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Evaluation of flat sheet and hollow fiber supported liquid membranes for fructose pertraction from a mixture of sugars

M. Di Luccio[a*], B.D. Smith[b], T. Kida[b], T.L.M. Alves[c], C.P. Borges[c]

[a]*Department of Food Engineering, URI-Campus de Erechim, Erechim, RS, 99700-000, Brazil*
Fax: +55-54-5209090, email: diluccio@uricer.edu.br
[b]*Dept. of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN, 46556, USA*
[c]*Chemical Engineering Program, COPPE, Federal University of Rio de Janeiro, RJ, 21945-970, Brazil*

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Abstract

This work investigates the use of supported liquid membranes (SLM) in the pertraction of fructose from a mixture of sugars contained in a fermentation broth. Membranes consisted in a porous polypropylene support impregnated with different kinds of carriers using 2-nitrophenyl octyl ether as solvent. Transport through flat sheet and hollow-fiber membranes was studied as a function of carrier and feed concentration. The results show that a boronic acid derivative yields the highest fructose selectivity and the hollow fiber supported liquid membrane (HFSLM) is more stable than the flat sheet system, also yielding higher fructose selectivities using lower carrier concentration. The HFSLM using a boronic acid as carrier was able to remove fructose selectively from a fermentation broth. Simulations of fructose removal from a fermentation broth were carried out using the experimental results obtained in this work. The results show that fructose removal from the fermentation broth can reduce microorganism inhibition and increase the system performance, although, further improvement in membrane stability and fluxes are still necessary.

Keywords: Fructose extraction; Supported liquid membranes; Fermentation

1. Introduction

Byproducts of high value have been proposed as an alternative to increase ethanol production profitability [1]. Fructose may be obtained as a byproduct of the selective fermentation of a mixture of glucose and fructose, which may result from the hydrolysis of sugar cane syrup. In such fermentation, glucose is converted to ethanol by a mutant *Saccharomyces cerevisiae* strain and fructose remains in the fermentation broth [2].

*Corresponding author

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In a fed-batch process, these products accumulate in the bioreactor, decreasing process performance due to inhibition of microorganism. Continuous removal of fructose and ethanol may keep the concentration of these products at sub-inhibitory levels [3]. Sugar separation is though a relatively difficult and costly task, since the most used commercial method for sugar separation frequently involves chromatographic processes [4]. Liquid membranes processes have been proposed to accomplish sugar separation [6–8]. This process combines solvent extraction and stripping in a single step and the transport mechanism is usually based on the facilitated diffusion. The simplest liquid membrane consists of an organic phase, which contains the carrier responsible for the transport of the desired component, placed between two aqueous phases.

The most attractive liquid membrane configuration for industrial applications is the supported liquid membrane (SLM). It consists in a polymeric microporous membrane, with the pores impregnated with a water immiscible organic solvent containing a carrier that has high affinity for the compound to be separated. In addition to the usual advantages of common membrane processes, as low energy demand, lower operating costs, easy scale up and operation, liquid membranes are highly selective.

It is then possible to use expensive carriers and/or solvents, and the process can be operated continuously. A major drawback with SLMs is membrane instability, due to the partition of the organic solvent/carrier to the aqueous phases. However, many studies have tried to overcome this problem with some success [9,10]. The hollow fiber geometry allows very high module packing densities, when they are compared to flat sheet, or to the tubular membranes. Hollow fiber modules also demand low investment and operating costs, due to the reduced equipment necessary, and they usually show favorable hydrodynamics that minimizes concentration polarization and membrane fouling [11].

Many studies have shown that quaternary ammonium salts and different kinds of boronic acids may be used as sugar carriers in liquid membranes [4,12–14], showing some selectivity for some sugars over other saccharides [15]. In this context, the main objective of the present study was to investigate the feasibility of removing fructose continuously from a fermentation broth using flat sheet and hollow fiber supported liquid membranes (FSSLM, HFSLM). The performance of different carriers is tested, and some preliminary simulations of fructose pertraction from the fermentation broth are presented.

