BUTYL ALCOHOLS

1. Introduction

Butyl alcohols encompass the four structurally isomeric 4-carbon alcohols of empirical formula $C_4H_{10}O$. One of these, 2-butanol, can exist in either the optically active $R(-)$ or $S(+)$ configuration or as a racemic ($\pm$) mixture [15892-23-6].

2. Physical and Chemical Properties

The butanols are all colorless, clear liquids at room temperature and atmospheric pressure with the exception of *t*-butyl alcohol which is a low melting solid (mp 25.82°C); it also has a substantially higher water miscibility than the other three alcohols. Physical constants (1) of the four butyl alcohols are given in Table 1.

Physical constants (2) for the optically pure stereoisomers of 2-butanol have been reported as follows:

	CAS Registry Number	d^t_4	n^{20}_D	$[\alpha]^{27}_D$
(S)-(+)-2-butanol	[4221-99-2]	0.8025^{27}	1.3954	+13.52
(R)-(-)-2-butanol	[14898-79-4]	0.8042^{25}	1.3970	−13.52

The most common azeotropes (3,4) formed by the butanols are given in Table 2. Butyl alcohol liquid vapor pressure/temperature responses (5,6), which are important parameters in direct solvent applications, are presented in Figure 1. Similarly, viscosity/temperature plots (1) for the four butanols are presented in Figure 2.

The butanols undergo the typical reactions of the simple lower chain aliphatic alcohols. For example, passing the alcohols over various dehydration catalysts at elevated temperatures yields the corresponding butenes. The ease of dehydration increases from primary to tertiary alcohol: *t*-butyl alcohol undergoes dehydration with dilute sulfuric acid at low temperatures in the liquid phase whereas the other butanols require substantially more stringent conditions.

With the exception of the *t*-butyl compound, the butyl alcohols are dehydrogenated to the corresponding carbonyl compounds when passed over copper or silver catalysts at temperatures around 300°C. Thus, *n*- and isobutyl alcohols are dehydrogenated to *n*- and isobutyraldehyde, respectively, while 2-butanol gives methyl ethyl ketone (2-butanone). Continued or more vigorous oxidation of *n*- and isobutyl alcohol yield the corresponding carboxylic acids whereas 2-butanol is degraded to acids of shorter chain length.

The butyl alcohols undergo esterification with organic acids in the usual manner in the presence of trace amounts of mineral acid catalysts. Esterification is fastest with *t*-butyl alcohol and slowest with the primary alcohols although *t*-butyl alcohol undergoes substantial dehydration in the presence of the typical acid esterification catalysts.

Table 1. **Physical Properties of the Butyl Alcohols (Butanols)**

| Common Name CAS Registry Number	n-Butyl alcohol [71-36-3]	Isobutyl alcohol [78-83-1]	sec-Butyl alcohol [78-92-2]	t-Butyl alcohol [75-65-0]
systematic name	1-butanol	2-methyl-1-propanol	2-butanol	2-methyl-2-propanol
formula	$CH_3(CH_2)_3OH$	$(CH_3)_2CHCH_2OH$	$CH_3CH(OH)C_2H_5$	$(CH_3)_3COH$
critical temperature, °C	289.90	274.63	262.90	233.06
critical pressure, kPa[a]	4423	4300	4179	3973
critical specific volume, m^3/kg mol	0.275	0.273	0.269	0.275
normal boiling point, °C	117.66	107.66	99.55	82.42
melting point, °C	−89.3	−108.0	−114.7	25.82
ideal gas heat of formation at 25°C, kJ/mol[b]	−274.6	−283.2	−292.9	−312.4
heat of fusion, kJ/mol[b]	9.372	6.322	5.971	6.703
heat of vaporization at normal boiling point, kJ/g[b]	43.29	41.83	40.75	39.07
liquid density, kg/m^3 at 25°C	809.7	801.6	806.9	786.6[c]
liquid heat capacity at 25°C, $kJ/(mol \cdot K)$[b]	0.17706	0.18115	0.19689	0.2198 at mp
refractive index at 25°C	1.3971	1.3938	1.3949	1.3852
flash point, closed cup, °C	28.85	27.85	23.85	11.11
dielectric constant, ε	17.5^{25}	17.93^{25}	16.56^{20}	12.47^{30}
dipole moment × 10^{30}, $C \cdot m$[d]	5.54	5.47	5.54	5.57
solubility parameter, $(MJ/m^3)^{0.5}$ [e] at 25°C	23.354	22.909	22.541	21.603
solubility in water at 30°C, % by weight	7.85	8.58	19.41	miscible
solubility of water in alcohol at 30°C, % by weight	20.06	16.36	36.19	miscible

