Biotechnology for Producing Fuels and Chemicals from Biomass

Volume II — Fermentation Chemicals from Biomass

Ruxton Villet, Editor

SERI

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

SERI/TR-621-754
UC Category: UC-61

BIOTECHNOLOGY FOR PRODUCING
FUELS AND CHEMICALS FROM
BIOMASS

VOLUME II - FERMENTATION CHEMICALS
FROM BIOMASS

RUXTON VILLET, EDITOR

FEBRUARY 1981

PREPARED UNDER TASK. NO. 1034.00

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Prepared for the
U.S. Department of Energy
Contract No. EG-77-C-01-4042

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

FOREWORD

As petroleum becomes scarcer and more costly, petroleum-derived chemicals will probably be increasingly displaced by chemicals produced from biomass. We describe the fermentative production of several large-volume chemicals and discuss to some extent economic feasibilities; more precise economic evaluations require detailed process engineering information which is not available at present.

Fermentation technology, before it was essentially superseded by petrochemicals several decades ago, depended on easily fermentable substrates such as sugar and starch. The cost of such feedstock is rising and constitutes about 60% of the overall cost of production of fermentation chemicals. It is important to develop biotechnological processes for the conversion of more inexpensive feedstocks such as cellulose and hemicellulose.

We hope that the information presented here, preliminary though it is, will be helpful to investors and entrepreneurs contemplating ventures in industrial chemistry based on renewable resources.

Approved for

SOLAR ENERGY RESEARCH INSTITUTE

Ruxton Villet, Branch Chief
Biotechnology Branch

Clayton Smith, Division Manager
Chemical and Biological Division

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

PREFACE

New industrial investment hinges on an adequate supply of capital. The latter is generated from a production surplus, the extent of which is related to the cost of available energy and materials (Villet 1981a). At present the chemicals industry is based on nonrenewable resources. As the availability of such resources declines and prices rise, market forces will motivate a quest for substitutes.

Sugars, which are feedstocks for production of chemicals via fermentation processes, can be obtained from an immense resource of biomass that is renewable by photosynthesis. It is likely, therefore, that because of the escalating price of crude oil, the raw materials supply base of the chemicals and fuels industry will modulate, perhaps dramatically, toward biomass.

Among various possible substitutes for petrochemicals, fermentation ethanol, for example, can serve as a fuel and as a basic chemical feedstock for other products such as ethylene, butadiene, acetaldehyde, and acetic acid. The demand for ethylene, a prime chemical feedstock derived from petroleum, is 11 million tonnes in the United States and approximately the same in western Europe. The price is 44¢/kg. With further increases in the price of ethylene as a consequence of the rising cost of crude oil, fermentation ethanol is likely to come into play as a key chemical feedstock.

To take advantage of a trend in market substitution toward fermentation chemicals, it is imperative to seek ways of resuscitating microbiological industry and, by the addition of sophisticated technology, make it competitive with the petrochemical industry. The total production in the United States of butadiene, acetic acid, acetone, isopropanol, ethanol, butanol, methyl ethyl ketone, glycerol, maleic anhydride, and fumaric acid is approximately 6.5 million tonnes, with a market value of about $3 billion. Less than 5% of these chemicals is produced fermentatively.

The potential for fermentation production is there, but biotechnological improvements are necessary to reduce the cost of production. The processes already developed are based on easily fermentable substrates, such as sugar and starch; the cost of such feedstocks can amount to as much as 70% of the total cost of production. Fermentation processes must be improved so that higher rates and yields are achieved. Development of the necessary microbial strains could be achieved in the near term. The energy efficiency of recovery processes, such as distillation, must also be improved (Nguyen and Heyman 1981). In the longer term, technology must be developed for the fermentation of relatively inexpensive but unconventional feedstocks, such as forage crops and woody biomass. Two options are (1) hydrolysis to produce sugars, followed by fermentation (Emert and Katzen 1979); and (2) a direct fermentation to chemicals using thermophilic anaerobes (Wang et al. 1978; Ng 1981).

In the United States the area of commercial timberland is 250 million hectares with an annual growth of 240 million metric tons of oil equivalent. Potential investors in a biomass-based chemicals/fuels venture must be assured of a well-managed and reliable wood fuel supply infrastructure. This requires considerable investigation. Forage crops as an alternative raw material supply have certain advantages, such as a relatively simple biotechnological processing due to lower lignification, an established culturing and harvesting technology, and an ability to thrive on drier terrain. A preliminary assessment of the economic potential of various herbaceous species for producing ethanol is encouraging (Moreira et al. 1981).

Another renewable resource that merits commercial interest is algal biomass (terrestrial and marine) (Tornabene 1981). For example, more than 50% of the dry weight of certain algal species is in the form of hydrocarbons and other lipids (Tornabene et al. 1980).

To establish an efficient biotechnological industry for chemicals and fuels manufacture, process development and research are needed (Villet 1979). An integration of science and engineering disciplines is essential, such as is incorporated in the design of the SERI Biotechnology Branch, with its range of R&D activity from modern genetic technology to biochemical engineering design and process scale-up (Villet 1981b; Grohmann and Villet 1981).

In Volume II of this overview of biotechnology for producing fuels and chemicals, four chemicals—acetone, butanol, acetic acid, and citric acid—are selected for a preliminary examination of the economic feasibility of fermentative production. In the past, before the advent of cheap petroleum and its highly efficient catalytic cracking technology, these chemicals were produced fermentatively in large volume. Approximately 90% of citric acid production worldwide continues to be fermentative. In addition to these larger-volume chemicals, 2,3-butanediol and propionic acid are included in this examination. Lactic acid, isopropanol, maleic anhydride, fumarate, and glycerol merit attention also and will be included in further SERI reports.
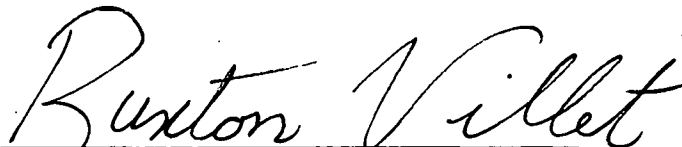
A difficulty in a survey of the economic feasibility of chemical production is the dearth of detailed process engineering economic information on the various fermentations. Precise, current process economic information, including associated sensitivity analyses and showing interactions among design variables, would be of immense value to the entrepreneur contemplating investment in particular biotechnological ventures.

The contributions to Volume II by A. E. Humphrey, E. J. Nolan, J. A. Phillips, D. L. Ristroph, G. F. Slatte, K. Grohmann, and R. B. Bailey are gratefully acknowledged.

REFERENCES

Emert, G. H.; Katzen, R. 1979. "Chemicals from Biomass by Improved Enzyme Technology." Proc. ACS/CSJ Joint Chem. Congr.; Hawaii.

Grohmann, K.; Villet, R. H. 1981. "Genetic Engineering of Microorganisms and Its Application in the Production of Chemicals and Fuels from Biomass." In preparation.

Moriera, A. R.; Linden, J. C.; Smith, D. H.; Villet, R. H. 1981. "Economic Outlook for the Production of Ethanol from Forage Plant Materials." ACS Benchmark Paper. Accepted for publication.

Ng, T. K. 1981. "Thermophilic Fermentation of Biomass." Adv. Biochem. Eng. In preparation.

Nguyen, X. N.; Heyman, E. C. 1981. "Computer Aided Analysis of Energy Consumption in Ethanol-Water Distillation Operations." Chem. Eng. Prog. In preparation.

Tornabene, T. G. 1981. "Microorganisms as Hydrocarbon Producers." In New Trends and Utilization of Solar Energy. Switzerland: Experientia.

Tornabene, T. G.; Holzer, G.; Peterson, S. L. 1980. "Lipid Profile of the Halophilic Alga, Dunaliella salina." Biochem. Biophys. Res. Commun. Vol. 96: p. 1349.

Villet, R. H. 1979. Biotechnology for Producing Fuels and Chemicals from Biomass: Recommendations for R&D. Vol. I. Synopsis and Executive Summary. SERI/TR-332-360. Golden, CO: Solar Energy Research Institute.

Villet, R. H. 1981a. "Biotechnology for a Renewable Resources Chemicals and Fuels Industry: Biochemical Engineering R&D." Chem. Eng. Prog. Accepted for publication.

Villet, R. H. 1981b. "Biotechnological R&D for Biomass Conversion to Chemicals and Fuels." In Developments in Industrial Microbiology. Accepted for publication.

Wang, D. I. C.; Cooney, C. L.; Wang, S. D.; Gordon, J.; Wang, G. Y. 1978. "Anaerobic Biomass Degradation to Produce Sugars, Fuels and Chemicals." Proc. 2nd Ann. Sympos. on Fuels from Biomass. Washington, D.C.: U. S. Department of Energy.

Ruxton Villet

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

SUMMARY

OBJECTIVE

The purpose of this report is to provide an overview of the possibilities and economic feasibility of producing selected chemical feedstocks by the fermentation of biomass. Six chemical feedstocks were selected for review. Four of them—acetone, butanol, acetic acid, and citric acid—were once produced in large volume by fermentation, and two of them—2,3-butanediol and propionic acid—could potentially be produced by fermentation.

DISCUSSION AND CONCLUSIONS

Acetone and Butanol

Butanol and acetone were produced commercially by fermentation until after World War II. During the postwar period the low cost of petrochemical feedstocks made the use of the oxo and aldol processes more attractive. No fermentation butanol or acetone has been produced in the United States since about 1952.

The main commercial use of acetone is as a solvent and chemical intermediate in the production of plastics and ketones. Butanol is used as a solvent in the paint and lacquer industry and as a precursor in plastics. The demand for these solvents has increased by a factor of almost three since the early 1960s. Since 1970, the cost of acetone has quadrupled and the cost of butanol has almost tripled. When prepared by fermentation, the production costs of these solvents are especially dependent on the feedstock and energy costs because yields tend to be low. For example, when corn or molasses is used, the feedstock cost amounts to about 60% of the total production cost. In view of the increasing cost of petrochemical feedstocks for these solvents, an updated analysis should be undertaken to determine the competitive position of fermentation in relationship to the oxo and aldol processes.

Acetic Acid

This important industrial chemical [1.3 billion kg (2.9 billion lb) were used in 1977] is currently produced commercially by liquid-phase hydrocarbon oxidation, acetaldehyde oxidation, or methanol carbonylation. However, acetic acid can be produced directly by fermentation, and it can be produced indirectly by oxidizing fermentation ethanol to acetaldehyde and then oxidizing acetaldehyde to acetic acid. The traditional fermentation process for manufacturing vinegar produces only about 7% to 8% acetic acid, which would have to be concentrated for commercial use; this pathway is not attractive because it is energy intensive. Acetic acid derived from ethanol oxidation is not yet economical because at present both acetic acid and ethanol are about the same price, 42¢ to 46¢/kg (19¢ to 21¢/lb).

No detailed information on process economics exists for the production of acetic acid by fermentation of biomass. The market for acetic acid could grow 5% to 7% per year. Production of acetic acid from biomass should be studied because the raw materials currently used are related to the petroleum industry and are, therefore, economically linked to oil.

Citric Acid

Since the early 1930s, fermentation has been the major process for the production of citric acid. At present, 90% of the 250 million kg (550 million lb) of citric acid manufactured in the world each year is produced by either submerged or surface fermentation. The cost of the substrates—molasses and other carbohydrates—is about 15% to 20% of the cost of the product, which is selling for about \$1.56/kg (71¢/lb) (hydrous citric acid). The major uses of citric acid are as an astringent in food production, as an agent for lowering pH in pharmaceuticals, and as a metal cleaner in industrial areas. The market for citric acid is expected to grow about 5%/yr; the growth may be greater if it is used as a substitute for phosphate in detergents.

2,3-Butanediol

This particular chemical is not now in large commercial production. During World War II, a major effort was undertaken to investigate its production by fermentation because it is a precursor to butadiene, a major ingredient of synthetic rubber. Work by J. A. Wheat in Canada proceeded to the pilot plant stage and was terminated after the end of the war.

A number of other useful chemicals can be obtained from 2,3-butanediol: methyl ethyl ketone (MEK), acetoin, diacetyl, and isocyanates (from which polyurethane foams may be obtained, although not economically at present). The production of MEK at \$507/tonne (\$460/ton) from butanediol does not appear economical at present. MEK can be condensed, however, to an eight-carbon ketone which in turn can be hydrogenated to octane isomers; this is an interesting application which, in light of potential fuel shortages, justifies a review of the process economics. Any carbohydrate source may be used to produce 2,3-butanediol by fermentation; the previous pilot studies used molasses.

Using the results of the pilot studies, a cost estimate was made by Wheat in 1952 for a plant daily producing about 4500 kg (10,000 lb) of 2,3-butanediol. The capital required was found to be \$2.78 million and the corresponding production cost was estimated to be 57¢/kg (26¢/lb) with no return on investment. This estimate was fairly well done from an engineering standpoint and deserves a review and an update for comparison with the contemporary economics for producing butadiene and MEK from other sources.

Propionic Acid

Propionic acid has never been produced industrially by fermentation, probably because the demand was small before 1950 (when the fermentation industry was at its peak) and because the cost of production by fermentation techniques is high, due largely to the low product concentration (21 g/L) and recovery and purification problems. The yield of acids from a typical propionic fermentation of sugar is around 84%, two-thirds of which is propionic acid. This means that if the raw material costs are not to exceed 50% of the production cost [estimated to be 37¢–40¢/kg (17¢–18¢/lb)], then sugar for a biomass conversion process must be available at 11¢/kg (5¢/lb) for the production of propionic acid to be economically feasible in today's market.

Propionic acid sells for 44¢–48¢/kg (20¢–22¢/lb) and has an annual demand of 45.4 million kg/yr (100 million lb/yr). It is used chiefly in the mineral salts form (calcium or sodium propionate) as a preservative. Approximately 9.1 million kg/yr (20 million lb/yr) are used for making cellulose ester plastics.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SERI

xiv

SECTION 1.0

ACETONE AND BUTANOL

1.1 BACKGROUND*

In 1861, Pasteur reported the formation of butanol during his studies of the bacterial fermentation of lactic acid and calcium lactate. The production of acetone from fermentation of potato starch by Bacillus macerans was first reported in 1905 by Schardinger. In the early 1900s, the synthetic rubber industry provided impetus for the commercial development of acetone/butanol fermentation. Synthetic rubber was produced by the polymerization of isoprene or butadiene. Isoprene was made from isoamyl alcohol obtained from fusel oil produced by ethanol fermentation; butadiene, eventually considered the best material for synthetic rubber manufacture, was prepared from butanol. Studies of the fermentative production of this butanol by Perkin and Weizmann of Manchester University and Fernbach and Schoen of the Pasteur Institute led to the discovery of an organism that fermented potato starch to amyl alcohol, butanol, ethanol, and acetone. Weizmann subsequently discovered an organism capable of fermenting other types of starches with a higher yield of solvents; this culture was eventually designated Clostridium acetobutylicum.

