

High selectivity microporous silica membranes for lactic acid dehydration

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Lactic acid (LA) has significant market potential for many industries including food, cosmetics, pharmaceuticals, medical and biodegradable materials. Production of LA usually begins with the fermentation of glucose but subsequent stages for the enrichment of lactic acid are complex and energy intensive and could be minimised using water selective membrane technology. In this work, we trialled a highly selective hydrostable carbonised template molecular sieve silica (CTMSS) membrane for the dehydration of a 15 vol% aqueous lactic acid solution with 0.1 vol% glucose. CTMSS membrane films were developed by dip-coating ceramic substrates with silica sols made using the acid catalysed sol-gel process. Permeation was performed by feeding LA/glucose solution to the membrane cell at 18°C in a standard pervaporation setup. The membrane showed selective transport of water from the aqueous feed to the permeate while glucose was not detected. CTMSS membrane permeate flux stabilised at 0.2 kg.m⁻².hr⁻¹ in 3.9 hours, and reduced LA to lower than 0.2 vol%. Flux through the CTMSS micropores was activated, displaying increased initial flux to 1.58 kg.m⁻².hr⁻¹ at 60°C. To enrich a 1 l.min⁻¹ stream to 85% LA in a single stage, a minimum membrane area of 324 m² would be required at 18°C. Increased operating temperature to 80°C significantly reduced this area to 24 m² but LA levels in the permeate stream increased to 0.5 vol%. The highly selective CTMSS membrane technology is an ideal candidate for LA purification. CTMSS membrane systems operate stably in aqueous systems leading to potential cost reductions in LA processing for future markets.

Introduction

Reducing the cost of purifying lactic acid (LA) could lead to a breakthrough in reduced production costs of many commercial products. Many industries utilise LA in producing their products. For the food industry, LA is considered safe and acts as a good preservative and pickling agent, while esters have been used as emulsifying agents in baking foods. In fact, LA has been used for a range of reasons in numerous applications including leather, textiles, food packaging, polymers, solder flux, adhesives, electroplating, detergents, cosmetics and medicines [1]. An interesting use of LA is in forming poly lactic acid, a readily biodegradable polymer which is not derived from fossil fuels. The global demand for LA in 2001 was 86,000 tons with growth expected to be 14% per year should polylactides and lactate esters become commercially successful [2]. LA is therefore seen as a major commercial product, with main drivers in food safety, health and the environment [3].

Lactic acid is produced from the fermentation of carbohydrates which can be sourced from renewables such as glucose or cornstarch. The carbohydrate undergoes fermentation with calcium hydroxide to produce calcium lactate. Sulphuric acid is then used to hydrolyse the lactate to lactic acid, leaving calcium sulphate to precipitate out. Lactic acid is then extracted

by esterification, distillation and hydrolysis. To reduce the cost of processing, several methods have been proposed for LA purification such as solvent extraction, adsorption, direct distillation and electrodialysis [4]. Solvent extraction can be costly and add further environmental issues due to the chemistry of the solvents. Distillation produces a highly corrosive lactic ester and self esterification leading to impurities can result. Electrodialysis is an expensive developmental technology and requires several pre-treatment stages:

- Ultrafiltration: to remove dissolved molecules from most particles and microorganisms. Cells must be removed first by filtering to prevent bacteria deposition on membrane surface;
- Decolourisation: dyes are removed to prevent dyes fixing on membrane leading to efficiency reduction; and
- Ion removal: Multivalent metal ions such as Ca, Mg, Fe, and Zn have to be removed from fermentation broth to prevent irreversible damage of electrodialysis membranes.

Selective extraction of water from lactic acid can be performed by molecular sieve silica (MSS) membranes. Such membranes have been shown to selectively permeate kinetically smaller kinetic gases such as He and H₂ over kinetically larger gases such as CO₂ and N₂ [5-7]. More recently however, researchers have been exploring the unique low adsorption, rigid inorganic microporous membranes for dehydration of water from alcohol solutions [8]. Performance in wet conditions however is a problem as silica is naturally soluble in water. Campaniello and co-workers trialled methyl templated membranes over 18 months, reporting major stability improvement over the standard silica membranes [9]. The advantage of inorganic silica membranes over organic is in their rigid oxide matrix, providing the required sieve structure while resisting degradation upon heating. For LA separation, the simplified mechanism is shown in Figure 1.

