CHEMICAL ENGINEERING TRANSACTIONS

VOL. 49, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Enrico Bardone, Marco Bravi, Tajalli Keshavarz

ISBN 978-88-95608-40-2; **ISSN** 2283-9216

DOI: 10.3303/CET1649003

Recovery of Butanol from ABE Fermentation Broth by Gas Stripping

Gabriele Lodi, Laura A. Pellegrini*

Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy.
laura.pellegrini@polimi.it

Because of the growing demand for renewable fuels, the production of butanol through acetone-butanol-ethanol (ABE) fermentation of lignocellulosic biomasses is attracting more and more research interest.
The major limit for an industrial-scale production of bio-butanol is the high separation cost, due to the presence of other fermentation products and to its low final concentration in the broth. In fact, microorganisms used in ABE fermentation suffer from product inhibition giving a low ABE final concentration in a batch process. The application of an in-situ recovery technique able to remove butanol during fermentation is a viable solution to solve the problem and improve the profitability of ABE fermentation.
In this context, gas stripping appears to be the most promising and cost-effective separation technique.
However, gas stripping usually also removes a large amount of water with butanol and requires a higher energy input because of its lower butanol selectivity if compared to other separation techniques. To improve the performance of the integrated fermentation-gas stripping process for butanol production, optimization of gas stripping conditions, and a better understanding of its effects on the ABE fermentation are needed. Several experimental studies on lab-scale gas stripping units are available in literature, but no process simulation studies are present.
This study regards the synthesis of the optimal process configuration for the in-situ recovery of butanol from a batch fermentation unit, in which the product is recovered from the fermentation broth by means of nitrogen gas stripping. A sensitivity analysis has been performed to study the effect of the gas flowrate on the separation performances. For the studied configuration a detailed simulation using Aspen Hysys$^{®}$ has demonstrated that it is possible to obtain a high selectivity to butanol that leads to a phase separation in the condensate, reducing the cost of the downstream process and indicating the potential and the profitability of the proposed process solution.

1. Introduction

Before the 1950s acetone, butanol and ethanol (ABE) fermentation by Clostridium acetobutylicum was the main route to produce butanol. This process began to decline due to the increasing of substrate cost and the appearance of a new, more economical, petrochemical route.
Today, almost all butanol is produced from petrochemical feedstock, although in some countries production continued through the fermentation route (Dürre, 1998).
The continuous increasing of greenhouse gas emissions and the resulting concerns about climate change, together with the availability of new renewable feedstocks, are leading to a growing interest in sustainable industry and, consequently, to a renewed interest in ABE fermentation.
Butanol can be used as a substitute of petroleum-derived fuel and shows several advantages over other biofuels produced by fermentation, like ethanol. As a matter of fact, butanol has a higher energy density, a lower vapour pressure, that makes it safer, and it is less corrosive. Moreover, butanol can be blended with gasoline in any proportion and can replace it without modification of car engines (Qureshi and Blaschek, 1999).

Please cite this article as: Lodi G., Pellegrini L.A., 2016, Recovery of butanol from abe fermentation broth by gas stripping, Chemical Engineering Transactions, 49, 13-18 DOI: 10.3303/CET1649003

ABE fermentation is performed at temperatures between 27-37 °C and 1 atm by a large variety of Clostridia strains that are able to ferment different sugars, including glucose, xylose, arabinose and mannose (Ezeji and Blaschek, 2008). Therefore, new renewable feedstocks like agricultural residues and forestry, which are abundant and inexpensive, can be used for the production of second-generation biofuels (Meesukanun and Satirapipathkul, 2014).

However, the microorganisms used in ABE fermentation suffer from product inhibition, mainly from butanol. Typically 20 g/L of total solvents, with a butanol concentration as low as 13 g/L, are achieved in the bioreactor during a batch process (Maddox, 1989), restricting the sugars concentration in the substrate to about 60 g/L.

These limitations deeply affect the costs of the process, both CAPEX due to the need of large process volumes and OPEX involved in downstream separations for product recovery, usually performed by distillation.

The application of an in-situ recovery technique, able to remove butanol from the fermentation broth during fermentation, currently appears to be the most viable solution to solve the problems related to ABE fermentation and to improve the profitability of the process (Ezeji et al., 2005).

