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Ethanol production in membrane distillation bioreactor

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Abstract

The batch fermentation combined with the removal of ethanol from the broth by means of membrane distillation process (MD) has been investigated. The porous capillary polypropylene membranes were used for the separation of volatile compounds from the feed (broth), formed as a result of fermentation. The elimination of these compounds allows increase in the productivity and the rate of conversion of sugar to ethanol, since they act as inhibitors. In the case of fermentation combined with the MD, the efficiency of 0.4–0.51 (g EtOH)/(g of sugar) and the production rate of 2.5–4 (g EtOH)/dm^3 h was achieved in relation to 0.35–0.45 (g EtOH)/(g of sugar) and 0.8–2 (g EtOH)/dm^3 h obtained in the classical batch fermentation. The ethanol flux obtained in membrane distillation varied in the range of 1–4 (kg EtOH)/m^2 per day and was dependent on the temperature and the feed composition.

Keywords: Membrane bioreactor; Fermentation; Ethanol; Membrane distillation

1. Introduction

Providing alternative liquid fuels is probably the most challenging aspect of the present search for oil substitutes. The ethanol production from biomass is one of the few plausible options which is available [1]. The fermentation reaction can be expressed as:

$$\text{sugar} + \text{nutrients} \overset{\textit{cells as catalyst}}{\rightarrow} \text{ethanol} + \text{cells} + \text{by-products}$$

The principal process in the ethanol production is the decomposition of sugar to ethanol and carbon dioxide through the glycolytic route. This reaction can be summarized as follows:

$$C_{12}H_{22}O_{11} \rightarrow 4C_2H_5OH + 4CO_2$$

The maximum theoretical efficiency of ethanol from this decomposition is 0.534 on a weight basis. The 0.48–0.5 conversion is typically achieved in practice since the residual is used in the production of yeast cell mass and other minor fermentation products (glycerol, acetaldehyde, fusel oils, etc.).

Many fermentations are inhibited by the high concentrations of products which is commonly known as 'end product inhibition'. In the case of ethanol fermentation the major limitation of the conventional process comes from ethanol inhibition. When the ethanol concentration in the fermentation broth reaches ca. 12% by volume, both a specific growth and the specific production rates of microorganisms decline, the cell density in the fermenter remains low, and a concentrated sugar solution cannot be completely fermented [2]. Therefore, the conventional process of ethanol production is limited by the above-mentioned phenomena. This problem can be solved by the integration of fermenter with a separator for both, the selective and continuous removal of the fermentation products (mainly ethanol).

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The applications of extraction in the liquid–liquid system is a frequently proposed solution [2–4]. The disadvantage of the extractive system is the contamination of ethanol with extractant as well as its toxic effect on the yeast. These problems may be partly solved by the application of membrane extractors [5]. In this case, the interfacial surface is maintained within the membrane pores, and the extraction takes place in the system of the two continuous phases. The advantage of this solution is the achievement of a high surface of the mass transfer. However, the disadvantages is the difficulty with maintaining the interfacial surface within the membrane pores [6]. This problem does not occur when the extractant is separated from broth by a hydrophobic membrane, the pores of which were filled with the gaseous phase [7]. The removal of ethanol from broth can be performed by pervaporation [8]. However, this process is mainly used for the removal of water from the concentrated ethanol solutions in order to obtain its dehydration [9].

