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Novel dual extraction process for acetone–butanol–ethanol fermentation

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ABSTRACT

One reason why butanol fermentation is not economically feasible has to do with the energy intensity of the product separation from the broth. In this study, a new approach for liquid–liquid extraction is presented. Several solvents, previously ignored because of their non-biocompatibility, were tested and a continuous process utilizing a novel, dual extraction with solvent regeneration is proposed. The optimal solvents for this process are from nine to eleven carbon alcohols used in conjunction with alkanes of approximately the same size. The ability to use non-biocompatible, but quite effective solvents offers a significant advantage, which is why a very low energy consumption of 3.76 MJ kg^{-1} butanol is achieved with this new process.

1. Introduction

1-Butanol can be produced from biomass via acetone, butanol, and ethanol (ABE) fermentation. During this process, solventogenic *Clostridium spp.* bacteria produce solvents, which are traditionally separated from the broth by distillation. This is an effective, robust, and well-known technology, but at the same time it is energy intensive [1]. Since the production of butanol by fermentation has been economically uncompetitive compared to the synthetic production route in the last decades, it is very important to minimize the operational costs of the fermentation route by using novel technologies [2,3]. Many alternative, cheaper separation methods for replacing the direct distillation have been reported in the existing literature, but so far none of them has been adopted on an industrial scale [3]. Some suggested methods for this purpose, along with the corresponding energy requirements, are as follows: 24.2 MJ kg^{-1} for steam stripping [4], 18.4 MJ kg^{-1} for traditional direct distillation [5], 13.3 MJ kg^{-1} for extraction with oleyl alcohol [5], 13.8 MJ kg^{-1} for gas stripping [4], 8.2 MJ kg^{-1} for adsorption–desorption [4], and 4.8 MJ kg^{-1} for extraction with mesitylene [5]. Other methods have also been suggested: These include pervaporation [6], perstraction [7], critical fluid extraction [8], adsorbtion [4], hollow-fiber reactors [9], reverse osmosis [10], liquid membranes [11], salt-induced phase separation [12], and continuous flash distillation [13].

Even though ABE fermentation has received a great deal of academic attention in recent years, a large number of authors have conducted their research with the easiest possible setup, thus contributing very little in terms of actual process enhancement. For example, when using extraction, methods where separation occurs simultaneously in the reactor have received much attention in the existing literature despite criticism from other authors, who point out that this is unpractical for large-scale production [14]. Another issue that is not often considered in the literature has to do with separating ABE products from the extraction solvent. Researchers often suggest using very high boiling extractants as the extraction solvent for ABE fermentation products. Such solvents include ionic liquids [8], vegetable oils [15], C-20 guerbet alcohol [16], and oleyl alcohol [1]. Using these kinds of solvents is not very economical, as high temperatures and low pressures are needed in distillation, which is energy intensive. And other methods, such as flash, offers only one separation stage which is not enough to get to the desired product purity [13]. Therefore smaller, more polar extractants, which are generally considered to be toxic to microbes, would be a much more energy efficient option for extraction solvents when the whole process is considered. The purpose of this study is to report results using a method that shows how effective, non-biocompatible solvents can be used to extract ABE fermentation products in a continuous process.

2. Materials and methods

2.1. Verification of the used liquid–liquid equilibrium (LLE) methods

Experiments to verify extraction simulations were performed. An aqueous mixture containing 1.2, 0.6, and 0.2 mass% of butanol, acetone, and ethanol, respectively, was mixed at a mass ratio of 4:1

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with the solvents tested. The experiments were kept at 37 °C with constant mixing for 24 h, after which both of the phases were analyzed using a gas chromatograph with a flame ionizing detector (GC-FID). The organic phase was further analyzed using a GC with mass spectrometer as a detector (GC–MS) to analyze the water content. The amount of water in the aqueous phase was calculated from material balance. The solvents selected for verifying the LLE methods were 1-heptanol, 1-octanol, and 1-decanol. These solvents were selected because they present different polarities within the scope of this work. The partition coefficients were calculated as the ratios of the mass fractions of the components in organic and aqueous phases.

2.2. Process simulations

Simulations were performed using Aspen plus software. The UNIFAC-LL activity coefficient model was used to model the liquid–liquid equilibria (LLE), while the NRTL model, with the pure component and binary interaction parameters taken from Aspen plus, was used for the vapor–liquid equilibria (VLE). During the simulations, a continuous broth flow rate of 1000 kg h^{-1} was assumed. Initial butanol concentration was varied from 4 to 12 g l^{-1}. The solvent mass ratio of the broth was 3:6:1 for acetone, butanol, and ethanol, respectively. The extraction columns were simulated using four ideal stages, and the extractions were performed adiabatically at approximately 37 °C. To make sure that the recycled broth was biocompatible, the amount of toxic solvent in the broth after the extractions was fixed at a very low value of 20 ppm. It can be assumed that this low solvent concentration does not have any effect on the microbes [5]. In the heat integration, the bottom streams of the distillation columns were used to heat up the feeds. The heat exchangers were assumed to operate with a 3 °C temperature difference between the incoming cold stream and the outgoing hot stream. The distillation columns consisted of 40 stages and the pressure profile inside the columns was from 1.3 to 1.0 bar. The flow rate of the first toxic solvent was varied and the energy needed per kilogram of separated butanol was calculated. In this way, the energetically optimal operating point could be found.

