Butanediol—A New Polyhydric Alcohol*

A. J. LIEBMANN
Schenley Research Institute, Inc., Lawrenceburg, Indiana

BUTANEDIOL has received very scant recognition in the technical literature. Up to very recently it was, at least in the United States, not much more than a laboratory curiosity and might have remained in comparative obscurity and neglect if the urgent need for butadiene as raw material for synthetic rubber had not arisen. Butanediol, with its four carbon chain, appeared as one of the likeliest intermediates on the road to butadiene.

Fulmer (1) and Kendall at Ames, Iowa (2), and Kluyver in his patent (3), had carried on a considerable amount of research on production of this diol by fermentation, but all work had been done on a small laboratory scale and with little attention to economical and mass production.

With the establishment of the Rubber Director's office and the organization of all technical resources for production of butadiene a concentrated effort resulted to produce butanediol from grain on a large scale under the auspices and direction of the War Production Board. A group of investigators was formed under the leadership of the Northern Regional Research Laboratory of the Department of Agriculture in Peoria with interchange of information.

Schenley Research Institute was a member of this group. First on a laboratory scale, and then in a generously sized pilot plant butanediol was produced, and some of it converted into butadiene. It is doubtful if the conversion of butanediol into butadiene will become one of major importance. On the other hand, butanediol itself, if produced at a reasonable price has great possibilities for many industrial applications.

The bacterial production of 2,3-butanediol involves two distinct steps:

1. The fermentation of a suitably prepared grain or sugar mash by a specific microorganism, and
2. The separation of the butanediol from the solids and other liquids in the fermented mash.

Two organisms have been shown to possess superior qualities for the production of butanediol: Aerobacter aerogenes and Aerobacillus polymyxa. The first of these bacteria readily ferments sugar, and the mashes must be prepared by hydrolyzing the starch in the grains prior to fermentation. The fermented beer contains the major metabolic product, butanediol, small amounts of acetylmethylcarbinol and ethanol and traces of lower aliphatic acids. Carbon dioxide and hydrogen are also produced during fermentation.

A. polymyxa can utilize starch directly and requires considerably less supplementary nutrient. This organism, however produces relatively large quantities of ethanol and proportionately less butanediol.

A COMPARISON of the main products formed during an aerogenes fermentation, a yeast fermentation, and a polymyxa fermentation are shown in Table 1. It is interesting to note that the butanediol produced by each organism is a different optical isomer of 2,3-butanediol. The isomerism of the various butanediols is shown in detail in Fig. 1. 2,3-Butanediol is the only member of the family which can exist in three isomeric forms: dextro, laevo, and meso. The diol produced by A. aerogenes consists of a mixture of about 20% dextro and 80% meso, whereas the diol produced by A. polymyxa is pure laevo.

TABLE 1
Summarized Equations

I. *Diol From Glucose (A. Aerogenes)*
$C_6H_{12}O_6 = C_4H_{10}O_2 + 2CO_2 + H_2$
100 gm. glucose = 50 gm. diol + 48.9 gm. carbon-dioxide +1.1 gm. hydrogen

II. *Ethanol From Glucose (Yeast)*
$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$
100 gm. glucose = 51.1 gm. ethanol + 48.9 gm. carbon-dioxide

III. *Three Parts Diol—Two Parts Ethanol From Glucose (A. Polymyxa)*
$5C_6H_{12}O_6 = 3C_4H_{10}O_2 + 4C_2H_5OH + 10CO_2 + 3H_2$
100 gm. glucose = 30 gm. diol + 20.44 gm. ethanol + 48.89 gm. carbon-dioxide + .67 gm. hydrogen.