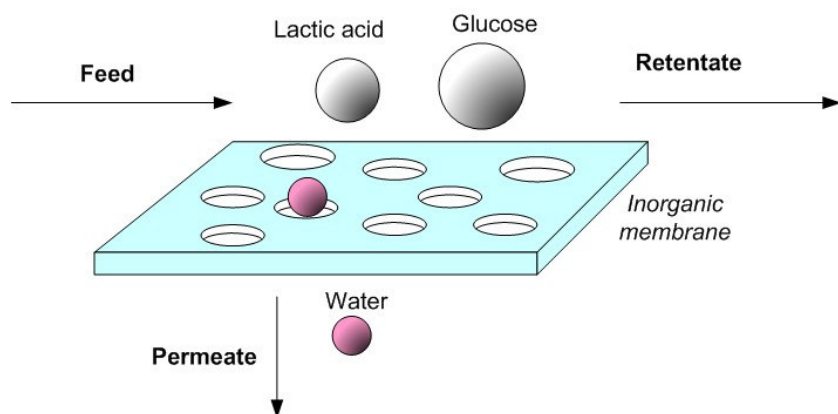


Figure 1: Simplified separation mechanism of inorganic membrane for dehydration of LA and glucose.

Our novel carbonised template MSS (CTMSS) material showed excellent hydrothermal resilience by inhibiting the micropore closing mechanism enabled normally by the free migration of silica [10]. In this work, we trial our CTMSS material formed over methyl templated silica to determine initial performance characteristics for lactic acid/glucose mixture dehydration. From this, we estimate the minimum membrane area required to dehydrate lactic acid to 85 vol% from 15 vol%.

Experimental

The CTMSS membranes were made according to our method described elsewhere [11]. In this method, porous ceramic substrates (25 × 10mm) comprising mostly of α -alumina are prepared for coating by first depositing a $\sim 1\mu\text{m}$ γ -alumina film. An intermediate sol is prepared using the acid-catalysed sol-gel process with methyl-triethoxy silane (MTES) as the methyl templated silica source. The sol is deposited by dip coating followed by calcination to 500°C. The final selective layer is made in a similar way, but with only tetraethyl orthosilicate (TEOS) in the sol-gel process, allowing specific tailoring of micropores suitable for sieving water molecules.

Lactic acid and glucose solutions of 15 vol.% and 0.1 vol.% respectively were used for the dehydration experiment in a membrane pervaporation setup. As shown in Figure 2, solution was fed to the membrane at $2\text{ mL}\cdot\text{min}^{-1}$ to avoid concentration polarisation effects. The permeate side was maintained at sub-atmospheric conditions by a 10^{-4} bar vacuum pump. Components that permeated through the membrane were caught in a liquid N_2 trap. The amount trapped over a 30 minute interval was measured to determine mass flow. The composition of LA and glucose was measured by first diluting in 2 mL of dionised water followed by analysis using a Perkin Elmer 200 HPLC with BIORAD HPX-87H column at 65°C and Perkin Elmer RI detector.

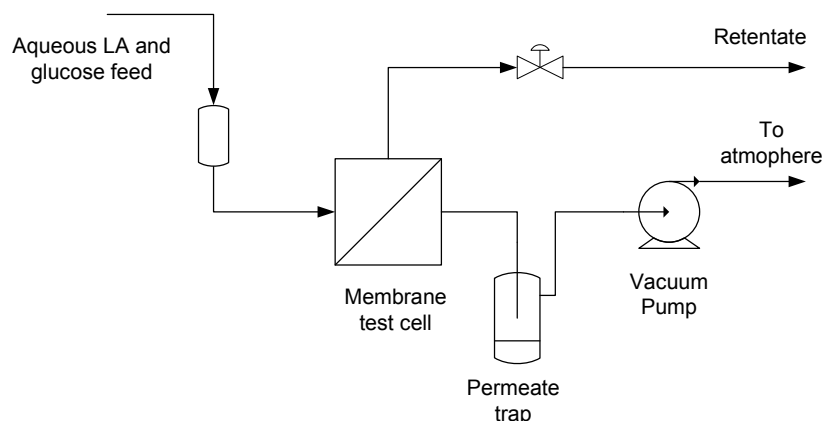


Figure 2: Schematic of the membrane pervaporation apparatus

Results and Discussion

The first test involved measuring the very first permeation and LA content changes to the permeate stream as shown in Table 1. LA increased by 30% upon stabilisation, and flux decreased by 35%. These values did not vary significantly up to the end of the test at 6.2 hours.

Table 1: Initial and stabilised flux and permeate LA concentration at 18°C

Test status	Time (hours)	Total flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$)	Permeate LA (ppm)
Initial	0.5	0.31	1400
Stabilised	3.9	0.20	2000

Glucose was not found in any trace amounts (ppm level) in the permeate for any experiment. This might be due to the full rejection of the larger molecule and glucose's low volatility. If some glucose diffused through the membrane it would remain on the membrane permeate side and not vaporise. Also, since glucose is much larger than the pore size of the membrane, this amount should be minor. No dried glucose was observed on the membrane after testing.