2. Experimental

The FSSLM were prepared by impregnating flat sheets of Accurel (thickness 25 m and pore size 0.2 m) with a solution of the carrier in 2-nitrophenyl octyl ether (NPOE), synthesized using the procedure described by Kemperman [16]. The membrane was impregnated with the carrier solution, and placed in a typical dialysis cell, that consists of two jacketed compartments of 100 mL. The effective membrane diameter for permeation was 4 cm. The sugars were analyzed by an enzymatic assay [17]. After 24 hours, the membrane was washed with deionized water for 20 hours, and a new experiment using the same conditions was started. Unless otherwise stated, the feed solution in all experiments consisted of an equimolar solution of the sugars in sodium phosphate buffer, 100 mol m^{-3}, pH 7.4. The strip solution consisted of the same buffer without any sugar. The slope of the straight line resulting from the plot of strip solution concentration vs. time was calculated for each sugar. Flux values were then obtained by multiplying the slope by the strip solution volume and dividing by the total membrane area [18]. The selectivity to fructose was defined simply as the ratio between the fructose and glucose fluxes.

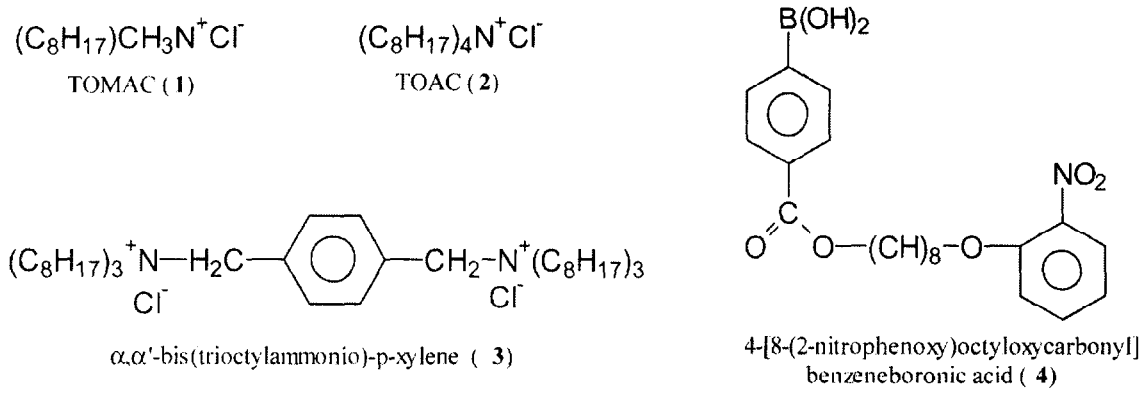

Fig. 1. Structure of the carriers.

The HFSLMs were prepared impregnating the support with a solution of the carrier in NPOE.

The support consisted of microporous hydrophobic polypropylene fibers (Hoescht-Celanese, internal diameter 292 m, wall thickness 26 m, and nominal pore diameter 0.05 m), assembled into a polypropylene tube (15 mm diameter and 25 cm length), sealed at each end with epoxy resin (Devcon). The feed and strip solutions were prepared in the same way as in the flat sheet experiments, and were pumped through the lumen and the shell side of the module, respectively. Quaternary ammonium salts and a boronic acid derivative were tested as carriers.

The salts tested were trioctylmethyl-ammonium chloride (TOMAC Aliquat 336), tetraoctylammonium chloride (TOAC), prepared at the lab from tetraoctylammonium hydroxide (Fluka); and one bisquaternary ammonium salt (BQAS), synthesized following the procedure described by Kida [6]. A boronic acid (BA) was synthesized following procedure described elsewhere [19].

The structure of each carrier is presented in Fig. 1.

3. Results

It can be observed from Table 1 that all the quaternary ammonium salt carriers showed similar fluxes and no selectivity for fructose. This behavior is possibly due to the binding mechanism between the carrier salts and the sugars, which is based on hydrogen bonding between the chloride that is associated with the quaternary ammonium cation and two adjacent hydroxyl groups of the sugar molecule [12]. The flux obtained using BQAS as carrier was the highest, since this carrier contains two binding sites for each molecule. For most cases, after washing the membrane and repeating the experiment lower fluxes were obtained. This is probably directly related to liquid membrane instability.