Membrane distillation (MD) can also be used for the separation of ethanol from the broth [10,11]. MD is the evaporation process of the volatile feed components through the air-filled pores of a hydrophobic membrane [10–12]. Generally, the membrane separates two aqueous solutions differing in temperature and composition. The primary requirements of the process is to sustain the gaseous phase in the membrane pores. The porous membranes used for MD are prepared from polymers, such as polytetrafluoroethylene, poly(vinylidene fluoride) or polypropylene, to comply with the requirements of non-wettability for several aqueous solutions. Membrane distillation can be applied successfully for water treatment and the concentration of the acid and salt solutions [13,14]. The driving force of the mass transfer through the membrane pores is a vapor pressure difference on both sides of membrane, which depends on the temperature and the solutions composition in the layers adjacent to the membrane. The separation mechanism in MD results from the feed solution/vapor equilibrium. The composition of permeate passing through the membrane is dependent on the partial pressure of respective components of the feed. In the case of non-volatile substances (such as NaCl), only water vapor passes through the membrane. The separation factor of dissolved substances in this case is close to 100%. However, when the feed contains more volatile components (e.g. HCl, EtOH) besides water, they all appear in the distillate collected on the other side of the membrane. The composition of permeate transported through the membrane in this case depends on the volatility coefficient values for the respective components of the feed. During membrane distillation of water-ethanol solution, the flux of both ethanol and water vapor through the membrane is obtained. However, at a given temperature, the volatility of ethanol is higher, therefore, the obtained distillate would be enriched in ethanol. For the dilute solutions of alcohol (up to 10%), it is possible to obtain the distillate with a 3–5 times higher ethanol concentration than in the feed. The application of bioreactor coupled with the system for membrane distillation enables to obtain a preliminary concentration of the product simultaneously with the removal of harmful metabolites.

The purpose of this work is to demonstrate the effect of membrane distillation application on the ethanol productivity in the fermentation membrane bioreactor.

2. Experimental

The experimental studies of sugar fermentation with simultaneous separation of the volatile products were carried out on the installation presented in Fig. 1. A tank with a working volume of 5.5 dm^3, located in a thermostat, constituted a bioreactor. The bioreactor was connected through a pump with a module for membrane distillation. The capillary module made from polypropylene membrane was used in this installation. The outside and inside diameters (d_{out}, d_{in}) of the capillary membranes amounted to 2.6 and 1.8 mm, respectively. These membranes have the pore sizes with a nominal and maximum diameter of 0.22 and 0.6 μm, respectively, and a porosity of ca. 73%. The effective membrane area amounted to 490 cm^2. The distillate cooled to 293 K (T_{D_ϵ}) flows through the inter-capillary space of the MD module. The feed (fermenting broth) flows inside the membranes. The inlet feed temperature (T_{F_ϵ}) was the same as the temperature of fermenting broth (T_B).

Two types of the batch fermentation experiments were carried out: the conventional free-cell fermentation as the standard process, and the fermentation in which the produced ethanol was removed continuously from the membrane bioreactor by membrane distil-

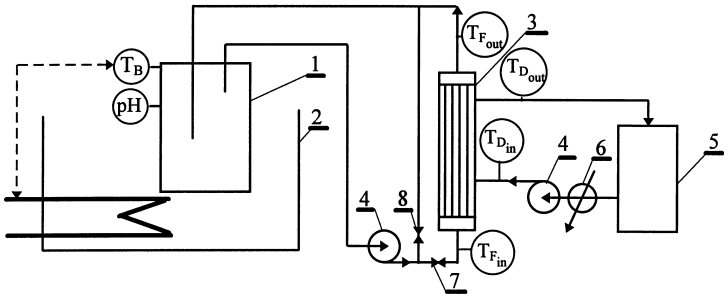

Fig. 1. Scheme of the experimental apparatus. 1, bioreactor; 2, thermostat; 3, MD module; 4, pump; 5, distillate tank; 6, heat exchanger; 7, valve 1; and 8, valve 2. T, temperature: D, distillate; F, feed; and B, broth.

lation. Both types of fermentation were performed at temperatures of 303 and 309 K, which were within the temperature range recommended for the utilized yeast.

A fermentation solution was prepared by pouring 5 dm^3 of sucrose solution (commercial product) dissolved in tap water, heated to the boiling point, with the addition of 0.5 g/dm^3 of urea. The sugar solutions with the concentrations of 50, 100 and 150 g/dm^3 were used in the studies. Subsequently, the liophilized yeast in the amount of 5 g/dm^3 was introduced into the solution at a temperature of 303 K. A commercially available dry distillery yeast (*Saccharomyces cerevisiae* — Bc 16a) manufactured in Poland were used as the microorganism. Rehydratation was performed for 30 min while the broth was periodically agitated. In order to perform the sterilization, the membrane bioreactor was flushed before the experiments with a 10% solution of H_2SO_4 followed by distilled water.