[a] To convert kPa to mm Hg, multiply by 7.50.
[b] To convert kJ to kcal, divide by 4.184.
[c] For the subcooled liquid below melting point.
[d] To convert $C \cdot m$ to debyes, divide by 3.336×10^{-30}.
[e] To convert $(MJ/m^3)^{0.5}$ to $(cal/cc)^{0.5}$, multiply by $0.239^{0.5}$.

Table 2. **Azeotropic Mixtures of the Butyl Alcohols**

Components	Weight %	Boiling point of mixture, °C
Binary azeotropes		
1-butanol		
water	42.4	92.6
n-butyl acetate	32.8	117.6
n-butyl formate	76.3	105.8
methyl isovalerate	67	113
cyclohexane	90	79.8
tetrachloroethylene	68	110.0
ethyl isobutyrate	83	109.2
toluene	68	105.5
isobutyl alcohol		
water	33	90
cyclohexane	86	78.1
benzene	91	79.8
toluene	56	101.1
2-butanol		
water	32	88.5
2-butyl acetate	13.7	99.6
Ternary azeotropes		
1-butanol	10	83.6
n-butyl formate	68.7	
water	21.3	
1-butanol	27.4	89.4
n-butyl acetate	35.3	
water	37.3	
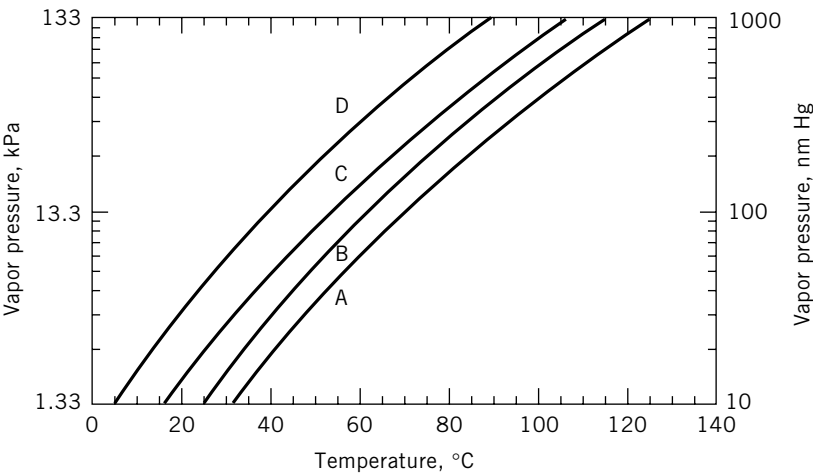
Fig. 1. Vapor pressure of butyl alcohols: A, *n*-butyl; B, isobutyl; C, *sec*-butyl; D, *t*-butyl. To convert kPa to mm Hg, multiply by 7.5.
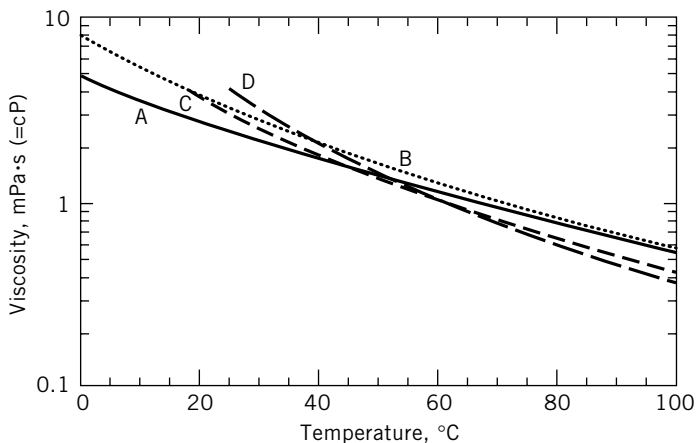
Fig. 2. Liquid viscosity of butyl alcohols: A, 1-butanol; B, isobutyl alcohol; C, 2-butanol; D, *t*-butyl alcohol.

