



Sustainability metrics of 1-butanol



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ABSTRACT

The production of chemicals from renewable resources often has to compete with a petrochemical process, optimized during several decades. Four sustainability metrics were used to compare the production of 1-butanol via the petrochemical and biobased processes: material efficiency, energy efficiency, land use and total costs. The selected petrochemical process is the oxo synthesis, i.e., the hydroformylation of propene, followed by the hydrogenation of the formed aldehydes with a yield of 95% 1-butanol. The selected biobased process is the anaerobic continuous acetone–butanol–ethanol (ABE) fermentation on glucose substrate from maize starch and a product recovery via distillation with a yield of 0.42 g ABE g⁻¹ glucose. The petrochemical process has significantly higher material and energy efficiencies, compared to the biobased process. For the biobased process, land is used to produce the biomass (0.29 ha ton⁻¹), while no land is used for the petrochemical process. Production costs are higher for the biobased process (1041 EUR ton⁻¹), compared to the petrochemical process (915 EUR ton⁻¹). Based on the four metrics, the petrochemical process is preferable to the biobased process. However, biomass for sustainable fuels and chemicals will be the only resource for future generations. The efficiency of the biobutanol production can be improved by altering upstream processes, by metabolic engineering, by decreasing byproduct formation and by improving in situ product recovery techniques.

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1. Introduction

1-Butanol or *n*-butanol is an aliphatic saturated C₄ alcohol with molecular formula C₄H₉OH (MW 74.12 g mol⁻¹). 1-Butanol is a colorless liquid with a characteristic odor. It is completely miscible with common organic solvents, but only sparingly soluble in water (7.7 wt% at 20 °C) [1]. The main effect of exposure to excessive concentrations is irritation of the mucous membranes and depression of the central nervous system. Animal studies have shown low acute oral, dermal and inhalation toxicity [1].

1-Butanol is a bulk chemical with a diverse use. It is used principally for surface coating [1]. It is used directly as solvent for varnishes or it is converted into derivatives that are used as solvents or monomers. 1-Butanol prevents blushing of certain coatings when they dry under humid conditions. It can also be used to regulate the viscosity and to improve the flow properties of varnishes. Butyl acrylate is since the 1990s an essential component of latex paints. 1-Butanol can also be used for the production of butylamines. It is used in the plastics and textile sector, for example as a coagulation bath for spinning acrylic fibers. The use of 1-butanol in 2010 was 30% in butyl acrylate, 25% in butyl acetate, 20% in plasticizers and resins, 15% as solvent and 10% in glycol ethers and esters [1].

A recent application of 1-butanol is its use as a direct replacement of gasoline or as a fuel additive. Biobutanol is expected to play an important role in the next generation of biofuels [2]. It is a better fuel than bioethanol due to the higher energy density of 1-butanol (29.2 MJ L⁻¹), compared to 19.6 MJ L⁻¹ for ethanol. 1-Butanol has also a lower tendency than ethanol to absorb water. It is also less corrosive for certain motor parts, compared to ethanol.

The 1-butanol capacity in the world in 2010 was 3.6 million tons [1]. However, there was an excess capacity for 1-butanol production with a plant utilization of 83% in 2010 [1].

2. Production

2.1. Petrochemical processes

For the production of 1-butanol, there are three petrochemical processes with industrial importance, as shown in Fig. 1: (a) the oxo synthesis, (b) the Reppe synthesis and (c) the crotonaldehyde hydrogenation [1,3].

The most important process is the oxo synthesis, i.e., the hydroformylation of propene, followed by the hydrogenation of the formed aldehydes. Carbon monoxide and hydrogen are added to the C–C double bond in the liquid phase in the presence of catalysts like Co, Rh or Ru. An isomeric aldehyde mixture of 1-butanol and 2-methylpropanal is obtained. Catalytic hydrogenation of the aldehydes leads to the formation of the corresponding alcohols. Until

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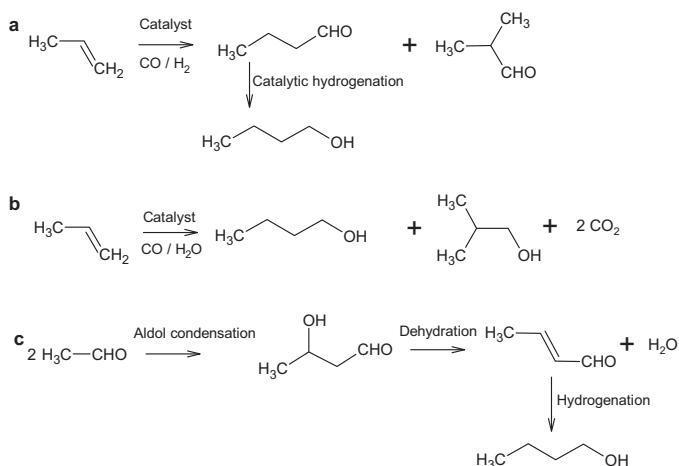


Fig. 1. Petrochemical processes for the production of 1-butanol: (a) oxo synthesis, (b) Reppe synthesis, and (c) crotonaldehyde hydrogenation [3].

the 1970s, a high pressure of $20\text{--}30 \times 10^6$ Pa CO/H_2 at $100\text{--}180^\circ\text{C}$ in the presence of a Co-catalyst was used. It yielded about 75% 1-butanol and 25% 2-methyl-1-propanol (or isobutanol). New processes at lower pressure of $1\text{--}5 \times 10^6$ Pa with a Rh-catalyst yielded up to 95% 1-butanol and 5% 2-methyl-1-propanol. In 2010, the biggest producers were BASF, Oxea Group and the Dow Chemical Company [1].