In the system used with MD, the fermentation process was carried out with periodic flow of broth through the MD module (valve 1 — open and valve 2 — closed; Fig. 1). The batch fermentation process was continuously carried out for 2–3 days, whereas the membrane distillation system was switch on for 5–6 h per day. The distillate side of MD installation was filled initially with distilled water (0.5 dm^3). Analyses of the sugar and alcohol contents in the broth were performed before switch-on, and after switch-off, of the MD system. The alcohol concentrations in the distillate obtained in MD were also determined over the same periods of time as previously. The permeate flux (ethanol + water vapor) transported through the membrane was determined by the measurement of an increase of distillate volume. The volume flux can be calculated from the equation:

$$N = \frac{V_D^2 - V_D^1}{At} 24 \quad (dm^3/m^2\ 24h) \tag{1}$$

where: V_D^1 is the volume of liquid in the MD system on the distillate side, at the start of MD process, dm^3; V_D^2 the volume of liquid in the MD system on the distillate side, at the end of MD process, dm^3; A the working area of membranes in the MD module, m^2, and t the number of working hours of the MD installation, h.

The ethanol flux (recalculated on 100% alcohol) was calculated based on the measurement of changes of both, the ethanol concentration in the distillate and the distillate volume:

$$N = \frac{V_D^2 c_{EtOH}^2 - V_D^1 c_{EtOH}^1}{At} 24 \quad (kg\ EtOH/m^2\ 24\,h) \tag{2}$$

where: c_{EtOH}^1 is the initial concentration of ethanol in distillate, (kg EtOH)/dm^3; and c_{EtOH}^2 the final concentration of ethanol in distillate, (kg EtOH)/dm^3.

For a comparison, each fermentation combined with membrane distillation was repeated for a disconnected MD system (valve 1 — closed and valve 2 — open; Fig. 1). The recirculation system during the conventional free-cell fermentation was start-up for 5–6 h per day, similarly as in the case of the fermentation with a connected MD system.

Analysis of the sugar content in the fermentation broth was performed using an Abbe refractometer. A sample previously centrifuged in order to remove the yeast cells, was then filtered through the MILLEX-HV membrane filter (manufactured by MILLIPORE), with a pore diameter of 0.45 μm. The filtrate (10 ml) was placed in the vacuum drier, for evaporation of ethanol at temperature 343 K and at pressure 0.03 MPa. The

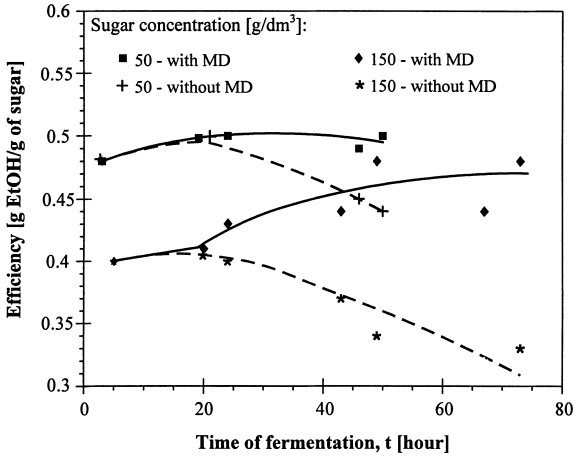

Fig. 2. Variations of the efficiency of the fermentation process carried out in the system with MD (solid line), without MD (broken line); for the broths with different initial concentrations of sugar. Fermentation temperature $T_B = 309$ K.

evaporation carried out for 30 min allowed to obtain about a 50% reduction of the sample volume. The loss of volume was refilled with distilled water and the refraction of solution was then measured. The sugar content was determined from the calibration curve.

The ethanol concentration in the broth and distillate was measured using a Shimadzu GC-14 gas chromatograph with a FID detector using a DB-WAX capillary column with a diameter of 0.53 mm and length of 30 m.

The pH measurement of broth was performed using an Elmetron CI-316 microcomputer pH-meter.

3. Results

The comparison of the experimental results obtained from the performed fermentations indicates, that the fermentation combined with the membrane distillation process proceeded considerably faster and with a higher efficiency.

