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The Design of a Membrane-Based Integrated Ethanol Production Process

Scientific Note

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Index Entries: Ethanol; pervaporation; microfiltration; cell recycle; process design.

INTRODUCTION

Alcohol production is an important topic in biotechnology. The research in this field aims at the development of efficient production schemes for alcohol as a fuel or beverage. In the case of fuel alcohol the validation of low-cost substrates or wastes also is aimed at. The efficiency of the production process depends on several aspects: operational simplicity, productivity and product concentration (cq. substrate consumption) in the fermentation, and product recovery. In a fermentation the productivity is proportional to the biocatalyst concentration, and techniques to retain the biocatalyst in the fermentation section must ensure a high productivity. In addition, product inhibition of the biocatalyst determines the productivity and the substrate consumption. These inhibition effects can be partly reduced by alcohol removal during fermentation. The in situ product recovery will result in an increase in the substrate consumption and, hence, a decrease in the amount of wastewater. Another advantage of this technology is that the recovery method is an economically feasible alternative to conventional distillation for purification of alcohol. Promising techniques for biomass retention are (auto)flocculation (200 m^3 scale [*1*]), immobilization (4 m^3 scale [2]), and microfiltration (0.8 m^3 scale [3]). In

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situ product recovery by stripping, combined with biomass retention by centrifugation, is applied in the Biostill-process (scale 150 m^3/d ethanol, [4]). A similar product-recovery technique is applied in the vacuferm process (*5*), but the low selectivity of both types of separation leads to relatively high recovery costs. Extraction has also successfully been used in continuous ethanol fermentations (*6*). The selectivity of extraction can be high; however, literature data suggest that the recovery of ethanol from the extract can be energy-consuming (*7*). A novel separation technique is pervaporation, in which an ethanol/water mixture is recovered from the broth by evaporation via a selective membrane. High-flux membranes are now available, which makes it possible to investigate pervaporation for laboratory-scale in situ product recovery.

In this study, some aspects of the design of an integrated ethanol production process with biomass retention by microfiltration and in situ ethanol recovery by pervaporation are highlighted. The operation of both units will shortly be described, and preliminary results with the integrated system will be presented. The observed fermentation kinetics are used for simulations of the optimal process configuration, and these systems will be evaluated from an economic and technological point of view.

MICROFILTRATION

Nowadays microfiltration can be considered a proven technology. On a commercial scale, membrane filtration is widely used (for example, in the dairy industry), and several studies in the literature report on cell retention in a fermentation by microfiltration. For some of the characteristics of microfiltration, *see* Table 1 and Fig. 1.

From a process point of view, the permeate flux is the key parameter in the design of a process. The flux depends on both defined conditions, such as the feed flow rate and the transmembrane pressure, and less-defined phenomena, such as concentration polarization and fouling. Usually backflushing techniques are used to maintain high and relatively constant fluxes, and in this sense microfiltration is an extensively instrumented unit operation.

PERVAPORATION

In the last decade, pervaporation has developed toward a separation technology that is also applied on a commercial scale (*8*). Pervaporation can profitably be used for the separation of mixtures of close-boiling liquids (azeotropes, isomers), and the removal of low concentrations of volatiles from mixtures.

Table 1
Use of Microfiltration and Pervaporation in a Fermentation

	Microfiltration	Pervaporation
Membrane type	Porous	Homogenous
Membrane material	Polymers, ceramics	Polymers, zeolites
Type of equipment	Tubular, plate and frame, spiral wound, hollow fibre	Plate and frame, hollow fibre
Driving force	Transmembrane pressure	Concentration gradient
Transport	Convection	Solution/diffusion
Product	Cell-free broth	Ethanol/water mixture
Fouling	Severe	Negligible
Operation	Relatively complicated	Simple
Sterilization	Steam, chemicals	50 % ethanol
Permeate flux	Up to 30 l/m²h at 150 g/l biomass	3 l/m²h at 30°C About factor 2 increase with 10°C increase
Selectivity[a].		4 (9): 5 wt% EtOH -> 16 % 17 (11): 5 wt% EtOH -> 47 % 47 (10): 5 wt% EtOH -> 71 %

a. Selectivity: $S = (1-x)/x \cdot y/(1-y)$, with x and y the mass fractions of ethanol in the broth and the pervaporate respectively. The selectivity is illustrated by a calculation of the pervaporate concentration of ethanol at an ethanol concentration in the broth of 5 wt%.

