



Review

Separation and purification of biobutanol during bioconversion of biomass

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ABSTRACT

Biofuels from biomass are becoming increasingly more important, due to the need for reduction in greenhouse gas (GHG) emissions, energy independence, and limited global availability and increasing demand and costs of fossil fuels. Butanol has several advantages over ethanol as a drop-in biofuel such as higher energy content, potential for higher blending percentage with gasoline, lower vapor pressure, and lower hygroscopy. It can be used in existing transportation fuel distribution infrastructure. Butanol can be produced by fermentation of carbohydrates derived from biomass using *Clostridium acetobutylicum* or *C. beijerinckii* under anaerobic conditions. There are still many unsolved challenges for making biobutanol technically, and economically viable. The unsolved challenges lie in severe product (especially butanol) inhibition during bioprocessing, which leads to low butanol yield and productivity, and very low final product concentration (<3 wt%), causing expensive downstream processing (product separation) costs. There are two ways for solving these problems. One is the modification of microorganisms for ABE (Acetone, Butanol and Ethanol) fermentation by genetic engineering, which could keep the microorganisms alive and active under higher concentration of products in the broth. This could significantly increase the product yield, productivity, and concentration and hence reduce the production costs. However, this is still an unrealized long term goal. Another approach is the development of efficient separation and purification processes for product recovery. And, even if the modification of microorganisms becomes a reality, product separation and purification will still remain a major critical challenge. In this study, an extensive review of separation and purification of butanol from fermentation broth is provided, including gas stripping, vacuum flash, liquid–liquid extraction, membrane solvent extraction or perstraction, membrane pervaporation, membrane distillation, thermopervaporation, reverse osmosis, adsorption, and integrated bioprocessing with various separation methods. It is concluded that membrane pervaporation, solvent extraction, and adsorption are the most energy-efficient approaches for removal of butanol from the ABE fermentation broths. It should be noted that this is not a strict comparison and it is suggested that each separation process should be optimized before comparison. Integration of bioreactors with these energy-efficient separation methods could significantly increase the product yield, productivity and concentration and hence lower the production cost. Butanol dehydration is also discussed. This review could be helpful in the research and development and commercialization of biobutanol as renewable drop-in biofuels and biochemicals.

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Abbreviations: [BMIM]⁺, 1-butyl-3-methylimidazolium; BTESE, 1,2-bis(triethoxysilyl)ethane; [DCA], dicyanamide; [DHSS]⁻, dihexylsulfosuccinate; [DMIM]⁺, 1-decyl-3-methylimidazolium; [FAP]⁻, tris(pentafluoroethyl)trifluorophosphate; ETES, ethyl triethoxysilane; [Hmim]⁺, 1-hexyl-3-methylimidazolium; [HOHmim], 1-(6-hydroxyhexyl)-3-methylimidazolium; IPA, isopropanol; [N1,8,8,8]⁺, methyltrioctylammonium; [NTF₂]⁻, bis(trifluoromethylsulfonyl)imide; OA, oleyl alcohol; [OMIM]⁺, 1-octyl-3-methylimidazolium; [P_{6,6,6,14}]⁻, trihexyltetradecylphosphonium; PDMS, poly(dimethyl siloxane); PE, polyethylene; PEBA, poly(ether-block-amide); PES-DVB, poly(4-ethylstyrene-co-DVB); [PF₆]⁻, hexafluorophosphate; [Phosph], bis(2,4,4-trimethylpentyl) phosphinate; PS-DVB, poly(styrene-co-divinylbenzene); PTMSP, poly(1-trimethylsilyl-1-propyne), membranes; TBP, tributyl phosphate; [TCB]⁻, tetracyanoborate; [THA]⁺, tetrahexylammonium; [TOA MNaph], tetraoctylammonium 2-methyl-1-naphthoate; β-CD, β-cyclodextrin.

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Nomenclature

C	concentration (g L^{-1} or mol L^{-1})	μ	viscosity (mPa s)
J	pervaporation permeate flux ($\text{kg m}^{-2} \text{h}^{-1}$)	γ	solvent–air interfacial tension (i.e., surface tension) or solvent–water interfacial tension (mN m^{-1})
K	distribution coefficient	β	separation factor of butanol/isobutanol (over water) for membrane pervaporation
K'	distribution coefficient	δ	thickness of membrane (μm)
K''	distribution coefficient		
m	mass (g) or mole numbers (mol)		
P	pressure (Pa)		
S	selectivity of an extracting agent (extractant) for the solute (butanol/isobutanol) over water	<i>Subscript</i>	
T	temperature	AP	aqueous phase
w	weight percent (wt%) or mass fraction (g g^{-1})	D	distribution
x	mole fraction	i	component
		OP	organic phase
		Perm	permeate side
<i>Greek letters</i>			
ρ	density (kg m^{-3})		

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1. Introduction

Biofuels from biomass are becoming increasingly more important, due to the need for reduction in GHG emissions, energy independence, and limited global availability and increasing demand and costs of fossil. Biobutanol as biofuel has several advantages over bioethanol such as higher energy content, lower vapor pressure, higher flash point (37°C vs. 15°C), lower hygroscopy, and better miscibility with gasoline [1–4]. Specifically, butanol contains 30% more energy content on a unit volume basis than ethanol ($27.83 \text{ MJ (L butanol)}^{-1}$ vs. $21.27 \text{ MJ (L ethanol)}^{-1}$) [5]. Life-cycle assessments by Swana et al. [4] show that the net energy return

associated with corn-to-biobutanol conversion is greater than that of the corn-derived bioethanol (6.53 MJ L^{-1} vs. 0.40 MJ L^{-1}). Butanol's lower vapor pressure and higher flash point represents that it is safer than ethanol, and being less hygroscopic means less corrosion to the fuel pipelines and equipments. Besides, butanol can be blended with gasoline at a higher percentage than ethanol. Current US regulations allow biobutanol to be blended at up to 16% by volume vs. 10% for ethanol (butamax.com). In addition, butanol is compatible with the current automobile engine design and can be used as a drop-in fuel and used in existing transportation fuel distribution infrastructure, making it an ideal candidate to replace gasoline [6,7]. In addition to being used as biofuel, butanol can

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