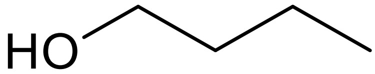
UK BioChem 10 – 10 n-Butanol

Name	n-butanol
Synonyms	butan-1-ol, 1-butanol, butyl alcohol
CAS Number	71-36-3
Molecular formula	$C_4H_{10}O$
MW	74.12 g mol^{-1}
Patents related to synthesis	279



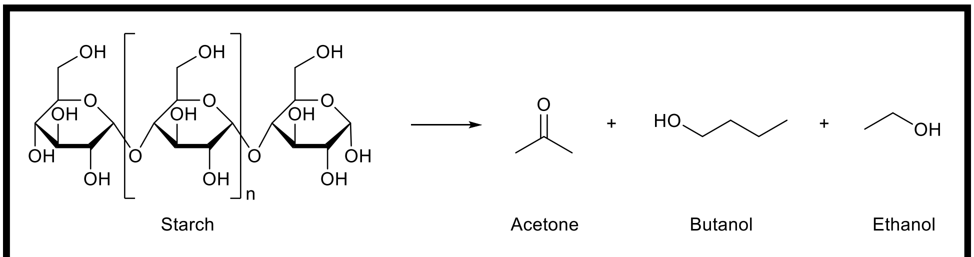
Why is it of interest?

Butanol is a simple C4 primary alcohol that is a promising bio-fuel for replacement/blending with petrol as opposed to the more commonly used alternative. This is as it has a higher energy content (29.2 MJ dm^3), lower volatility (117 °C) and is not as soluble in water compared to ethanol, it also has a comparable octane number (87) to that of petrol (95-98). Butanol is recognised protic solvent, with wide use within the paints and coatings industry. It is also employed as a reactive solvent in the formation of esters, with butyl acetate and butyl acrylate being notable high volume examples. Functional change of the -OH group can yield a variety of useful derivatives, with dehydration to 1-butene a prominent example.

Feedstocks for butanol

n-Butanol is already produced on an industrial scale from fossil resources *via* propylene hydroformylation. However before this process became established in the 1950, fermentation was the principal production route for butanol.[1] This process required bacteria of the *clostridium* genus and utilised 1st generation feedstock, principally starch. Free sugars can also be used as a feedstock, but require pre-processing, where as corn, sugar cane, sugar beet and potatoes have also all been used to directly produce n-butanol with this bacteria.[2] Second generation biomass feedstock has also been utilised either with pre-treatment followed by hydrolysis to free sugars and then fermentation or by combining the final steps simultaneously.[3] Additionally taking ethanol , dehydrogenating, coupling and then hydrogenating is also an area under much research due to the ease of quantitatively fermenting C2 alcohol from both sugars and increasingly from secondary biomass at industrial scale.

Highlighted routes of production



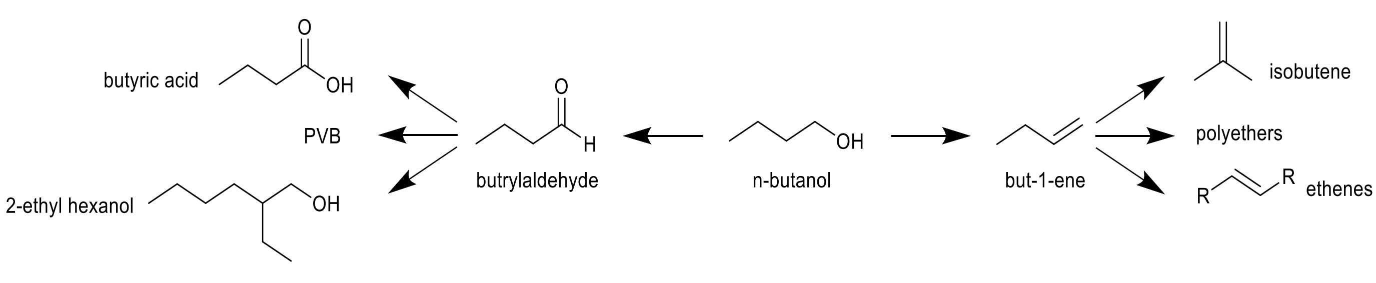
The early patented route to produce bio-butanol was termed the Weizmann process, which was implemented principally to produce acetone for munitions as part of the WW1 war effort. At the time n-butanol was considered an unwanted side product. This process is now more commonly referred to as ABE fermentation as the 3 products, acetone, butanol and ethanol, are produced in a 3:6:1 ratio by mass, alongside carbon dioxide and hydrogen. Here the issues are concentration of free sugar and n-butanol, both of which inhibit the overall process. As such the best yields are achieved with low feedstock loading and continual removal of the n-butanol. This has issues of low product concentration, high water footprint and high energy costs. The highest reported yield of n-butanol *via* this process is 45.9% (AE 45.7%, RME 21%) although this is alongside yields of acetone (29.4%) and ethanol (12.4%) by-products (total 3-product yield of 87.6%).[4] The best reported 2nd generation feedstock yields gave an overall ABE yield of 0.41 g per gram of free sugar, corresponding to 0.28 g per gram of wheat straw. With relation to just the n-butanol, this is 0.16 g per g of wheat straw with the bacteria consuming both C6 and C5 sugars (from cellulose and hemicellulose), equating to a yield of 51.6%. The highest yield reported for n-butanol from free sugar *via* ethanol is 36.9% (AE 40.1%, RME 14.8%) over a heterogeneous calcium hydroxyapatite catalyst at high temperature and conducted in the gas phase.