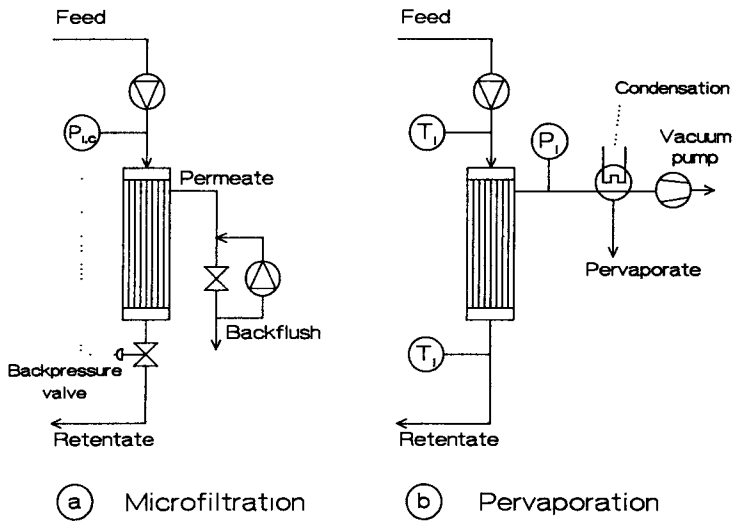

Fig. 1. Schematic diagram of (a) microfiltration and (b) pervaporation.

The mass transfer in pervaporation membranes is based on the solution-diffusion mechanism. A homogeneous, nonporous membrane is used, through which a compound diffuses only when it dissolves to a certain extent in the membrane.

At the downstream side of the membrane, the compound is evaporated in a vacuum, and the vapor is trapped in a condensor. The components of a liquid mixture can be separated, based on their difference in solubility and diffusivity in the membrane.

Pervaporation with a hydrophobic membrane can be applied in an alcoholic fermentation for the in situ recovery of ethanol. Other medium constituents, such as microorganisms, proteins, salts, and the like, are rejected by the membrane. Volatile byproducts in the fermentation, such as the higher alcohols and esters, will also be recovered. In general these compounds dissolve well in the membrane, and they show a relatively high flux compared with ethanol. This phenomenon can play an important role in the case of production of alcohol for consumption or in the use of pervaporation for the dealcoholization of beverages. For more details on pervaporation, *see* Table 1 and Fig. 1.

From a process point of view, the pervaporate flux and the selectivity are the key parameters in designing a process. Current commercial composite membranes based on silicone rubber show a total flux of about 3 L/m^{2}h at 30°C and an ethanol/water-separation selectivity of 4 (SEMPAS Membrantechnik GmbH, Horb, FRG [*9*]). The flux can be increased by decreasing the membrane thickness or by increasing the feed temperature, but, at very high fluxes, transport limitation of vapors at the downstream side may occur. Membrane materials that have a higher selectivity than pure silicone rubber ($S=7$) have already been reported, e.g., silicone copolymers ($S=46$, [*10*]). The addition of silicalite, a hydrophobic zeolite, to silicone rubber can lead to a higher selectivity ($S=17$, [*11*]). These data illustrate that in the future several improvements in membrane materials and equipment may be expected.

PROCESS CONFIGURATION

Microfiltration and pervaporation have been coupled to free-cell ethanol fermentations to investigate the operational characteristics of the integrated system and to elucidate the fermentation kinetics. Two process schemes were studied and are shown in Fig. 2. In the first scheme (Fig. 2a), only pervaporation is coupled to the fermenter. This simple concept can be used in a batch, fed-batch, or continuous mode. Pervaporation decreases the ethanol concentration, and the reduction of inhibition enables the conversion of a concentrated feed. In the continuous mode, a bleed is used to prevent the accumulation of potential inhibitors, such as byproducts and salts. In this system the biomass concentration is increased

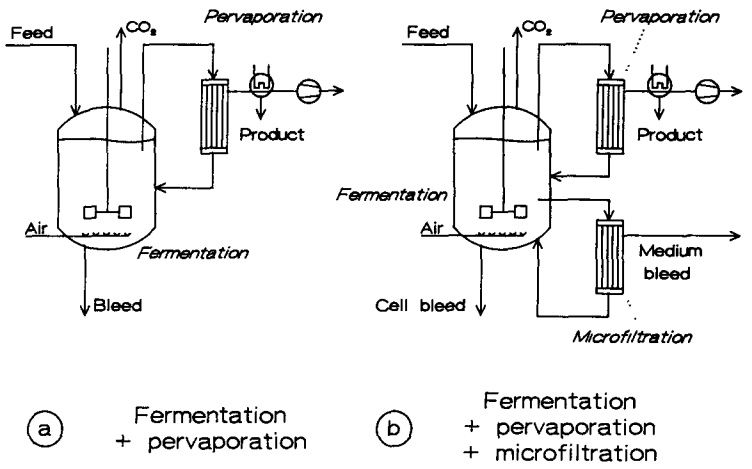

Fig. 2. Schematic digram of integrated processes: (a) pervaporation coupled to the fermentation; (b) pervaporation and microfiltration coupled to the fermentation.

as a result of the removal of water in the recovery section. However, cells are also removed with the bleed, and the resulting biomass concentration is a function of the feed, bleed, and product flows. In the second scheme (Fig. 2b) pervaporation is combined with microfiltration, which makes it possible to control the biomass concentration independently. A bleed is used to remove an excess of cells, and a medium bleed is used to remove an excess of accumulated medium components and/or water.