In fact, by removing toxic solvents from the culture at a rate similar to that at which they are formed, it should be possible to ferment more concentrated sugar solutions, reducing capital costs, because of the higher fermenter productivity, and operating costs for product recovery (Maddox, 1989).

Product removal techniques include gas stripping (Groot et al., 1989), liquid-liquid extraction (Barton and Daugulis, 1992), adsorption (Nielsen and Prather, 2009) and pervaporation (Matsumura et al., 1988).

Gas stripping has several advantages in comparison with the other technologies because it is simple to operate and to scale up, it does not require expensive equipment or chemicals, it does not remove nutrients and reaction intermediates from the broth and it is not harmful to cells. (Ezeji et al., 2003). In gas stripping, an inert gas is contacted with the fermentation broth, capturing the solvents, and is then passed through a condenser. Here the stripped components condense, while the gas can be recycled to the stripping section.

The application of gas stripping results in the use of concentrated sugar solutions in the fermenter (Qureshi and Blaschek, 2001), in a reduction in butanol inhibition and in higher sugar utilization (Maddox and Qureshi, 1995), reducing process volumes. The concentration of the butanol in the recovered stream is higher than in the fermentation broth.

However, gas stripping usually also removes a large amount of water with butanol and requires a higher energy input, because of its lower butanol selectivity if compared to other separation techniques (Oudshoorn et al., 2009; Qureshi et al., 2005; Vane, 2008). Nevertheless, some authors (Xue et al., 2013) have experimentally demonstrated that it is possible to obtain a phase separation in the condenser, giving a butanol-rich organic phase that would reduce the subsequent purification cost. Thus, to improve the performance of the integrated fermentation-gas stripping process for butanol production, optimization of gas stripping conditions, and a better understanding of its effects on ABE fermentation are needed.

In this respect, a lot of experimental work has been performed (Qureshi and Blaschek, 2001), but no computer simulations are available in literature. The aim of the present paper is to define a process configuration for the in-situ gas stripping removal of ABE from fermentation broth. Computer simulations with a reliable thermodynamic package have been performed with Aspen Plus®, in order to analyse the effect of the operating conditions of the stripping section on solvents recovery for process optimization.

2. Thermodynamic framework

In order to simulate the downstream process, it is fundamental to set up a thermodynamic model able to predict the phase equilibria involved in the separation. The ABE mixture contains many polar compounds and therefore shows a strong non-ideal behavior, with several azeotropic binary systems. Moreover, butanol and water exhibit a miscibility gap, whose correct representation is fundamental for the proper description of the separation process. Thus, the thermodynamic model must be able to properly describe both vapor-liquid equilibrium and liquid-liquid equilibrium. Because of the strong non-ideality of the mixture and of the low pressure level involved in the separation process, an indirect method was chosen. This is based on the NRTL model for the calculation of the activity coefficients in liquid phase and on the RK EoS for the calculation of the fugacity coefficients in the vapor phase. The considered components were only those effectively removed from the broth, namely acetone, butanol, ethanol, water, and the stripping agent, nitrogen. Firstly, the capability of the model to reproduce phase equilibria using default parameters implemented in Aspen Plus® was checked (Figure 1). In order to improve the model predictions, the model parameters were regressed over a large set of binary and ternary vapor-liquid and liquid-liquid equilibrium data. Nitrogen was treated as a Henry component and its Henry's constants were kept equal to default values. A comparison between the model predictions with default and optimized parameters for the main mixture is shown in Figure 1.

It can be seen that the model capability of predicting either vapor-liquid equilibrium or liquid-liquid equilibrium is strongly improved by the use of optimized parameters.

