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Review

Fermentative production of butanol: Perspectives on synthetic biology

Sonil Nanda[a], Dasantila Golemi-Kotra[b], John C. McDermott[b], Ajay K. Dalai[c], Iskender Gökalp[d], Janusz A. Kozinski[a,*]

[a] Department of Earth and Space Science and Engineering, York University, Ontario, Canada
[b] Department of Biology, York University, Ontario, Canada
[c] Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatchewan, Canada
[d] Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), Centre National de la Recherche Scientifique (CNRS), Orléans, France

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ABSTRACT

Apprehensions relating to global warming, climate change, pollution, rising energy demands as well as fluctuating crude oil prices and supply are leading to a shift in global interest to find suitable alternatives to fossil fuels. This review aims to highlight the many different facets of butanol as an advanced next-generation transportation biofuel. Butanol has fuel properties almost on a par with gasoline, such as high energy content, low vapor pressure, non-hygroscopic nature, less volatility, flexible fuel blends and high octane number. The paper reviews some recent advances in acetone-butanol-ethanol fermentation with special emphasis on the primary challenges encountered in butanol fermentation, including butanol toxicity, solvent intolerance and bacteriophage contamination. The mechanisms for butanol recovery techniques have been covered along with their benefits and limitations. A comprehensive discussion of genetic and metabolic engineering of butanol-producing microorganisms is made for the prospective development of industrially-relevant strains that can overcome the technical challenges involved in efficient butanol production.

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Contents

Introduction

Awareness concerning the production of renewable transportation fuels has been growing rapidly. Waste biomasses that have tremendous potential to supplement the production of alternative biofuels include lignocellulosic feedstocks (e.g. agricultural and forestry residues), algae, municipal solid wastes, sewage sludge, industrial effluents and cattle manure [1–3]. Biobutanol, especially *n*-butanol (C_4H_9OH) is a four carbon primary alcohol that is gaining attention as a gasoline substitute. Butanol is often considered as a next-generation biofuel over ethanol (C_2H_5OH) that can be derived from lignocellulosic feedstocks through microbial fermentation. The many advantages of biobutanol are illustrated in Fig. 1. In contrast to ethanol, which is usually blended up to 85% with gasoline, butanol can be used in its pure form or blended at

* Corresponding author at: Lassonde School of Engineering, York University, Toronto, Ontario, M3J 1P3, Canada.
E-mail address: janusz.kozinski@lassonde.yorku.ca (J.A. Kozinski).

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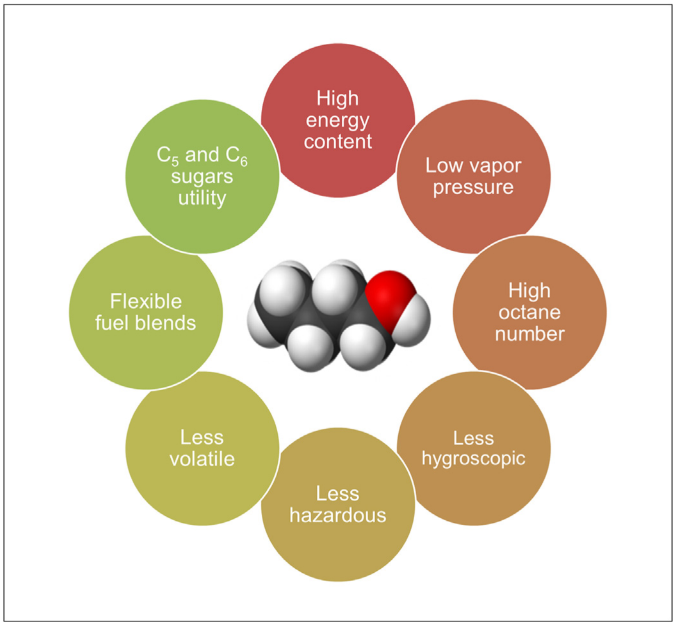

Fig. 1. Advantages of butanol as an advanced next-generation biofuel.

relatively higher concentrations [4]. Biobutanol is often referred to as a drop-in fuel that can be used in existing motor engines and vehicular infrastructures without mechanical tailoring.