Many works have investigated liquid membrane instability causes and its effects on membrane performance. The flux decrease is normally attributed to partition of carrier molecules to the aqueous phases, and its increase is often related to the solvent leaching to the aqueous phases [9].

The fluxes obtained using the boronic acid derivative are slightly lower than the ones

Table 1
Results from FSSLM transport experiments using different carriers

Entry	Membrane	Feed (mol m^{-3})[1]	Glucose flux (10^8 mol m^{-2} s^{-1})	Fructose flux (10^8 mol m^{-2} s^{-1})	Fructose selectivity[2]
1	20 wt% TOMAC	100	20.6 (32.8)[3]	12.2 (26.9)	0.60 (0.82)
2	20 wt% TOAC	100	34.3 (22.3)	25.9 (21.1)	0.76 (0.94)
3	20 wt% BQAS	100	53.7 (35.7)	34.7 (27.3)	0.64 (0.76)
4	50 mol m^{-3} BA	100	15.0 (17.6)	9.46 (8.57)	0.63 (0.48)
5	50 mol m^{-3} BA	300	19.6 (46.5)	15.6 (37.5)	0.79 (0.81)
6	250 mol m^{-3} BA	100	3.7 (2.1)	51.4 (20.4)	14.0 (9.81)
7	250 mol m^{-3} BA	300	6.6 (3.5)	55.3 (10.7)	8.3 (3.0)

1) Equimolar concentration of glucose and fructose in sodium phosphate buffer100 mol m^{-3}, pH 7.4. Strip solutions: same buffer without the sugars. 2) Flux fructose/flux glucose. 3) Values in parenthesis represent the flux after washing the membrane for 20 h. 4) Standard deviations±5%.

Table 2
Results from HFSLM transport using boronic acid 4 as carrier

Entry	Membrane (mol m^{-3} BA)[1]	Feed (mol m^{-3})[2]	Glucose flux (10^8 mol m^{-2} s^{-1})	Fructose flux (10^8 mol m^{-2} s^{-1})	Fructose selectivity[3]
1	50	100	0.14	2.4	16.9
2	50	300	0.72	9.6	13.4
3	150	100	1.1	9.4	8.5
4	150	300	1.7	26.4	15.8
5	250	100	1.2	22.8	19.8
6	250	300	2.7	29.1	10.6
7	250	500	3.1	42.0	13.6

1) Liquid membrane: boronic acid 4 in NPOE, different concentrations. 2) Feed solutions: equimolar concentration of glucose and fructose in sodium phosphate buffer 100 mol m^{-3}, pH 7.4. Strip solutions: same buffer without the sugars. 3) Fructose flux/glucose flux. 4) Flux fructose/flux glucose. 4) Standard deviations±5%.

obtained using the quaternary ammonium salts. The chemical similarity of the carrier and solvent probably decreases the diffusion coefficient of the carrier-solute complex into the organic phase. One can also note that the transport using boronic acid carrier did not show selectivity for fructose for lower concentration of the carrier. However, when the concentration of the carrier is increased, there is an increase in fructose flux and a drastic change in selectivity. Although the reason for such behavior is not yet well clear, some speculations regarding the transport mechanism and membrane stability can be made. The onset observed on the fructose flux may be related to the moving site relay mechanism [20].

In such mechanism, the carrier molecules have a limited mobility in the organic phase, and the solute "jumps" from each carrier molecule to another. If the transport is mainly ruled by this mechanism, a minimum amount of the carrier is necessary for the transport to occur, since below this concentration the distance between carrier molecules will be too

large for the "jumping". On the other hand it was demonstrated that when moderate flow conditions and a support with smaller pore size are used, high fructose selectivity could already be obtained using 50 mol m^{-3} of the carrier.

This suggests that the carrier is being leached out of the organic phase very quickly in the flat sheet membrane system, causing the transport of fructose to be ineffective. The possibility that both phenomena are occurring in the system cannot be avoided.

The increase of feed concentration leads only to slight increase in fluxes (entries 4/5 and 6/7). This is possibly due to the fact that most of the carrier content in the organic phase might be already saturated with the solute, at the feed concentration of 100 mol m^{-3} [18,20].