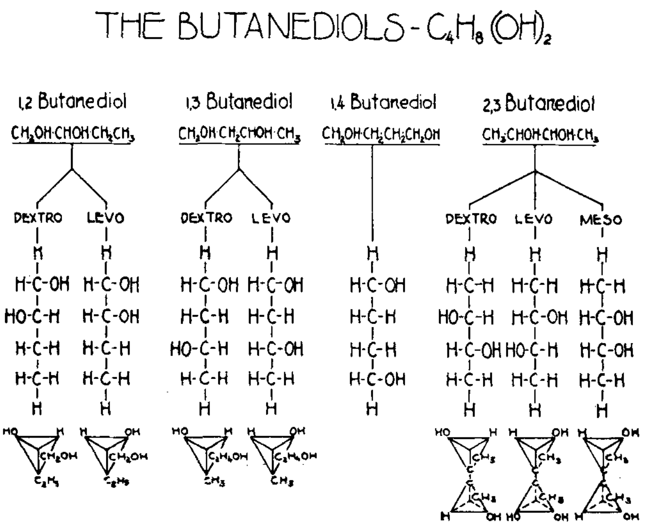


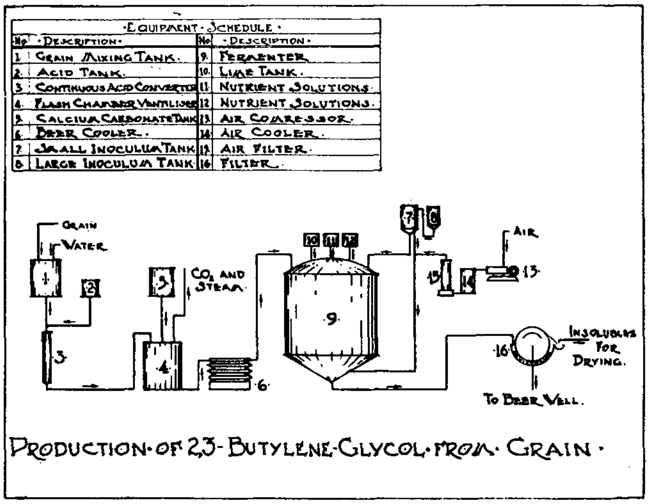
FIG. 1.

The significantly lower yield of butanediol obtained from the polymyxa fermentation practically eliminates this method as a competitor of the aerogenes fermentation unless the laevo isomer is specifically wanted. The supplementary formation of ethanol by A. polymyxa is of no particular advantage since ethanol can be more easily and more efficiently produced by yeast fermentation. A quantitative comparison of butanediol yields by each organism from different raw material sources is shown in Table 2. The yield of butanediol from A. aerogenes is about 50% greater than that from A. polymyxa. Unless otherwise noted, the following discussion will be concerned with A. aerogenes fermentation.

Although molasses is the most logical raw material for the aerogenes fermentation, grains were employed exclusively in development work due to the unavailability of molasses for such use during the last three years. In the case of grain (see Fig. 2), after milling to proper size, the starch in the grain is converted to sugars by sulphuric or hydrochloric acid using

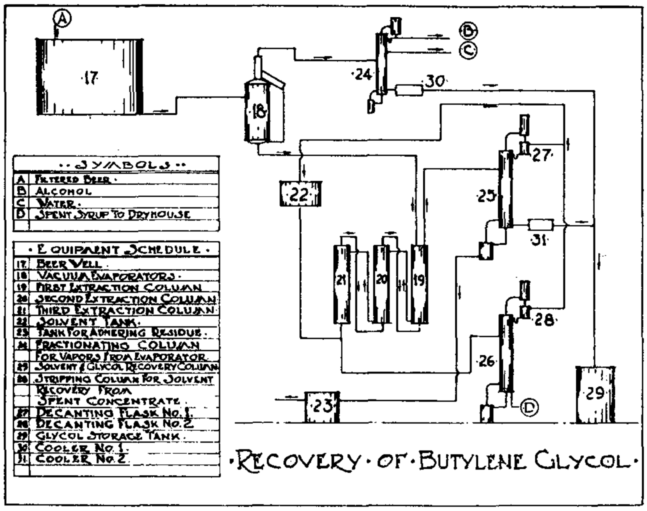
---

* This paper was presented at the Chicago meeting of the American Oil Chemists' Society, October 25-27, 1944.



