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Bioethanol Production in Membrane Bioreactor (MBR) System: A Review

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Abstract

World is facing not only atmospheric pollution but also climate changes as consequences of the use of petroleum fuels and progressive depletion of non-renewable energy resources. Therefore, biofuels as ethanol derived from biomass through fermentation are becoming more significant. The concentration of ethanol in the fermentation broth can range from 1 to 15 wt% depending upon the source of biomass and hydrolysis process. The water content of ethanol in broth must be reduced from 85 to 99 wt% to less than 1.3 wt% water to produce fuel grade ethanol. Distillation is the traditional technology for the recovery of ethanol from these dilute biomass fermentation broth which needs a high amount of energy. As an alternative, pervaporation is a membrane separation method that can be coupled with fermentation to remove ethanol from the fermentation broth continuously. Combining fermentation with pervaporation in addition to water and energy savings, will also reduce product inhibition by keeping the ethanol concentration in the broth low and simplify downstream processing as the ethanol recovered will be more concentrated. Overall, this review paper demonstrates that membrane bioreactor can serve as a highly selective, cost and energy saving technology in the bioethanol industry.

Keywords: Bioethanol, MBR, Pervaporation, Fermentation.

1. Introduction

The global production of bioethanol showed an upward trend over the last 25 years with a sharp increase from 2000. Worldwide annual production capacity in 2005 and 2006 were about 45 and 49 billion litres, respectively and total output in 2015 is forecast to reach over 115 billion litres. Brazil was for a time the largest bioethanol

producing country, but in 2005, the United States passed Brazil and became the world's number one ethanol producer. Bioethanol production from non-food biomass resources as feedstock is of particular relevance in countries with large populations and growing gasoline consumption such as Brazil, Egypt, China and India. As per report of *RFA* (2012) America is the largest producer of bioethanol (19,568 MG) followed by Brazil (5,577 MG), Europe (1,139 MG) and India (573 MG). About 3.9 billion litres of ethanol can be produced from rice straw and bagasse in China and India. **[1]**. Intense research has been carried out for obtaining efficient fermentative organisms, low cost fermentation substrates, and optimal environmental conditions for fermentation to occur. The different fermentation systems used are batch, continuous, fed-batch and semi-continuous, immobilised systems and MBR systems. The MBR systems, in addition to water and energy savings, can continuously remove ethanol from the fermentation process thereby accelerating fermentation and increasing throughput without the installation of additional tank.

2. Fermentation Systems

Ethanol can be produced by four main types of industrial operations: batch, continuous, fed-batch and semi-continuous. In batch fermentation, substrate and yeast culture are charged into the bioreactor together with nutrients. Major advantages of batch systems are that it does not require much control, can be accomplished with unskilled labour, complete sterilization and management of feedstocks are easier **[2].** The other advantage of batch operation is the greater flexibility that can be achieved by using a bioreactor for various product specifications.

In the continuous process, feed containing substrate, culture medium and other required nutrients are pumped continuously into an agitated vessel where the microorganisms are active. The product, which is taken from the top of the bioreactor, contains ethanol, cells, and residual sugar **[2].** Fermentation systems operated in continuous mode of operation offer a number of advantages compared to batch processes, generally resulting in enhanced volumetric productivity and, consequently, smaller bioreactor volumes and lower investment and operational costs. **[2]** The major drawback is that yeasts cultivated under anaerobic conditions during long time diminish their ability to synthesize ethanol. In addition, at high dilution rates enabling elevated productivities, the substrate is not completely consumed and yields are reduced **[3]**.

In fed-batch operation, the feed solution, which contains substrate, yeast culture and the required minerals and vitamins, are fed at constant intervals while effluent is removed discontinuously. The main advantage of the fed-batch system is that intermittent feeding of the substrate prevents inhibition. If the substrate has an inhibitory effect, intermittent addition improves the productivity of the fermentation by maintaining a low substrate concentration. It is essential to keep the culture volume constant in continuous operation, whereas there is volume variation in the fed-batch processes.