The advent of World War I dramatically increased the demand for acetone in the manufacture of cordite, an explosive. Because the increased demand could not be met by the wood-distilling industry, the production of acetone by the fermentation of maize, using C. acetobutylicum, was commercialized in England, India, Canada, and the United States. Before the war ended, plantation production of natural rubber had increased to an extent that made synthetic rubber production economically unfeasible. Consequently, the demand for butanol was low and the quantities of this solvent produced during the fermentation production of acetone (2 parts butanol/1 part acetone) presented a severe waste disposal problem.

After World War I, the demand for acetone dropped and production was drastically curtailed. However, plant operation was restarted when demand increased for butanol in the manufacture of butyl acetate. (Butyl acetate was used as a solvent for the nitrocellulose lacquers required by the rapidly expanding automobile industry.)

In the early 1930s, the isolation of Clostridium saccharobutylicum, a culture capable of metabolizing sucrose, was reported by Woodruff et al. and by McCoy. This discovery, and the continued demand for butanol, led to construction in Philadelphia, Baltimore, Puerto Rico, and England of new plants utilizing molasses as the raw material.

With increased production of plastics and synthetic fibers, rayon, and lacquers, the demand for acetone and butanol continued to grow. Various synthetic processes, based on petrochemical raw materials, were developed. Today, for economic reasons, all acetone and butanol in the United States is produced from petrochemicals; all fermentative production in the United States has ceased.

---

*From: Gabriel 1928; Gabriel and Crawford 1930; McCutchan and Hickey 1954; Nathan 1919; Ross 1961; Wynkoop 1943; Wynkoop 1957.

1.2 PHYSICAL PROPERTIES

Acetone, the simplest and most important of the ketones, is a colorless, flammable liquid and is miscible in all proportions with water and with organic solvents such as ether, methanol, ethanol, and esters. Butanol, a primary alcohol, is a colorless liquid. It has a solubility of 8 wt % in water and is miscible with most common organic solvents. Some selected physical properties of acetone and butanol are listed in Table 1-1.

Table 1-1. PHYSICAL PROPERTIES OF ACETONE AND BUTANOL

Property	Acetone	Butanol
Formula	CH_3COCH_3	$CH_3(CH_2)_2CH_2OH$
Alternative names	dimethyl ketone, 2-propanone	1-butanol, n-butyl alcohol
Formula weight	58.079	74.12
Melting point at 101.3 kPa, or 1 atm (°C)	-94.6	-90.2
Boiling point at 101.3 kPa (°C)	56.1	117.7
Specific gravity, 20°C/4°C	0.7899	0.8098
Heat of vaporization [kJ/kg (cal/g)]	501.1 (119.7)	591.5 (141.3)
Specific heat of liquid [kJ/kg K (cal/g K)]	2.60 (0.62)	2.34 (0.56)
Heat of fusion [kJ/kg (cal/g)]	98.08 (23.42)	125.3 (29.93)

1.3 APPLICATIONS

Acetone is used as a chemical intermediate in the manufacture of methyl methacrylate, methyl isobutyl ketone, diacetone alcohol, bisphenyl A, and the vitamin intermediate methyl butanol. It is also used as a solvent for vinyl or acrylic resins, alkyd paints, varnishes, lacquers, inks, and nitrocellulose and cellulose acetate. The relative amounts of acetone consumed for these various uses are given in Table 1-2.

The major uses for n-butanol are as a solvency enhancer in the formulation of nitrocellulose lacquers; as a latex, in the form of butyl acrylate; and as a precursor to butyl acetate, butyl glycol ether, and dibutyl phthalate. A breakdown of its applications is given in Table 1-3.

Table 1-2. DISTRIBUTION OF USES OF ACETONE

Use	% of Total
Manufacture of:	
Methacrylates	33-34
Methyl isobutyl ketone	13-14
Bisphenyl A	5-6
Methyl butynol	5
Others (methylisobutylcarbinol, hexyleneglycol, isophorone, diacetone alcohol, mesityl oxide)	9-12
Solvent for:	
Resins, paints, lacquers, varnishes	16-18
Processing use	5
Cellulose acetate	4-5
Other	1-10

Table 1-3. DISTRIBUTION OF USES OF n-BUTANOL

Use	% of Total
Manufacture of:	
Butyl acrylate	21
Glycol ethers	18
Dibutyl phthalate	10
Solvent for:	
General use	22
Amine resins	5
Other	24

1.4 CURRENT COMMERCIAL PRODUCTION (CHEMICAL)

1.4.1 Acetone*

All acetone is currently produced by two synthetic routes: the cumene hydroperoxide process and the catalytic dehydrogenation of isopropanol. In the cumene hydroperoxide process, used for producing phenol as well as acetone, benzene is first alkylated to cumene, which is oxidized in a series of reactors at 80°-130°C to cumene hydroperoxide. The hydroperoxide, after concentration, is then cleaved under acid conditions at 60°-100°C to phenol and acetone. After neutralization or ion exchange, the products are recovered by distillation. The primary product is phenol; 0.40-0.45 kg of acetone per kg of cumene is produced as coproduct.

The catalytic dehydrogenation of isopropanol is an endothermic reaction carried out in a tubular reactor at 327°C. A conversion of 97 wt % is theoretically possible; in actual operation, conversions of 75-95 mol % have been attained. A number of by-products may be formed in addition to acetone and hydrogen: propylene, mesityl oxide, diisopropyl ether, acetaldehyde, propionaldehyde, and other hydrocarbons and carbon oxides. The product steam is cooled, noncondensable gases are scrubbed with water, and acetone and isopropanol are recovered by fractional distillation. After concentration, the isopropanol is recycled to the reactor.

As of 1976, 60% of U.S. acetone production was based on the cumene hydroperoxide process. Production of acetone by this process is tied to the demand for phenol. Production by isopropanol dehydrogenation meets most of the additional acetone requirements. Supply and demand curves and cost data for acetone are given in Fig. 1-1. Manufacturers, their approximate capacities, and the technology used in production as of 1977 are listed in Table 1-4.

1.4.2 n-Butanol**

All U.S. production of this chemical is currently based on two synthetic routes: the oxo process and the aldol process. In the oxo process, propylene is reacted with carbon monoxide and hydrogen at 140°-170°C and 27-30 MPa (270-300 atm) in the liquid phase and in the presence of a catalyst to yield a mixture of n- and iso-butyraldehydes. The isomeric forms of the aldehyde are separated by distillation, and the n-butyraldehyde component is then reduced with hydrogen over a fixed-bed catalyst at 130°-160°C and 3-5 MPa (30-50 atm). The crude butanol is purified by distillation. If operated for the production of butyraldehyde, the process yields 100 kg of n-butyraldehyde and 11 kg of n-butanol per 102 kg of propylene. If the process is operated for the exclusive production of n-butanol, the yield is 100 kg of n-butanol per 92 kg of propylene.

In the aldol process, acetaldehyde, produced either by the direct oxidation of ethylene or by the dehydrogenation of ethanol, is reacted with base at 5°-25°C to form acetaldol. The reaction mixture is then acidified and distilled to dehydrate the acetaldol to

---

*From: Chemical Marketing Reporter 1963-1979; Nelson and Webb 1979.

**From: Chemical Marketing Reporter 1963-1979; Sherman 1979.

4

SERI
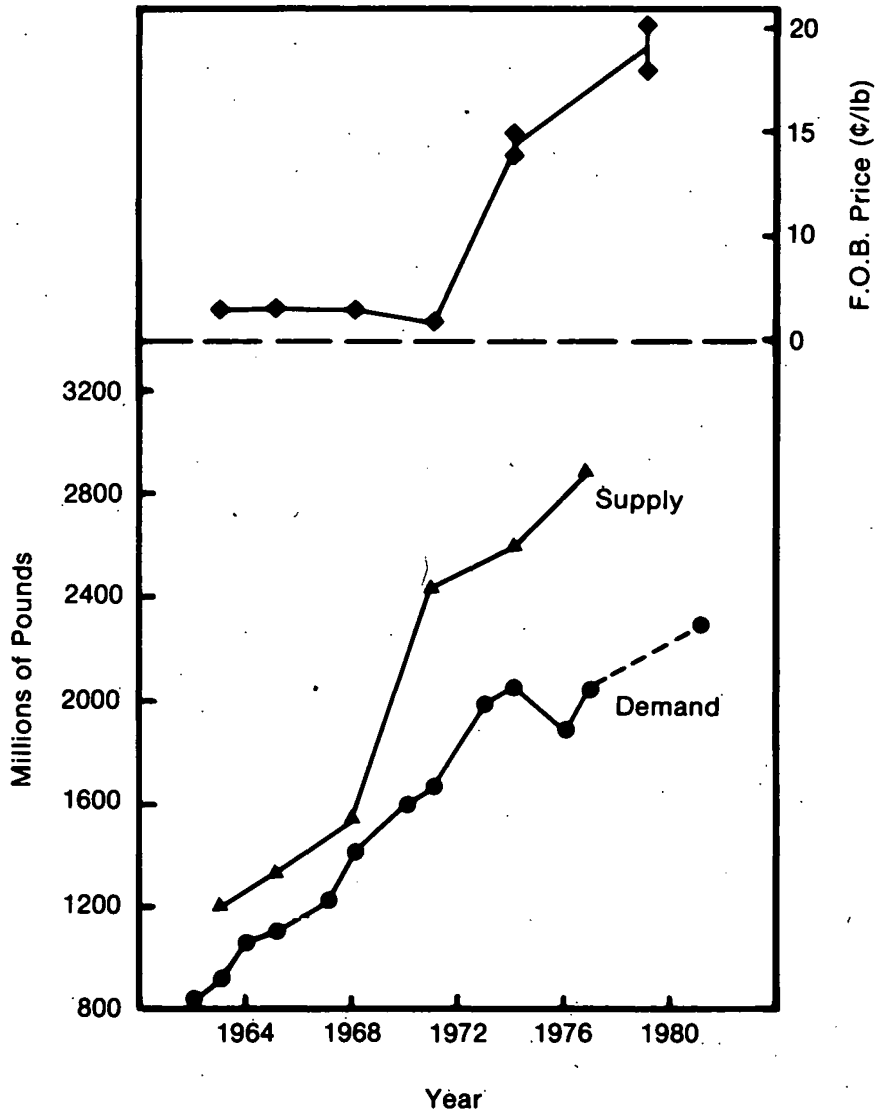
CONVERSION FACTOR: lb × 0.45 = kg

Figure 1-1. Supply, Demand, and Cost Data for Acetone

Table 1-4. MANUFACTURERS OF ACETONE (1977)

Manufacturer	Capacity (10^6 kg/yr)
Allied Chemical Corp.	149-150
Chevron Chemical Co.	14-15
Clark Chemical Co.	24
Dow Chemical Co.	127
Eastman Chemical Products, Inc.	36
Exxon Chemical Co.	64
Georgia Pacific Corp.	73-77
Monsanto	136
Shell Chemical Co.	271-408
Skelly Oil Co.	26
Union Carbide Corp.	199-235
USS Chemicals	88-91
TOTAL	1207-1389

CONVERSION FACTOR: 10^6 kg/yr x 2.20 = 10^6 lb/yr.

Table 1-5. MANUFACTURERS OF n-BUTANOL (1978)

Manufacturer	Capacity (10^6 kg/yr)
Celanese Chemical Co.	140
Conoco Chemicals Div.	2
Dow Badische Co.	45
Eastman Chemical Products, Inc.	140
Ethyl Corp.	2
Oxochem	30
Shell Chemical Co.	90
Union Carbide Corp.	120
TOTAL	460

CONVERSION FACTOR: 10^6 kg/yr x 2.20 = 10^6 lb/yr.

crotonaldehyde (2-butanol). The unsaturated aldehyde is catalytically hydrogenated to butanol at 200 kPa (30 psi) and 180°C.

Almost two-thirds of n-butanol is produced from butyraldehyde by the oxo process; the remaining quantity is derived from crotonaldehyde via the aldol process. Supply and demand curves and cost data for n-butanol are given in Fig. 1-2. A list of manufacturers and their approximate capacities as of 1978 is presented in Table 1-5.

1.5 FERMENTATIVE PRODUCTION

1.5.1 Fermentation of Starches*

Initial commercial development of acetone/butanol fermentation in the early 1900s depended on the bacterial conversion of potato starch to the solvents. After the discovery of Cl. acetobutylicum by Weizmann, corn was used instead as the raw material. Later, molasses became the chief feedstock; the sugar was cheaper, and solvent ratios were improved.

Like other members of its genus, Cl. acetobutylicum is a spore-forming rod commonly isolated from soil, manure, roots of leguminous plants, cereals, decayed wood, corn stalks, sewage, or river-bottom mud. It has been used to produce acetone and butanol from diverse carbohydrate sources, including various grains, nuts, sugars, and food wastes. Some of these materials can be fermented after the starch is made soluble; others require hydrolysis. The most commonly used raw material for Cl. acetobutylicum fermentation is corn.

Sufficient nitrogen for the fermentation is supplied by the carbohydrate feedstock. A requirement for biotin and p-aminobenzoic acid has been demonstrated but, again, sufficient quantities are supplied by the feedstock.

A process flow diagram for the production of acetone and butanol from corn is given in Fig. 1-3. Cultures of Cl. acetobutylicum are prepared on a starch medium for inoculation into the fermentation vessel in a manner identical to that for sugar fermentation (see Sec. 1.5.2). Corn is degermed and the kernels ground to coarse meal; oil may be extracted. The ground meal is mixed with water to a concentration of 6%–10% corn and cooked for 2 hours to sterilize the mash and solubilize the starch. After cooling to 37°C, the mash is pumped into the final fermentation stage of 2.3 to 19×10^5 L (6 to 50×10^4 gal) capacity and inoculated with the prepared culture. The fermentation is conducted at 37°C under anaerobic conditions. After 48–72 hours of fermentation, the beer, containing about 2.5% mixed solvents, is pumped to a distillation column. The solvents are recovered by further fractionation of the overheads from this column. The bottoms are concentrated by evaporation and dried for recovery of the stillage.

