Biotechnology Advances 33 (2015) 1493–1501

Contents lists available at ScienceDirect

Biotechnology Advances

journal homepage: www.elsevier.com/locate/biotechadv

Research review paper

Current status and prospects of industrial bio-production of n-butanol in China

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ARTICLE INFO

Available online 27 October 2014

Keywords:
n-Butanol
Fermentation
China

ABSTRACT

n-Butanol is an important bulk chemical. Commercial fermentative production of n-butanol has been applied more than 100 years ago but is currently more costly than production from propylene and syngas. Renewed interest in biobutanol as a biofuel has spurred technological advances to the fermentation process. This article reviewed the recent status including the commercialization, pilot production and R&D activities of n-butanol fermentation in China. Long-term bio-production of n-butanol as a next generation biofuel and biochemical from biomass waste and steel mill off-gas needs technology breakthroughs and more environmental concerns from policymakers.

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1. Introduction

n-Butanol (or butyl alcohol) is a four-carbon, straight chained alcohol, and it is an important chemical precursor for paints, polymers, and plastics. The global market for n-butanol was estimated to be 3.8 million tons in 2012, with an estimated worth of approximately $7 billion, which is forecast to grow by 4.6% from 2013 to 2018. China consumed around 34.8% of the global n-butanol demand in 2012, and approximately 60% of its consumption came from imports.[1] Fermentative butanol production has a long history, which can be traced back to World War I, and was once one of the largest fermentation industries (Jones and Woods, 1986; Schiel-Bengelsdorf et al., 2013). The process is also called ABE fermentation because three products, acetone, butanol, and ethanol, are normally produced in a ratio of 3:6:1, respectively, by solventogenic clostridia. The decline of industrial ABE fermentation began in the 1950s due to the rapid rise of the petrochemical

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http://dx.doi.org/10.1016/j.biotechadv.2014.10.007
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Table 1
Techno-economic comparison of n-butanol and ethanol from various feedstocks.[a]

Feedstocks		Carbon cost (\$/mol carbon)[b]	Theoretical carbon yield (mol carbon/mol butanol)[c]	Ethanol cost (\$/kg)		n-Butanol cost (\$/kg)
Petrochemical route	Propylene/syngas/H_2	0.018	4 (Xue, 2005)	–		1.52[d]
First generation feedstock	Corn	0.018	6	0.55 (Pfromm et al., 2010)		2.342 (Pfromm et al., 2010); 1.87[e]
Second generation feedstock	Corn stover, etc.	0.003–0.0017	6	Enzymatic hydrolysis and fermentation 1.16–1.04 (Piccolo and Bezzo, 2009); 0.72 (Tao et al., 2014)	Gasification and microbial fermentation 1.79–1.60 (Piccolo and Bezzo, 2009)	0.99 (Tao et al., 2014); 1.32[g]
	Corex off-gas	0.0012	12	0.66[f]	–	
	Blast furnace gas	0.0007	12	–	–	

[a] The exchange rate of US dollars to RMB is calculated as 6.

[b] The price of propylene and syngas was estimated as 1667 \$/ton, $0.12\,\$/\mathrm{Nm}^3$ from online data on April 2014 (http://info.1688.com/detail/1161506338.html). The price of corn was estimated as 400 \$/ton from the average price in 2014 (http://www.yz88.cn/sz/301037.shtml). The corn stover price was estimated as 63–36 \$/ton from previously published data (Piccolo and Bezzo, 2009). The price of Corex off-gas and blast furnace gas was provided by Baosteel Group Corporation as $0.033\ \$/\mathrm{Nm}^3$ and $0.008\ \$/\mathrm{Nm}^3$, respectively.

[c] The theoretical carbon yield was calculated based on the fermentative pathways as indicated in Fig. 2.

[d] The feedstock price was estimated as indicated in a and the other cost was provided by our industrial collaborators and listed as follows. Hydrogen, $0.23\ \$/\mathrm{Nm}^3$; steam, 16.7 \$/ton; electricity, 0.14 \$/kW; catalyst, 3% of the raw material; and fixed costs, 15% of the overall cost. The overall cost was estimated based on the unit consumption of raw materials and utilities of low-pressure Davy/Dow process published previously (Xue, 2005).

[e] The overall cost of corn-based n-butanol was provided by the North China Pharmaceutical Group Corporation and the Tianguan Group in China from their factory and pilot output, respectively.

[f] The data was provided by Baosteel Group Corporation from the output of Baosteel/LanzaTech demo pilot (http://finance.yahoo.com/news/lanzatech-baosteels-100-000-gallon-130000931.html) of ethanol production from off-gases in 2013.

[g] The cost of cellulosic n-butanol was provided by Lignicell Refining Biotechnologies Ltd. from the pilot output.

industry, and nearly all ABE fermentation processes had ceased by the 1960s, except in China, Egypt, the Soviet Union, and South Africa (Gu et al., 2011; Ni and Sun, 2009; Zverlov et al., 2006). China was one of the few countries that maintained industrial ABE fermentation because of its economic and political situation at that time. In 1955, the first ABE fermentation factory, the Shanghai solvent factory, started to use corn to produce ABE. During the next 30 years, approximately 30 ABE fermentation factories, with an annual production of 3000–10,000 tons, were built in various provinces, including Beijing, Jiang Su, Tian Jin, Yun Nan, Shan Xi, Zhe Jiang, He Bei, Shan Dong, Ji Lin, etc. As a result, the annual production of ABE reached 170,000 tons (Chiao and Sun, 2007; Ni and Sun, 2009).