It is also observed that the fluxes for the membrane containing 250 mol m^{-3} of carrier are strongly decreased after washing, showing that even though the carrier is very lipophilic, its partition on the aqueous phases is still high, causing membrane to degrade.

Table 2 shows the results for HFSLMs. It can be noted that the fluxes through FSSLM were higher than HFSLM, probably due to smaller pore size of the HF support. Nevertheless, even at low boronic acid concentrations, the transport using this geometry was fructose selective (entries 1 and 2).

This result may be attributed to increased membrane stability. In the hollow fiber system the pore size of the support is maller and the disturbance caused at the membrane surface by the flow is probably lower than in the flat sheet cell, preserving the membrane stability during the experiment.

Considering that in HF the flow conditions are limited to laminar (feed was pumped through the fiber lumen) and that the FS system is well stirred, a higher mass transfer resistance in the case of HF system is expected, leading also to lower fluxes. Previous workers have shown that the shear stress at the membrane surface disturbs the stability of aqueous/organic interface, inducing emulsion formation and gradually removing the organic solution out of the pores [9].

Another trend observed in Table 2 is the flux increase with the feed concentration. This result is expected if the carrier is not saturated with solute, so that as the solute concentration increases, the chemical potential gradient across the membrane is also increased.

It was possible to obtain a fructose flux almost two times higher, when the feed concentration was increased from 100 to 500 mol m^{-3} (entries 5–7). Although it has been reported that high concentrations of carriers might decrease the flux, due to viscosity increase [21], this behavior was not observed in the concentration range investigated.

In both feed concentrations studied, the flux increased with the carrier concentration. Using 250 mol m^{-3} of BA, it was possible to obtain a fructose flux more than tenfold higher than when 50 mol m^{-3} was used.

This result is similar to that obtained with FSSLMs. Selectivities to fructose showed a tendency to decrease with feed concentration.

This behavior is possibly related to the stoichiometry of the sugar complex formation. Norrild and Eggert [22] have shown that the higher the ratio sugar:boronic acid, the larger was the probability of complex formation with other isomeric forms of the sugar.

In this case, the increase in glucose concentration might include complex formation with other glucose isomeric forms, thus increasing its flux and changing selectivity. The HFSLM system could be operated for at least 48 h without significant changes in fluxes and selectivities.

After that time there is a 50% drop in fluxes and selectivity, but the membranes still show high fructose selectivity up to 168 h of operation, as can be observed in Fig. 2.

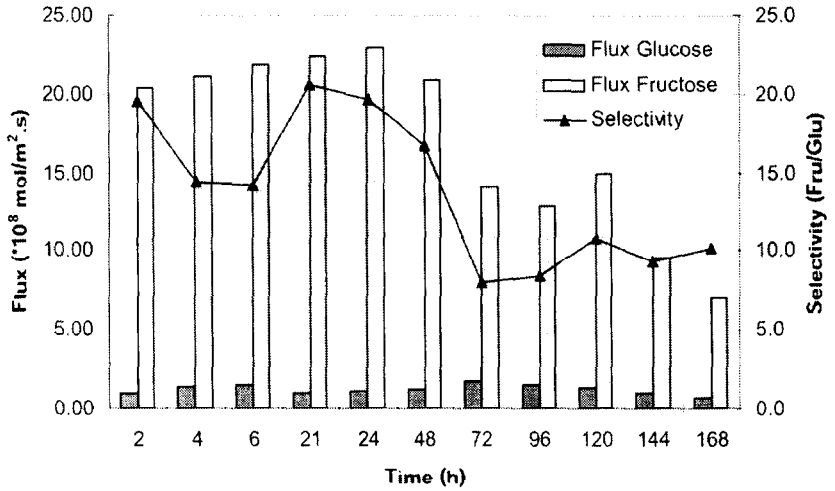

Fig. 2. Long term permeation experiment using 250 mol m^{-3} of boronic acid in the hollow fiber system. Feed concentration 100 mol m^{-3} of each sugar in sodium phosphate buffer 100 mol m^{-3} and pH 7.4. Strip solution: same buffer without sugars.

