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A Critical Review and Evaluation of Bioproduction of Organic Chemicals

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ABSTRACT

Dependence on petroleum as the primary feedstock for production of chemicals cannot continue indefinitely. Bioconversion could provide an alternate route to production of organic chemicals. A wide range of commodity chemicals and potentially new chemicals can be produced via bioconversion of biomass. However, before large-scale bioproduction of organic chemicals becomes a reality, issues related to economics, feedstock availability, environment, and energy requirements must be addressed. In this paper, these issues are discussed, and promising potential candidates for bioproduction are identified. Research needs are briefly addressed.

Index Entries: Bioconversion; chemicals; fermentation; organics; review.

INTRODUCTION

The primary feedstock for production of organic chemicals is petroleum. Dependence on petroleum cannot continue indefinitely. Total proven reserves of oil (worldwide) are about 150 billion tons. As of 1990, about 75 billion tons of oil remain. The current consumption rate is about 3.6 billion tons/year (*1*). At this rate, proven oil reserves will be depleted in about 20 years. Certainly, new oil reserves may be discovered, and oil consumption will decrease as supplies decline (and prices rise); therefore, oil will be available for some time. However, the conclusion remains the same—alternatives to oil are needed.

Oil supplies in the United States are also being depleted, and the US is becoming increasingly dependent on oil imports. In 1990, imports will

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provide about 42% of US oil consumption and could provide 54–67% by the year 2010. Overall US energy consumption is projected to rise about 25%, to between 104 and 113 quadrillion Btu (quads), by 2010. At the same time, US crude oil production is expected to decrease about 4 million barrels/day (*2*). The flow of imported oil can be interrupted, and the price of imported oil can rise dramatically. Even without a repeat of the dramatic events of the 1970s, many analysts expect the price of oil to rise steadily. The US Department of Energy estimates that the real price of oil could triple between 1990 and 2010 (*3*).

Development of alternative feedstocks for the production of organic chemicals would be prudent. Living systems consume, process, and produce thousands of organic chemicals using carbohydrates as the primary carbon and energy source; therefore, it is reasonable to conclude that bioconversion could provide a non-petroleum-dependent route to production of organic chemicals. The potential of a bioconversion-based organic-chemicals industry has received ongoing evaluation (*1,4–16*); opinions vary. Based on a review of the literature, relevant issues are discussed, potential products are described, needed research is identified, and conclusions are provided. This review is necessarily brief; more details are presented in ref. *16*.

THE ORGANIC-CHEMICALS INDUSTRY

The primary feedstocks for the production of organic chemicals are petroleum and natural gas. The current organic-chemicals industry is flexible, established, and well integrated into the economy. Current facilities are large-scale; hence, they exploit the economies of scale. Various competing routes exist for the production of most chemicals, which keeps production costs and prices low. Production and consumption patterns of organic chemicals are interrelated. The current industry produces high-purity products at relatively low cost. These factors constitute significant barriers to new production routes (e.g., bioconversion).

In 1985, the US organic-chemicals industry produced about 144 billion kg of products, with a value of over $110 billion. About 390 organic chemicals are produced at levels >500,000 kg/yr. The top five chemicals for 1988 account for ~24% of US production. About half the products account for 98% of the total production (*14*). US production and price data (for 1988) for 53 high-volume organic chemicals are presented in Table 1 (*16,17*).

THE ISSUES

Several factors are creating interest in the production of fuels and chemicals via bioconversion. Bioconversion routes may reduce consumption of petroleum feedstocks, which are expected to decline in supply and

Table 1
High-Volume Organic Chemicals Production in U.S.
(Millions of Pounds per Year, 1988) and Prices ($/Pound)[a]