1-Butanol and isobutyl alcohol are aminated with ammonia over alumina at 300–350°C to give the corresponding mono-, di-, and tributylamines.

3. Manufacture

The principal commercial source of 1-butanol is *n*-butyraldehyde [123-72-8], obtained from the Oxo reaction of propylene. A mixture of *n*- and isobutyraldehyde [78-84-2] is obtained in this process; this mixture is either separated initially and the individual aldehyde isomers hydrogenated, or the mixture of isomeric aldehydes is hydrogenated directly and the *n*- and isobutyl alcohol product mix separated by distillation. Typically, the hydrogenation is carried out in the vapor phase over a heterogeneous catalyst. For example, passing a mixture of *n*- and isobutyraldehyde with 60:40 H_2:N_2 over a CuO–ZnO–NiO catalyst at 25–196°C and 0.7 MPa proceeds in 99.95% efficiency to the corresponding alcohols at 98.6% conversion (7,8) (see BUTYRALDEHYDES; OXO PROCESS).

In a process which is now largely of historical interest, 1-butanol has been produced from ethanol [64-17-5] via successive dehydrogenation (to acetaldehyde [75-07-0]), condensation (to crotonaldehyde [4170-30-3]) and hydrogenation.

$$CH_3CH_2OH \longrightarrow CH_3CHO \longrightarrow CH_3CH{=}CHCHO \longrightarrow CH_3CH_2CH_2CH_2OH$$

Alternatively, the intermediate acetaldehyde (qv) for this process was obtained from ethylene by the Wacker process (9). A small amount of *n*-butyl alcohol is produced in the United States by the Ziegler-Natta chain growth reaction from ethylene [74-85-1] (10).

The earliest commercial process to 1-butanol, still practiced extensively in many Third World countries, employs fermentation of molasses or corn products with Clostridium acetobutylicum (11–13). Acetone and ethanol are obtained as coproducts.

A fermentation route to 1-butanol based on carbon monoxide employing the anaerobic bacterium, Butyribacterium methylotrophicum has been reported (14,15). In contrast to other commercial catalytic processes for converting synthesis gas to alcohols, the new process is insensitive to sulfur contaminants. Current productivities to butanol are 1 g/L, about 10% of that required for commercial viability. Researchers hope to learn enough about the bacteria's control mechanisms to be able to use recombinant DNA to make the cells produce more butanol.
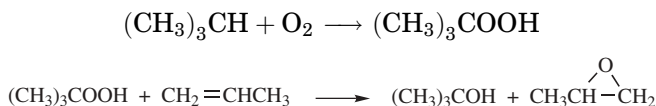
A novel route to 1-butanol from butadiene has been disclosed in the recent patent literature [36]. Butadiene is converted catalytically initially into a mixture of linear and branched butenyl ethers. These are isomerized to the linear butenyl ether, which is subsequently converted into the linear butyral, which is finally hydrogenated to 1-butanol. Alternatively, the intermediate acetal can be hydrolyzed to n-butyraldehyde. High overall efficiencies to n-butanol or n-butyraldehyde are claimed.