The major products are butanol, acetone, ethanol, carbon dioxide, hydrogen, and riboflavin-containing feeds. From normal fermentation, solvent ratios of 60% butanol, 30% acetone, and 10% ethanol are obtainable. Yields are 1 kg of mixed solvents from 4.3 kg of corn or 1 kg of mixed solvents from 2.9 kg of starch. The solvent ratio and

---

*From: Beesch 1953; Killeffer 1927; McCutchan and Hickey 1954; Peterson and Fred 1932; Ross 1961; Wynkoop 1957.
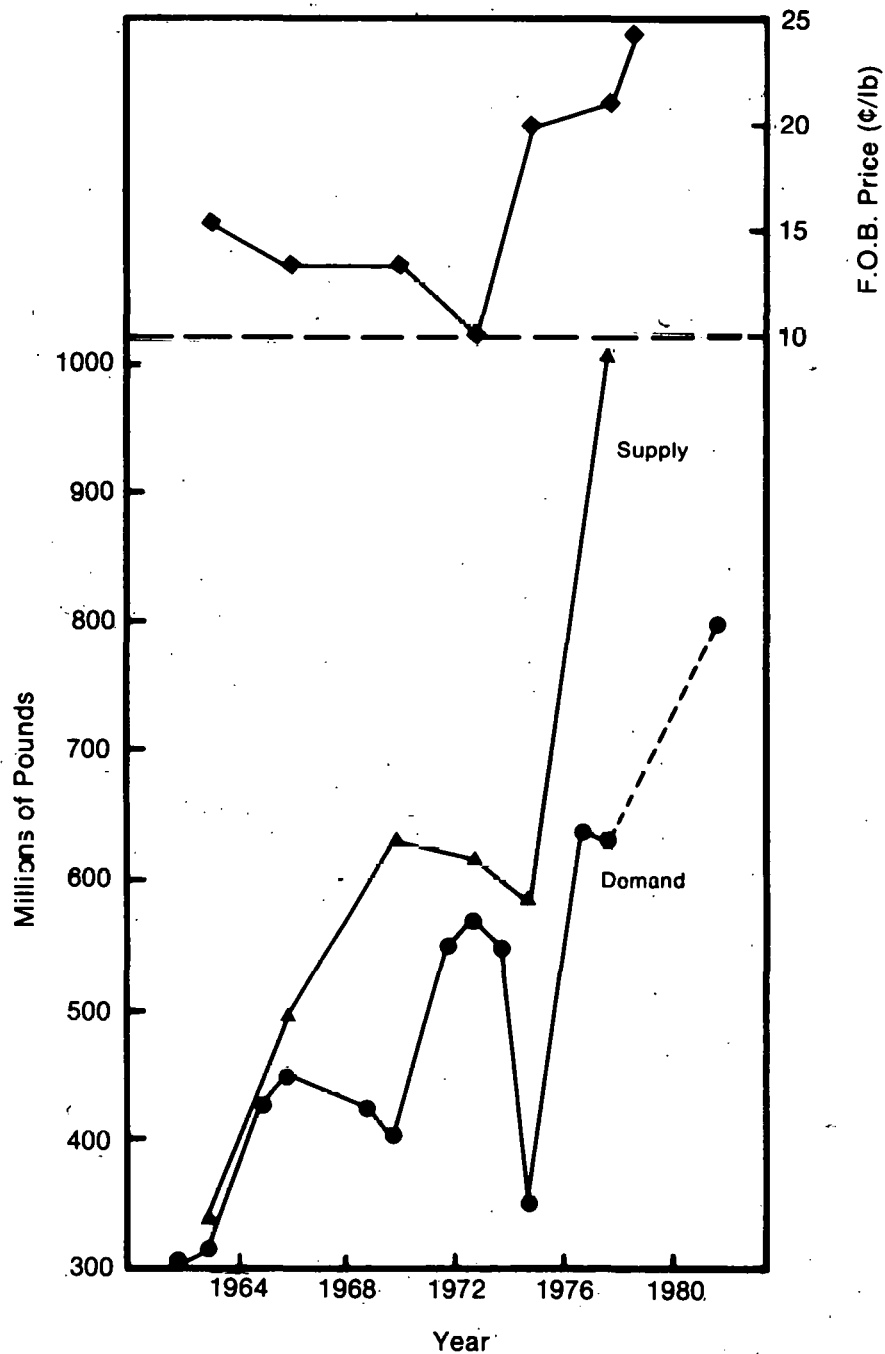
Figure 1-2. Supply, Demand, and Cost Data for Butanol

CONVERSION FACTOR: lb × 0.45 = kg
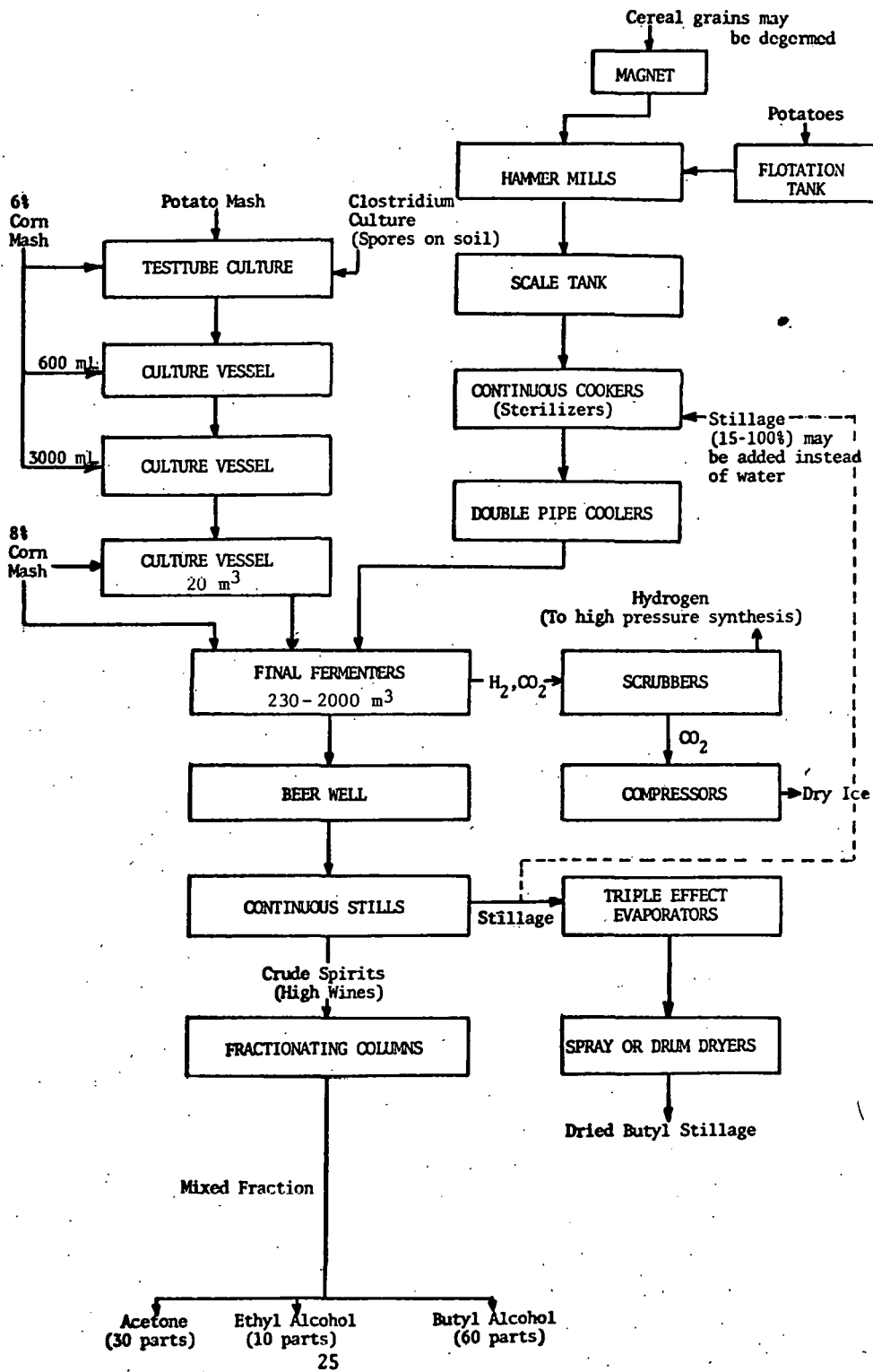
Figure 1-3. **Flow Sheet for the Production of Acetone and Butanol by the Fermentation of Starch**

yield depend on the feedstock, the culture of bacteria, the contaminants, the recycle of stillage, and the added chemicals. The stillage can be used as animal feed; feed values of various stillage fractions are given in Table 1-6.

1.5.2 Fermentation of Sugars*

Numerous strains of Clostridia can be used to ferment molasses or sugar to acetone and butanol. The cost of such feedstocks at present, however, tends to make this fermentation process unattractive. Yields of 33%-35% total solvents based on the sugar added are obtainable. The final solvent distribution is 65%-68% n-butanol, 30%-33% acetone, and 2%-5% ethanol.

The saccharolytic members of the Clostridium genus that have been isolated are listed in Table 1-7. Each of these bacteria is unique in the carbohydrate source fermented, the nitrogen source utilized, and the type and distribution of solvents yielded. All are spore-forming rods isolated from soil, manure, roots of leguminous plants, cereals, decayed wood, cornstalks, or sewage.

Many different saccharine materials can be used as carbohydrate sources. The most common are invert or blackstrap molasses. Invert, or "high test," molasses is evaporated sugar cane juice that contains all the original sugar of the juice in an inverted form. Blackstrap molasses is the syrup left after recovery of crystalline sucrose from concentrated sugar cane juice. In addition, saccharolytic Clostridia can be used to ferment sucrose, glucose, beet molasses, citrus molasses, hydrol, sulfite waste liquor, or starch-containing grains. Some are capable of fermenting starch directly under suitable conditions with almost full yields of solvents.

Nitrogen for the fermentation process is supplied as ammonia or degraded protein, depending on the organism. Sources of ammonia are ammonium hydroxide, ammonium sulfate, monoammonium phosphate, or ammonium nitrate. Cheap sources of degraded protein are cornsteep liquor, yeast autolysate, and de-oiled soybeans. Sufficient phosphates are usually supplied by the feedstock; in case of deficiency, phosphate may be supplied as calcium acid phosphate, monoammonium phosphate, or any other soluble form of phosphate.

Figure 1-4 is a process flow diagram of a typical acetone/butanol fermentation of sugars (Beesch 1952). Heat-shocked cultures of Clostridium spores are incubated in a sterilized potato glucose medium at 31°C (87°F) for 20-24 hours. The culture is then aseptically transferred to 600 mL of sterilized molasses mash and allowed to ferment for 20-24 hours. The culture is then transferred to molasses mash in a 4000-mL Erlenmeyer flask, allowed to ferment for 20-24 hours, and inoculated into an 18.9 kL (5000 gal) tank for preparation for the final fermentation tank.

The molasses to be used in the final fermentation is mixed with water and steam to a concentration of 5%-7% sugar. The mash is sterilized at 107°C for 60 minutes in continuous cookers. After cooling to 31°-32°C, the mash is pumped into a final fermenter of $2.3-19 \times 10^5$ L (60,000-500,000 gal) capacity and inoculated with the prepared culture. The fermentation proceeds at 31°C under anaerobic conditions for 36-48 hours. The fermented beer, containing about 2% mixed solvents, is then pumped to a distillation

---

*From: Beesch 1952; McCutchan and Hickey 1954; Ross 1961; Wynkoop 1957.

Table 1-6. FEED VALUES RECOVERABLE FROM THE ACETONE/BUTANOL FERMENTATION OF WHOLE GROUND CORN

Stillage Fraction	% Dry Matter in Stillage	Yield (kg/100 kg dry grain)		% Protein (Dry Basis)	% Fat (Dry Basis)	% Fiber (Dry Basis)	% Ash (Dry Basis)	Riboflavin (μg/g)
		Dry Feed	Protein					
Solids after evaporation of whole stillage	2.32	36.8	10.80	32.8	14.2	4.9	4.1	41
Dried solids on 40-mesh screen	0.34	8.6	1.0	19.1	16.9	16.6	1.5	6
Solids through 40-mesh screen	1.95	31.0	9.20	38.8	11.1	1.5	5.2	46
Solids after centrifugation of material through 40-mesh screen	0.31	4.9	1.36	22.9	10.8	5.3	1.6	16
Dried effluent from centrifuge	1.68	26.6	7.85	42.1	11.4	0.4	6.4	31

SOURCE: Beesch 1953.

Table 1-7. SACCHAROLYTIC CLOSTRIDIA USED IN THE ACETONE/BUTANOL FERMENTATION

Bacteria	Carbohydrate Source	Nitrogen Source	Additional Nutrients	Product Solvent Ratios (%)			
				Butanol	Acetone	Ethanol	Isopropanol
Cl. saccharobutylacetonicum	blackstrap molasses	$(NH_4)_2SO_4$	corn gluten	64	36	--	--
Cl. saccharoacetobutylicum	cane molasses	degraded protein	--	68-73	26-32	1-3	--
	louisiana molasses	$(NH_4)_2SO_4$	$CaCO_3$	68-73	26-32	1-3	--
	cuban molasses	$(NH_4)_2SO_4$	gluten meal	68-70	20-32	1-3	--
	invert molasses	NH_3	--	76	22	2	--
	blackstrap molasses	NH_3	--	70	25	5	--
	molasses	NH_3	--	73	23	4	--
Cl. inverto-acetobutylicum	louisiana molasses	ammonium salts	alkalies	66-70	27-31	2-3	--
Cl. saccharobutyl-acetonicum-liquefaciens	blackstrap molasses	$(NH_4)_2SO_4$	$CaCO_3$, P_2O_5	58-74	24-36	2-6	--
	cuban molasses	$(NH_4)_2SO_4$	$CaCO_3$, P_2O_5	60-69	26-35	3-4.5	--
	molasses	NH_3	--	69	28	3	--
Cl. celerifactor	invert molasses	NH_3	$CaCO_3$	60	38	2	--
Cl. granulobacter-acetobutylicum	molasses	ammonium salts	corn gluten, $CaCO_3$	60-75	25-30	1-10	--
Cl. madisonii	cuban blackstrap molasses	NH_4OH, $(NH_4)_2SO_4$	$CaCO_3$	75-76	17-20	4-6	--
	blackstrap molasses	NH_3	--	76	18	6	--
Cl. saccharoacetoperbutylicum	invert molasses	$(NH_4)_2SO_4$	$CaCO_3$, P_2O_5	69-76	18-25	2-7	--
		NH_4OH	P_2O_5				
B. tetryl	invert molasses	NH_3	--	70	20	5	--
B. butacone	blackstrap molasses	animal & vege table protein	--	65	38	2	--
	beet molasses	complex nitrogen	--	70	28	2	--
Cl. saccharobutylicum	blackstrap molasses	--	$CaCO_3$	65-80	18-34	--	1-2
Cl. viscifaciens	invert molasses	--	$CaCO_3$	66	3	--	31
Cl. propyl butylicum	invert molasses	NH_3	$CaCO_3$	69-70	4-17	--	14-28
		$(NH_4)_2SO_4$	$CaCO_3$, K_2HPO_4, $MgSO_4$	65-70	5-10	3-4	16-20
Cl. saccharobutyl-isopropyl-acetonicum	invert molasses	degraded protein	--	60-70	30-38	--	trace-10 (high pH)
				65-80	2-20	--	10-30 (low pH)
	cane & beet molasses	$(NH_4)_2SO_4$	$CaCO_3$	60-85	15-40	--	0.1-4.0
Cl. acmylosaccharo-butylpropylicum	invert molasses	$(NH_4)_2SO_4$	$CaCO_3$, P_2O_5	65-72	trace	2-4	26-32
		NH_4OH	P_2O_5				
B. saccharobutylicum	invert molasses	--	$CaCO_3$	75	3	--	35

SOURCES: Beesch 1952; Ross 1961.