The changes of efficiency during the fermentation as a function of the process parameters are shown in Fig. 2. The tendencies of the efficiency changes indicate that, for the first 20 h (without MD), the efficiency of the fermentation process increases until it reaches a certain maximum. This efficiency is dependent on the sugar concentration in the broth: ca. 0.41 (g EtOH)/(g of sugar) and 0.5 (g EtOh)/(g of sugar) for the solutions with 150 (g of sugar)/dm^3 and 50 (g of sugar)/dm^3, respectively. This results from the achievements of the optimal conditions of the growth and activity of yeast. During further fermentation, the inhibiting effect of products formed in the process becomes pronounced. In the case of fermentation without the removal of these products, a continuous decrease of the process efficiency was observed for a longer period of time (dotted lines).

The fermentation combined with the membrane distillation process, however, behaved differently (solid lines). During MD, the transport of volatile products of fermentation across the porous membrane occurs. As a result, the advantageous working conditions of yeast are maintained. Therefore, the efficiency of the fermentation exhibited a continuously growing tendency, approaching a theoretical value of 0.53 (g EtOH)/(g of sugar). The calculated values of efficiencies in the respective intervals of time were clearly dependent on the state of working of the MD system (switch on/switch off). The MD system was start-up for the first time (for a period of 5–6 h) after about 20 h of fermentation. This caused a significant increase of the process efficiency, which is expressed by the scattered points in Fig. 2. The points placed beneath the solid lines represent the state when MD installation was switched off, whereas the points above these lines represent the results obtained for working MD system. The process efficiency was also increased for the subsequent intervals of work of the MD system, namely after ca. 43 and 67 h of fermentation. The highest efficiency close to 0.51 (g EtOH)/(g of sugar) was obtained for a solution of 50 (g of sugar)/dm^3. A slightly lower efficiency of about 0.47 (g EtOH/(g of sugar) was obtained for a solution of 150 (g of sugar)/dm^3. The efficiency of sugar conversion to ethanol during the switch-off periods of the MD system was stabilized, exhibiting only a slight variations of declining. In this period, the concentration of inhibiting by-products in the broth increases. Thus, the fermentation efficiency was reduced (points beneath solid lines).

The performance of fermentation in the membrane bioreactor, in comparison with the classical tank reactor, allowed not only to increase the process efficiency, but also resulted in a higher rate of conversion of sugar into ethanol, which is shown in Fig. 3. The

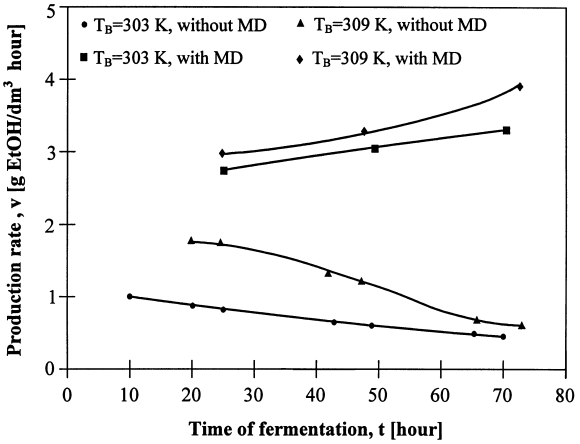

Fig. 3. Variations of the fermentation rate in the system with/without MD. The broth compositions: 5 (g of yeast)/dm^3, and 150 (g of sugar)/dm^3.

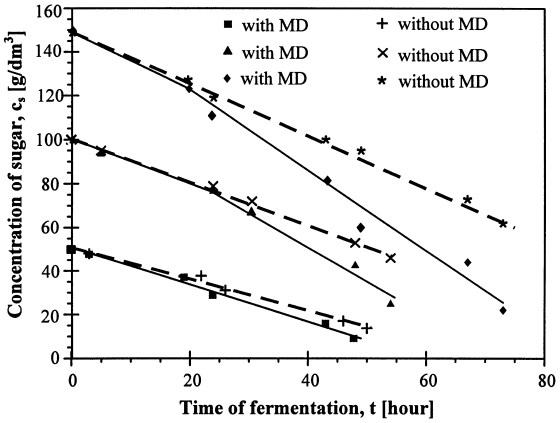

Fig. 4. Variations of sugar concentrations in the broths with different initial concentrations, fermenting in the system with/without MD. Fermentation temperature $T_B = 309$ K.