In both process configurations, ethanol fermentations were performed with *Saccharomyces cerevisiae* CBS 8066 and with a glucose solution as the feed. The total fermentation volume was about 1.5 L, and the fermentation temperature was 30°C. Microfiltration was carried out with a 0.1-m^2 hydrophilic hollow-fiber membrane module (X-Flow, Hengelo, The Netherlands). Pervaporation was carried out with membrane modules with pervaporate flows of 0.07–0.15 L/h at 30°C and selectivities of 3–4 (SEMPAS Membrantechnik GmbH, Horb, FRG). The ethanol/water vapors were condensed under vacuum at a cooling temperature of 0°C. More details about the experimental setup will be published in forthcoming papers.

RESULTS

Preliminary fermentation results are summarized in Table 2. In both integrated systems, the glucose consumption could be increased by a factor of two compared with a conventional continuous fermentation. In the system with microfiltration and pervaporation, the biomass concentration could be increased to 150 g/L and the productivity to 32 g/Lh.

Table 2
Fermentation Results With the Membrane-Based Integrated Systems

	Biomass concentration (kg/m^3)	Substrate consumption (kg/m^3)	Productivity (kg/m^3h)
Continuous fermentation	7	150	2
Continuous + pervaporation	35	350	13
Continuous + pervaporation + microfiltration	150	358	32

A mathematical model has been derived to describe the kinetics of the fermentation. The model is used for design, optimization, and control purposes. First, the mass balances for biomass, substrate, and product were derived over the system with the feed, cell bleed, medium bleed, and product flows. With these mass balances, the fermentation data could be described using the kinetic equations below.

A linear inhibition of the growth rate by ethanol is found at concentrations of 50–70 g/L. (All fermentations were carried out at an excess of glucose and with ethanol inhibition as the limiting factor.) Therefore, the biomass production rate (r_X in kg/m^3h) is given by:

$$r_X = \mu \cdot C_X = \mu_{max} \cdot (1 - C_P/C_P^{max}) \cdot C_X \quad (1)$$

The sugar consumption rate (r_S in kg/m^3h) can be modeled satisfactorily with the linear relation. Depending on the growth rate, the yield of biomass on substrate (Y_{SX}) ranges from 0.005 to 0.05 g/g.

$$r_S = r_X/Y_{SX} = r_X/Y_{SX}^{max} + m_S \cdot C_X \quad (2)$$

The ethanol production rate (i.e., the ethanol productivity; r_P in kg/m^3h) is linked to the substrate consumption rate via the yield of ethanol on substrate (Y_{SP}). This yield of ethanol on substrate yield depends on the yield of biomass on substrate according to the elemental balance (*12*): the yield of ethanol on substrate increases when the growth rate decreases, and was found to range from 0.38 to 0.44 g/g.

$$r_P = Y_{SP} \cdot r_S \quad (3)$$

In the system with product recovery, byproducts and salts will accumulate, and this will have an inhibitory effect on the activity of the yeast (*see also* ref. [*5*]). Particularly, a decrease in the maximal growth rate (μ_{max}) and ethanol concentration (C_P^{max}) can be expected in the system with pervaporation compared with a system without pervaporation.

The systems with pervaporation and microfiltration were easy to operate, and continuous fermentations could be run for >2 mo. The microfiltration unit showed a constant flux of about 0.7 L/h. The flux and selectivity of the pervaporation modules were constant, indicating that no fouling occurs. There are indications, however, that the transport of carbon dioxide from the medium affects the downstream pressure in the modules that can influence the flux.

SIMULATIONS

In this discussion some aspects of a membrane-based integrated ethanol-production process relevant to the technological and economical feasibility on a large scale will be considered. All simulations were based on the kinetic model.