In semi-continuous processes, a portion of the culture is withdrawn at intervals and fresh medium is added to the system. In the continuous processes it is essential to maintain a constant culture volume, whereas there is volume variation in semi-

continuous processes. This method has some of the advantages of the continuous and batch operations. There is no need for a separate inoculum vessel, except at the initial startup. Time is also not wasted in non-productive idle time for cleaning and resterilization. Another advantage of this operation is that not much control is required. However, there is a high risk of contamination and mutation due to long cultivation periods and periodic handling. Furthermore, since larger reactor volumes are needed, slightly higher investment costs are required. **[4]**

3. Fermentation with Immobilized Cell System

One of the strategies used for improving the fermentation is the immobilization cell technology that allows the implementation of continuous processes with higher yields and productivities and with increased cell concentrations **[3]**. As a result, shorter residence time and smaller reactor size can be employed. Other major advantages include prolonged cellular stability, increased ethanol yield, increased tolerance to high substrate concentration, reduced end product inhibition, easier product recovery leading to decreased energy demands and process expenses, regeneration and reuse of cells for extended periods in batch system, feasibility of continuous processing, and reduction of risk of high cell densities. **[5]**

The main factors influencing the immobilisation behaviour of the cells and their productivity are the surface characteristics of the carrier including pore size, particle size, water content, hydrophilicity etc**.** The most widely used immobilization methods are based on cell entrapment in gels, such as carrageen and Ca alginate **[6,7]**. Other methods are based on passive adhesion to the surfaces, such as glass beads, stainless steel wire spheres. **[8].** Apart from these various lignocellulosic materials have been tried as microbial support. Some examples are orange peel, wooden chips or blocks, sorghum baggase, rice husk, wild sugarcane, wheat starch granules.

The main drawback of cell entrapment system is the instability of Ca-alginate against phosphates and the disruption of gel particles due to CO_2 evolution during fermentation **[8].** For the adhesion or adsorption system, as the cells attach to the carriers' surface by electrostatic interactions or covalent binding of the cells, the two major drawbacks are the limitation of the biomass loading by the carriers surface, and the effect of various factors that can cause cell desorption thereby limiting the operational stability. Lignocellulosic support carriers have advantages in terms of cost, safety, and waste treatment but the main drawback is the non uniform structure, often present in a particulate, powder or chip form.

4. Ethanol Recovery

Generally, for ethanol recovery, distillation is the industry standard for separating water from ethanol and is an energy intensive process, accounting for a significant portion of the total energy usage in an ethanol plant. Existing distillation systems also require high volumes of cooling water, resulting in about four gallons of water used for every gallon of ethanol produced **[9].** Fermenting yeast cannot tolerate more than about 10-12% by volume of ethanol therefore in order to achieve complete conversion, it is necessary to start with a relatively dilute sugar solution. Inhibition affects the overall

productivity of the yeast cells and the ethanol yield of the fermentation process. The large amount of water carried through the process results in high costs for large process equipment for fermentation and subsequent separation of ethanol by distillation, which needs a high amount of energy **[10]**. It has been recognized that if ethanol separation is combined with fermentation there will be a reduction in the cost of process. If the ethanol is removed as soon as it is formed, the ethanolic deactivation of yeast cells can be overcome, as the ethanol concentration can be constantly kept low with no additional dilution required **[11].**

5. Fermentation in MBR System

Membrane bioreactors (MBR) with different configurations have been implemented for simultaneous separation of fermented products using pervaporation technique. Pervaporation is well known as an efficient separation method for separation of ethanol water azeotropic mixtures, compared to distillation **[12].**

High alcohol-water selectivities are critical to the energy efficiency of pervaporation. There are some reports in the literature discussing about continuous ethanol production by pervaporation using different cultures, membranes and configurations. Chen et al**. [13]** have investigated ethanol production by *Saccharomyces`cerevisiae* in a continuous and closed-circulating fermentation (CCCF) system using a PDMS pervaporation membrane bioreactor. An ethanol volumetric productivity of 1.39 g/l.h has been obtained in the third cycle, with a yield rate of 0.13 h^{-1}. Also, Ding et al. **[14]** have employed similar configuration for ethanol fermentation with similar results. Nomura et al. **[15]** have studied the removal of ethanol from fermentation broth by silicalite zeolite membrane. They have shown that separation efficiency of the silicalite membrane is disturbed during operation. Ikegami et al. **[16]** have shown that by a coupled fermentation/pervaporation process using a silicalite membrane, which is selective for ethanol, 85% (v/v) ethanol solution could be obtained and the process exhibited about a 20% increase in an average glucose consumption rate

Little data is found in the literature regarding ethanol production in batch MBRs. Ikegami et al. reported a very interesting data that pervaporation flux drastically decreased to 33% of that for an ethanol/water solution with increasing glucose concentration and decrease in the total flux was resulted from a lowering of the water flux **[17]**. The amount of ethanol that was recovered was nearly constant and independent of the glucose concentration. As a result, the separation factor towards ethanol increased from 23 to 137. They also suggested that glucose was not adsorbed by the membrane material, the silicalite powder hence glucose molecules strongly inhibit the adsorption of water molecules into the silicalite membrane.

