Glucose, xylose, ethanol, acetic acid |
| Costridium thermohydrosu/furicum | Glucose, xylose | Ethanol, acetic acid, lactic acid |
| chizosaccharomyces pombe | Xylulose | Ethanol |
| /uyveromyces lactis | Xylulose | Ethanol |
| Pachysolen tannophilus | Glucose, xylose | Ethanol |
| hermobacteroides saccharolyticum | Xylose, glucose | Ethanol |
| hermoanaerobacter ethano/icus | Glucose, xylose | Ethanol, acetic acid, lactic acid |
| /ostridium acetobuty/icum | Glucose, xylose, arabinose | Acetone, butanol |
| /ostridium aurianticum | Glucose | Isopropanol |
| Vostridium thermoaceticum | Glucose, fructose, xylose | Acetic acid |
| Nostridium propionicum | Alanine | Propionic acid, acetic acid, acrylic acid |
| eromonas hydrophilic. , | Xylose | Ethanol, 2,3-butanediol |
| Dunaliella sp | | Glycerol |
| spergil/us niger | | Citric acid |
| erobacter aerogenes | Glucose | 2,3-butanediol |
| Bacillus polymyxa | | 2,3-butanediol |

Le Office of Technology Assessment, from L. K. Ng, R. M. Busche, C. C. McLohalo, et al., "Production of Feedstock Chemicals," Science 219:733.740, 1963; J.C. Linden and A Moreira, "Anaerobic Production of Chemicals," Bask Biology of New Develo~rnerrts In Blotec/mo/o~y (New York: Plenum Press, 1963); and D. I. C. Wang, Massachusetts Institute of Technology, personal communication, 1952.

identification of the genes that control the synthesis of these chemicals. With such knowledge, it will be possible in some instances to employ rDNA technology or cell fusion methodology to yield microorganisms with improved bioconversion efficiencies. Improvements of these microorganisms by genetic manipulation at present are limited to a few cases. Examples include the development of a **pseudomonas putida** plasmid that codes for proteins that hydroxylate chemicals and the development of rDNA plasmids in **E3cherichia coli** that provide the genes that code for enzymes that convert fumarate to succinate (21).

In developing commercial bioprocesses, a major need is for micro-organisms with characteristics such as tolerance to increased levels of products during bioprocess reactions;* better efficiency of sugar utilization; faster rates of production; tolerance to higher temperatures, so that separation and purification methods (which often require elevated temperatures) can be coupled with bioprocesses; * * selected drug tolerance, so that growth of contaminant bacteria can be inhibited by drug treatment; and better growth on a variety of biomass sources (26). Another major need is the identification of plasmids that can be used as vectors for the transmission of useful genetic information.

[&]quot;The most commonly used micro-organism for ethanol fermentation is yeast, which tolerates ethanol concentrations up to about 12 percent. Since the purification of ethanol from such dilute solutions is costly, a desirable goal is to develop organisms (and thus enzymes) whose tolerance to end products is higher. Such organisms could be used as hosts for cloned bioconversion genes.

^{• •} A combination of **bioprocessing** and purification **could** be **imple**mented whereby products are continuously removed and collected. In this case, the high temperatures would minimize contamination by other organisms and avoid product concentrations high enough to kill the **micro-organisms** (13,37).

International research activities

Biomass-related research in the United States is conducted by the Department of Energy (DOE), the National Science Foundation, and private companies. Programs within DOE include the Biomass Energy Technology- program, which examines the technical feasibility of innovative biomass feedstock production and conversion technology; the Alcohol Fuels program; and the Biological Energy Research program (within DOE's Office of Basic Energy Science), which funds research on genetic manipulation of plants for increased biomass production and of micro-oganisms for improved bioprocessing. DOE's Energy Conversion and Utilization Technologies (ECUT) group recently started a program in biocatalysis specifically in response to the potential use of rDNA organisms in chemical production processes. The goal of this generic applied research program is to build "biocatalysis technology to enable industry to displace a significant level of nonrenewable resource requirements by [the year] 2000" (33). The ECUT program focuses on research on scale-up of bioprocesses, monitoring continuous bioprocesses, bioreactor design, and downstream product separation.

The Reagan administration's proposed fiscal year 1984 budget is not generous to biomass conversion for energy programs. The budget requests \$17.3 million to support '(fundamental R&D" in this area, a small increase of \$1.3 million (8.1 percent) from fiscal year 1983. Alcohol fuels R&D, formerly budgeted separately, would be combined with biomass energy programs (25), Since some of this R&D relates to studies of microbial chemical production, any change in Federal support for R&D of biomass energy will effectively alter R&D for biological commodity chemical production. The only DOE program specifically directed toward the use of new biotechnology, the ECUT program, received no funding for fiscal year 1984.