depicted results demonstrated that, in case of the membrane bioreactor, the amount of ethanol obtained from 1 dm^3 of broth for 60 min is 2–3 times larger in comparison with the classical fermentation. The elevation of temperature from 303 to 309 K accelerates the rate of fermentation process and, therefore, the concentration of inhibiting compounds (not only ethanol) also increases. The production rate decreased rapidly when the fermentation products were not removed, which is represented by the line $T_B = 309$ K without MD, in Fig. 3. This phenomenon did not occur in the membrane bioreactor system (line: $T_B = 309$ K, with MD), because the products formed in the fermentation process were removed by MD.

The changes of the sugar concentration in the broth during the fermentation are presented in Fig. 4. In the case of fermentation carried out in a classical mode, the rates of the changes of sugar concentrations are less pronounced than in the membrane bioreactor. A considerable increase of the rate of sugar loss in broth was observed during the work of the MD system. Therefore, a substantial reduction of fermentation time can be achieved in comparison with the classical batch fermentation.

The results shown in Fig. 5 indicate that the ethanol flux (recalculated on 100% alcohol) across the membrane in MD is essentially dependent upon the broth temperature and increases along with an increase of ethanol concentration in the broth. The driving force for the ethanol transport in MD (partial pressure difference) increases both, with the increase of temperature and feed concentration. The influence of sugar concentration in the broth on the magnitude of the ethanol stream is negligible.

As fermentation follows the successive doses of sugar are converted for ethanol and its concentration in the broth increases. The rate of ethanol production in membrane bioreactor was higher; thus, the ethanol concentration in the broth was also higher (see Fig. 6). However, this did not involve such a noticeable inhibiting effect, since the obtained concentration of ethanol

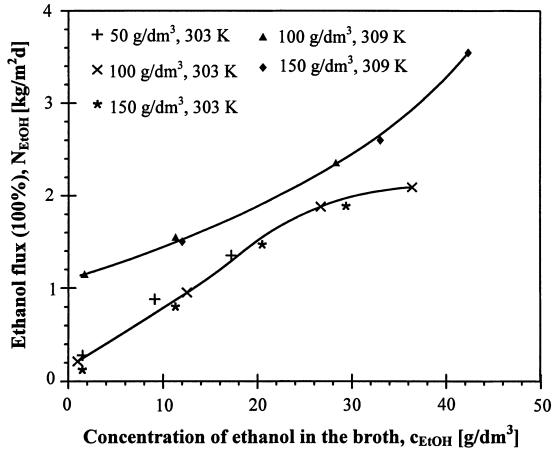

Fig. 5. The magnitude of obtained ethanol fluxes (recalculated on 100%) as a function of the temperature and ethanol concentration in the broths differing in the initial concentrations of sugar.

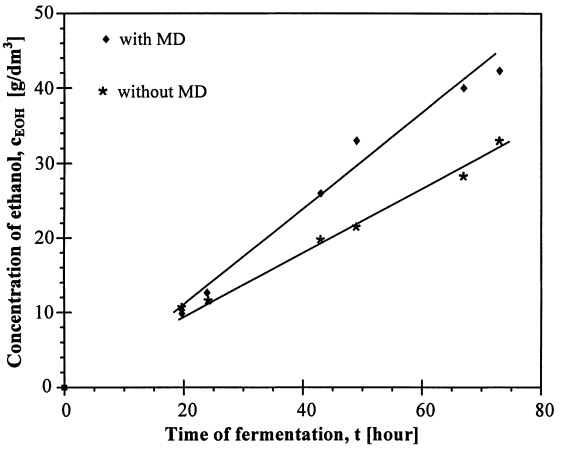

Fig. 6. Variations of ethanol concentration in broths with 150 g/dm^3 initial concentrations of sugar fermenting in the system with/without MD. Fermentation temperature $T_B = 309$ K.