Different operating conditions, such as flow rate, temperature, feed composition and permeate pressure affects the pervaporation performance **[18].** R.H. Bello et al, reported that the parameters of both the performance analysis of the membrane, permeate flux and the pervaporation separation index (PSI) were higher at lower flow rates. When the flow rates were increased, these parameters decreased. The increase in flow rate negatively affects the diffusion of the ethanol molecules in the membrane, which reduces the mass flux of permeate.

The partial pressure difference (driving force) increases with increased temperature, and the PDMS polymer chains are more flexible, which results in more free volume between the chains, which, in turn, facilitates the diffusion of molecules **[19,20].** As a result, the mass flow of the permeate increases, and the selectivity of the membrane decreases. In this context, higher permeate fluxes are obtained, as are consequently lower selectivity values. R.H. Bello et al, reported that when the feed temperature was increased from 22 to 30 °C, an increase of 10% was observed for the mass flux of the permeate, along with an 8% decrease in the selectivity of the membrane.

Mohammadi et al. **[21]** reported that the degree of swelling of the membrane increases with the feed, which adversely affects the selectivity, and, as a result, more water can be permeated. In addition, the increase in the concentration of ethanol in the feed causes an increase in the flux of ethanol in the permeate, which increases its concentration in this stream. This phenomenon is explained as a result of the increased ethanol concentration improving the adsorption of this component to the membrane; as a result, the membrane becomes swollen, which reduces the selectivity. The permeate flux and separation factor, which is also called selectivity, indicate the performance of the membrane under analysis, which means that, with higher permeate fluxes, the process of pervaporation is less efficient. Wu et al. **[18]** observed high permeate flux rates, with minimum and maximum values of 220 and 409 g/m².h for concentrations of 51.3 and 88.4 g/L, respectively. In contrast, selectivity was reduced to 7.7 and 5.7 for the minimum and maximum concentration values of ethanol, respectively.

Jiratananon et al. **[20]** have stated that, as permeate pressure increases, the driving force for permeation of the ethanol molecules decreases, which results in a decrease in the mass flow of the permeate. According to R.H. Bello et al, a decrease of 64% at a pressure of 20 mmHg and 95% at 45 mmHg in relation to a maximum of 5.85 g/m².h were obtained for the permeate flux at a permeate pressure of 5 mmHg.

Separation factors of PDMS, PTMSP, composite membranes, and zeolite are reported to be in the range of 4.4–10.8, 9–26, 7–59, 12–106, respectively. However, the ethanol–water separation factors in some other cases might exceed these ranges. For instance, the separation factor of ethanol over water is 218, when using a silicate zeolite membrane where ethanol (98.2 wt %) at permeate is continuously obtained from the fermentation broth of 20 wt% ethanol **[15].** In general, the ethanol–water separation factors are largely ranked in the following order: PDMS< PTMSP < composite membranes < zeolite membranes. To date, hydrophobic zeolite membranes are commercially available, while polymeric membranes (PDMS, PTMSP) and composite membranes are still under investigation. Zeolite membranes are more expensive than polymer membranes, but zeolite membranes have higher separation factors and flux than polymer membranes. Therefore, zeolite membranes may be more cost effective on per unit ethanol basis **[11].**

According to **Sherry l. Schmidt et al. [17]** PTMSP membrane shows a distinct advantage over conventional PDMS membranes in ethanol removal. The flux with PTMSP is about three-fold higher and the concentration factor is about twofold higher than the corresponding performance achieved with PDMS under similar conditions. The performance of PTMSP with fermentation broths shows a reduction in both flux

and concentration factor relative to ethanol-water mixtures. However, the PTMSP membranes promise increased resistance to fouling in operation with cell containing fermentation broths.

6. Conclusion

With an aim of reducing overall water consumption and making recovery process energy and cost efficient, MBR system seems to be an emerging technology. Studies can be carried out to explore the possibility of in situ integration of pervaporation with fermentor by using an ethanol selective membrane at the wall surface of bioreactor so that the fermentation is carried out in the bioreactor and ethanol is selectively removed through the membrane wall surface and the water consumption is minimised.

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