As of December 11, 1997, the total U. S. capacity of 1-butanol was 8,111 t per year. Capacity for an additional 733,000 t per year of n-butyl alcohol is operated in Western Europe, and an additional 320,000 t in Southeast Asia (Japan, China and Korea) (10).

Commercial isobutyl alcohol is made almost exclusively from the hydrogenation of isobutyraldehyde obtained by the hydroformylation of propylene. However, this alcohol is also commonly obtained as a coproduct in the Fischer Tropsch synthesis of methanol (16,17).

2-Butanol is produced commercially by the indirect hydration of n-butenes. However, current trends are towards the employment of inexpensive Raffinate II type feedstocks, ie, C-4 refinery streams containing predominantly n-butenes and saturated C-4s after removal of butadiene and isobutylene. In the traditional indirect hydration process, n-butenes are esterified with liquid sulfuric acid and the intermediate butyl sulfate esters hydrolyzed. DEA Mineraloel (formerly Deutsche Texaco) currently operates a 2-butanol plant employing a direct hydration of n-butenes route (18) with their own proprietary catalyst.

The Arco Propylene Oxide Process produces t-butyl alcohol as a coproduct of propylene oxide [75-56-9] when isobutane is used as a starting material.

$$(CH_3)_3CH + O_2 \longrightarrow (CH_3)_3COOH$$

$$(CH_3)_3COOH + CH_2{=}CHCH_3 \longrightarrow (CH_3)_3COH + CH_3CH\overset{O}{-}CH_2$$

The process can be modified to give predominantly or solely t-butyl alcohol. Thus, t-butyl hydroperoxide (and t-butyl alcohol) produced by oxidation of isobutane in the first step of the process can be decomposed under controlled, catalytic conditions to give gasoline grade t-butyl alcohol (GTBA) in high selectivity (19−22).

$$(CH_3)_3COOH \xrightarrow{\text{Mo catalyst}} (CH_3)_3COH + \frac{1}{2}O_2$$
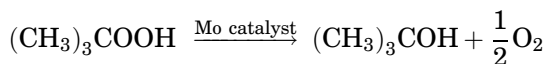
The oxygen released is recycled to the isobutane oxidation step. GTBA contains some methanol and acetone coproducts and is used as a blending agent for gasoline.

The other significant industrial route to *t*-butyl alcohol is the acid catalyzed hydration of isobutylene (24), a process no longer practiced in the United States. Raffinate I, C-4 refinery streams containing isobutylene [115-11-7], *n*-butenes and saturated C-4s or C-4 fluid catalytic cracker (FCC) feedstocks (23) may be employed.

4. Uses

The largest volume commercial derivatives of 1-butanol in the United States are *n*-butyl acrylate [141-32-2] and methacrylate [97-88-1] (10). These are used principally in emulsion polymers for latex paints, in textile applications and in impact modifiers for rigid poly(vinyl chloride). The consumption of *n*-butanol in the United States for acrylate and methacrylate esters was 270,000 t in 1997(10).

Butyl glycol ethers, the largest volume derivatives of *n*-butyl alcohol used in solvent applications (10), are obtained from the reaction of 1-butanol with ethylene oxide. The most important of these derivatives, 2-butoxyethanol, is used principally in vinyl and acrylic paints as well as in lacquers and varnishes. It is also employed in aqueous cleaners to solubilize organic surfactants. 2-Butoxyethanol [111-76-2] has achieved some growth at the expense of the lower alkoxyethanols (ie, methoxy and ethoxyethanol) because of 2-butoxyethanol's lower toxicity.

1-Butanol is used as a direct solvent in paints and other surface coatings. It acts synergistically with butyl acetate as a latent solvent system for nitrocellulose lacquers and thinners to give a solvent system stronger than either solvent alone. Other direct solvent applications for *n*-butyl alcohol are in the formulation of pharmaceuticals, waxes, and resins. Slightly more 1-butanol is consumed in western Europe in direct solvent applications than in the production of butyl acrylate and methacrylate in contrast to the United States where the acrylate and methacrylate esters are the predominent end products.