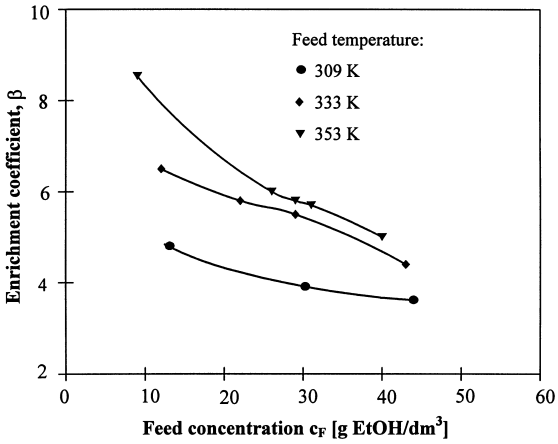

Fig. 7. The dependence of the enrichment coefficient on the ethanol concentration in broths and the feed temperature.

(50 g/dm^3), is not harmful for the yeast activity [2]. The results presented in Fig. 6 suggest that, in our experimental systems, the course of fermentation process is not only affected by ethanol concentration, but also by the presence of other by-products. These compounds are frequently volatile, therefore, they can be also removed by MD process.

During the ethanol separation from broth by MD, simultaneously it is concentrated in the permeate. The value of the enrichment coefficient reached is expressed as:

$$\beta = \frac{c_P}{c_F} \equiv \frac{V_D^2 c_D^2 - V_D^1 c_D^1}{c_F (V_D^2 - V_D^1)} \quad (3)$$

where: c_P is the ethanol concentration in the permeate; c_F the ethanol concentration in the broth; it being illustrated in Fig. 7. For the examined range variation of ethanol concentration in the broth, the β value strongly depends on the feed temperature in the MD process. Fourfold increase of ethanol concentration in the permeate was obtained for the fermentation temperature $T_B = 309$ K. An elevation of distillation temperature $T_{F_\in}$ to 353 K enables the achievement of a sixfold increase of the permeate concentration. The dependence of partial pressure on the temperature is exponential; thus, along with elevation feed temperature the growth of the driving force is achieved. Unfortunately, a thermal death of applied yeast takes place at a temperature of 353 K. The enrichment coefficient reaches a higher values for the distillation of diluted solutions. This results from a well-know behaviour of alcohol. Ethanol is a non-polar component; therefore, it is accumulated in the diluted aqueous solution at the free surface of liquid (feed/membrane interface). This surface constitutes the vaporization surface in the MD process.

The initial pH value of fermenting broths was close to six and is systematically lowered during the fermentation process. After running the fermentation process for 24 h, the pH of broths approaches the value of 4, and during the next hours of its duration the pH decreases only slightly, up to a final value of 3.8. Low values of pH may validate the occurrence of bacterial infection in the examined systems, which results in a decrease in the conversion of sugar to ethanol. In spite of a similar distribution of the changes of pH values in the fermenting broths performed with or without the MD process, considerably higher values of the efficiency of transformation of sugar into ethanol were obtained in the former case.

The application of the membrane reactor allows to remove from the broth not only ethanol but also the other by-products of fermentation. The presence of these products in the MD distillate caused an odour characteristic of unrefined ethanol. Substantial amounts of carbon dioxide are also transported through the membrane. The removal of above-mentioned compounds, which like ethanol are the inhibitors of fermentation, was surely the reason for the observed advantages resulting from the performance of fermentation in the membrane bioreactor.

4. Conclusion

The membrane distillation can be successfully applied for the removal of volatile components from the fermenting broths. During several months of MD module work, a negative influence of separated broths on the hydrophobic polypropylene membrane mounted in it has been not observed.

The performance of fermentation in the membrane bioreactor allows for a considerable acceleration of its course and increases its efficiency through the selective removal of fermentation products formed. The efficiency of conversion of sucrose to ethanol obtained in the experiments amounted to 0.47–0.51 (g EtOH)/(g of sugar) for the fermentation carried out with the MD system, whereas it was 0.35–0.45 (g EtOH)/(g of sugar) for the fermentation carried out without the removal of its products.

The application of the membrane bioreactor allows to perform the fermentation of concentrated sugar solutions, which normally lead to a significant increase of the ethanol concentration in the classical reactors.

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