Optimization of the Fermentation

Calculations for systems with microfiltration and pervaporation show that high ethanol productivities of 50–60 kg/m^{3}h can be obtained at high product and bleed flows. The simulations were based on a biomass concentration of 150 kg/m^3. This concentration was found to be the practical limit with respect to the viscosity of the broth and the carbon dioxide release from the broth. At a pervaporation selectivity of 4, the substrate concentration in the feed is limited to about 400 kg/m^3, since most of the water introduced with the feed is removed in the recovery section. At higher selectivities the substrate consumption can be increased, and then the accumulation of byproducts and salts is less severe.

Process Configuration

Simulations show that it is advantageous to couple microfiltration directly to the fermentation and to apply pervaporation to the cell-free broth. In this case the temperature of the pervaporation may be increased, and a higher flux will be obtained. The membrane area for pervaporation will then be smaller, although the area for microfiltration will be larger, since higher recirculation rates are required. This concept is shown in the scheme in Fig. 3, which also includes some scale-up aspects. The fermentation is divided into a growth phase in the first fermenter and an ethanol-formation phase in the second fermenter (*see also* ref. [3]). In the second fermenter a high ethanol concentration can be obtained, which will reduce the membrane area and the recovery costs. The microfiltration units are placed in a separate loop with a high recirculation rate to reduce fouling. The pervaporation units, including a trimheater, are also placed in a separate loop with a high recirculation rate to maintain a constant high temperature and flux. The process may be scaled up by using several loops with membrane modules.

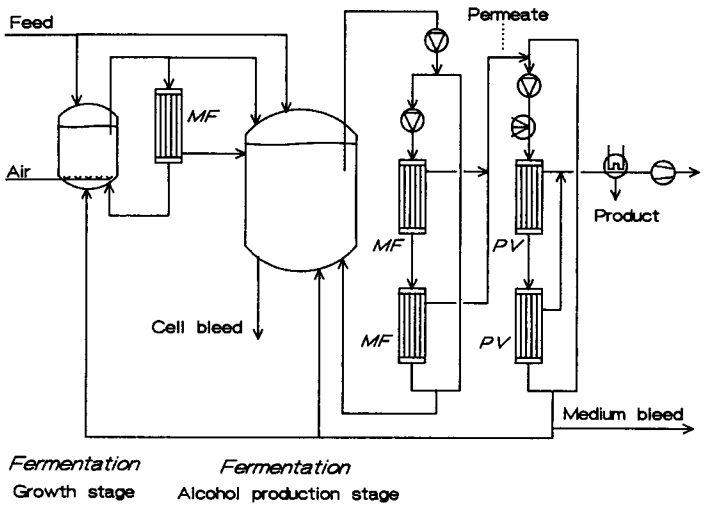

Fig. 3. Proposed process scheme for operation on a large scale. MF, microfiltration; PV, pervaporation.

Economics

A computer program was written for the estimation of the economics of the integrated processes described in this paper. Results are presented for a scheme as depicted in Fig. 3 with ethanol purification to 99.5% by distillation and (azeotropic) pervaporation. It was calculated that the optimal substrate consumption rate for the fermentation should be about half the maximal rate and that the substrate concentration in the feed should be maximal for economic processing. For a process on a 50-m^3 scale (productivity, 60 kg/m^3h; substrate concentration in the feed, 350 kg/m^3) a microfiltration area of about 2000 m^2 and a pervaporation area of over 3000 m^2 were calculated, based on a selectivity of 4 for pervaporation. Further assumptions were that the price of all membrane modules is \$500 m^2 (lifetime 3 yr), the microfiltration flux is 30 L/m^2h, and the pervaporation flux is 5 L/m^2h. In this case, an ethanol price, excluding substrate costs of about 0.40 \$/kg, is calculated. With silicone/silicalite membranes with a selectivity of 17 (*11*) and a substrate concentration of 500 kg/m^3 in the feed, the produce price is about 0.25 \$/kg ethanol. In the review article by Maiorella et al. (*13*) on ethanol production schemes, a minimal ethanol production price of \$0.20/kg, excluding substrate costs, was calculated for a process with in situ product recovery by extraction.

CONCLUSIONS

By applying pervaporation and microfiltration to an ethanol fermentation, the substrate consumption was greater by a factor of two and the productivity by a factor of 15 than that in a conventional continuous cul-

ture. The fermentation data can be described adequately by a kinetic model. The membrane techniques are relatively easy to operate, and fouling occurs in microfiltration modules, but not in pervaporation modules.

Simulations show that the fermentation performance can further be improved and that the process configuration can be optimized to reduce the membrane area. On a large scale a membrane area as high as 2000–3000 m^2 may be needed, which may give rise to logistic problems.

With the presently available equipment, commercial ethanol production with membrane-based integrated systems is not economically feasible. The flux of existing pervaporation membranes may be acceptable; however, the selectivity is still too low to make pervaporation competitive with other separation techniques.

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