Equipment Schedule			
No.	Description	No.	Description
1	Grain Mixing Tank.	9	Fermenter.
2	Acid Tank.	10	Lime Tank.
3	Continuous Acid Converter	11	Nutrient Solutions.
4	Flash Chamber Ventilizer	12	Nutrient Solutions.
5	Calcium Carbonate Tank	13	Air Compressor.
6	Beer Cooler.	14	Air Cooler.
7	Small Inoculum Tank	15	Air Filter.
8	Large Inoculum Tank	16	Filter.

FIG. 2.



Symbols	
A	Filtered Beer.
B	Alcohol
C	Water.
D	Spent Syrup To Dryhouse

Equipment Schedule	
17	Beer Well.
18	Vacuum Evaporators.
19	First Extraction Column
20	Second Extraction Column
21	Third Extraction Column
22	Solvent Tank.
23	Tank for Adhering Residue.
24	Fractionating Column for Vapors from Evaporator.
25	Solvent & Glycol Recovery Column
26	Stripping Column for Solvent Recovery from Spent Concentrate.
27	Decanting Flask No. 1.
28	Decanting Flask No. 2
29	Glycol Storage Tank.
30	Cooler No. 1.
31	Cooler No. 2

FIG. 3.

either a batch or continuous process. After pH adjustment to 6.1 with calcium carbonate and calcium hydroxide, the mash is cooled and transferred under sterile conditions to a fermenter to which are simultaneously added urea, salts, and inoculum. The temperature of the fermentation is maintained between 88-90°F. and continuously aerated and agitated. After 36 hours the fermentation is completed, and, the mash contains between 3.6 to 4.2% butanediol, 0.2% ethanol, and traces of acetylmethylcarbinol and organic acids.

The separation of the butanediol from all the other constituents of the mash is complicated by the secondary aim of recovering the spent grain from the mash in a form suitable for animal feed. Five different recovery processes were studied by the research groups investigating the problem:

1. Solvent extraction in a liquid—liquid countercurrent operation.
2. Spray drying.
3. Drum drying.
4. Kerosene distillation.
5. Vapor-phase steam extraction.

Solvent extraction (See Fig. 3): The beer is concentrated by evaporation to about one-fifth its original volume, and the concentrate extracted with butanol in a countercurrent column. The butanol phase, containing the butanediol and some water, is then fractionated and the diol collected separately.

Spray drying: The beer is concentrated by evaporation to about one-fourth to one-fifth its original volume, and the heated concentrate flashed into a vacuum chamber. The vapors, consisting of steam and diol, are directly fractionated and the diol collected separately. The residue solids can be used for animal feed.

Drum drying: After concentrating the beer by evaporation, the syrup is dried on the surface of a steam-heated rotating drum, either at atmospheric pressure or under vacuum. The vapors, consisting of steam and diol, are directly fractionated as above. The residue solids can be used for animal feed.

Kerosene distillation: After concentrating the beer by evaporation, the syrup is added to hot kerosene and the distillate of the mixture cooled. The kerosene in the distillate is decanted after cooling and the residual aqueous phase containing the diol fractionated.

Vapor-phase steam extraction: The beer is concentrated by evaporation to about one-quarter to one-fifth of its original volume and the heated syrup passed into a plate column through which steam under high pressure is injected at the bottom. The butanediol is removed by scrubbing in the vapor stage and then fractionated and cooled separately. The residue solids removed from the bottom of the steam column can be used for animal feed.

The physical properties of the butanediol produced by the A. aerogenes and the A. polymyxa are shown in Table 3.