Chemical	Production	Price	Bioproduction?
Ethylene	36,562[a]	0.13 to 0.34[a]	Possible
Propylene	19,966	0.14 to 0.24	Possible
Ethylene dichloride	13,652	0.16 to 0.19	Possible
Benzene	11,840	0.12 to 0.30	
Ethylbenzene	9,936	0.22 to 0.50	
Terephthalic acid, dimethyl ester	9,604		
Vinyl chloride	9,056	0.17 to 0.28	
Styrene	8,588	0.21 to 0.54	
Methanol	7,343	0.04 to 0.09	Possible
Formaldehyde[b]	6,730	0.26 to 0.31	Possible
Toluene	6,470	0.10 to 0.17	
p-Xylene	5,598	0.19 to 0.30	
Ethylene oxide	5,365	0.35 to 0.65	Possible
Ethylene glycol	4,899	0.31 to 0.83	Possible
Cumene	4,800	0.14 to 0.30	
Methyl tert-butyl ether	4,680	0.20 to 0.24	
Phenol, synthetic	3,528	0.25 to 0.62	Possible
1,3-Butadiene	3,194	0.12 to 0.26	Possible
Acetic acid	3,164	0.25 to 0.31	Yes; not used
Propylene oxide	3,110	0.48 to 0.51	Possible
Acrylonitrile	2,576	0.36 to 0.46	Possible
Vinyl acetate	2,561	0.36 to 0.43	
Cyclohexane	2,319	0.16 to 0.25	
Acetone	2,285	0.24 to 0.30	Yes; not used
Adipic acid	1,590	0.57 to 0.67	Possible
Isopropyl alcohol	1,418	0.21 to 0.31	Yes; not used
Caprolactam	1,261	0.85 to 0.91	
n-Butanol	1,194	0.34 to 0.40	Yes; not used
Phthalic anhydride	1,141	0.27 to 0.48	
Methyl methacrylate	1,098	0.62 to 0.62	
Bisphenol A	1,077	0.67 to 1.00	
Aniline	1,032	0.33 to 0.68	
o-Xylene	945	0.14 to 0.24	
Propylene glycol	930	0.40 to 0.62	Possible
Dodecylbenzene	851	0.45 to 0.47	
Carbon tetrachloride	759	0.24 to 0.36	
2-Ethylhexanol	731	0.35 to 0.42	
Methyl chloroform	724	0.40 to 0.42	
Acrylic acid	691	0.57 to 0.67	Possible
Toluene diisocyanates	620	1.01 to 1.28	
Ethanolamines	611		Possible
Ethanol, synthetic	574	0.16 to 0.32	Yes
Chloroform	524	0.34 to 0.38	
Methyl ethyl ketone	506	0.24 to 0.50	Possible
Methylene chloride	504	0.26 to 0.35	
Perchloroethylene	495	0.28 to 0.31	Possible
Maleic anhydride	429	0.53 to 0.67	Possible
Methyl chloride	428	0.25 to 0.26	
Glycerol, USP Grade	370	0.64 to 0.91	Yes; not used
Dioctyl phthalate	334	0.40 to 0.48	
Citric acid	235	0.83 to 1.25	Yes
1,4-Butanediol	225	0.80 to 0.96	
Ethyl chloride	152	0.24 to 0.35	

[a] Production data for 1988 (16, 17); prices for 1986 through 1989 (16).

[b] Formaldehyde (37% solution, production and price in dry pounds).

increase in real costs. Bioconversion can use biomass (lignocellulose, which is plentiful; agricultural products; and wastes) as feedstocks. Biomass represents a potentially sustainable feedstock. The environmental effects of bioconversion may be relatively benign. Recent advances in molecular biology have increased the potential of bioconversion.

However, before large-scale bioproduction of organic chemicals emerges, several issues must be addressed. These issues are discussed under four headings: Economics, Feedstock Availability, Environment, and Energy Balances.

Economics

The primary issue (and barrier) facing a bioconversion-based organic-chemicals industry is unfavorable economics. At the present time, most bioconversion processes for production of commodity organic chemicals cannot compete with traditional, petroleum-based processes (*4,6,8,10, 12,14*). The ratio of oil costs to biomass costs must increase substantially and the cost of bioconversion processes must decrease substantially before bioproduction can economically be used to produce organic chemicals. According to Jimenez and Chaves (*12*), even a 50% increase in petroleum prices (with no change in biomass costs) is not sufficient to give bioconversion an economic advantage. Palsson et al. (*6*) estimate that the oil-to-biomass feedstock cost ratio must be in the range of 3:1 to 5:1 before bioconversion of biomass can compete with petroleum-based processes. Boyles (*10*) essentially writes off the potential future of bioconversion. In summary, coal and natural gas are in plentiful supply and are likely to be used before biomass for energy and chemicals production.