SERI
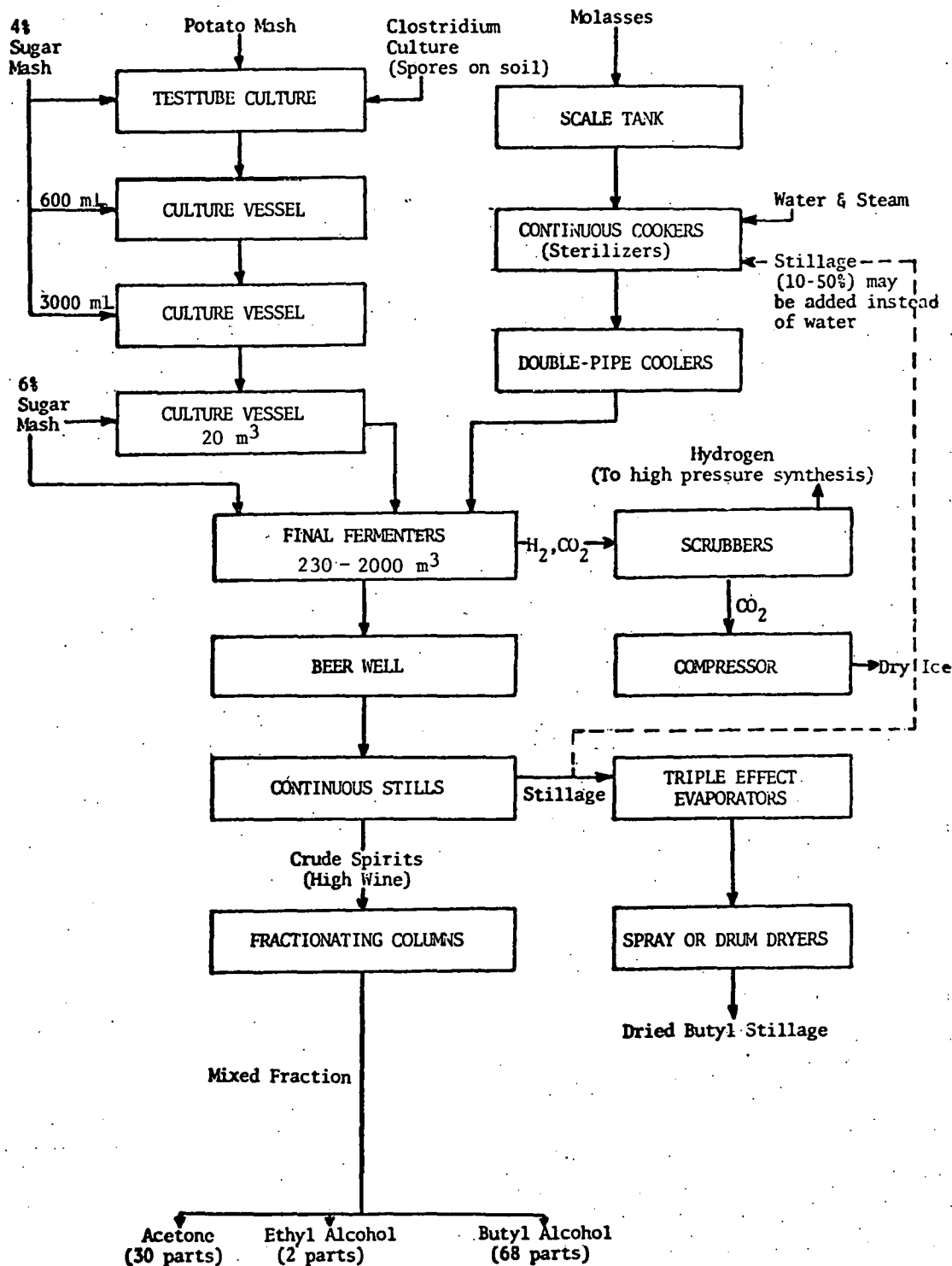
Figure 1-4. Flow Sheet for the Production of Acetone and Butanol by the Fermentation of Sugar

column from which a 40% solvent mixture is taken off overhead and distillers' slops are removed as bottoms. The solvents are further concentrated by fractional distillation. Stillage obtained from the initial distillation step is concentrated by evaporation and dried.

As in starch fermentation, the major products formed in the acetone/butanol fermentation of sugars are n-butanol, acetone, ethanol, carbon dioxide, hydrogen, and riboflavin-containing feeds from the fermentation residue. The solvent ratio and yield depend on the same factors noted in the discussion of starch fermentation. In the normal fermentation of sugars, a ratio of 68% butanol, 30% acetone, and 2% ethanol can be obtained. The yield is 15.6 kg of mixed solvents from 100 kg of molasses. The stillage is suitable for admixing with other materials for use as animal feed; recoverable feed values of this material are given in Table 1-8. In addition, this stillage may be recycled to the fermentation process to supply additional nitrogen and buffer substances; used in the manufacture of plastics; concentrated, dried, and burned to an ash high in potassium; or used as a binder in foundry work.

There is a need to expand the range of feedstocks to include cellulose and hemicellulose.

1.6 REFERENCES

Beesch, S. C. 1952. "Acetone-Butanol Fermentation of Sugars." IEC Engr. Proc. Dev. Vol. 44: pp. 1677-1682.

Beesch, S. C. 1953. "A Microbiological Process Report: Acetone-Butanol Fermentation of Starches." Appl. Microbiol. Vol. 1: pp. 85-95.

Chemical Marketing Reporter. 1963-1979.

Gabriel, C. L. 1928. "Butanol Fermentation Process." IEC. Vol. 20: pp. 1063-1067.

Gabriel, C. L.; Crawford, F. M. 1930. "Development of the Butyl-Acetonic Fermentation Industry." IEC. Vol. 22: pp. 1163-1165.

Killeffer, D. H. 1927. "Butanol and Acetone from Corn: A Description of the Fermentation Process." IEC. Vol. 19: pp. 46-50.

Langlykke, A. F.; Van Lanen, J. M.; Fraser, D. R. 1948. "Butyl Alcohol from Xylose Saccharification Liquors from Corncobs." IEC. Vol. 40: pp. 1716-1719.

Lee, S. B. 1949. "Fermentation." IEC. Vol. 41: pp. 1868-1879.

Lee, S. B. 1950. "Fermentation." IEC. Vol. 42: pp. 1672-1690.

Leonard, R. H.; Peterson, W. H.; Ritter, G. J. 1938. "Butanol-Acetone Fermentation of Wood Sugar." IEC. Vol. 30: p. 1251.

McCutchan, W. N.; Hickey, R. J. 1954. "The Butanol-Acetone Fermentations." Industrial Fermentations. Edited by L. A. Underkofler and R. J. Hickey. Vol. I. New York: Chemical Publishing Company, Inc.

Table 1-8. FEED VALUES RECOVERABLE FROM ACETONE/BUTANOL FERMENTATION OF INVERT AND BLACKSTRAP MOLASSES

Stillage Fraction	Type of Molasses	% Dry Matter in Stillage	Yield (kg/100 kg molasses)		% Protein	% Fat (Dry Basis)	% Ash	Riboflavin (μg/g)
			Dry Feed	Protein				
Total solids after evaporation of stillage	invert	1.15	17.7	6.5	36.8	0.31	12.1	52
	blackstrap	2.71	28.6	6.0	20.8	0.14	23.2	38
Solids recoverable by centrifugation	invert	0.17	2.6	2.0	77.6	2.00	4.8	49
	blackstrap	0.22	2.3	1.3	57.5	2.60	7.2	27
Dried effluent from centrifuge	invert	0.96	14.8	4.1	28.1	0.0	13.4	54
	blackstrap	2.50	26.3	4.2	16.0	0.0	25.9	37

Nathan, F. 1919. "The Manufacture of Acetone." J. Soc. Chem. Ind. Vol. 38: pp. 271-273T.

Nelson, D. L.; Webb, B. P. 1979. "Acetone." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. 1. New York: John Wiley & Sons; pp. 179-190.

Peterson, W. H.; Fred, E. B. 1932. "Butyl-Acetone Fermentation of Corn Meal: Interrelations of Substrate and Products." IEC. Vol. 24: pp. 237-242.

Ross, D. 1961. "The Acetone-Butanol Fermentation." Prog. Ind. Microbiol. Vol. 3: pp. 73-90.

Sherman, P. D. 1979. "Butyl Alcohols." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. 4. New York: John Wiley & Sons; pp. 338-345.

Sjolander, N. O.; Langlykke, A. F.; Peterson, W. H. 1938. "Butyl Alcohol Fermentation of Wood Sugar." IEC. Vol. 30: pp. 1251-1255.

Underkofler, L. A.; Christensen, L. M.; Fulmer, E. I. 1937. "Butyl-Acetonic Fermentation of Xylose and Other Sugars." IEC. Vol. 28: pp. 350-354.

Waksman, S. A.; Kirsh, D. 1933. "Butyric Acid and Butyl Alcohol Fermentation of Hemicellulose- and Starch-Rich Materials." IEC. Vol. 25: pp. 1036-1041.

Wiley, A. J.; Johnson, M. J.; McCoy, E.; Peterson, W. H. 1941. "Acetone-Butyl Alcohol Fermentation of Waste Sulfite Liquor." IEC. Vol. 33: pp. 606-610.

Wynkoop, R. 1943. "n-Butanol and Acetone." IEC. Vol. 35: pp. 1240-1242.

Wynkoop, R. 1957. "The Acetone-Butanol Fermentation." Microbial Technology. Edited by H. J. Peppler. New York: Reinhold Publishing Corporation.

SECTION 2.0

ACETIC ACID

2.1 BACKGROUND

Acetic acid is an important industrial chemical, as evidenced by the 1977 nameplate capacities of the U.S. producers listed in Table 2-1. A total of 1.16 billion kg (2.55 billion lb) of acetic acid was produced in 1977. The market growth has historically been 4.5% per year and is projected to increase to 5%-7% per year through 1981. In June 1979, the contract price was 42¢/kg (19¢/lb) (Chemical Marketing Reporter 1979).

Table 2-1.   U.S. ACETIC ACID PRODUCTION IN 1977

Producer	Capacity (million kg acetic acid)
Borden, Gelsmar, La.	45
Celanese, Bay City, Tex.	95
Celanese, Clear Lake, Tex.	180
Celanese, Pampa, Tex.	250
Eastman, Kingsport, Tenn.	180
FMC, Bayport, Tex.	20
Monsanto, Texas City, Tex.	180
Publicker, Philadelphia, Pa.	40
Union Carbide, Brownsville, Tex.	290
Union Carbide, Taft, La.	40
TOTAL	1320

SOURCE: Chemical Marketing Reporter 1977.

CONVERSION FACTOR: 2.20 x mass in kg = mass in lb.

2.2 PHYSICAL PROPERTIES

Acetic acid is a colorless, pungent liquid and a moderately strong acid which, when concentrated, is highly corrosive. Miscible with water in all proportions above 17°C, it is digestible or biodegradable when dilute. Selected physical properties are listed in Table 2-2. Dilute acetic acid is commonly found in nature as a fermentation product; in this form it is called "vinegar," a word derived from the French term for sour wine.

2.3 APPLICATIONS

Acetic acid is used chiefly in the production of several industrial chemicals (see Table 2-3).

SΞ⩴I

Table 2-2. PHYSICAL PROPERTIES OF ACETIC ACID

Property	Acetic Acid
Formula	CH_3COOH
Molecular weight	60
Melting point (°C)	16.6
Boiling point at 101.3 kPa (°C)	117.9
Specific gravity at 20°C	1.051
Specific heat [J/kg K (Btu/lb °F)]	2.04 (0.487)
Heat of fusion [kJ/kg (Btu/lb)]	195.0 (83.9)
Heat of vaporization [kJ/kg (Btu/lb)]	394.7 (169.7)

Table 2-3. DISTRIBUTION OF USES OF ACETIC ACID

Use	% of Total
Chemical production	
Vinyl acetate	45.0
Cellulose acetate	23.0
Acetic esters	12.0
Purified terephthalic acid and dimethyl terephthalate	10.0
Textile processing	3.0
Chloracetic acid	2.5
Miscellaneous	4.5

2.4 CURRENT COMMERCIAL PRODUCTION (CHEMICAL)

Vinegar is produced by biological methods, but virtually all industrial acetic acid is produced by acetaldehyde oxidation, liquid-phase hydrocarbon oxidation, or methanol carbonylation from petroleum feedstocks (Lowry and Aguilo 1974; Schwerdtel 1970; Lowenhoem and Moran 1975; McMahon 1976; Conner and Allgeier 1976; Wagner 1978. When methanol carbonylation is used to produce acetic acid, natural gas is oxidized to methanol and CO_2. An iodide-promoted rhodium catalyst is used for the BASF version of this process. Methanol and CO_2 are introduced into a reactor vessel at a temperature of about 175°C and pressure of 1460 kPa (200 psig). The reaction takes place with a 99% yield based on methanol and 90% based on CO_2. The product is cooled and flashed to 1120 kPa (150 psig). The gas is scrubbed with feed methanol to recover methyl iodide, and then the gas is vented. The liquid is sent to an acid recovery system to evaporate esters and catalyst in a distillation train. Azeotropic distillation removes water and formic acid. The resulting product is glacial acetic acid.