Most n-butanol produced today is synthetic and derived from a petrochemical route based on propylene oxo synthesis, in which aldehydes from propylene hydroformylation are hydrogenated to yield n-butanol. Synthetic butanol production costs are linked to the propylene market and are extremely sensitive to the price of crude oil (Green, 2011).

According to the current situation of n-butanol industries in China, the petrochemical process has cost advantages over the traditional fermentation route. As listed in Table 1, the cost of the petrochemical process is about \$1.52/kg n-butanol, while that of traditional ABE fermentation is about \$1.87/kg. However, counting the prospective feedstocks and theoretical carbon utilization yield, the theoretical feedstock costs of bioprocessing are much lower than that of the petrochemical process, and the lowest of which were estimated at \$0.11/kg (from blast furnace gas, $0.0007 * 12 * 10^3/74$) and \$0.97/kg n-butanol ($0.018 * 4 * 10^3/74$), respectively, as listed in Table 1. Although there are currently many challenges regarding the industrialization of bioprocessing, with the increasing attention of the Government on the utilization of renewable and even waste resources, as well as the progress of the process technology, the bio-production of n-butanol promises to have a competitive edge. Currently, China is one of the few countries that are able to industrially ferment n-butanol. The article will review the recent status, including the commercialization, pilot testing and R&D activities, of industrial bio-production of n-butanol in China. The necessity and possibility of developing alterative feedstocks, and the strain improvement strategies to decrease the cost of bio-butanol fermentation will also be discussed.

2. Targets to be improved for bio-butanol

The traditional n-butanol fermentation process mainly uses corn liquefaction, semi-continuous fermentation, and product distillation, etc. as indicated in Fig. 1 (First Generation Biobutanol). Feedstock and utilities (mainly steam cost for distillation) account for the largest costs, 66% and 16%, respectively, of the whole process (Fig. 2). Three targets related to the aforementioned costs can be improved. These include the high cost of sugars from feedstock, and the low butanol selectivity and titers of butanol in fermentation broth.

Traditional ABE fermentation uses starchy feedstocks (such as corn) or molasses as preferred substrates, while corn is mainly used in China (Table 1). Taking corn as an example, according to an economic assessment based on an average industrial ABE plant from China in 2008, the

Fig. 1. First generation and second generation n-butanol processes and their corresponding microbial n-butanol fermentation pathway. Fermentative sugars from first generation feedstock is mainly glucose while from corn stover are glucose, xylose, and arabinose, that metabolite through the Embden–Meyerhof–Parnas or pentose phosphate pathway, followed by two reported n-butanol synthesis pathways as i) fermentation pathway, that naturally exists in solventogenic clostridia, and ii) the artificial a-keto-valerate pathway (Ranganathan and Maranas, 2010). The theoretical carbon yield of the above pathway is 6 mol carbon per mol butanol. The syngas or waste gas metabolite through the Wood–Ljungdahl pathway, followed by the fermentation pathway to synthesize butanol, and the theoretical carbon yield is 12 mol carbon per mol butanol. 1. phosphoglucose isomerase; 2. 6-phosphofructokinase; 3. fructose-1,6-bisphosphatase; 4. fructose bisphosphate aldolase; 5. triose phosphate isomerase; 6. glyceraldehyde-3-phosphate dehydrogenase; 7. phosphoglycerate kinase; 8. phosphoglycerate mutase; 9. enolase; 10. pyruvate kinase; 11. pyruvate dehydrogenase or pyruvate:ferredoxin oxidoreductase; 12. Thiolase; 13. 3-hydroxybutyryl–CoA dehydrogenase; 14. Crotonase; 15. Butyryl–CoA dehydrogenase/electron transferring flavoprotein complex or trans-2-enoyl–CoA reductase; 16. CoA–acylating aldehyde dehydrogenase; 17. alcohol dehydrogenase; 18; xylose isomerase; 19. xylulokinase; 20. L-arabinose isomerase; 21. L-ribulokinase; 22. ribose 5-phosphate isomerase; 23. L-ribulose-5-phosphate 4-epimerase A; 24. transketolase; 25. transaldolase; 26. transketolase; 27. threonine deaminase; 28. 2-isopropylmalate synthase; 29. 2-isopropylmalate hydro-lyase; 30. 2-isopropylmalate hydrolyase; 31. 3-isopropylmalate dehydrogenase; 32. 2-ketoacid decarboxylase; 33. citramalate synthase; 34. 2-isopropylmalate hydrolyase; 35. 2-isopropylmalate hydro-lyase; 36. 3-isopropylmalate dehydrogenase; 37. hydrogenase; 38. CO dehydrogenase; 39. formate dehydrogenase; 40. formyl–THF synthetase; 41. methenyl–THF cyclohydrolase; 42. methylene–THF dehydrogenase; 43. methylene–THF reductase; 44. methyltransferase; 45. CO dehydrogenase/acetyl–CoA synthase. Co-FeS–P: corrinoid iron–sulfur protein; Fd: ferredoxin; THF: tetrahydrofolate; 2[H]: reducing equivalents (e.g. NADH or NADPH).