Lest the picture appear too bleak, commodity and specialty organic chemicals are presently produced via bioconversion (*16*). Petroleum-based processes for the production of citric acid cannot compete with fermentation (*18*), which makes citric acid a unique organic chemical. The fuel-ethanol industry is established and growing, in large part because of tax credits given to automotive fuels that contain ethanol. Large quantities of acetic acid and lactic acid are produced by fermentation in the food industry; these production quantities are not included in chemical production figures. In addition, corn sweeteners (glucose and fructose syrups) are produced via enzymatic conversion of corn starch; US production of high-fructose corn syrup exceeds 900 million kg/yr (*11*). Xanthan gum and other microbial polysaccharides used as food additives are also produced by fermentation. Vast quantities of methane are produced as a byproduct of wastewater treatment; a substantial fraction of this biogas is (or can be) used for on-site heating and electricity generation.

Feedstock Availability

Potential feedstocks for a bioconversion-based organic-chemicals industry include lignocellulose, cellulose, hemicellulose, lignin, starch (and

Table 2
Estimated Collectible Supply of Potential Biomass Feedstocks[a]

Biomass Feedstock	Production (Million Dry Tonnes/yr) Current (1980s)	Potential
Feedstock Crops		
Wood (lignocellulose)	350	1420
Starch crops	94	1460
Sugar crops	12	---
Forage grasses	22	380
Subtotal	478	3260
Waste Sources		
Agricultural	350	350
Animal/Livestock	240	300
Industrial	160	250
Municipal (MSW)	160	240
Forestry/Milling	85	130
Sewage	10	15
Miscellaneous	50	80
Subtotal	1055	1365
TOTAL	1530	4625

[a]Based on Lynd (1) and other references in Leeper and Andrews (16).

other polysaccharides), sugars (glucose, sucrose, lactose, and xylose), and other organic compounds. Sources of these materials include feedstock crops (wood, grain, sugar crops, forage grasses) and wastes.

Biomass feedstock availability is often cited as a barrier to production of fuels. However, most studies conclude that biomass availability is not a barrier to production of chemicals from biomass. As seen from Table 2 (*1,16*), the potential US supply of collectible biomass feedstocks is 1500–4600 million dry tons. This quantity of biomass could be converted to 185–575 billion kg of organic chemicals (assuming 50% carbohydrate content and 25% overall yield). Current US production of organic chemicals and polymers is 145 billion kg. The supply of biomass feedstocks appears to be sufficient to support a bioconversion-based organic-chemicals industry (*1,8,12,14*). The world supply of cellulose may be sufficient to support a bioconversion-based fuels industry (*1,13*). Biomass currently provides ~15% of the world's total energy supply (*19*).

Lignocellulose is usually identified as the most promising feedstock for bioproduction of fuels and chemicals for the long term, primarily because of its abundance and potentially low cost (*1,4,8,12,20*). However, lignocellulose requires extensive pretreatment. Pretreatment technology has not been well demonstrated; hence, the costs of converting lignocellulose to chemicals are uncertain: capital and operating costs appear to be high. Corn and other grains require relatively little pretreatment, but crop-production costs are high and environmental impacts may be high. Wastes may be inexpensive, but collection and transportation costs are high. Wastewaters contain fermentable components in dilute solution; concentration of either the feedstock or the product is necessary, which increases process costs. A feedstock mixture consisting largely of coal and natural gas, with a limited amount of biomass feedstocks, will probably emerge.

Environment

Bioconversion may have a smaller environmental impact than traditional production of chemicals. Use of biomass as a feedstock for chemicals can reduce the net production of carbon dioxide, since production of biomass consumes carbon dioxide. If managed correctly, production of greenhouse gases can be substantially reduced by producing chemicals and fuels via bioconversion of biomass. In addition, bioconversion can utilize wastes as feedstocks, and, thus, make a contribution to waste-minimization efforts. The byproducts of bioconversion are generally benign compounds. However, biomass production could have a major impact on soil erosion, especially for production of grain crops, such as corn (*21–23*). Production of lignocellulose and forage grasses should have minimal impact on the environment (*1*).