Butanol is considered to have superior fuel properties to ethanol that make it a better replacement for gasoline. Table 1 summarizes some significant fuel properties of butanol, ethanol and gasoline. The energy value of butanol (29.2 MJ/L) is 30% greater than that of ethanol (21.2 MJ/L) and 10% lesser than that of gasoline (32.5 MJ/L). On the other hand, the octane ratings (research octane number, RON and motor octane number, MON) of butanol are much closer to gasoline, indicating some similar fuel properties. The air-to-fuel ratio of butanol (11.2) is much closer to that of gasoline (14.7) [7]. Ethanol is highly oxygenated (35% oxygen content) compared to butanol (22% oxygen content) [8]. Compared to ethanol, the restorative qualities of butanol as a fuel are non-sensitivity to water, less corrosiveness, lower volatility, less flammability and reduced toxicity to physical exposure. Moreover, butanol's low vapor pressure enables its use in existing gasoline transport pipelines and filling stations without considerable retrofitting. Furthermore, the rising crude oil prices and aggregating concerns over pollution and global warming have renewed a common interest in the biological production of butanol as an alternative fuel.

Table 1
Fuel properties of ethanol, butanol and gasoline.

Property	Gasoline	Ethanol	Butanol
Chemical formula	H, C_4–C_{12}	C_2H_5OH	C_4H_9OH
Molecular weight (g/mol)	114.23[a]	46.07	74.12
Density at 20 °C (g/m^3)	0.7	0.789	0.81
Acidity (p K_a)	–	15.9	16.1
Viscosity at 25 °C (mPa s)	0.6	1.074	2.573
Flash point (°C)	−43	17.2	35
Auto-ignition temperature (°C)	280	365	343
Calorific value (MJ/L)	32.5	21.2	29.2
Air-fuel ratio	14.7	9	11.2
Research octane number	91–99	129	96
Motor octane number	81–89	102	78
Heat of vaporization (MJ/kg)	0.36	0.92	0.43
Specific gravity at 15.6 °C	0.72–0.78	0.79	0.81
Boiling point (°C)	125[a]	78.4	117.4
Melting point (°C)	−56.6[a]	−114	−89.8
Lower heating value (MJ/kg)	43.4	26.9	34.3
Higher heating value (MJ/kg)	46.5	29.8	37.3
Reid vapor pressure (psi)	8–15	2.3	0.3
Solubility in water (%) at 25 °C	–	100	7.3
Oxygen content (%)	0	35	22

References: Dürre [4]; Lee et al. [5]; Surisetty et al. [6]; MacLean and Lave [7]; Szulczyk [8].
[a] The value is represented for octane as a major component of gasoline.

Approximately 10–12 billion pounds of butanol are generated every year through petrochemical routes [9], which currently accounts for a nearly $7–8.4 billion market [5]. Moreover, butanol is expected to achieve about 20% of the global gasoline and diesel requirements in the near future. The current worldwide demand for butanol exceeds 1.2 billion gallons per annum, which is valued at over $6 billion [10]. The market for butanol is expanding at the rate of 3% per year [5], which is predicted to reach $9.9 billion by 2020 [11].

Recently, GranBio (Brazilian Biotech Company in Alagoas) and Rhodia (Solvay International Chemical Group in Belgium) announced their partnership to produce butanol from sugarcane bagasse in an impending refinery in Brazil [12]. The biorefinery is envisaged to produce 100 kt of solvents every year. Butamax™ Advanced Biofuels, a joint endeavor of British Petroleum (London, UK) and DuPont (Delaware, USA), is developing sustainable technologies to make butanol an inexpensive, high-value and drop-in biofuel for the future transportation market. Butamax™ technology is intended for converting polysaccharides from different feedstocks including corn and sugarcane into butanol using some existing biorefining facilities [13]. Furthermore, some global enterprises that have lately announced their endeavors in commercializing butanol as a next-generation biofuel include Butamax™ (a joint venture of British Petroleum and DuPont), GreenBiologics (Oxon, UK), Cobalt Biofuels (California, USA), Tetravitae Bioscience Inc. (Illinois, USA), Gevo (Colorado, USA), METabolic EXplorer (Clermont-Ferrand, France), Butalco (Fürigen, Switzerland) and Cathay Industrial Biotech (Shanghai, China).

Although promising, the butanol biorefining process suffers from several drawbacks such as solvent toxicity towards fermenting microorganisms, lesser yields, expensive recovery technologies and metabolic intolerance of butanol-producing bacteria. This review aims to highlight the advantages of butanol

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