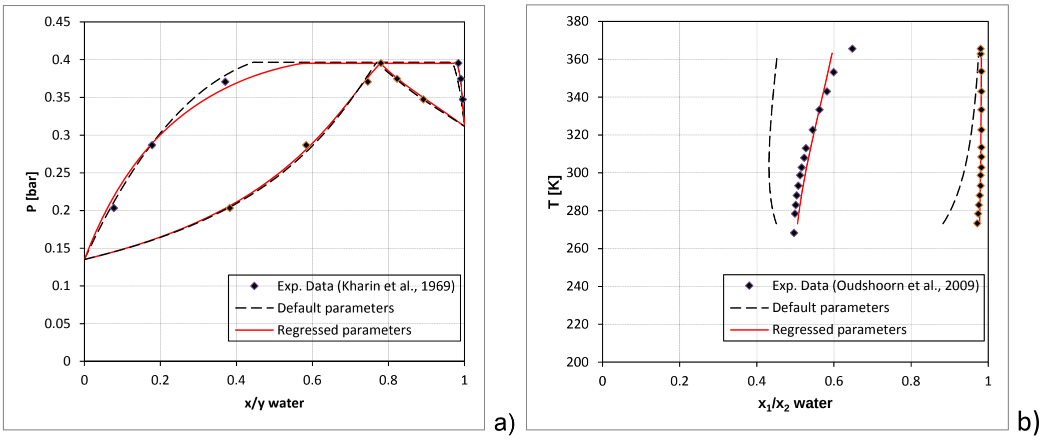

Figure 1: Comparison of thermodynamic equilibrium predictions using Aspen Plus® NRTL-RK model with default parameters (dotted line) and with regressed ones (solid line). a) Water-butanol vapour-liquid equilibrium at 343.13 K. b) Water-butanol liquid-liquid equilibrium at 1 bar.

3. Process description

In the gas stripping process, fermentation products are removed from the broth by contacting it with an inert gas stream. Either nitrogen or the fermentation gases themselves (CO_2 and H_2) can be used for this operation (Groot et al., 1989; Ezeji et al., 2003). Attention should be paid in the use of fermentation gases, since carbon dioxide could solubilise in the fermentation broth and decrease its pH, a parameter that plays a key role during ABE fermentation (Maddox, 1989; Dahlbom, 2011). Therefore, nitrogen has been preferred as stripping agent.

Gas stripping can be performed either bubbling the gas through the fermenter or in an external column (Groot et al., 1989; Ezeji et al., 2003). An external stripper represents a more appropriate design, because of the higher performances of a multistage unit compared with a single equilibrium stage. Moreover, with this configuration it is possible to use nitrogen as a stripping agent while maintaining a beneficial fermentation gas, positive head-space pressure.

In the studied configuration the fermentation broth is withdrawn from the fermenter and sent to a stripping column: here the ABE mixture is stripped with nitrogen, passing from the liquid phase to the vapour phase. The fermentation broth is then recycled to the reactor, while the vapour phase is sent to the condenser. Here the stripped compounds are condensed and the regenerated nitrogen is recycled to the stripping column. A nitrogen make-up is required to compensate the amount of gas that remains dissolved in the product stream. The condensed ABE mixture has a higher butanol concentration than the initial fermentation broth. If the global composition of condensate falls in the liquid-liquid demixing region, a phase separation occurs, giving an organic phase rich in acetone, butanol and ethanol and an aqueous phase rich in water. The condensate is collected in a decanter in which the two liquid phases can be separated and sent to a distillation train for further separation. The lean fermentation broth exiting from the stripping column can be recycled to the fermenter. A schematic representation of the proposed process is shown in Figure 2.

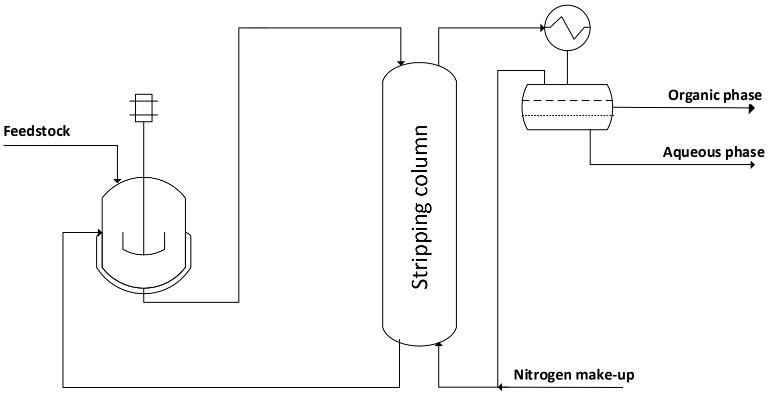

Figure 2: Process flow diagram of the integrated stripping unit for recovery of butanol from fermentation broth.