Butyl acetate [123-86-4], one of the more important derivatives of *n*-butyl alcohol produced commercially, is employed as a solvent in rapid drying paints and coatings. In some instances, butyl acetate, $C_6H_{12}O_2$, has replaced ethoxyethyl acetate [111-15-9] due to the latter's reported toxicity and teratogenicity. Butyl acetate is used in leather treatment, perfumes, and as a process or reaction solvent and is also used extensively with wood coatings, maintenance coatings, and in coatings for containers and closures.

Additional commercial markets for 1-butanol include plasticizer esters (eg, dibutyl phthalate), butylated melamine–formaldehyde resins, and mono-, di-, and tributylamines.

Historically, isobutyl alcohol was an unwanted by-product of the propylene Oxo reaction. Indeed, isobutyraldehyde the precursor of isobutyl alcohol was occasionally burned for fuel. However, more recently isobutyl alcohol has replaced *n*-butyl alcohol in some applications where the branched alcohol appears to have preferred properties and structure. However, supplies of isobutyl alcohol have declined relative to overall C-4 alcohols, especially in Europe, with the conversion of many Oxo plants to rhodium based processes which give higher normal to isobutyraldehyde isomer ratios. Further the supply of

isobutyl alcohol at any given time can fluctuate greatly, since it is the lowest valued derivative of isobutyraldehyde, after neopentyl glycol, methyl isoamyl ketone and certain condensation products (10).

The principal industrial application for isobutyl alcohol is as a direct solvent replacement for 1-butanol. It is also used as a process solvent in the flavor and fragrance, pharmaceutical, and pesticide industries. The maximum employment of isobutyl alcohol was in the mid-1980s when it had a distinct price advantage over 1-butanol (10). More recently, however, with increased demand for other value added derivatives of isobutyraldehyde, the price differential between iso-butyl and *n*-butyl alcohols has diminished resulting in a switching back by some consumers to 1-butanol.

Some commercially important isobutyl derivatives include isobutyl acetate, employed as a replacement solvent for *n*-butyl acetate; zinc dialkyldithiopho-sphate (ZDPP) lube oil additives; isobutyl acrylate [106-62-8] and methacrylate [97-86-9] monomers; isobutylamines; and amino resins (qv).

t-Butyl alcohol, obtained from hydration of Raffinate I, can be dehydrated and subsequently refined to high purity, polymer-grade isobutylene (25). How-ever, the major use of *t*-butyl acohol is to produce methyl *t*-butyl ether (MTBE) gasoline additive by initial dehydration of *t*-butyl alcohol to isobutylene which is subsequently reacted with methanol in the presence of an acid catalyst (see ESTERS ORGANIC).

t-Butyl alcohol is employed as a feedstock in Japan to make methyl metha-crylate monomer. In one such process (26), the alcohol is oxidized (in two steps) to acrylic acid, which is then esterified with methanol. In a similar process (27), *t*-butyl alcohol is oxidized in the presence of ammonia to give methacrylonitrile [126-98-7]. The latter is hydrolyzed to methacrylamide [79-39-0] which then reacts with methanol to yield methyl methacrylate [80-62-6].

The glycol ethers obtained from *t*-butyl alcohol and propylene oxide, eg, 1-*t*-butoxy-2-propanol, have lower toxicities than the widely employed 2-butoxyetha-nol and are used in industrial coatings and to solubilize organic components in aqueous formulations (28).

2-Butanol is employed almost exclusively to make the solvent methyl ethyl ketone [78-93-3], accounting for almost 90% of its global use [10]. In analogy to the primary butanols, 2-butanol is also employed as a direct solvent, as well as a blend with aromatic hydrocarbons, ketones and other alcohols.