Current applications of butanol

The major current use of n-butanol is as a solvent, where it is applied in paints and coatings to reduce viscosity and improve film forming. n-Butanol has begun to be incorporated in fuel in the US, but take up has been slower than expected.[6] The reaction of n-butanol with ethylene oxide produces a range of glycol ethers which are widely used in paints, cosmetics and as de-icers by the aviation industry. Other solvents such as butyl acetate also have significant markets. Butanol can be readily esterified to give plasticisers such as dibutyl phthalate (DBP), although this is coming under increased regulation as a suspected endocrine disruptor.[7] Other butyl esters are widely applied, with butyl acrylate and butyl methacrylate being high volume chemicals in the production of emulsion polymers, binders and adhesives.

Future markets and applications

Obviously the largest potential market for n-butanol is as a road fuel either being blended with or directly replacing petrol without the need to mechanically alter any vehicle, although the price of reduced performance and increased consumption.[8] The potential volumes here are incredibly large, but the value of the product is low, meaning production would have to become considerably cheaper than at present. Higher value however can be gained through greater functionality and butanol offers a range of easily accessible compounds that can act as drop in replacements to current technology. Dehydration of bio-ethanol to bio-ethene is a commercial reality and similarly n-butanol can be reacted to give but-1-ene in high yield.[9] This can be used to gain a variety of alkenes through metathesis, be isomerised to give isobutene (which is the current building block for a vast array of chemical compounds) or be polymerised directly. Butanol can also be converted into butyraldehyde which can be used to form branched alcohols, polyvinyl butyrate (PVB) and butyric acid.[10]



References: **1.** US1315585A, **2.** DOI.org/10.1038/sj.jim.7000114 **3.** DOI.org/10.1016/j.biombioe.2007.07.004
4. DOI.org/10.1007/s12010-009-8770-1 **5.** WO2012035772 (A1), **6.** https://afdc.energy.gov/fuels/emerging_biobutanol.html,
7. https://www.echa.europa.eu/web/guest/substances-restricted-under-reach/-/dislist/details/0b0236e1807e2d0d,
8. DOI.org/10.1016/j.rser.2016.11.213, **9.** EP1953129 (A1), **10.** CN105439786 (A)

Additional feedstocks

Three sets of feedstock have been investigated to determine how much of each would be required to supply a 20 kton butanol plant. These figures would also produce roughly 10 kton of acetone and 3 kton of ethanol per annum, *i.e.* 33 kton ABE plant.

First generation biomass

The crops presented are those that are most intensively farmed in the UK, principally as food crops, although a small percentage of wheat, maize and sugar beet are also utilised in industrial applications. Sugar cane figures are from Brazil.*

crop	ktons needed to supply a 20 kton n-butanol plant	ktons produced per annum (UK)	% required
wheat	141.8	14837	0.96
barley	141.8	7169	1.98
maize	139.8	3054	4.58
sugar beet	608.7	8325	7.31
potatoes	591.3	5075	11.65
field beans	574.9	965	59.58
oats	156.8	875	17.92
sugar cane*	1034.9	666925	0.16

Energy crops

Both Miscanthus and short rotation coppice are primarily grown for energy generation in biomass boilers. Data here for the latter has been generated using willow as this is the crop most commonly used. Forestry waste is material left in woodland post harvesting and generally is 10-15% by mass compared to the lumber harvested. The average value has been used here and only softwood has been considered. Unlike other fermentations, here both the cellulose and hemicellulose components are utilised.

crop	ktons needed to supply a 20 kton n-butanol plant	ktons produced per annum (UK)	% required
forestry waste	356.8	1340.88	26.61
miscanthus	146.1	87.50	166.99
short rotation coppice	161.1	28.20	571.19

Second generation biomass

These are by-products of food production which contain an appreciable quantity of cellulose that can be depolymerised to give sugars for use in the synthesis of platform molecules. Unlike other fermentations for some of the UKBioChem10, for n-butanol both the cellulose and hemicellulose components are utilised. Additionally included is the steam autoclaving of municipal solid waste (the Wilson process), the organic fraction of which is converted into a fibre, rich in free sugars.

feedstock	ktons needed to supply a 20 kton n-butanol plant	ktons produced per annum (UK)	% required
wheat straw	200.6	3828	5.24
barley straw	240.7	1850	13.01
maize stover	162.6	916	17.75
oilseed rape straw	188.0	379	49.58
oat straw	222.8	247	90.31
MSW	767.1	15734	4.88