TABLE 3

Physical Properties of Isomers of 2,3-Butanediol (4)

	I	II
	Aerobactor Aerogenes Fermentation	Bacillus Polymyxa Fermentation
Color	Appx. 80% meso 2,3-butanediol Appx. 20% dextro 2,3-butanediol	laevo 2,3-butanediol
	Colorless	Colorless
Boiling point (u45 mm.)	180-182° C.	179-180° C.
Melting point	+ 25° C.	+ 19° C.
Density (25° C.)	1.000 g./ml.	0.990 g./ml.
Specific Rotation (23° C., D)	+ 1.06	—12.85
Refractive Index (18° C.)	1.4387	1.4340
Viscosity (25° C.)	118 cp.	41.0 cp.

2,3-Butanediol exhibits certain characteristics which lend itself to immediate applications for indus-

TABLE 2

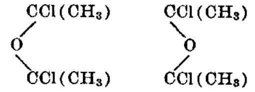
Theoretical and Practical Yields

Raw Material	Organism	Theoretical		Practical in Beer		Practical Recovered	
		Diol	Alcohol	Diol	Alcohol	Diol	Alcohol
Corn	A. aerogenes	17.8 lbs./bu.	....	15.5 lbs./bu.	....	14.0 lbs./bu.	....
Molasses*	A. aerogenes	3.5 lbs./gal.	....	3.0 lbs./gal.	....	2.8 lbs./gal.	....
Wood Sugar	A. aerogenes	50.0 lbs./cwt.	....	35.0 lbs./cwt.	....	....	....
Corn	A. polymyxa	10.7 lbs./bu.	7.3 lbs./bu.	10.0 lbs./bu.	7.0 lbs./bu.	9.0 lbs./bu.	6.8 lbs./bu.

* 1 gallon molasses = 11.8 lbs. = 7.08 lbs. sugar.

TABLE 4

Halogenated Derivatives of 2,3-Butanediol

1. Halogenated butanols	2-chloro-3-butanol	$CH_3 \cdot CHCl \cdot CH(OH) \cdot CH_3$
2. Dihalogenated butanes	2,3-dichlorobutane	$CH_3 \cdot CHCl \cdot CHCl \cdot CH_3$
3. Halogenated butyl esters	2-chloro-isobutyl acetate	$CH_3 \cdot CHCl \cdot CH(OOC \cdot CH_3) \cdot CH_3$
4. Halogenated butyl ethers	2-chloro-3-methoxy butane	$CH_3 \cdot CHCl \cdot CH(OCH_3) \cdot CH_3$
5. Halogenated tetra-methyl dioxanes	Tetrachloro-tetramethyl dioxane	

trial use. Its hygroscopicity and low vapor pressure can be utilized for moistening and softening of such varied materials as glue, gelatin, casein, paper, tobacco, composition cork, and textile fibers. It shows possibilities as an excellent solvent for certain dyes, gums, resins, and essential oils.

The laevo 2,3-butanediol produced by the A. polymyxa produces a marked depression in freezing point when mixed with water. A solution of 80% laevo butanediol and 20% water freezes at —35°F. This mixture can therefore be used as an anti-freeze for cooling systems where low temperatures are encountered. The presence of two functional groups in the butanediol molecule produces various reactions with poly-functional organic compounds. In this respect butanediol can be used for production of polymers.

THE chemical derivatives of 2,3-butanediol have been studied in considerable detail and a large number of such derivatives have been prepared on laboratory scale. The family of halogenated substitutes of butanediol are shown as five classes in Table 4, together with examples for each group. These compounds, by structural analogy and from studies of those members which have actually been prepared, exhibit physical characteristics which indicate uses in lacquers, printing inks, synthetic perfumes, flavors, and as a solvent for oils, fats, waxes, and resins. Furthermore, these halogenated compounds may be useful intermediates in the production of synthetic rubber, drugs, and pharmaceuticals. Finally, these compounds may be used for organic syntheses.

The esters of butanediol can be divided into two classes as shown in Table 5. The esters of mono-basic acids can be used in synthetic perfumes and flavors and as solvents for the lacquer industry. These compounds have further uses as extracting agents and varnish removers. The compounds resulting from the reaction of dibasic acids yield polymers in the field of thermoplastic resins. Various types of resins can be obtained by co-polymerizing with different diols and by using mixtures of different dibasic acids.