2.2.1. Dual extraction method

Many thorough articles have been published on the solvent selection in ABE product extraction. However, extractants that are slightly soluble in water have been almost completely ignored. In traditional extraction systems, these kinds of solvents would become expensive, since much of the solvent would be lost during the extraction. Another important reason is that these solvents would most likely be poisonous to the microbes. However, these problems can be overcome if the toxic solvent dissolved in the fermentation broth is extracted in another extraction unit, as shown in Fig. 1. The aqueous, butanol-rich reactor output stream, BROTH, is extracted in the Extraction1 using a non-biocompatible solvent, which has a high distribution coefficient for butanol. The solvent containing the extracted ABE products and some water continues as stream ORG1. The bottom flow of Extraction1, AQ1, is the aqueous fermentation broth leaving the extraction column and it contains the ABE products, which were not extracted with traces of the toxic extraction solvent. To remove this non-biocompatible solvent from the broth, a second extraction is performed. The non-toxic extractant, SOLV2, removes traces of the toxic solvent from the broth so that the fermentation broth can be safely recycled back to the reactor. After both extractions the aqueous fermentation broth, AQ2, contains the non-extracted ABE products, and small amounts of the extraction solvents. The solvent stream of the second extraction, ORG2, contains the solvent used in the second extraction, the extracted toxic solvent and trace amounts

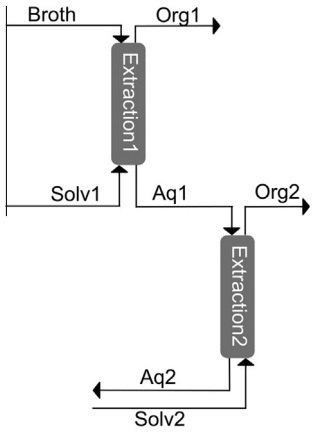

Fig. 1. Novel dual extraction method.

of ABE products and water. Since the ABE products are mainly separated during the first extraction, the amount of solvent used there primarily determines the extraction capacity, whereas the efficiency of the second extraction primarily determines the toxicity of the recycled fermentation broth. This kind of dual extraction system enables the use of extraction agents with distribution coefficients that are several times higher than has previously been reported. This means that significantly smaller amounts of solvents are needed to achieve the desired extraction efficiency. The ability to use these very powerful solvents could significantly improve the economics of the downstream separations of an ABE process.

Using two extraction solvents to enhance the ABE fermentation is not an original or new idea. But usually the two solvents are mixed together in order to lower the toxicity of a high-capacity solvent [17]. A method where a non-biocompatible solvent could be used without fear of inhibiting the growth or even of killing the microbes has so far not been reported in the existing literature. The problem in using this kind of dual extraction process is that the product mixture consists of not one, but two additional components that need to be separated from the mixture. If distillation is the choice for the downstream purification method, this means that additional distillation columns will be needed.

2.2.2. Solvent selection

Prior studies have concluded that the optimal extraction solvent is non-toxic for the microorganisms used, immiscible in water, non-emulsion forming, non-azeotrope forming, inexpensive, readily available and that it should have a high affinity towards butanol [1,18]. The biocompatibility issue has been the most severe constraint in solvent selection [17,19]. On the other hand, the water solubility of a solvent goes usually hand in hand with its biocompatibility: for the most part, the more water soluble a solvent, the higher its toxicity to the microbes. This also means that biocompatibility is inversely linked to the selectivity and capacity of the extraction process. In other words, more polar, non-biocompatible solvents can dissolve larger amounts of ABE products and water than less polar, non-toxic solvents [20]. Ezeji et al. [1] claims that water in the product stream will affect the product separation costs. For this reason, its minimization is essential.

To find the best solvent for the first extraction, a number of studies were reviewed [5,15,17,18,21–26]. The chemical groups considered in these articles were alkanes, alkenes, aldehydes, ketones, aromatic components, triglycerides, acids, alcohols, esters, ethers, halogen components, and chemical mixtures that are difficult to categorize, such as gasoline and kerosene. Easily evaporable solvents such as diethyl ether were ignored because the conditions would need to be rather harsh before they could be utilized in a