4. Process simulation and analysis of the stripping column operating conditions

The proposed process configuration was simulated with Aspen Hysys®, importing the thermodynamic model implemented in Aspen Plus®. For process simulations, a typical broth composition obtained at the end of a batch fermentation process and reported in Table 1 has been used.

Table 1: Fermentation broth composition.

Component	g/L
Acetone	3.25
Butanol	14.5
Ethanol	2.10
Total density	1016

For the gas stripping section, the effect of the G/L ratio (the ratio between the broth and nitrogen flowrates) on products recovery and purity has been investigated. Simulations have been carried out considering a stripping column with ten ideal-stages and varying the G/L ratio in an appropriate range. The temperature of the condenser was fixed at 3 °C, to prevent solid phase formation.

Figure 3a shows the composition of the gas stream from the stripping column, normalized with respect to the stripped components. It can be seen that, with low G/L ratios, a higher butanol selectivity is obtained. Increasing the G/L ratio, the selectivity decreases due to the increasing water removal from the fermentation broth.

According with the Raoult law, the recovery of butanol at the condenser decreases in the same way, giving the overall condensate composition shown in Figure 3b. For values of G/L lower than 0.84 the concentration of butanol is high enough to allow a phase separation in the condenser, giving an organic butanol-rich phase and an aqueous phase. The composition of the two phases is quite constant with the G/L ratio and is reported in Table 2.

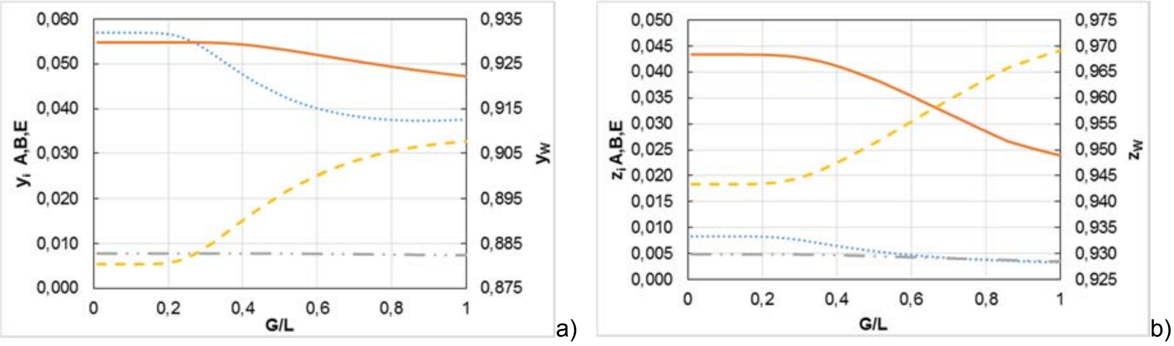

Figure 3: a) Composition of the gas stream exiting from the stripping column. Mole fractions are normalized with respect to the stripped components. b) Global composition of the condensate: (······) acetone, (——) butanol, (— ·· —) ethanol and (------) water.

Table 2: Mole fractions of stripped components in the liquid phases exiting from the condenser.

Component	Organic phase	Liquid phase
Acetone	0.016	0.005
Butanol	0.398	0.028
Ethanol	0.013	0.004
Water	0.572	0.962

For appropriate values of the gas flowrate it is possible to obtain a phase separation in the condenser, giving an organic phase with a concentration of butanol of nearly 40 %, namely two orders of magnitude greater than the starting concentration in the fermentation broth. From the composition of the aqueous phase, it is possible to see that also in this phase the butanol concentration is ten times the initial value in the broth.