The family of nitrogen derivatives of butanediol can be divided into three classes as shown in the table. The amins are useful as emulsifying agents, gas purifiers, and in softening and moistening agents. These compounds may also be used for synthesis of dyestuffs, pharmaceuticals, and fatty acid detergent soaps. Due to the presence of the primary amino groups, these compounds will readily undergo reaction with functional groups and thus may be a source of many derivatives in the synthetic organic field. The nitrates of butanediol may be used as dynamite modifiers and explosives.

The family of oxides derived from 2,3-butanediol may be divided into two sub-classes as shown in the table. Butylene oxide may be able to replace the valuable ethylene oxide in various syntheses due to the fact that the compound is a liquid at room temperature and has two additional methyl groups as compared to ethylene oxide. It can be predicted that butylene oxide will be a valuable reactant in the preparation of such derivatives as halogenated alcohols, amines, substituted amino compounds, acids, and aldehydes. The butylene oxide itself may possibly be used as a fumigating agent. Tetramethyldioxane, prepared in substantial quantities in our laboratory, is an excellent solvent for cellulose derivatives, resins, oils, waxes, lacquers, and varnishes. Its camphor-like aroma may be useful in pharmaceuticals and drugs.

TABLE 5

Esters of 2,3-Butanediol

1. Esters of monobasic acids	Butylene-2,3-diacetate	$CH_3 \cdot CH(OOCCH_3) \cdot CH(OOCCH_3) \cdot CH_3$
2. Esters of dibasic acids	Succinic acid polyester of butanediol	$[COOH \cdot (CH_2)_2 \cdot COO \cdot CH(CH_3) \cdot CH(CH_3)OH]_x$

Nitrogen Derivatives of 2,3-Butanediol

1. Butanolamines	2-amino-3-butanol	$CH_3 \cdot CH(NH_2) \cdot CH(OH) \cdot CH_3$
2. Diamino butanes	2,3-diamino butane	$CH_3 \cdot CH(NH_2) \cdot CH(NH_2) \cdot CH_3$
3. Nitrates of butanediol	Butane-2,3-dinitrate	$CH_3 \cdot CH(ONO_2) \cdot CH(ONO_2) \cdot CH_3$

Oxide Derivatives of 2,3-Butanediol

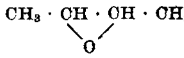
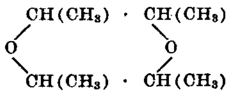
1. Butylene oxide	
2. Tetramethyl dioxane	

TABLE 6

Ether Derivatives of 2,3-Butanediol

1. Hydroxy isobutyl ethers	2-hydroxy-3-methoxy butane	$CH_3 \cdot CH(OH) \cdot CH(OCH_3) \cdot CH_3$
2. Diethers of butanediol	2-methoxy-3-ethoxy butane	$CH_3 \cdot CH(OCH_3) \cdot CH(OC_2H_5) \cdot CH_3$
3. Ester-ethers of butanediol	3-methoxy isobutyl acetate	$CH_3 \cdot CH(OOCCH_3) \cdot CH(OCH_3) \cdot CH_3$
Ketonic Derivatives of 2,3-Butanediol		
1. Butanolene	Acetylmethyl carbinol	$CH_3 \cdot CO \cdot CH(OH) \cdot CH_3$
2. Butanediones	Diacetyl	$CH_3 \cdot CO \cdot CO \cdot CH_3$
3. Butanone	Methyl ethyl ketone	$CH_3 \cdot CH_2 \cdot CO \cdot CH_3$
Olefinic Derivatives of 2,3-Butanediol		
1. Mono-enes	1-butene	$CH_2 \cdot CH \cdot CH_2 \cdot CH_3$
2. Di-ene	1,3-butadiene	$CH_2 \cdot CH \cdot CH \cdot CH_2$