5. Quality Specifications and Analysis

With the exception of gasoline grade *t*-butyl alcohol (GTBA), whose purity is typi-cally 93–94% the butanols are generally marketed in bulk in the pure isomeric form. ASTM specifications (29) for *n*-, iso- and *sec*-butyl alcohol are given in Table 3. Butanol specification purity is routinely obtained by gas chromatogra-phy (30).

A cosmetics industry specification for *t*-butyl alcohol (31) is 99.5% alcohol, a maximum 0.002% acidity (as acetic acid), a maximum of 0.1% water, and a max-imum of 0.001% nonvolatile matter.

Table 3. **ASTM Specification for Butyl Alcohols**

ASTM standard	*n*-Butyl D 304-85	Isobutyl D 1719-86	*sec*-Butyl D 1007-85	Specification method
apparent specific gravity				
20/20°C	0.810−0.813	0.802−0.804	0.809−0.809	D268
25/25°C	0.807−0.810	0.794−0.801	0.804−0.806	
color (Pt−Co), max	10	10	10	D1209
distribution range,[a] °C	117 ± 1.7	107.9 ± 2	98−101	D1078
nonvolatile material, mg/100 mL, max	5	5	5	D1353
water, wt % max	0.1	0.2	0.5	D1364 and 1476
acidity, as acetic acid, wt % max	0.005	0.003	0.002	D1613

[a] At 101.3 kPa = 760 mm Hg.

6. Health, Safety, and Environmental Considerations

All four butanols are thought to have a generally low order of human toxicity (32). However, large dosages of the butanols generally serve as central nervous system depressants and mucous membrane irritants. Animal toxicity and irritancy data (32) are given in Table 4.

The reported odor threshold limits (33) for *n*-, iso, *sec*- and *t*-butyl alcohol are 0.83, 1.6, 2.6, and 47 ppm, respectively.

Flammability characteristics (1) of the four butanols are given in Table 5.

Table 4. **Animal Toxicity and Irritancy Data for Butanols**

	LD_{50} rats, mg/kg, oral	LD_{50} rabbits, g/kg, intravenous	Inhalation	Eye injury to rabbits
1-butanol	4.36	5.3	8,000 ppm for 4 h (all rats survived)	5 µL (severe corneal damage)
isobutyl alcohol	3.4	0.6	10,600 ppm for 6 h (all mice survived)	one drop caused moderate to severe irritation
2-butanol	6.5	0.8	16,000 ppm for 4 h (5 of 6 rats died)	severe corneal injury (rabbit)
t-butyl alcohol	3.6	1.5 (mouse)		

Table 5. **Flammability Characteristics of the Butanols**

	Flash point, °C	Autoignition temperature, °C	Explosive limits, vol %	
			lower	upper
n-butyl	2−3	342.85	1.4	11.2
isobutyl	28	426.85	1.7	10.9
sec-butyl	21	405.85	1.7	9.8
t-butyl	11	477.85	2.4	8.0

All four butanols are registered in the United States on the Environmental Protection Agency Toxic Substances Control Act (TSCA) Inventory, a prerequisite for the manufacture or importation for commercial sale of any chemical substance or mixture in quantities greater than a 1000 pounds (454 kg). Additionally, the manufacture and distribution of the butanols in the United States are regulated under the Superfund Amendments and Reauthorization Act (SARA), Section 313, which requires that anyone handling at least 10,000 pounds (4545 kg) a year of a chemical substance report to both the EPA and the state any release of that substance to the environment.

7. Storage and Handling

The C-4 alcohols are preferably stored in baked phenolic-lined steel tanks. However, plain steel tanks can also be employed provided a fine porosity filler is installed to remove any contaminating rust (34).

Storage under dry nitrogen is also recommended since it limits flammability hazards as well as minimizing water pickup. There is a report of an explosion occurring during distillation of a sample of aged 2-butanol (35), suggesting that dangerous levels of peroxides can form in 2-butanol on storage in air.

Piping and pumps used for transfer of the butanols can be made of the same metal as tanks. Centrifugal pumps with explosion-proof electric motor drives are recommended (34).

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