Energy Balance

The energy balance of producing fuels and chemicals from biomass is still a matter of debate. Biomass production, collection, and transportation consume petrochemicals—fuels, fertilizers, pesticides, and herbicides. Bioconversion processes, e.g., lignocellulose hydrolysis, are energy-intensive. Product recovery can consume tremendous energy (e.g., butanol recovery). In general, grains and sugars have higher energy density, but also have higher production-energy requirements, than lignocellulose, grasses, and wastes. On the other hand, lignocellulose, grasses, and wastes have higher collection, transport, and pretreatment energy requirements. Each specific potential application requires analysis to determine its overall energy balance.

For example, Chambers et al. (*24*) performed a comprehensive analysis of the energy requirements of ethanol production from corn. Depending on the assumptions (and including the energy value of the byproduct), ethanol from corn requires 13.1–24.2 GJ/m^3 (47,000–87,000 Btu/gal) of ethanol. Based on a petroleum-only balance, ethanol production requires 9.5 GJ of petroleum/m^3 (34,000 Btu/gal). Corn production constitutes a substantial fraction of the total energy requirement (13.1–20.2 GJ/m^3 [47,000–74,000 Btu/gal], which corresponds to 4.9–7.6 MJ/kg [119,000–184,000 Btu/bushel] of corn). Since the heat of combustion of ethanol is about 21.5 GJ/m^3 [77,000 Btu/gal], Chambers et al. (*24*) conclude that producing ethanol from corn can result in a net energy gain (especially if the use of petroleum feedstocks is limited in the conversion steps). Based on Lockeretz et al. (*21*), corn production in the corn belt requires about 2.1 MJ/kg (51,000 Btu/bushel); this energy input can be reduced to about 1.0 MJ/kg (23,000 Btu/bushel) by use of alternative farming techniques.

POTENTIAL PRODUCTS

Organic chemicals can be produced via three general bioconversion routes: (a) microbial fermentation of carbohydrates, (b) enzymatic or microbial (one-step) conversion of intermediates and (c) microbial or enzymatic conversion followed by catalytic conversion (i.e., combined conversion). Organic chemicals of significant industrial interest, including ethylene and propylene, can be produced via one or more of the above bioconversion routes. Potential routes to various organic chemicals are provided in ref. *16*.

Bioconversion can compete with the existing chemicals industry by direct substitution or by indirect substitution; each approach has advantages and disadvantages (*5*). In direct substitution, a new production route (e.g., bioconversion) is developed for a chemical that is currently in the marketplace; the new production route competes for market share directly with existing routes. Production of ethylene from ethanol is an example of direct substitution. Direct substitution does not require development of new markets; the product already has demonstrated uses. If a new process has a sufficient economic advantage, its product can take over the existing market. However, direct substitution competes with existing production capacity, which has a significant advantage over new technology. Candidates for direct substitution include acetaldehyde, acetic acid, acetone, acrylic acid, adipic acid, 1,3-butadiene, *n*-butanol, ethanol, ethyl acetate, ethylene, glycerol, isopropanol, maleic anhydride, methanol, methyl ethyl ketone, phenol, and propylene.

A potential bioconversion-based chemicals industry based primarily on direct substitution is described by Busche (*14*). In this scenario, about 93% of US organic chemicals are supplied from biomass feedstocks via bioproduction of ethanol (for conversion to ethylene and other C-2 derivatives), isopropanol (for conversion to propylene and other C-3 derivatives), *n*-butanol (for conversion to butenes), polyhydric alcohols (e.g., 2,3-butanediol for conversion to butadiene), acetone, acetic acid, fumaric or malic acid, and glycerol. Although this scenario is technically possible, it is not presently economically feasible (*14*).

In indirect substitution, a new chemical, which has a use similar (or superior) to that of a chemical used currently, is produced; if the new chemical is better than the currently-used chemical, then the current chemical is indirectly displaced. The production of a new polymer that is biodegradable (e.g., lactic acid copolymers or polyhydroxybutyrate, a microbial polysaccharide) is an example of indirect substitution. Indirect substitution does not involve direct competition with existing chemical markets; therefore, bioconversion products may enter the marketplace by this route. However, markets for potential products are not established, and a great deal of product-development research may be required for each product. Indirect substitution may allow development of entirely new products with new uses.