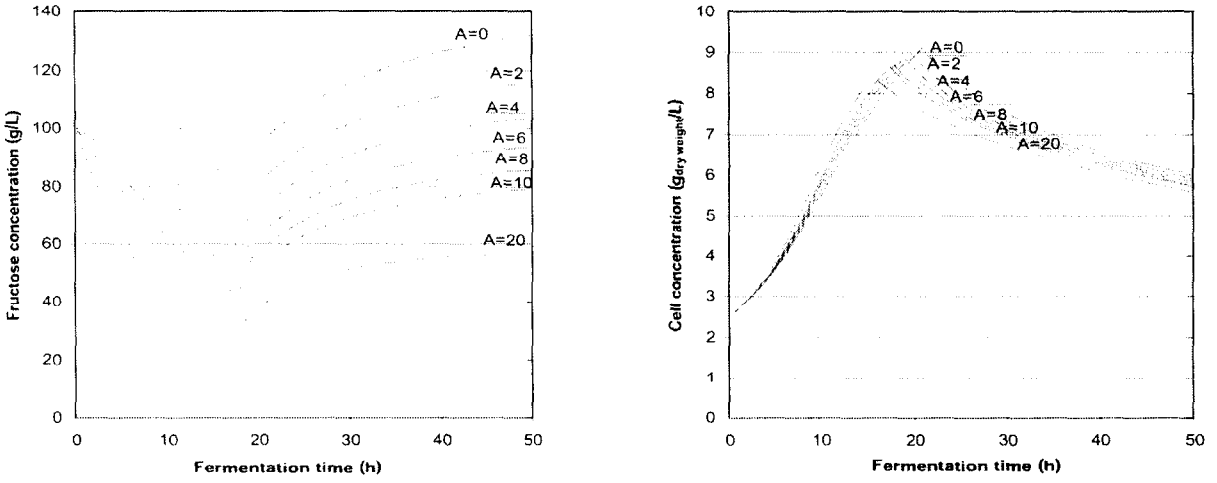

Fig. 3. Effect of liquid membrane area on fructose and cell concentrations in-side a bioreactor coupled to HFSLM system.

Computer simulations using parameters estimated from experimental data of selective fermentations of glucose and fructose mixtures [3] and the experimental fluxes and selectivities obtained in this work using HFSLM, were carried out.

The model considered a HFSLM system using 250 mol m^{-3} of the boronic acid derivative with fructose selectivity of 12, which was considered constant during all the operation. The bioreactor volume was 1 L and the initial concentrations of glucose and fructose was 100

g/L for each sugar. The feed contained 160 g/L in each sugar and it was started when glucose concentration in the bioreactor reached 5 g/L, which was about after 17 h of operation. The simulations yielded curves of concentration of glucose, fructose, ethanol and cells as function of time.

Fig. 3 shows the results for fructose and cell concentration progress with time for different liquid membrane areas tested. It is interesting to note that the HFSLM was able to decrease fructose concentration in the bioreactor. Nevertheless, the necessary area to keep the concentration of this sugar under the initial concentration is very high, due to the low fructose flux of the liquid membrane. Fructose removal has two opposite effects on cell concentration. When membrane area is increased, the inhibition is lowered and then the growth rate is increased (curve slopes).

On the other hand, a high membrane area also implies in higher removal of glucose as well. Therefore, the final cell concentrations are decreased, due to the lower availability of the substrate in the medium. Ethanol production and glucose consumption rates are also increased with the membrane area (results not shown), due to the decrease of microorganism inhibition with fructose removal from the fermentation broth.

4. Conclusions

In this work the pertraction of fructose from mixtures of fructose and glucose using flat sheet and hollow fiber supported liquid membranes (FSSLM and HFSLM) was studied. Two kinds of carriers were tested in the flat sheet system, quaternary ammonium salts and a boronic acid hydrophobic derivative. The latter showed the best fructose extraction properties. The flat sheet system produced fructose/glucose selectivities up to 14, while in the hollow fiber system fructose fluxes 20 times higher than glucose were obtained, using low carrier concentrations.

Preliminary tests show that a HFSLM using boronic acid as carrier was able to extract fructose from a fermentation broth. Simulation results showed that the HFSLM coupled to a bioreactor is capable of decreasing microorganism inhibition by fructose accumulation in the medium, although future work needs to improve membrane stability and increase the fructose flux.

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