Acetaldehyde is produced from an ethylene feedstock and then processed into about 35% of the acetic acid currently used in the United States. To produce acetic acid from

acetaldehyde, oxygen-enriched air and acetaldehyde are fed into a reactor at 66°C and 101.3 kPa (1 atm), where they undergo a three-step chain reaction. The process is about 95% efficient with very few by-products. The only other significant equipment involved in the process are distillation towers used for recovery of unreacted acetaldehyde and glacial acid.

2.5 FERMENTATIVE PRODUCTION

Biomass may be thermochemically converted (pyrolyzed) or biologically fermented to produce acetic acid. Pyrolysis or gasification of biomass is a chemical process and is not discussed further in this report. Acetic acid can be produced by the fermentation of biomass in five different ways:

(1) anaerobic gasification of biopolymers to methane and CO_2, followed by methanolic carbonylation to acetic acid;

(2) anaerobic yeast fermentation of hydrolyzed biopolymers to ethanol, followed by oxidation to acetaldehyde and then to acetic acid;

(3) anaerobic yeast fermentation of hydrolyzed biopolymers to ethanol, followed by aerobic bacterial fermentation to acetic acid;

(4) anaerobic bacterial homofermentation of biopolymers; and

(5) anaerobic bacterial heterofermentation of biopolymers with simultaneous production of ethanol and other acids.

The first method essentially involves an anaerobic digestion to produce methane or synthetic natural gas (SNG). This material may then be fed into a standard methanol carbonylation facility.

The second alternative for biological production of acetic acid is quite possibly the most favorable. It involves well-known technology. A standard fermentation is used to produce ethanol, which is subsequently oxidized to produce acetaldehyde. The acetaldehyde can then be oxidized to acetic acid using existing technology and facilities (see Sec. 2.4).

The third method, ethanol fermentation followed by acetic acid fermentation, is the process currently used for vinegar production. The semibatch process as it is operated today is discussed by Conner and Allgeier (1976) and in an article in Chemical Engineering (1960). Molasses, nutrients, and 1% ethanol are used to start a submerged aerobic fermentation. The concentration of ethanol is kept at about 1% until the acetic acid concentration nears 10%-11%. When properly planned, the process results in a final concentration of ethanol of less than 0.5%, and the concentration of acetic acid is about 10%. The fermentation is ended and the acetic acid is extracted. This mixture of extractant and acetic acid is then put through a distillation chain to recover both. The process sequence is shown in Fig. 2-1. A major drawback to this process for acetic acid production is the energy-intensive distillation step. The five possible alternatives for this concentration/purification are:

(1) straight distillation (expensive),

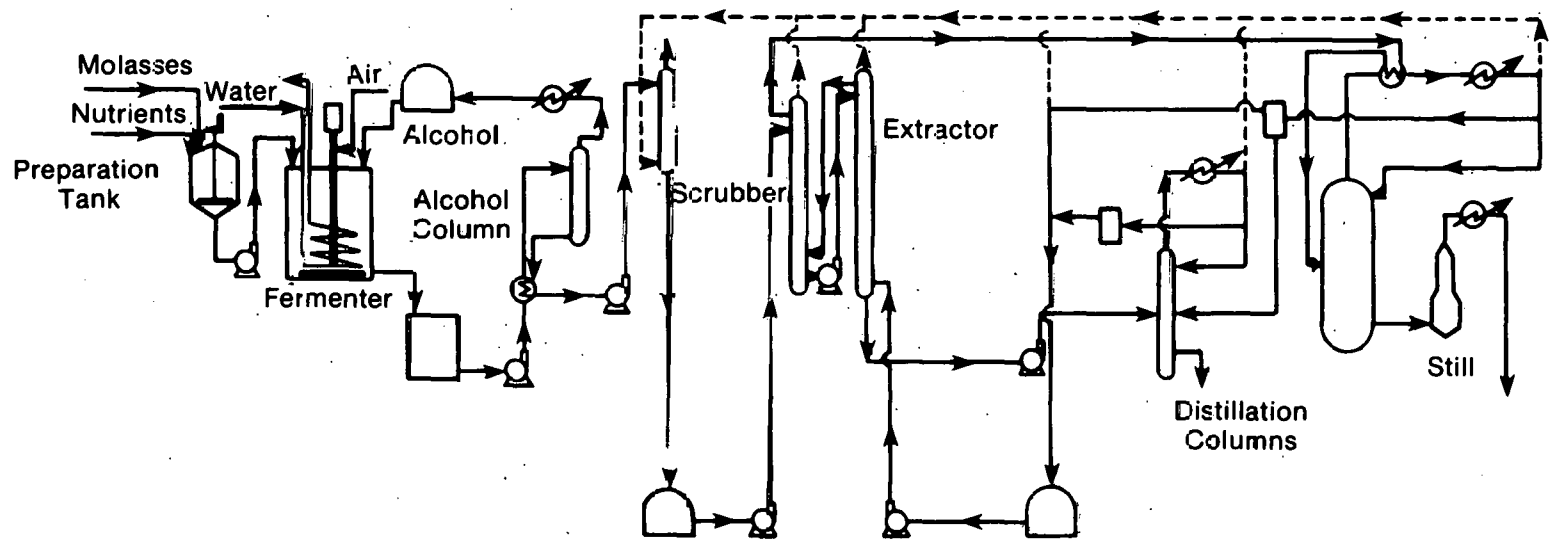(2) liquid-liquid extraction,

(3) azeotropic distillation,

Figure 2-1. Conventional Acetic Acid Fermentation

(4)   extractive distillation, and

(5)   a combination of (1) with either (2) or (3).

Any of these concentration trains adds substantially to the cost of acetic acid production. Membrane separation is yet to be developed.

The fourth process, anaerobic bacterial homofermentation of biopolymers, may become quite important. Although organisms have been found that can produce a maximum of 15 g/L acetic acid in 80 hours during anaerobic fermentation, no technology using them has been developed. A minimum of five years of developmental work is anticipated before the economic feasibility of this method of acetic acid production can be demonstrated.

The fifth method, heterofermentation of carbohydrates to acetic acid, presents a number of purification problems. The separation and purification problems are significant in any of the five fermentation processes because of the large amounts of water involved, but these problems are multiplied in this case by the presence of other organic products, and the yield of acetic acid is lower than in the methods previously discussed. For these reasons this process has received less attention than the others.

2.6 ECONOMICS

The process technology for the direct fermentation of biomass to acetic acid by either homofermentative or heterofermentative means has not yet advanced far enough to allow definitive statements about feasibility. The traditional vinegar technology followed by concentration steps is technically feasible but currently cannot compete with synthetic production. The ethanol contribution (raw material cost) to the cost of acetic acid is 42¢/kg (19¢/lb) if the ethanol is valued at 38¢/L ($1.44/gal). The processing and profit costs are not included here, and, as noted earlier, the June 1979 price of acetic acid was 42¢/kg (19¢/lb). The ethanol/acetaldehyde/acetic acid pathway is also technically feasible; however, this pathway is victim to the same economic problem. The cost of the ethanol stock, added to the cost of production and separation, makes the cost of the acetic acid too high to be competitive with contemporary methods of production. It should be mentioned, however, that when the cost of acetaldehyde produced from petroleum reaches the cost of ethanol, this pathway may be the most feasible alternative. This is a consequence of the facilities already available to produce acetic acid from acetaldehyde; only the ethanol and acetaldehyde units would need to be constructed, thus allowing a substantial savings in capital cost. The methanol carbonylation process has the same economic advantages because carbonylation plants already exist. However, the SNG feedstock will probably be produced from municipal or agricultural wastes with the stipulation from the suppliers that the SNG be used for energy for the waste supplier. Also, whereas the raw material for ethanol should be more available to the acetaldehyde plant sites, wastes for SNG production are costly to transport and SNG probably will be used wherever it is generated rather than piped to other locations.

The overall feedstock and utility requirements to produce one metric ton (one short ton) of acetic acid by ethanol fermentation (third method) are given in Table 2-4. Note that about 0.9 kg of ethanol and about 0.5 kg of molasses are required to obtain 1 kg of acetic acid. In view of the relatively large utility requirements [about 12.6 kg of steam per litre of acetic acid (105 lb/gal) and 760 L of water per litre of acetic acid, a solvent extractive process might be more economical than conventional distillation. Anticipated

future production of ethanol by fermentation at prices significantly less than 26¢/L ($1.00/gal) merits review and an updating of the economics of this acetic acid process.

Table 2-4. UTILITY REQUIREMENTS TO PRODUCE ONE METRIC TON OF ACETIC ACID BY SUBMERGED ETHANOL FERMENTATION

Utilities and Material	Quantity (kg)
Molasses	500
Ethyl alcohol (95%)	858
Ammonium sulfate	10
Ethyl acetate	30
Steam	5 kg/kg acetic acid
Water	330 kg/kg acetic acid

CONVERSION FACTOR: 2.20 x mass in kg = mass in lb.

2.7 REFERENCES

"Acetic Acid by Submerged Fermentation." 1960 (5 Sept.). Chem. Eng. pp. 50-52.

Chemical Marketing Reporter. 1977 (11 Apr.).

Chemical Marketing Reporter. 1979 (30 June).

Conner, H. A.; Allgeier, R. J. 1976. "Vinegar: Its History and Development." Adv. Appl. Microbiol. Vol. 20: pp. 91-133.

Gosh, S.; Packer, M.; Roess, A.; Conrad, J.; Van Ryzin, Z. 1977. "Anaerobic Processes." Water Pollution Control Federation J. Vol. 49: pp. 1019-1040.

Hawkes, D.; Horton, R.; Stafford, D. 1976 (Mar.). "The Application of Anaerobic Digestion to Producing Methane Gas and Fertilizer from Farm Wastes." Process Biochemistry. pp. 32-36.

Keenan, J. D.; Kormi, I. 1977. "Methane Fermentation of Brewery By-Products." Biotechnol. and Bioeng. Vol. XIX: pp. 867-878.

Lowenhoem, F. A.; Moran, M. K. 1975. Industrial Chemicals. Edited by Faith, Keyes, and Clark. Wiley Interscience; pp. 8-15.

Lowry, R. P.; Aguilo, A. 1974. "Acetic Acid Today." Hydrocarbon Processing. Vol. 53 (No. 11): pp. 103-113.

McMahon, K. S. "Acetic Acid." 1976. Encyclopedia of Chemical Processing and Design. Edited by J. J. McKetta and W. A. Cunningham. Vol. 1: pp. 216-240.

Schwerdtel, W. 1970. "Make Acetic Acid from n-Butenes." Hydrocarbon Processing. VoL 49 (No. 11): pp. 117-120.

Wagner, F. "Acetic Acid." 1978. Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. 1: pp. 120-147.

SERI⚙

SERI ☀

SECTION 3.0

CITRIC ACID

3.1 BACKGROUND

Citric acid was first isolated by Scheele, who crystallized it from lemon juice in 1784. Almost a hundred years later, in 1880, it was first synthesized by Grimous and Adam from glycerol. In 1893, Wehmer discovered that certain fungi produce citric acid when grown on sugar solutions, thus indicating the possibility of citric acid production by fermentation.

In spite of Wehmer's discovery, the commercial production of citric acid in the early 1900s was not by fermentation, but by extraction from lemon juice. In 1917, Currie published a paper describing the production of citric acid from sucrose by the fermentation by <u>Aspergillus niger</u> on the surface of the media. Because of this and other work, in the 1920s surface fermentation became the main commercial process for the production of citric acid, and the United States became the largest producer.

No one produced citric acid by submerged fermentation until the first breakthrough in 1930. Amelung (1930) reported that when submerged cultures of <u>Aspergillus japonicus</u> were aerated, good yields of citric acid were obtained. These yields, however, were not as high as those from surface fermentation. Several years later, Perquin (1938) showed that the concentration of certain substances, such as zinc and potassium, affected the yield of citric acid. With the incorporation of this idea of nutrient deficiency, a number of successful submerged fermentation processes for citric acid production were developed.

Currently, 90% of citric acid is produced by either submerged or surface fermentation (the remaining 10% is extracted from lemon juice or pineapple wastes). Today, about 180 million kg/yr (400 million lb/yr) are produced in the United States and about another 68 million kg/yr (150 million lb/yr) in the rest of the world. Most new plants use submerged fermentation, but older plants using a surface process are still operating.

3.2 PHYSICAL PROPERTIES

Anhydrous citric acid is a tricarboxylic acid with no optical activity. The molecular formula is $C_6H_8O_7$. It forms colorless and translucent crystals and has a melting point of 153°C. It is a strong organic acid with a rather high first dissociation constant of 8.2 x 10^{-4} at 18°C.

Citric acid is sold in a number of different forms. The most common are the anhydrous, the monohydrated, and the sodium, ammonium, calcium, or potassium salts.

3.3 APPLICATIONS

Uses of citric acid in the United States are listed in Table 3-1. As a food, it is used chiefly as an astringent additive; i.e., to produce a tart taste in jellies, soft drinks, canned fruits and vegetables, wines, and dairy products. Because citric acid reduces the pH of a substance, it is used also as a preservative. In the pharmaceutical industry citric

acid is used to make medicines more palatable as well as to provide a low pH to enhance the activity of preservatives. Another use is to create effervescence by producing CO_2 from the reaction of citric acid with a bicarbonate-carbonate source. Its industrial applications range from use as a sequestering agent of metal ions to metal cleaning. Citric acid is rapidly biodegradable and has detergent-building properties; therefore, it has found some use in laundry and cleaning powders as a replacement for phosphates.

Table 3-1. DISTRIBUTION OF USES OF CITRIC ACID IN THE UNITED STATES

Use	% of Total
Food	64-68
Pharmaceuticals	13-17
Industrial processes	8-12
Exports	7-10

The worldwide production of citric acid is expected to increase about 5%/yr for the next 5 to 10 years. This increase could be larger if citric acid becomes more commonly used as a substitute for phosphate in detergents.

3.4 CURRENT COMMERCIAL PRODUCTION (FERMENTATIVE)

As noted in Sec. 3.1, citric acid may be produced by either surface or submerged fermentation. In surface fermentation, spores of a strain of the fungus Aspergillus niger are blown across the surface of media in large shallow pans. The pans are about two to three inches deep and are not shaken or stirred. After about two to five days, the surface is completely covered by a mat of the organism, and in about seven to ten days the fermentation is complete. The conditions for fermentation are a temperature of 25°C-30°C and a low pH, which usually drops to below pH 2 as the fermentation progresses. The yields of citric acid based on the amount of sugar consumed depend on the substrate. Explicit data from current industrial-scale processes are not available. Table 3-2 summarizes yields obtained at the laboratory scale. In surface culture systems the liquid is poured from the pans at the end of the fermentation. The remaining mycelial mat is washed, and the wash liquid is added to the fermented solution. The citric acid is recovered and purified.