The family of ether derivatives of butanediol can be divided into three sub-classes as shown in Table 6. The hydroxy ethers can be used as modified solvents similar to the "cellosolve" and "carbitol" solvents now in wide use in the chemical industries. Furthermore, the hydroxy ethers are excellent solvents for the cellulose compounds, resins, and dyes. The di-ethers may be used for extraction processes in removing fats, waxes, and oils and have the advantage of being somewhat soluble in water. These di-ethers may also be utilized for degreasing and dewaxing materials. The third class suggests uses as solvents in lacquers, varnish removers, and printing inks. It may further be used as a plasticizer in synthetic resin preparations.

The family of ketones derived from butanediol are divided into three classes as shown in the table. The keto-alcohols are versatile intermediates in the synthesis of organic derivatives due to the presence of the two functional groups. The di-ketones may be used as solvents and intermediates in the synthesis of dyes, drugs, resins, and pharmaceuticals. These compounds also have the property of carrying the aroma of butter, vinegar, coffee, etc. The monoketones shown as the third class may be used as solvents in the lacquer, ink, resin, and plastic industries.

The family of olefinic derivatives of 2,3-butanediol, obtained by the pyrolysis of the diol, may be used as intermediates in the synthesis of medicinals, drugs, dyes, and other synthetic preparations. Butadiene is one of the most important derivatives of the diol and is at present the major constituent in the production of buna-S rubber. The production of butadiene from 2,3-butanediol has been studied intensively and has been carried through the pilot plant stage. It has been shown that an over-all yield of approximately 80% of the butanediol can be converted into butadiene of high purity by pyrolyzing the diacetate ester of 2,3-butanediol.

If sufficient demand can be developed to warrant production of butanediol on a sufficiently large scale, there is every indication that it may be produced at a price of 10 to 12 cents per pound and possibly even considerably less. Butanediol should receive the attention of the chemical industry as a promising material in itself and as an intermediate.

Acknowledgment

The author wishes to express his appreciation to the staff of the Schenley Research Institute for their assistance in the technical work, especially to George de Becze and Maurice Rosenblatt, who have also contributed to the preparation of this paper.

LITERATURE CITED

(1) Fulmer, E. I., Nelson, V. E., and Sherwood, F. F., J.A.C.S., *43*, 191-9 (1921).

(2) Kendall, A. R., "The Biochemistry of the Production of 2,3-Butylene Glycol by Fermentation," Graduate Thesis, Iowa State College, 1934.

(3) Kluyver, A. J., and Scheffer, M. A. (to Th. Hermanus Verhave), U. S. Patent 1,899,156 (Feb. 28, 1933).

(4) Morell, S. A., and Auerheimer, A. H., J.A.C.S. *66*, 792 (1944).

Refining Committee Report
1943 - 1944

THE activities of the Refining Committee for the year 1943-4 are covered by the published minutes of two meetings held during the year, the first at Peoria on July 7-8, 1943 (*Oil and Soap*, Sept., 1943, Vol. XX, No. 9, pages 183-189), and the second in Chicago on October 5, 1943 (*Oil and Soap*, April, 1944, Vol. XXI, No. 4) and by three subcommittee reports which are attached. This final report of the Committee repeats, for purpose of emphasis, certain important discussions, resolutions, and recommendations, some of which will be passed on by the Uniform Methods and Planning Committee and, if approved, will be presented to the Society.

The proposed centrifugal method of refining was discussed at considerable length at the Refining Committee meeting, July 7-8, 1943, Peoria, Ill., and a subcommittee, consisting of Sorensen (chairman), James, Freyer, Kruse, Kiess, and Sanders, prepared a resolution, during a recess of the Committee, carrying, in part, the points given below:

1. That the Committee suggest that further development work on the centrifugal refining method be continued at a later date at the Northern Regional Laboratory.
2. That the Committee continue studies on modification of the present A.O.C.S. cup methods through subcommittees now collaborating with the Northern Regional Laboratory and that the new recommended procedures