Differing emphasis is placed on the biological production of chemicals and fuels by the governments of foreign countries. The United Kingdom funds biotechnological applications to chemical production processes through several governmental departments. The Canadian Development Corporation is pursuing technology development for producing ethanol from aspen wood (\$21 million over 5 years), and several other Canadian Government agencies are addressing chemical and energy production from biomass. Japan, France, and Sweden also have Government-funded programs pursuing the use of biomass as a feedstock for chemicals and energy (33).

Profiles of recent U.S. patent activity indicate widespread attention by private inventors and companies in the United States and other countries to biomass conversion, particularly in areas related to hydrolysis of starch to sugar, the production of higher value-added chemicals such as amino acids from microbial systems, and improvements in bioprocess systems such as enzyme immobilization (32). Organizations with the most U.S. patents in starch hydrolysis and related bioprocesses include CPC International Inc. (U.S.), with 21; A. E. Staley Manufacturing Co. (LJ.S.), with 18; A. J. Reynolds Tobacco Co. (U.S.), with 8; France's National Agency for the Funding of Research (L' Agence Nationale de Iralorisation de la Recherche); Anheuser-Busch, Inc. (U.S.), and Havashibara Biochemical Laboratories, Inc. (Japan), with 7 each; and Novo Industri A/S (Denmark) and Miles Laboratories Inc. (U.S.), with 5 each (32). Even though patents in starch hydrolysis do not give a conclusive view of future biotechnological applications to the commodity chemical industry, they do indicate that U.S. companies are the predominant developers of the bioprocess technology underlying the utilization of starch biomass.

Conclusion

The production of low-value-added, high-volume commodity chemicals demands the use of the most economic production schemes available. The most economic schemes for chemical and energy production at present favor the use of petrochemical feedstocks. In the future, however, decreasing petroleum supplies, increasing oil prices, and technological advances in biomass utilization may foster a transition to the use of feedstocks derived from biomass. Such a transition is not expected to occur on an industrywide scale in the near future, but bioprocesses are being used to produce significant amounts of fuelgrade ethanol from corn and other crops economically.

Because of the potential for disruption of the existing industrial structure, the complex interrelationships that characterize the production of commodity chemicals will affect the success of the introduction of particular compounds produced by microbial bioprocesses. Projected bioprocessing costs of commodity chemicals and the structure of the chemical industry have been investigated by B. O. Palsson, et al, (23). These investigators concluded that the potential exists for a smooth introduction of four microbial products (ethanol, isopropanol, n-butanol, and 2,3-butanoO into the U.S. chemical industry, and that these products may foster other bioprocess development. In order for this transition to take place, however, either the costs of producing these products must be reduced (about 20 to 40 percent of their existing costs) or the price of petroleum must rise. Reducing the costs of production of chemicals from biomass is a prerequisite to commercial success in all case studies thus far.

U.S. Government support for applications of biotechnology to the conversion of biomass is decreasing, while high levels of government support are provided in several competitor countries, particularly Japan and the United Kingdom. U.S. companies appear to be active in developing certain biotechnological applications, but most of this activity as reflected in patents is concentrated in applications to starch conversion, with primary emphasis on higher value chemicals which are expected to be produced before biomass-based commodity chemicals are made. Some companies in the united States and other countries are active in bioprocess development, but given the current slow pace of R&D in microbial systems that perform the chemical conversions, these processes will not be applicable in the chemical industry for some years.

Priorities for future research *

Biotechnology will be a key factor in developing economic processes for the conversion of biomass to commodity chemicals. A number of priorities for research that will improve the efficiency of the conversion of biomass to useful chemicals can be identified:

• bioprocess improvements, including the use of immobilized cell and enzyme systems and improved separation and recovery methods, ** an area especially important to the production of commodity chemicals because incremental improvements in bioprocess technology will be readily reflected in the price of these chemicals.

- screening programs to identify micro-organisms (and their biochemical pathways) useful to processes such as commodity chemical synthesis, cellulose hydrolysis, lignin degradation, and catalysis of reactions that utilize byproducts that are currently unmarketable;
- developing host/vector systems that facilitate increased production of commodity chemicals by gene amplification and increased gene expression of desired products and that allow

^{*}Many of these suggestions are from Rabson and Rogers (24), • See *Chapter 3: The Technologies* for a more extensive discussion.

the transfer of genes into industrially important micro-organisms;

- understanding the structure and function of the cellulase and ligninolytic activities of micro-organisms;
- understanding the mechanism of survival of micro-organisms in extreme environments, such as high temperature, high pressure, acid, or salt;
- understanding the mechanism of cell tolerance to alcohols, organic acids, and other organic chemicals;

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- understanding the genetics and biosynthetic pathways for the production of commodity chemicals, especially for the strict anaerobic bacteria such as the methanogens and the clostridia;
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