A major difference between submerged and surface fermentation is that air must be supplied to the submerged culture, usually at a rate of 0.5 to 1.5 vvm, to provide adequate oxygen. Typical results for a submerged fermentation are shown in Fig. 3-1. The pH drops from 3 or 4 to about 2 during 5-14 days of fermentation. The concentration of citric acid is usually 8 to 10 g/L. Some yields for submerged fermentation on different substrates are shown in Table 3-2; these yields are for the fermentation step only and range from about 70% in 4 days to 95% in 6 to 10 days.

The media are the same for submerged and surface fermentation. The sugar is present in concentrations of 15% to 25% w/v. Nitrogen is present as an inorganic salt, or it is

Table 3-2. PRODUCTION OF CITRIC ACID BY ASPERGILLUS NIGER

Substrate	Submerged Fermentation			Surface Fermentation		
	Yield (%)	Time (h)	References	Yield (%)	Time (h)	References
Sucrose	80	165	Currie 1917	63	216	Prescott and Dunn 1959
Glucose	71	168	Prescott and Dunn 1959	90	200	Prescott and Dunn 1959
Cane Molasses	64	192	Prescott and Dunn 1959	70	240	Johnson 1954
Beet Molasses	64	216	Clement 1952	50	240	Prescott and Dunn 1959

NOTE: These are laboratory-scale yields based on the amount of sugar consumed for the fermentation step only.
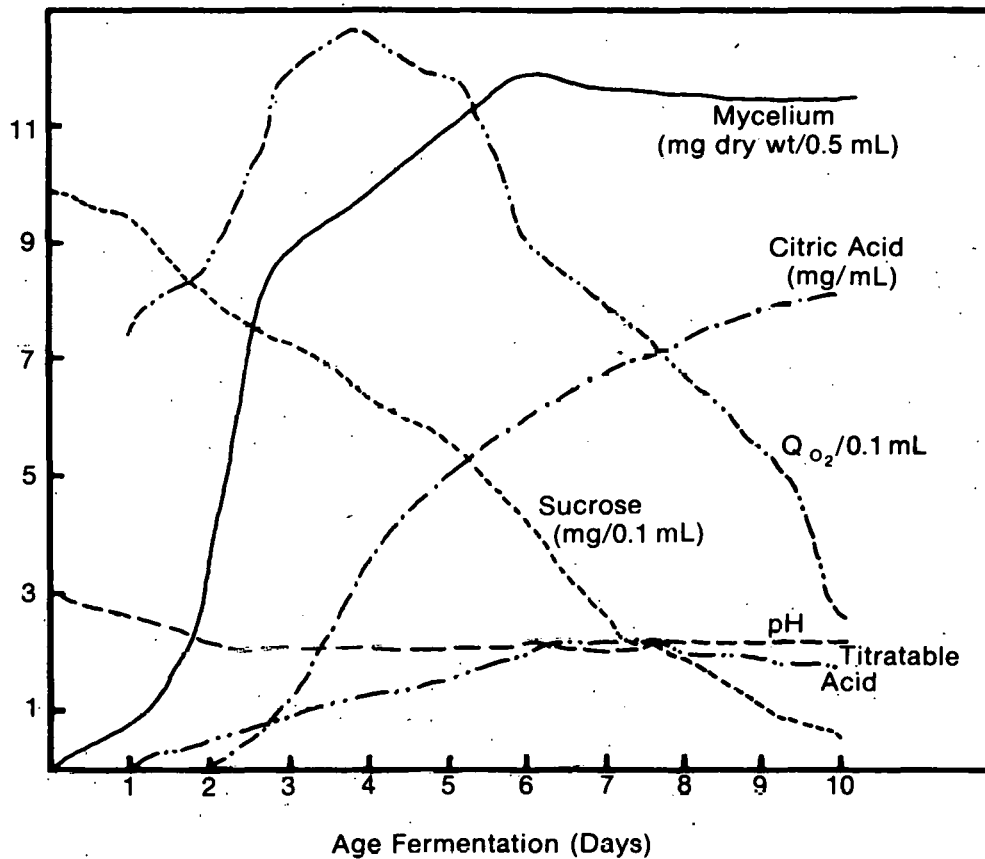
Figure 3-1. Submerged Fermentation of Aspergillus Niger

supplied with the substrate (molasses) in an organic form but in a concentration not exceeding 0.08% to 0.09% w/v. The concentrations of other inorganic ions, such as phosphate, iron, manganese, magnesium, and zinc, must be carefully controlled to obtain good citric acid yields. Magnesium is usually supplied as $MgSO_4 \cdot 7H_2O$ at about 0.1% and potassium as KH_2PO_4 at 0.05% to 0.2%. Iron concentrations should not exceed 2 to 5 mg/L.

Although most citric acid is produced industrially by either of the above fermentations using Aspergillus niger, other processes have been developed for different organisms and substrates. The Takeda process employs a Candida yeast growing on normal paraffins in long deep tanks (60-metric-ton capacity). The citric acid is continuously precipitated as the calcium salt. This is the only alternate method used commercially today. Several others have been described but not developed because of their lack of commercial viability. See Table 3-3 for yield data and references for three of these alternate processes.

Table 3-3. ALTERNATE ORGANISMS FOR CITRIC ACID PRODUCTION

Organism	Substrate	Yield (%)	Time (h)	References
Candida	Levulose (15% w/v)	35	72	Fried 1972
Candida oleophila	Glucose (5% w/v)	77	96	Izuka 1971
Bacillus licheniformis	Levulose (10% w/v)	42	120	Sardinas 1973

Whether a plant operates a submerged or surface fermentation or extracts citric acid from lemon juice, the product is recovered and purified usually by one of three methods: (1) direct crystallization after concentration of the filtered liquor, (2) precipitation as calcium tetrahydrate, or (3) solvent extraction. Precipitation is the most commonly used method, and a flow diagram and material balance for the process is shown in Fig. 3-2. Miles Laboratories owns the patent for the only solvent extraction process. The solvent is a mixture of normal octyl alcohol, synthetic isoparaffins, petroleum hydrocarbons, and tridecyl amine. The yield obtained by most plants is 75-80 g citric acid/100 g sugar.

Citric acid is produced in about 30 countries. In the United States there are two commercial producers. Table 3-4 lists the processes and capacities of the plants located in the United States.

Table 3-4. U.S. MANUFACTURERS OF CITRIC ACID (1977)

Manufacturer	Process	Substrate	Capacity (10^6 kg/yr)
Miles Labs., Inc.			
Dayton, Ohio	submerged fermentation	dextrose	11.3
Elkhart, Ind.	submerged fermentation	dextrose	11.3
Pfizer, Inc.			
Brooklyn, N.Y.	surface fermentation	beet molasses	74.8
Groton, Conn.	surface/submerged fermentation	beet molasses	74.8
Southport, N.C.	Takeda fermentation	n-paraffin	--
	fermentation	beet molasses	---

CONVERSION FACTOR: 2.20 x mass in kg = mass in lb.

3.5 ECONOMICS

The price of hydrous citric acid rose from 54.0¢/kg (24.5¢/lb) in 1950 to $1.09/kg (49.5¢/lb) in 1976 and $1.56/kg (71¢/lb) in 1979. A kilogram (pound) of anhydrous citric acid sold for 58.4¢ (26.5¢) in 1950 and $1.37 (62¢) in 1979 (from the Chemical Marketing Reporter 1950-1976 and communication with industry). The price of citric acid is very

Water

Acid Mold

Molasses

Nutrient

Air

Lime

Sulfuric acid

| Mixer | | Fermentation Chamber | | Settling Tank | | Precipitator and separator | | Filter | | Acidulator |

Sludge

Calcium Oxalate
Charcoal

Waste

Spent char

| Filter | | Purifier | | Evaporator | | Filter |

Calcium sulfate

| Dryer | | Filter | | Crystallizer |

Citric acid

Mother liquor

30

Reaction

$$C_{12}H_{22}O_{11} \text{ or } C_6H_{12}O_6 + H_2O \xrightarrow[\text{air}]{\text{Organism}} C_6H_8O_7 + CO_2 + H_2O$$

Sucrose or dextrose

Citric acid

35%–65% (w/w) yield

Material Requirements

Basis - 1 metric ton citric acid

Molasses	4000 kg
Nutrients	5 to 15 kg
Sulfuric acid 95%	700 kg
Lime	500 kg

Figure 3-2. Production of Citric Acid from Molasses by Fermentation

dependent on the cost of the three raw materials: molasses, dextrose, and n-paraffins. For example, between 1973 and 1974 the prices of raw materials went up 100%; the price of citric acid climbed 25% in the same period and 61% by 1975 (from the U.S. Department of Agriculture 1973-1977, <u>Chemical Marketing Reporter</u> 1973-1977, and communication with industry).

3.6 REFERENCES

Amelung, H. 1930. <u>Chem. Ztg.</u> VoL 54: p. 118.

Buelow, G. H.; Johnson, M. J. 1952. <u>Ind. Eng. Chem.</u> Vol. 44 (No. 12): pp. 2945-2946.

<u>Chemical Marketing Reporter.</u> 1950-1977.

Clement, M. T. 1952. <u>Corn Jour. Tech.</u> Vol. 30: pp. 82-88.

Currie, J. N. 1917. <u>Jour. BioL Chem.</u> VoL 31 (No. 1): pp. 15-37.

Fried, J. H. 1972 (4 Jan.). U.S. Patent 3,632,476.

Izuka, H. 1971 (23 Nov.). U.S. Patent 3,622,455.

Johnson, M. J. 1954. "The Citric Acid Fermentation." <u>Industrial Fermentations.</u> Edited by L. A. Underkofler and R. J. Hickey. VoL 1. New York: Chemical Publishing Co., Inc.

Perquin, L. H. C. 1938. <u>Beijdrage Tot de Kennis der Oxydative Dissimilatie van Aspergillus Niger van Teighem.</u> Thesis. Delft, Netherlands: Technische Hogeschool, W. D. Meinema.

Prescott, S. C.; Dunn, C. G.; eds. 1959. "The Citric Acid Fermentation." <u>Industrial Microbiology.</u> 3rd ed. New York: McGraw-Hill.

Sardinas, J. L. 1973 (2 Jan.). U.S. Patent 3,708,399.

U.S. Department of Agriculture. 1973-1977. <u>Molasses Market News.</u>

SERI☀

SECTION 4.0

2,3-BUTANEDIOL

4.1 BACKGROUND

One of the earliest references to butanediol was made by Henninger (1882), who isolated this compound from wine, believing it to be isobutylene glycol (Underkofler and Hickey 1954). Later investigations found that pure yeast fermentations yield small quantities of 2,3-butanediol. Production of 2,3-butanediol by the bacterium Aerobacter aerogenes was shown in 1906 (Harten and Walpole 1906). Subsequent studies in 1926 (Donker 1926) showed that this diol could also be produced by fermentation using Bacillus polymyxa. It was not until 1933, however, that Fulmer et al. (1933) demonstrated the commercial potential of producing 2,3-butanediol by using Aerobacter aerogenes.

The critical need to produce synthetic rubber during World War II brought about a coordinated search for techniques for producing butadiene by several universities, the Northern Regional Research Laboratories of the USDA, the National Research Council of Canada, and seven commercial firms. Much of the work focused on the Aerobacter and B. polymyxa fermentations to produce 2,3-butanediol, with interest in converting the butanediol to butadiene. But chemical synthetic routes to produce methyl ethyl ketone (MEK) and butadiene were more competitive economically than fermentative production of 2,3-butanediol followed by chemical conversion. This fermentation process, therefore, was never fully developed at a commercial level.

4.2 PHYSICAL PROPERTIES

2,3-butanediol, also called dimethylene glycol, 2,3-dihydroxybutane, or 2,3-butylene glycol, is a viscous liquid that is both colorless and odorless. The molecular formula is $CH_3CHOHCHOHCH_3$. There are three stereoisomeric forms—the levorotory, dextrorotary, and meso isomers—all of which can be obtained by fermentation.

Selected physical properties of the butanediol stereoisomers are listed in Table 4-1. Properties of the dextrorotary isomer are assumed to be the same as those of the levorotary isomer except for the sign of rotation of polarized light. Note the significant differences between the properties of the meso and levo isomers.

Table 4-1. SELECTED PHYSICAL PROPERTIES OF 2,3-BUTANEDIOL

Property	Levorotary	Mesorotary	Racemic (equimolar meso and levo)
Boiling point at 99.3 kPa ($^\circ$C)	179–182	181–182	177
Melting point ($^\circ$C)	19.0	34.4	7.6
Density at 25°C (g/mL)	0.9869	0.9939	--
Viscosity at 35°C (kg/m s x 10^3)	21.8	65.6	--

SOURCE: Underkofler and Hickey 1954.

4.3 POTENTIAL APPLICATIONS

Potential applications of 2,3-butanediol and some of the respective costs are shown in Fig. 4-1. Note that the differences between the cost of butanediol and the costs of some of the products obtainable from it are quite substantial.

Both the meso and optically active isomers form hydrates with water. The levo isomer hydrate crystallizes at about -60°C and can therefore be used as an antifreeze. The meso isomer hydrate is stable to only about -10°C. Hence, it is of some interest to establish which organisms produce which isomers, since the meso isomer is useless as an antifreeze. Ward et al. (1944) identified the levo form as the main product of the fermentation of grain mashes by B. polymyxa, whereas a mixture of the meso and levo isomers is produced by B. subtilis and P. hydrophilia (see Table 4-1). Liebmann (1945) suggests that either isomer could be used as a moistener for glue, tobacco, and casein.

The most interesting use for 2,3-butanediol is as a precursor for the production of 1,3-butadiene. Any of the isomers, or a mixture, is suitable as a feedstock. As can be seen in Fig. 4-1, the production of butadiene from the diol cannot yet compete economically with production from naphtha sources. 1,4-butanediol is the diol of particular value for polymer applications; the potential for producing it chemically from fermentation products remains to be investigated.

Butanediol can be esterified to produce precursors of urethane foams, but it must compete with ethylene products. This is not yet economically practical even considering a likely increase in ethylene prices beyond 44¢/kg.

Catalytic dehydration of 2,3-butanediol yields methyl ethyl ketone (MEK), a major solvent for resins and lacquers. Also, MEK can be condensed to an eight-carbon ketone which can in turn be hydrogenated to give octane isomers. The current price of MEK—$360-$420/metric ton—does not permit its production from butanediol. If butanediol could be manufactured from an inexpensive feedstock (municipal solid waste, for example), then production of octane isomers from diol-derived MEK could be attractive.