Table 3
Analysis of Selected Chemicals Produced via Bioconversion

Product	Product[a] Price ($/kg)	Theoretical Yield (kg/kg)	Potential Return ($/kg)	Return[b] Ratio ($/$)
Methane	0.15	0.27	0.04	infinite
Xanthan gum	12.69	0.90	11.42	78
Itaconic acid	3.96	0.72	2.85	19
Fructose[c]	1.81	1.00	1.81	12
Citric acid	2.20	1.12	2.47	11[d]
Gluconic acid	0.93	1.09	1.01	7
Ethanol[e]	0.37	0.51	0.19	1.3
Ethanol[f]	0.57	0.51	0.29	1.9

[a]Price data (25).
[b]Return ratio based on glucose at $0.148/kg (corn at $3/bushel), unless otherwise specified.
[c]Fructose in high fructose corn syrup (HFCS); price assumes glucose in HFCS has no value, HFCS at $0.90/kg, and 50% HFCS.
[d]Based on sucrose at $0.216/kg (i.e., molasses at $110/tonne, 51% sucrose).
[e]Actual market price of ethanol at $0.367/kg ($1.10/gallon).
[f]Effective ethanol price including tax credits equals $0.567/kg ($1.70/gallon).

A simple approach has been applied to identify potentially promising candidate organic chemicals for economical production via bioconversion. Two terms are defined for a candidate organic chemical: potential return and return ratio. The potential return (PR) is defined as theoretical yield (kg product/kg feedstock) times market value ($/kg product). The PR provides an estimate of the maximum potential monetary return per unit of feedstock. The return ratio (RR) is the PR divided by the cost of feedstock; the RR allows comparison of processes that use different feedstocks. If the feedstock is a waste (with no value), then the RR is infinite. Additional important factors in identifying promising candidates include actual production costs (obtainable yield, separation requirements, difficulty of purification, special materials, and so on) and market considerations (market size, profitability, number of producers, and the like).

The proposed approach to analyzing candidate chemicals may, nonetheless, provide a straightforward, simple method for preliminary screening of many candidate products. In this way, the number of chemicals for which detailed economic analyses will be necessary can be reduced. Detailed economic and market analyses are still needed for the candidate chemicals passing this initial screening. Candidate chemicals passing the more rigorous analyses should then be selected for research and development efforts.

In order to gain insight into the utility of PR and RR, the approach is applied in Table 3 to organic chemicals currently produced via bioconversion (25). Except for ethanol and methane, these chemicals have high market values, theoretical yields, PRs, and RRs. Ethanol probably provides the lower feasible limit for PR and RR, at about $0.26/kg carbohydrate feedstock and about 2, respectively. Methane, produced in large volumes as a byproduct of wastewater treatment, is included in Table 3. Methane has an extremely low PR; yet, it is produced because of low feedstock and

Table 4
Analysis of Selected Chemicals Being Studied or Considered for Production via Bioconversion

Product	Product[a] Price ($/kg)	Theoretical Yield (kg/kg)	Potential Return ($/kg)	Return[b] Ratio ($/$)
Lactic acid	2.33	1.00	2.33	16
Glycerol	1.85	0.88	1.63	11
PHB[c]	1.10[d]	0.85	0.94	6
Propionic acid	0.73	0.70	0.51	3.5
Acrylamide	2.26	1.34	3.04	3[e]
Acetone	0.66	0.53	0.35	2.4
n-Butanol	0.84	0.41	0.34	2.3
Isopropanol	0.57	0.44	0.25	1.7
2,3-Butanediol	0.35	0.55	0.19	1.3
Butadiene	0.57	0.33	0.19	1.3
n-Butene	0.62	0.31	0.19	1.3
Ethylene	0.53	0.31	0.16	1.1
Propylene	0.42	0.31	0.13	0.9

[a]Price data (25).
[b]Return ratio based on glucose at $0.148/kg (corn at $3/bushel), unless otherwise specified.
[c]PHB: polyhydroxybutyrate.
[d]Assumed price, based on competition with polyethylene (25).
[e]Feedstock is acrylonitrile at $0.96/kg.

recovery costs. Methane is a gas that bubbles out of the digester broth. Methane provides insight into the importance of considering several factors when analyzing potential candidates for bioproduction. High PR and RR values indicate that economically competitive production via bioconversion may be possible.