1-Butanol can also be produced by the Reppe synthesis, i.e., the carbonylation of propene, developed by Reppe in 1942. In this process, propene, carbon monoxide and water react at a pressure of $0.5\text{--}2 \times 10^6$ Pa and a temperature of 100°C in the presence of a catalyst (tertiary ammonium salt or polynuclear iron carbonyl hydrides) [1]. 1-Butanol and 2-methyl-1-propanol are directly formed in a ratio of 86:14. The Reppe process was not as successful as the oxo synthesis with the Co catalyst despite the more favorable ratio of *n*-butanol to isobutanol and the milder reaction conditions. This was due to the more expensive process technology.

Until the 1950s, the petrochemical route for production of 1-butanol was based on an aldol condensation of acetaldehyde, followed by a dehydration and subsequent hydrogenation of crotonaldehyde. With the development of the oxo synthesis, this process was abandoned. The aldol condensation was performed at ambient temperature and pressure in the presence of alkaline catalysts. The dehydration was induced by acidification with acetic or phosphoric acids and subsequent distillation. The hydrogenation was performed in the gas or liquid phase with a Cu catalyst. About 1000 kg of 1-butanol were obtained from 1350 kg of acetaldehyde [1].

2.2. Biobased process

The biological formation of 1-butanol has a long history [2], starting in 1862 with a fermentation report of Pasteur [4]. The acetone–butanol–ethanol (ABE) fermentation became the second largest biotechnological process ever performed, only beaten in volume by ethanol fermentation. During World War I, acetone helped the ABE fermentation to an industrial breakthrough for the preparation of cordite, used in munition during the war. Weizmann patented the production of acetone and alcohols from starchy material by a mixed culture of mainly *Clostridium acetobutylicum* in 1915. There was almost no use of butanol during the war. After the war, 1-butanol was used for the production of butyl acetate, a solvent for quick-drying lacquers, needed in large amounts by the growing automobile industry. Up to 1950, about two thirds of the butanol supply in the world came from the biological process.

The largest plant was located in the USA with a total ABE fermentation capacity of $18\,168\text{ m}^3$. Facilities in South Africa and the former Soviet Union (using lignocellulose hydrolysates) operated until the 1980s and until 2004 in China (using continuous culture technology). The decline of the fermentation process was caused by increasing substrate costs (molasses) and low crude oil prices, leading to cheaper petrochemical production [2]. Recently, the ABE fermentation has gained renewed interest from the biofuel point of view.

Butanol can be produced from various commercial raw materials like molasses, whey permeate and corn [5]. Mostly clostridia (strictly or moderately anaerobic, spore-forming, Gram-positive bacteria) perform the ABE fermentation from glucose or starch in a complex manner. The most widely studied clostridia are *C. acetobutylicum* and *C. beijerinckii*. During the acidogenic growth phase, organic acids like lactic, acetic and butyric acid and H_2 and CO_2 are formed. In the stationary, solventogenic phase, acetone, 1-butanol and ethanol are produced [6]. In a typical fermentation with *C. acetobutylicum*, the total ABE concentration is 20 g L^{-1} in an ABE ratio of 3:6:1 and a yield of $0.29\text{--}0.33\text{ g ABE g}^{-1}$ glucose [5]. Qureshi and Blaschek [7] reported on a fermentation with the mutant strain *C. beijerinckii* BA101 with a total ABE concentration of 33 g L^{-1} in a ABE ratio of 3:16:1 and a yield of $0.40\text{--}0.50\text{ g ABE g}^{-1}$ glucose.

Most of the enzymes and corresponding genes have been characterized. To reduce the relatively high substrate costs, cheap low-grade agricultural substrates that cannot be used for food or feed are favored [6]. Also lignocellulosic substrates are investigated, but solventogenic clostridia cannot hydrolyse cellulose, so a hydrolytic pretreatment of the lignocellulose is required. Due to the inhibitory effects of butanol, the final product titers and the initial carbohydrate concentrations are relatively low, while byproduct formation (acetone and ethanol) complicates the downstream processing. Several strategies are investigated to overcome these problems. Metabolic engineering is investigated to target increased product specificity (less byproducts) and increased 1-butanol titers, while in situ product removal can be used to reduce product inhibition. The default technology for recovery of biobutanol is distillation, the most energy intensive step in the entire production process [8]. For 1-butanol, energetic gains are expected by combining it with a selective and efficient primary recovery step. Therefore, integrating the fermentation with the first step of the downstream process by using a suitable in situ product recovery technique is an interesting strategy to overcome the above described problems. The energy consumption, overall economics, robustness and long-term performance of the integrated technology will define the success of such integrated process schemes and should be studied in more detail.

3. Metrics

To compare the petrochemical process with the biobased process for 1-butanol, four sustainability metrics were chosen:

Table 1
Material balance for a 1-butanol fermentation plant [5].

| | kg |
|-------------------|------------------|
| Feed | |
| Glucose | $3.7\text{E}+08$ |
| Product | |
| Butanol | $1.2\text{E}+08$ |
| Acetone | $2.4\text{E}+07$ |
| Ethanol | $7.5\text{E}+06$ |
| Gases | $2.3\text{E}+08$ |
| Fiber and protein | $8.8\text{E}+07$ |
| Germ/oil | $2.0\text{E}+07$ |
| Cell mass | $4.2\text{E}+07$ |
| Polysaccharide | $3.2\text{E}+07$ |

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