Catalytic dehydrogenation of 2,3-butanediol yields diacetyl and hydrogen almost quantitatively. The reaction is independent of the diol isomer. In view of the current market price of diacetyl—about $20,000/metric ton—a review of the possibility of producing this material from 2,3-butanediol seems warranted.

4.4 CURRENT COMMERCIAL PRODUCTION

2,3-butanediol is not commercially produced at present.

4.5 FERMENTATIVE PRODUCTION

Organisms that produce 2,3-butanediol are shown in Table 4-2 with their respective substrates and the amounts of the different stereoisomers produced. The production of 2,3-butanediol by fermentation has never been commercialized, although extensive pilot plant work was completed by J. A. Wheat and associates at the National Research Laboratories in Ottawa, Canada; the results were published in the Canadian Journal of Research (Wheat et al. 1948). Wheat (1953) subsequently proposed the design of a commercial plant to produce 4600 kg (10,200 lb) of butanediol per day using 27,000 kg (60,000 lb) of molasses.

Carbohydrate
$80/ton (Molasses) to $320/ton (Sucrose)

CHEMICAL SYNTHESIS
2-Butene
($120/ton)

Synthetic Rubber

FERMENTATION

2,3-BUTANEDIOL
($7,500/ton)

Butadiene
($380/ton)

Styrene
($460/ton)

Isocyanates

Flexible Polyurethane Foams

Antifreeze
(2-isomer)

Acetoin
and
Diacetyl
($20,000/ton)
and H_2

Methyl Ethyl
Ketone
($400/ton)

Other
Products

Isocyanates

Polyester
Polyols

Solvent
for Lacquers,
Vinyl Resins

Octane
($980/ton)

C_4 Stream

Aviation
Fuel Blend

Diethylene Glycol
($410/ton)

Ethylene Glycol
($460/ton)

Glycol
Ethers

Paints,
Inks

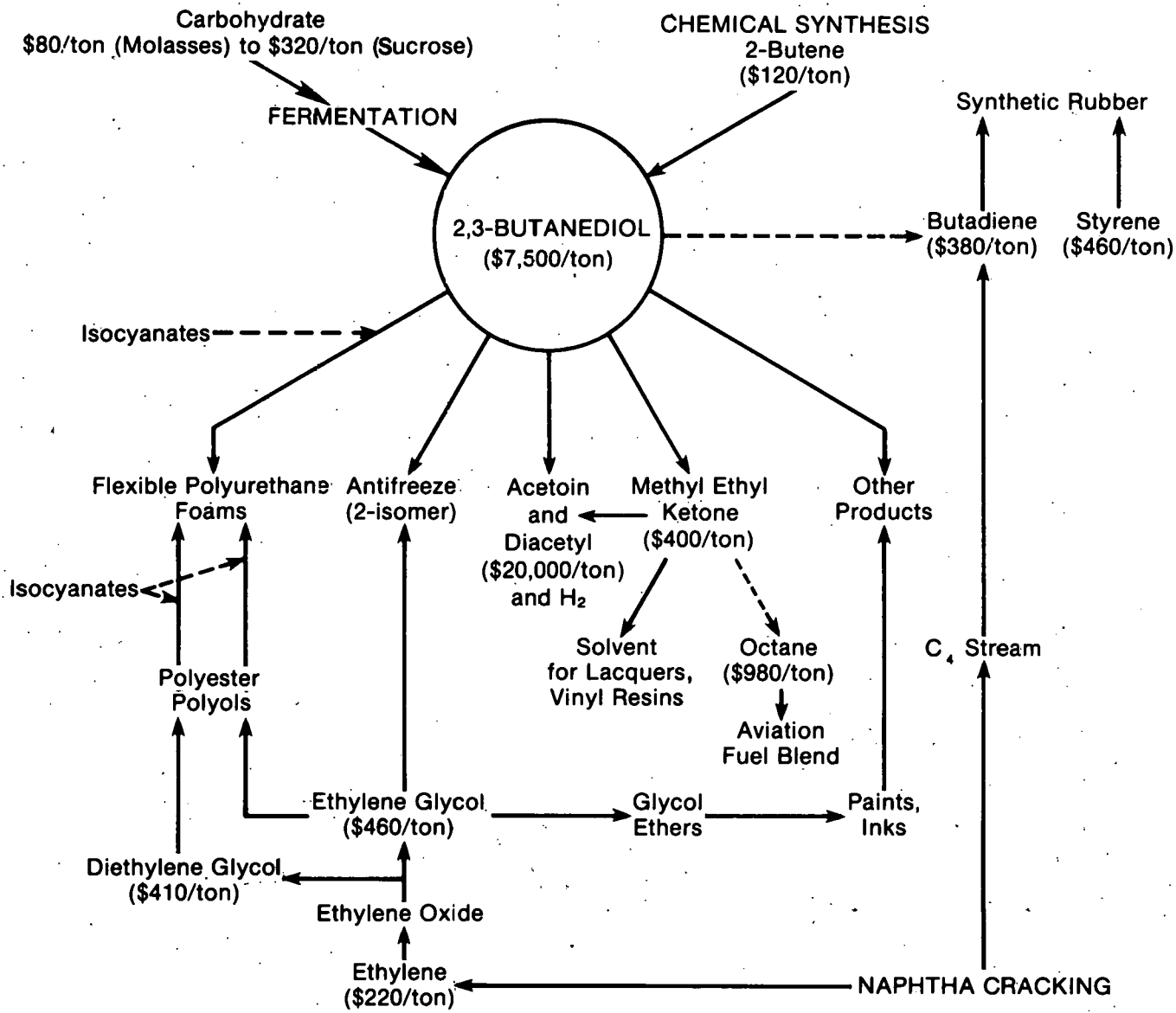Ethylene Oxide

Ethylene
($220/ton)

NAPHTHA CRACKING

Figure 4-1. Applications of 2,3-Butanediol

Table 4-2. ORGANISMS PRODUCING 2,3-BUTANEDIOL

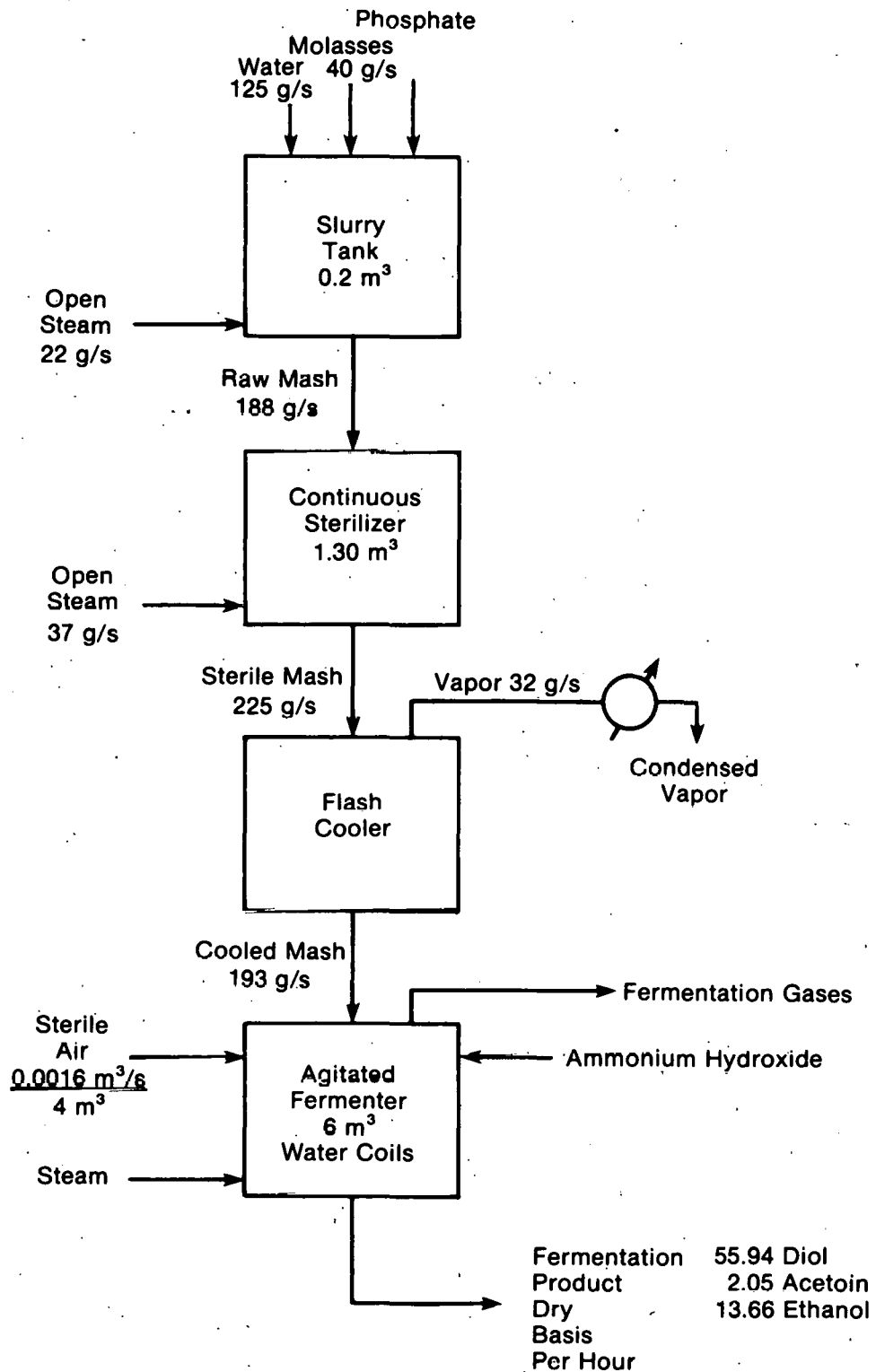| Organism	Stereoisomer of 2,3-Butanediol	Raw Material
Aerobacter aerogenes	5% to 14% dextrorotary; remainder meso	beet, cane, and glucose; citrus molasses; blackstrap sucrose; acid-hydrolyzed cornstarch; wood hydrolysate; acid-hydrolyzed wheat; sulfite waste liquor
Bacillus polymyxa	levorotary; D(-)	beet, citrus, and cane molasses; cornstarch: barley sulfite waste liquor; whole wheat sulfite waste liquor
Bacillus subtilis	~65% D(-); remainder meso	blackstrap; cane and beet molasses; glucose
Pseudomonas hydrophilia	48% meso; 2% levo; 50% racemic	blackstrap; cane and beet molasses; glucose; sulfite waste liquor
Aeromonas liquifaciens	--	blackstrap; cane molasses
Serratia marcescens	mainly meso	beet molasses; sulfite waste liquor; glucose
Distillers yeast	65% levo; remainder meso (possibly some dextro)	

SOURCE: Underkofler and Hickey 1954.

The pilot plant for producing 2,3-butanediol was designed to accommodate 3300-L (880-gal) batches of sugar beet molasses mash. The capacity of the fermentation vessel was 5700 L (1500 gal). Foam breakers, cooling coils, separation devices, and automatic temperature and pH controls were provided in the vessel. Separate experiments were conducted using Aerobacter aerogenes and Pseudomonas hydrophilia. Yields ranged from 143 to 187 kg of diol per 1000 kg of sugar beet molasses. Fermentation efficiencies ranged from 77% to 98%. Approximately 98% of the sugar was converted.

Figure 4-2 is a block diagram of the pilot plant process. A charge of molasses [51%-57% invert sugar, about 540 kg (1200 lb)] was diluted to 7.25% sugar to give about 3300 L (880 gal) of mash. To give a phosphorous pentoxide concentration of 0.02%, 1.8 kg (4 lb) of triple phosphate were added. Flow rates are shown in Fig. 4-2. The mash was sterilized in a continuous "cooker" with a residence time of 1.7 minutes. The pressure of the live steam was 1460 kPa (200 psig). One batch of mash was sterilized in six hours.

The mash was transferred to a flash cooler, and vapor was condensed in a jet-eductor/condenser from which water was discharged through a barometric leg to a well. Cooled mash was transferred to the fermenter by gravity flow. A 3.7-kW (5-hp) motor ran a vaned disk at 420 rpm for mixing in the baffled fermenter. A jacket and a cooling coil helped control the temperature of the fermenter. Air was admitted to the fermenter through a porous stainless steel disk, 5 cm (2 in.) in diameter, placed just below the agitator center. The exhaust gas was sampled, but no experimental gas analysis was reported. Foaming occurred during fermentation but was controlled by the addition of about 800 mL of corn oil to the inoculum. The pH was controlled by adding ammonium hydroxide to the fermentation broth when necessary.

The results of 19 fermentation experiments are given in Wheat (1953). The sugar fermented varied from 95% to 99.9% with A. aerogenes and from 93.8% to 99.8% with P. hydrophilia. Fermentation efficiencies ranged from 77% to 96.6% with A. aerogenes and from 76.2% to 98.1% with P. hydrophilia. The reasons for the variations in efficiency are not known. The ratio of diol plus acetoin to ethanol varied from 2.21 to 6.43 with A. aerogenes and from 1.81 to 5.65 with P. hydrophilia. Laboratory experiments established that aeration decreases the production of ethanol and increases the quantity of acetoin; pilot plant experiments, however, did not support this. Wheat concluded that foaming during the fermentation caused liquid carry-over into the exhaust gas lines, thereby contributing to an inaccurate determination of the amount of product.

After fermentation, the mash was pumped to a stripping column 0.6 m (two feet) in diameter and containing 22 plates, as shown in the recovery block diagram of Fig. 4-3. A closed steam coil supplied heat. Discharge from the bottom was transferred to a 3800-L (1000-gal) slops holding tank. This material was then concentrated in a vertical tube evaporator with a heat transfer area of 12.7 m^2 (137 ft^2). Vapor from the evaporator was scrubbed to remove diol in a 0.3-m (1-ft) diameter copper rectifying column containing 33 plates. When the diol concentration reached 20% during evaporation, the syrup was removed continuously and transferred to the stripping and scrubbing columns. These columns were 0.3 m (1 ft) in diameter and 6.1 m (20 ft) high and were packed with Raschig rings. Open steam flow to these columns was regulated automatically. Syrup rates varied from 0.23 to 0.39 kg/m^2 s (172 to 290 lb/ft^2 h) and steam-to-syrup ratios varied from 2.46 to 3.56. Mass-transfer coefficients could not be calculated because the effect of solids on the vapor/liquid equilibria was not known. To estimate how long the stripping column could be operated, syrup containing 16.9% diol and 52% solids was stripped in a 0.15-m (6-in.) column at 0.28 kg/m^2 s (205 lb/ft^2 h) for 80 hours. No general trend was noted in the pressure drop, so it was concluded that the column could probably operate a week before cleaning. The average height of a transfer unit was found to be 1.17 m (3.84 ft) with 98.5% of the resistance in the gas film.