The results of applying this approach to chemicals currently being studied or considered are shown in Table 4 (*25*). Production of olefins (butadiene, butenes, ethylene, and propylene) via dehydration of the corresponding alcohol has low PR and RR values; olefins are low-value chemicals and are produced from carbohydrates in low yield. Acetone, butanol, butanediol, and isopropanol also have low PRs and RRs because of low values and yields. Acetone–butanol fermentation was once the commercial route to these two chemicals and has been studied for years. A RR >2 is not sufficient to make the acetone–butanol fermentation feasible; these solvents are produced at low concentration, which leads to high separation costs. On the other hand, lactic acid, glycerol, and polyhydroxybutyrate appear to be promising candidates for bioproduction.

Lactic acid, for instance, could enter the marketplace in significant quantities via indirect substitution. Lactic acid can be copolymerized to produce biodegradable polymers (*26*). The production of lactic acid by fermentation is a well-established technology. However, the cost of lactic acid production and recovery by fermentation must be reduced before large-scale production by bioconversion will be feasible. The current price of lactic acid is $2.33/kg (*25*). If lactic acid is to be used as a bulk monomer, its price must drop significantly (to <$1.00/kg).

Glycerol is produced from propylene and by isolation from animal fats and oils. In 1988, US production of USP-grade (propylene) glycerol was 169 million kg. Total US glycerol production, including crude glycerol,

Table 5
Analysis of Selected Potential Chemicals for Production via Bioconversion

Product	Product[a] Price ($/kg)	Theoretical Yield (kg/kg)	Potential Return ($/kg)	Return[b] Ratio ($/$)
Succinic acid	9.60	0.66	6.28	42
Adipic acid	1.47	1.70	2.50	17[c]
Maleic acid	3.00	0.64	1.92	13
Fumaric acid	1.70	0.97	1.65	11
Malic acid	1.82	0.74	1.35	9
Adipic acid	1.47	1.73	2.54	9[d]
Acrylic acid	1.42	0.80	1.14	8
Butyric acid	1.67	0.59	0.99	7
Adipic acid	1.47	0.63	0.93	6
Maleic anhydride	1.52	0.54	0.82	6
Formaldehyde	0.61[e]	1.00	0.61	6[f]
Ethylene oxide	1.38	0.59	0.81	5.5
Acrolein	1.36	0.53	0.73	5
Formaldehyde	0.61[e]	0.94	0.58	4
Acetic acid	0.64	1.00	0.64	4
Acetaldehyde	1.02	0.59	0.60	4
Propylene oxide	1.20	0.48	0.58	4
Ethyl acetate	0.90	0.59	0.53	3.6
Vinyl acetate	0.87	0.48	0.42	2.8
Butyraldehyde	0.84	0.45	0.38	2.6
Methyl ethyl ketone	0.66	0.54	0.36	2.4
Methanol	0.11	2.00	0.22	1.4[g]

[a]Price data (25).
[b]Return ratio based on glucose at $0.148/kg (corn at $3/bushel), unless otherwise specified.
[c]Feedstock is hexane at $0.15/kg.
[d]Feedstock is cyclohexane at $0.295/kg.
[e]Price on pure basis; actually sold at 37%.
[f]Feedstock is methanol at $0.107/kg.
[g]Feedstock is methane at $0.154/kg.

was about 1.6 billion kg in 1979. Glycerol sells for about $1.40–1.85/kg (25). Glycerol is used in foods, drugs, cosmetics, tobacco products, gaskets and cork products, and various other areas (*27*). Glycerol can be produced by fermentation (*16*). Feedstocks include glucose, hydrolyzed starch, fructose, and xylose. Glycerol has not been produced by fermentation since World War II because of the low cost of chemical routes, the low yield of fermentation, and the cost of glycerol recovery from fermentation broth. Fermentation-based glycerol may have difficulty entering the marketplace in competition with production of crude glycerol from fats, which is a highly profitable route to glycerol.

Polyhydroxybutyrate (PHB) is a microbial polysaccharide. Production of PHB provides a potential direct route to biodegradable polymers. PHB can be produced from carbohydrates and other feedstocks by several microorganisms (*28*).

Additional organic chemicals that can be produced via bioconversion are shown in Table 5 (25). Of the chemicals with RR >4 (and which can be produced from carbohydrates), several are high-volume chemicals (production in million kg/yr): formaldehyde (3059), ethylene oxide (2439), acetic acid (1438), propylene oxide (1414), adipic acid (723), acrylic acid (314), and maleic anhydride (195). Ethylene oxide and propylene oxide are made from the corresponding olefin, which is produced at lower cost from traditional feedstocks than from carbohydrates; therefore, these two chemicals are not considered promising candidates for production via bioconversion. Additional candidate organic chemicals are discussed below.