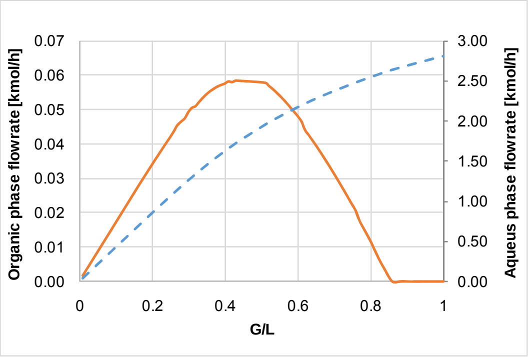

Figure 4: Flowrates of the organic phase and aqueous phase exiting from the condenser unit: (——) organic phase, (------) aqueous phase.

Figure 4 shows that the organic phase flowrate initially increases with the G/L ratio. Then, due to the increase of the overall water content in the condensate, the organic phase decreases until it vanishes for G/L greater than 0.84. The ratio between the organic phase and the aqueous phase shows a maximum for G/L equal to 0.5. Despite the concentration of butanol in the aqueous phase is much lesser than in the organic phase, the amount of the former is significantly greater than the organic phase and contains at least 60 % of the condensed butanol. Even under optimal condition, due to the high disproportion between the two phase flowrates, the recovery of butanol only from the organic phase is too low, with a maximum value of 6.5 %. Thus, in order to obtain a higher butanol recovery, it is necessary to treat both the streams. It is worth noting that in the aqueous phase the concentration of butanol is one order of magnitude higher than in the starting fermentation broth. Therefore the energy requirement to recover butanol from this stream will be still lower.

Figure 5 shows the total recovery of butanol obtainable from both the organic and the aqueous phases, in the hypothesis to recover all the butanol contained in the two streams. The total recovery shows a maximum for the G/L value corresponding to the maximum of organic phase flowrate, allowing to recover more than the 20 % of butanol contained in the fermentation broth. Finally, it is worth underlying that a complete recovery of butanol from the fermentation broth is not required, since the products remaining in the liquid phase are recycled to the fermenter, without any loss. Conversely, a good product recovery accompanied with high purity is preferable to reduce the energy requirement of the subsequent distillation train.

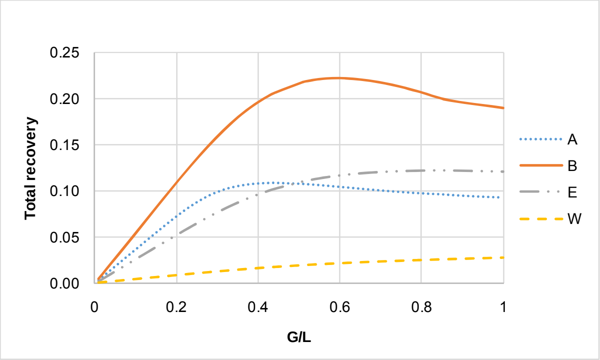

Figure 5: Total recovery of the stripped components obtainable treating the two liquid phases exiting from the condenser: (······) acetone, (——) butanol, (— ·· —) ethanol and (------) water.

5. Conclusions

In this work, the value of gas stripping as an in-situ product removal technique from ABE fermentation broth is demonstrated. The described technique uses nitrogen as stripping gas and performs the separation in an external stripping column, in which only the volatile compounds are removed. A sensitivity analysis on the recycle gas flowrate has been performed, showing that the selectivity on butanol removal during gas stripping varies in the range 9-13. Hence, in addition to the butanol removal from the broth, the technique represents a concentration step with a positive effect on the overall product recovery process, usually performed by distillation, reducing the total separation costs. Furthermore, it has been shown that, for certain values of G/L ratio, a phase separation occurs in the condenser, giving a butanol-rich organic phase and an aqueous phase. This would furthermore reduce the downstream separation costs. Future activities will include the synthesis and the simulation of the distillation train, in order to assess the overall energetic consumption of the separation process. Then the positive effect of this recovery technique on the ABE fermentation, in terms of reduction of product inhibition and increase in reactor productivity, will be studied by integrating the separation process model with a batch reactor one, in which an overall kinetics for butanol production will be implemented.

Reference

Aznar M., Araújo R. N., Romanato J. F., Santos G. R., d'Ávila S. G., 2000, Salt effects on liquid-liquid equilibrium in water+ ethanol+ alcohol+ salt systems, Journal of Chemical & Engineering Data 45, 1055-1059.