Figure 4-2. Block Diagram for Pilot Plant Fermentation of 2,3-Butanediol
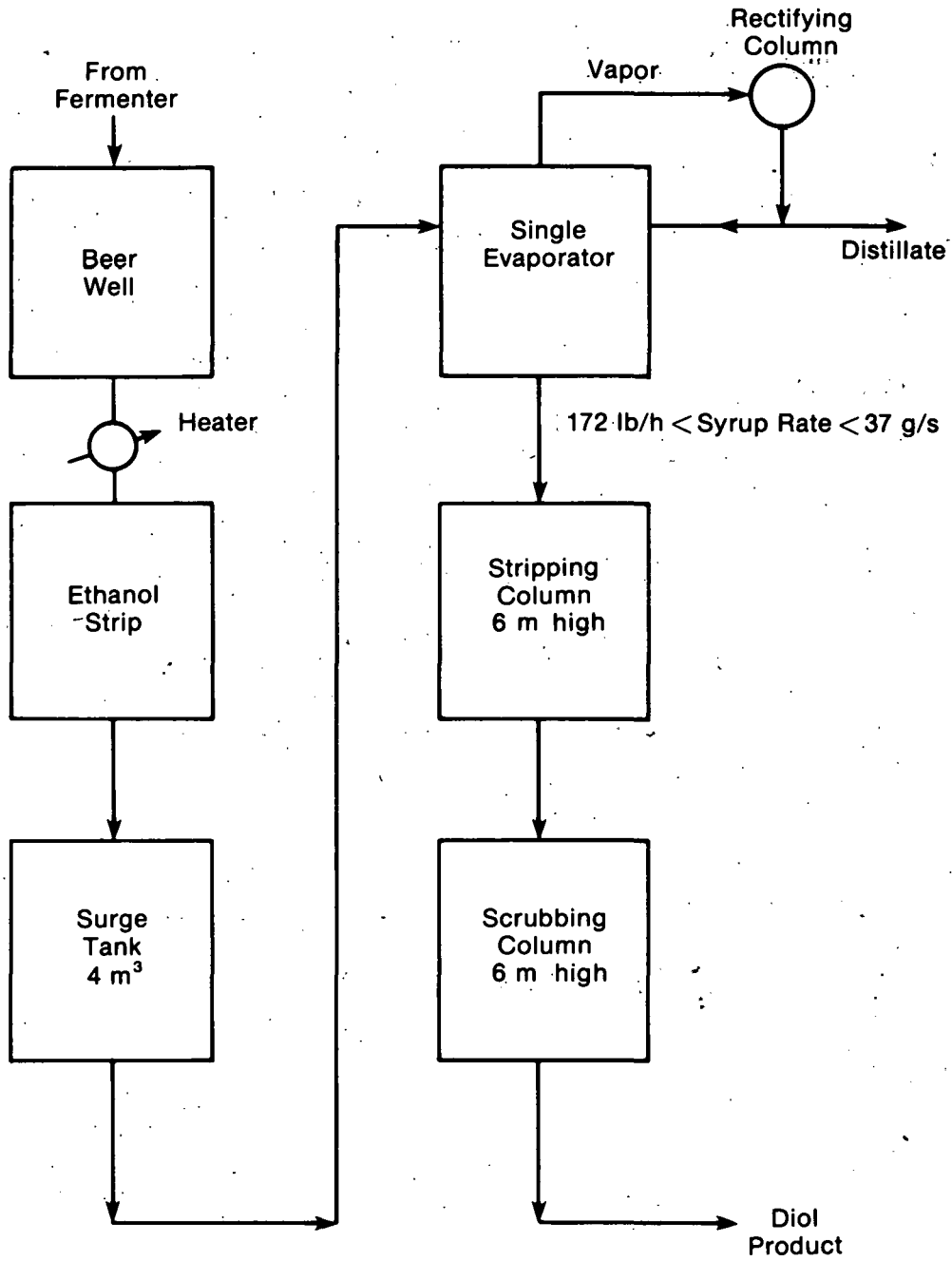
CONVERSION FACTORS: m × 3.28 = ft
g/s × 7.94 = lb/h
m³ × 264 = gal.

Figure 4-3.   Block Diagram for 2,3-Butanediol Recovery

For purifying the diol from the scrubber product, the following steps were found satisfactory:

(1) Sodium hydroxide was added to the scrubber product and a portion distilled and fractionated at atmospheric pressure into a water fraction containing 50% to 60% diol.

(2) The crude diol was vacuum-distilled into water and impure diol.

(3) Sodium hydroxide was added to the impure diol, which was again vacuum-distilled, leaving the "second residue."

4.6 ECONOMICS

Wheat (1953) estimated the cost of a commercial plant to produce 1699 kg (10,196 lb) of 2,3-butanediol daily from 10,000 kg (60,000 lb) of molasses. His initial estimate was approximately $2.78 million, based on his pilot plant data and June 1952 prices. A breakdown of the capital costs involved is given in Table 4-3. The corresponding costs for utilities and labor on a daily basis in 1952 are given in Table 4-4.

When depreciation, interest, taxes, insurance, and maintenance were added to the cost of raw materials, a total operating cost of 57¢/kg (26¢/lb) of diol was obtained with no return on investment (ROI). When working capital was included and a 20% ROI assumed, a selling price of $1.07/kg (48.5¢/lb) resulted. 2,3-butanediol has not yet been available in commercial quantities, but in view of the increasing costs of petrochemicals and the potential applications of butanediol, a review of its production and potential appears advisable.

4.7 REFERENCES

Donker, H. J. L. 1926. Ph.D. dissertation. Delft, Netherlands.

Fulmer, E. I.; Christensen, L. M.; Kendall, A. R. 1933. Industrial and Engineering Chemistry. Vol. 25: p. 798.

Harten, A.; Walpole, G. S. 1906. Proceedings of the Royal Society (London). Vol. 77B: p. 399.

Henninger, A. C. 1882. Comptes Rendu. Vol. 95: p. 94.

Liebmann, S. J. 1945. Oil and Soap. Vol. 22: p. 81.

Underkofler, L. A.; Hickey, R. J. 1954. Industrial Fermentations. Vol. 2. New York: Chemical Publishing Co.

Ward, G. E.; Pettijohn, O. G.; Lockwood, L. B.; Loghill, R. D. 1944. J. American Chemical Society. Vol. 66: p. 541.

Wheat, J. A. 1953. Industrial and Engineering Chemistry. Vol. 45: p. 2387.

Wheat, J. A.; Leslie, J. D.; Tomkins, R. V.; Milton, H. E.; Scott, D. S.; Ledingham, G. A. 1948. Canadian Journal of Research. Vol. 26F: p. 469.

**Table 4-3. SUMMARY OF CAPITAL COSTS FOR A
PLANT PRODUCING 4625 KG/DAY
(10,196 LB/DAY) OF 2,3-BUTANEDIOL
(JUNE 1952)**

Expense	Cost ($)	% of Total
Land and improvements	51,180	1.84
Buildings	126,550	4.55
Process equipment	1,133,620	40.79
Process piping	380,550	13.69
Instruments	190,340	3.93
Electrical installations	81,040	2.92
Service facilities	205,370	7.39
TOTAL PHYSICAL COST	2,087,650	75.11
Contingency	196,890	7.09
Insurance and taxes	56,060	2.12
Engineering	435,830	15.68
TOTAL OTHER COSTS	691,780	24.89
TOTAL COSTS	2,779,430	100

**Table 4-4. SUMMARY OF UTILITY AND LABOR
COSTS FOR A PLANT PRODUCING
4625 KG/DAY OF 2,3-BUTANEDIOL
(JUNE 1952)**

Item	$/Day	¢/kg (¢/lb) Diol
Steam	330.00	6.8 (3.1)
Water	52.00	1.1 (0.5)
Power	31.50	0.7 (0.3)
Labor	318.66	6.8 (3.1)
TOTAL	732.16	15.4 (7.0)

SERI☉

SECTION 5.0

PROPIONIC ACID

5.1 BACKGROUND

The isolation of microorganisms capable of producing propionic acid by fermentation was first described in 1898 by von Freudenreich and Orla-Gensen. Propionic acid is produced from pyruvate via succinate by Propioni bacteria. These bacteria are responsible for the characteristic flavor and eye formation in Emmenthaler cheese. They are gram positive, non-spore-forming, nonmotile facultative aerobes. Materials fermented include lactose, sucrose, maltose, glucose, arabinose, xylose, dextrin, and starch.

5.2 PHYSICAL PROPERTIES

The chemical formula for propionic (or propanoic) acid is $CH_3CH_2CO_2H$. It has a melting point of -21°C and a boiling boint of 141°C. It is freely soluble in water.

5.3 APPLICATIONS

Table 5-1 lists the relative amounts of propionic acid used for various applications. Propionic acid is increasingly used in herbicides. In reaction with phenylmercuric acetate, a paint fungicide, phenylmercuric propionate is produced. The use of propionic acid as a grain preservative has been demonstrated and is FDA acceptable. Cellulose propionate is used as a thermoplastic. Esters of propionic acid are used in the perfume industry. If ethylene and propylene prices rise dramatically, production of cellulose esters from biomass could become economically feasible; they could be produced by fermentation of sugar syrups derived from cellulose and hemicellulose.

Table 5-1. DISTRIBUTION OF USES OF PROPIONIC ACID

Use	% of Total
Ca^+ and Na^+ propionates	28
Herbicides	24
Grain preservatives	20
Cellulose propionate plastics	18
Miscellaneous	10

5.4 CURRENT COMMERCIAL PRODUCTION

Propionic acid generally is produced by the oxidation of propionaldehyde derived from petrochemicals. A DuPont process for manufacturing propionic acid involves reacting a mixture of ethanol, ethyl ether, and carbon monoxide at high pressure. The 1980 demand

is expected to be 45 million kg/yr (100 million lb/yr). This demand is increasing at a rate of 8.7%/yr. Table 5-2 lists companies currently producing propionic acid.

Table 5-2. U.S. MANUFACTURERS OF PROPIONIC ACID

Producer	Annual Capacity (10^6 kg)
Union Carbide, Texas City, Tex.	68
Eastman, Kingsport, Tenn.	32
Celanese, Pampa, Tex.	6.8
IMC Chemical Group, Sterlington, La.	1.4
TOTAL	108.2

CONVERSION FACTOR: 2.20 x mass in kg = mass in lb.

Most propionic acid plants also have the capability to produce valeric and isopentanoic acids when the demand for propionic acid is low. At present, propionic acid sells for 44¢-48¢/kg (20¢-22¢/lb) in tank car lots.

5.5 FERMENTATIVE PRODUCTION

High yields of propionic acid can be obtained by fermentation of wood sugars by bacteria of the genus Propioni. The Columbia Cellulose Co., Ltd., of Canada developed a process for the fermentation of sulfite waste liquor to propionic acid using Propioni bacterium arabinosum ATCC 4968. The fermentation was carried out at 35°-38°C in limestone-packed column fermenters. The feed contained 25 g/L of fermentable sugars. A conversion of 84% was obtained, and the primary products were propionic acid and acetic acid in the ratio of two to one. A residence time of 54 hours was required for maximum conversion. The resultant mixed calcium salts of propionic and acetic acids were separated by fractional crystallizations, and the acetic acid was purified by ion exchange chromatography.

5.6 ECONOMICS

No economic data on the fermentation process can be found in the literature. Columbia Cellulose never went beyond the pilot plant stage, and the process is not currently competitive with the petrochemical process. Furthermore, the fermentation product does not meet the "water white" specification of the air-oxidized propionic acid without the addition of a costly charcoal dieolonization step.

Unfortunately, Propioni bacteria appear to be inhibited at relatively low concentrations of acid (21 g/L). For the fermentation process to be economical, mutant strains must be developed that can withstand an acid concentration of 50 g/L and that have repressed or inhibited acetic acid production.

5.7 REFERENCES

Gutcho, S. Chemicals by Fermentation. Noyes. pp. 17-19.

Wayman, J.; Martin, M. E.; Grad, C. 1962 (4 Dec.). U.S. Patent 3,067,107. Assigned to
    Columbia Cellulose Co., Ltd.

Document Control Page	1. SERI Report No. TR-621-754	2. NTIS Accession No.	3. Recipient's Accession No.

4. Title and Subtitle

Biotechnology for Producing Fuels and Chemicals from Biomass. Vol. II - Fermentation Chemicals from Biomass

5. Publication Date

February 1981

6.

7. Author(s)

Ruxton Villet, editor

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

10. Project/Task/Work Unit No.

1034.00

11. Contract (C) or Grant (G) No.

(C)

(G)

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered

Technical Report

14.

16. Abstract (Limit: 200 words) The technological and economic feasibility of producing some selected chemicals by fermentation is discussed: acetone, butanol, acetic acid, citric acid, 2,3-butanediol, and propionic acid. The demand for acetone and butanol has grown considerably. They have not been produced fermentatively for three decades, but instead by the oxo and aldol processes. Improved cost of fermentative production will hinge on improving yields and using cellulosic feedstocks. The market for acetic acid is likely to grow 5%-7%/yr. A potential process for production is the fermentation of hydrolyzed cellulosic material to ethanol followed by chemical conversion to acetic acid. For about 50 years fermentation has been the chief process for citric acid production. The feedstock cost is 15%-20% of the overall cost of production. The anticipated 5%/yr growth in demand for citric acid could be enhanced by using it to displace phosphates in detergent manufacture. A number of useful chemicals can be derived from 2,3-butanediol, which has not been produced commercially on a large scale. R&D are needed to establish a viable commercial process. The commercial fermentative production of propionic acid has not yet been developed. Recovery and purification of the product require considerable improvement. Other chemicals such as lactic acid, isopropanol, maleic anhydride, fumarate, and glycerol merit evaluation for commercial fermentative production in the near future.

17. Document Analysis

a. Descriptors Acetic Acid; Acetone; Alcohol Fuels:T2; Biomass:T1; 2,3-Butanediol; Butanols; Citric Acid; Economics; Feasibility Studies:Q3; Fermentation:Q1,T3; Production:Q2; Propionic Acid; Alcohols; Bioconversion; Carboxylic Acids; Energy Sources;Fuels; Glycols; Hydroxy Acids; Hydroxy Compounds; Ketones; Monocarboxylic Acids; Organic Acids; Organic Compounds; Renewable Energy Sources; Synthetic Fuels; Aerobic Bacteria; Anaerobic Bacteria; Chemical Feedstocks; Feedstocks; Stillage

c. UC Categories

61

18. Availability Statement
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

19. No. of Pages

46

20. Price

$4.50