Formaldehyde can be produced via enzymatic conversion of methanol (*29*). Methanol can be produced from methane, which can be produced from carbohydrates. Therefore, production of formaldehyde from carbohydrates is possible. This route may warrant investigation.

Acetic acid production by microbial conversion is a well-known, established technology (*30*). Bioconversion is not presently competitive for production of acetic acid as a chemical.

Adipic acid is produced via conversion of cyclohexane to cyclohexanol and cyclohexanone via air oxidation, followed by nitric acid oxidation to produce adipic acid. Adipic acid production in the US was 659 million kg in 1985 (*31*). Its price is $1.32–1.47/kg (*25*). About 90% of the adipic acid produced in the world is used to make nylon-6,6, the polyamide formed by condensation polymerization of adipic acid with hexamethylenediamine. The remaining uses of adipic acid include applications in plasticizers, resins,plastics, foams, and as a food acidulant. Most nylon manufacturers produce the adipic acid and hexamethylenediamine used in their processes. Adipic acid can be produced by two combined routes (*16*). In one potential route, 2,3-butanediol (produced via bioconversion) is converted by chemical catalysis to 1,3-butadiene, which is then converted to adipic acid. In another potential route, C_{10}–C_{16} fatty acids (produced by fermentation) are converted to alkanes by electrolytic decarboxylation or by enzymatic decarboxylation, followed by microbial (*Candida tropicalis*) conversion of the resulting *n*-alkanes to adipic acid. Bioconversion-based adipic acid may have difficulty entering the marketplace; for the most part, adipic acid is currently produced by nylon manufacturers for their own use.

Acrylic acid is produced from propylene, which is converted to acrolein via catalytic oxidation, followed by conversion to acrylic acid by air oxidation. In 1981, US production of acrylic acid was about 314 million kg (*4*); its current market price is $1.39–1.45/kg (*25*). Acrylic acid is used to produce several polymers and polymer emulsions. Acrylate polymer emulsions are used as coatings, finishes, and binders for leather, textile, and paper products; in the preparation of interior and exterior paints, floor polishes, and adhesives; and for other industrial coatings. Acrylic acid can also be produced from acetic acid, propionic acid, and methane (*32*), which are products of bioconversion. Therefore, acrylic acid can be produced via bioconversion and combined routes.

Maleic anhydride can be produced via dehydration of malic acid (*33*). Since malic acid can be produced via fermentation of carbohydrates (*34*), maleic anhydride can be produced from carbohydrates.

RESEARCH NEEDS

According to Busche (*8,14*), fermentation is presently uneconomical for production of (most) chemicals; in the future, fermentation of biomass can become feasible for production of commodity and specialty chemicals. Research and development of biomass conversion to produce chemicals and fuels is justified and should be viewed as a national insurance policy by the US (*14*).

As a basic goal, research must focus on overcoming the economic barriers to expansion of bioconversion. Further analyses to determine promising feedstock/product combinations are needed. Advances in biomass production (greater yield and/or lower energy requirements) are needed. Complete and optimum feedstock utilization is essential to the economic feasibility of bioconversion; for lignocellulose utilization, studies on hemicellulose and lignin conversion are needed. For other feedstocks, similar studies are needed. In addition, research related to upgrading the value of bioconversion byproducts are needed; such studies could result in increased revenues for bioconversion processes. Process studies and analysis are needed to integrate and optimize processes and reduce processing costs. Product-recovery studies are also essential. Perhaps products that are easy to recover should be identified (e.g., gases); methane is a case in point. More detailed discussions of research needs in biotechnology and bioconversion for chemicals production are provided by Leeper and Andrews (*16*) and OTA (*35*).

CONCLUSIONS

Bioconversion will enter the chemical industry via niches. The niches will be determined by a combination of economic and environmental factors. Therefore, federal research and development should be directed toward high-volume chemicals that have a potential to compete in the market place. Production of fuels could become necessary in the future. Research on chemicals production will provide insight into the production of fuels via bioconversion.

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