

Pervaporative Butanol Fermentation

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Butanol can be manufactured by chemical synthesis or by bacterial fermentation of carbohydrate-containing materials. Today the principal commercial source of n-butanol is n-butyraldehyde, obtained from the Oxo reaction of propylene. When crude oil price was sky-rocketed in late 70's and subsequently the price of petrochemical products raised, butanol production from renewable resources such as agricultural and forestry products once gained research interests.

An important difficulty with the butanol fermentation process is the strong toxicity of the major product, butanol, to the producing microorganism. When chemical engineering concepts were introduced into this fermentation system, many different ways of in-situ butanol removal from the fermentor have been developed to avoid inhibitory effect of butanol (*Mattiason and Holst, 1991; Park and Geng, 1992*).

Pervaporation is a new actively growing membrane process (*Fleming and Slater, 1992*) and applied to simultaneous fermentation and separation. Pervaporation is a combined process of permeation and evaporation. Components of interest permeate through the membrane and subsequently evaporate at the other surface of the membrane because their partial pressure on the permeate side is lower than saturation vapor pressure. The driving force for pervaporation is generated by applying a vacuum or by using an inert carrier gas. Pervaporation uses either solvent-selective or water-selective membranes which modify the vapor-liquid equilibrium (V.L.E.) of the system. Pervaporation applied to butanol fermentation need to use solvent-selective membranes first to extract butanol from a dilute aqueous solution. After we obtain a more concentrated butanol permeate from solvent-selective separation, we need to process the permeate further by

using water-selective membranes. The latter is called dehydration process (water removal from liquid organics) and accounts for the majority of plants built to date. However, membranes and processes for selective removal of organics from aqueous streams became also commercially available around 1989. The best known of the commercial processes is the GFT process for dealcoholization of beers, wines and liquors. Pervaporation seems to be a suitable method to remove butanol from water-butanol mixture because of its high selectivity and because it can separate the azeotrope mixtures.

The goal of simultaneous fermentation and separation is to raise the product formation by increasing the sugar consumption. In doing so, the composition of the fermentation broth changes after operation over a period of time and adverse production conditions may develop. In the case of pervaporative butanol fermentation, acetic acid and butyric acid will accumulate in the fermentor and their concentrations can be increased to the toxic levels during fed-batch fermentation. This implies that we need to avoid organic acid accumulation in the medium to achieve our goal of increasing butanol production. However, this cannot be accomplished easily because pervaporation membranes for butanol removal are not efficient in removing organic acids. Moreover, because of the interesting physiology of the butanol producing microorganisms organic acid formation is an indispensable biochemical reaction for energy generation in the cell. And organic acid removal is not beneficial for solvent production because butanol production initiates only when butyric acid concentration reaches a certain level. We found a way of avoiding acid accumulation by using a new strain of *Clostridium acetobutylicum* B18 producing a lower amount of organic acids.

We showed that pervaporation using a silicone tubing module was efficient for the removal of butanol and acetone from dilute aqueous solutions (*Geng and Park, 1994*). The module was made of silicone tubing (1.95 mm outside diameter and 240 μm thick walls) that was woven through the holes on two flat autoclavable plastic holders horizontally mounted in a fermentor. The module was immersed in one liter make-up

solutions or fermentation broth at 32°C. Air was supplied at a controlled rate through the lumen side of the tubings using an air pump. The flux of each solvent component was linearly dependent on its solution concentration. At the concentration range studied in our work, solvent diffusivities were independent of each other and increased at higher sweep air flow rates. Organic acid removal by pervaporation was inefficient for butyric acid (20% removal) and negligible for acetic acid. However, the acids did not accumulate up to toxic levels because *C. acetobutylicum* B18 produced little organic acids and recycled existing organic acids efficiently. With a limited separation capacity (surface area 0.17 m²) we could maintain butanol concentration in the fermentation broth below 4.5 g/L. The glucose consumption rate with pervaporation was 2.0 g/L-h, which was faster compared to that without pervaporation. The amount of glucose consumption was nearly three fold compared with batch fermentation without product removal, and butanol was produced steadily during fed-batch operation for 80 hrs.

One limitation of our study was low butanol flux (4 g/m²-h at 6 g/L of butanol concentration), which can be increased by employing thinner membranes. Development and application of membranes with higher butanol flux will further improve the efficiency of our pervaporation system.

Engine performance test using butanol fuel blends showed that butanol can be used as a gasoline or diesel fuel supplement in percentages ranging from 0 to 20 percent and 0 to 40 percent, respectively, without significantly affecting unmodified engine performance (Miller *et al.*, 1981). A more interesting finding is that solvent mixture of ABE fermentation was shown as efficient spark ignition engine fuel. Solvent mixtures of butanol (51wt%), acetone (25 wt%) and ethanol (6 wt%) with some water (18 wt%) produced power and thermal efficiency roughly equivalent to gasoline provided the engine is operated in performance regions where mixture maldistribution is not severe (Schrock and Clark, 1983). This means that the mixture of ABE fermentation product can possibly be used as an engine fuel after simple concentration by pervaporation. This will improve

the economics of fermentation butanol production because we can eliminate the steps necessary to separate butanol from acetone and ethanol. It is also reported that oxides of nitrogen (NO_x) emissions were substantially lower for mixture of butanol, acetone and ethanol (*Schrock and Clark, 1983*).

The economic viability of fermentation process producing low value added material such as butanol is particularly dependent upon the oil price, feed stock cost, capital investment and separation cost. The process described in this article markedly improved downstream processing and it opened a possibility of continuous operation in a fed-batch mode. With other efforts on using lower value feed stock I expect that pervaporative butanol fermentation will be commercially viable in the future.

Literature Cited

- (1) Fleming H.L.; Slater, C.S. In *Membrane Handbook*; Ho, W.S.W.; Sirkar, K.K. Eds.; Van Nostrand Reinhold; 1992; p 132.
- (2) Geng, Q.; Park, C.-H. *Biotechnol. Bioeng.* **1994**, *43*, 978.
- (3) Kühn, I. *Biotechnol. Bioeng.* **1980**, *22*, 2393.
- (4) Mattiasson, B.; Holst, O., Eds. *Extractive Bioconversions*; Marcel Dekker, Inc.: New York, 1991.
- (5) Miller, G.L.; Smith, J.L.; Workman, J.P. *TRANSACTIONS of the ASAE* **1981**, *24*, 538.
- (6) Park, C.-H.; Geng, Q. *Separation and Purification Method* **1992**, *21*, 127.
- (7) Schrock, M.D.; Clark, S.J. *TRANSACTIONS of the ASAE* **1983**, *26*, 723.