Barton W.E, Daugulis A.J., 1992, Evaluation of solvents for extractive butanol fermentation with Clostridium acetobutylicum and the use of poly(propylene glycol) 1200, Appl. Microbiol. Biotechnol. 36, 632-639.

Dahlbom S., Landgren H., Fransson P., 2011, Alternatives for Bio-Butanol Production, Lunds Universitet feasibility study. Lund, Sweden.

Dürre P., 1998, New insights and novel developments in clostridial acetone/ butanol/ isopropanol fermentation, Appl. Microbiol. Biotechnol. 49, 639-648.

Ezeji T.C., Qureshi N., Blaschek H.P., 2003, Production of acetone, butanol and ethanol by Clostridium beijerinckii BA101 and in situ recovery by gas stripping, World Journal of Microb. & Biotech. 19, 595–603.

Ezeji T.C., Qureshi N., Blaschek H.P., 2008, Fermentation of dried distillers' grains and soluble (DDGS) hydrolysates to solvents and value-added products by solventogenic clostridia, Bioresource Technology 99, 5232–5242.

Ezeji T.C., Qureshi N., Blaschek H.P., Karcher P.M., 2005, Improving performance of a gas stripping-based recovery system to remove butanol from Clostridium beijerinckii fermentation, Bioprocess Biosyst Eng 27, 207–214.

Groot W. J., Van der Lans R.G.J.M., Luyben K.C.A.M., 1989, Batch and continuous butanol fermentations with free cells: integration with product recovery by gas-stripping, Applied Microb. & Biotech. 32, 305-308.

Kharin S. E., Perelygin V. M., Remizov G. P., 1969, Liquid-Vapor Phase Equilibrium in Ethanol-n-Butanol and Water-n-Butanol Systems, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 12, 424-428.

Maddox I.S., 1989, The Acetone-Butanol-Ethanol Fermentation: Recent Progress in Technology, Biotechnology and Genetic Engineering Reviews 7, 189-220.

Matsumura M., Kataoka H., Sueki M., Araki K., 1988, Energy saving effect of pervaporation using oleyl alcohol liquid membrane in butanol purification, Bioprocess Engineering 2, 93-100.

Meesukanun K., Satirapipathkul C., 2014, Production of Acetone-Butanol-Ethanol from Cassava Rhizome Hydrolysate by Clostridium Saccharobutylicum BAA 117, Chemical Engineering Transaction 37, 421-426.

Nielsen D.R., Prather K.J., 2009, In situ product recovery of n-butanol using polymeric resins, Biotechnology and Bioengineering 102, 811-821.

Oudshoorn A., Van der Wielen L.A.M., Straathof A.J.J., 2009, Assessment of Options for Selective 1-Butanol Recovery from Aqueous Solution, Ind. Eng. Chem. Res. 48, 7325-7336.

Qureshi N., Blaschek H.P., 1999, Butanol recovery from model solution/fermentation broth by pervaporation: evaluation of membrane performance, Biomass and Bioenergy 17, 175–184.

Qureshi N., Blaschek H.P., 2001, Recovery of butanol from fermentation broth by gas stripping, Renewable Energy 22, 557–564.

Qureshi N., Hughes S., Maddox I.S., Cotta M.A., 2005, Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption, Bioprocess and Biosystems Engineering 27, 215-222.

Qureshi N., Maddox I.S., 1998, Reactor Design for the ABE fermentation using cells of Clostridium acetobutylicum immobilized by adsorption onto bonechar, Bioprocess Eng. 3, 69-72.

Ruiz F., Prats D., Gomis V., 1984, Quaternary liquid-liquid equilibrium. Water-ethanol-1-butanol-chloroform at 25 degree C. Experimental determination and graphical representation of equilibrium data, Journal of Chemical and Engineering Data 29, 147-151.

Santos F. S., d'Ávila S. G., Aznar M., 2001, Salt effect on liquid–liquid equilibrium of water+ 1-butanol+ acetone system: experimental determination and thermodynamic modeling, Fluid phase equilibria 187, 265-274.

Vane L.M., 2008, Separation technologies for the recovery and dehydration of alcohols from fermentation broths, Biofuels Bioproducts and Biorefining 2, 553-588.