The behaviour of the permeation at 60°C is shown in Table 2. Initially, there was a major benefit to flux without compromise to the amount of LA in the permeate compared to the results at room temperature (Table 1). Flux increased by 5 fold while the amount of LA was actually 65% of the low temperature value. In this process, the water was assisted initially more than LA giving rise to a more diluted LA in the permeate. Permeation through the tight spaces of micropores is governed by an activated process, which has been rigorously applied for diffusion of single gas species in microporous membranes [7, 12-14]. More recently, groups have utilised vapour liquid equilibrium (VLE) from thermodynamic principles to quantify each component's driving pressure on the feed (liquid) side [15-17]. More modelling studies are however needed to represent the unique molecular scale diffusion process with low temperature liquids.

Table 2: Initial and stabilised flux and permeate LA concentration at 60°C

Test status	Time (hours)	Total flux (kg.m ⁻² .hr ⁻¹)	Permeate LA (ppm)
Initial	0.5	1.58	790
Stabilised	5.4	0.46	1720

At stabilisation however, the flux and permeate LA concentration reached a steady state. The flux was now only 2.3 fold greater than the stabilised value at 18°C, so some advantage of the activated process remained evident. Also, LA in the permeate was 86% of its 18°C stable value indicating still some advantage of the temperature activated process. At both conditions, there was 4-5 hours before stable performance was observed. Our past studies on the CTMSS material showed hydrostable performance at 200°C in steam conditions, but some permeance was lost [11] within the first few hours due to water adsorbing on the pore surface as the surface was still hydrophilic [10].

In the practical sense, increasing the temperature assisted the flux through the membrane having great implications for reducing unit size. Temperature test results were used to predict the minimum membrane area required to dehydrate 15 vol.% LA solution to 85 vol.% in a 1 l.min⁻¹ total feed flow basis. Result of these estimates are shown in Table 3.

Table 3: Predicted membrane performance with 1 l.min⁻¹ feed basis with 15 vol.% LA and retentate of 0.2 mL.min⁻¹ with 85 vol.% LA. Total pressure drop 1 bar.

T (°C)	Minimum area (m ²)	Permeate LA (ppm)
18	324	2000
50	77	5400
80	24	5100

In this modelling, $0.2 \text{ mL}\cdot\text{min}^{-1}$ of retentate exited the membrane containing the 85 vol.% solution of LA. The amount of LA rejected to perform the separation is shown in the right hand column. Based on our results, there are vast reductions in membrane area by operating at a higher temperature. According to the result in Table 2, LA was reduced in the permeate operating at 60°C . Further studies are underway to explore the change to LA structure upon heating which may effect the permeation through a molecular sieve membrane. In any case, it is therefore possible to dehydrate LA/glucose solutions with silica membranes, and with these and further results, an optimal design could be configured to achieve most efficient separation.

Conclusions

Lactic acid is a valuable product which can be used in many industries. Its purification steps are however process intensive and complicated. Hydrostable CTMSS membranes derived from silica were shown to remove lactic acid from aqueous streams containing glucose. Stable performance was recorded after 6.5 hours and the LA in the permeate was no more than 2200 ppm starting with 15 vol.%. Temperature greatly improved the total flux through the membrane, but there was a trade-off observed in increased LA rejected. From these results, at 80°C , 24 m^2 of membrane area would be required to process the LA solution to 85 vol.% with a feed flow of $1 \text{ L}\cdot\text{min}^{-1}$. With correct process design, silica membranes might find application in LA processing for product cost reduction.

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References

- [1] N. Narayanan, P. K. Roychoudhury and A. Srivastava. L (+) lactic acid fermentation and its product polymerization, *Electronic Journal of Biotechnology* [online] 7 (2004) cited 14-Feb 2006
- [2] Nextant Biotech Routes to Lactic Acid/Polylactic Acid
- [3] PURAC PURAC builds lactic acid plant in Thailand
- [4] X. Sun, Q. Wang, W. Zhao, H. Ma and K. Sakata. Extraction and purification of lactic acid from fermentation broth by esterification and hydrolysis method, *Separation and Purification Technology* In Press, Corrected Proof (2006)
- [5] R. J. R. Uhlhorn and A. J. Burggraaf. Gas Separations with Inorganic Membranes. In: R. R. Bhave *Inorganic Membranes: Synthesis, Characteristics, and Applications*. New York, NY: Van Nostrand Reinhold, 1991:155
- [6] R. S. A. de Lange, J. H. A. Hekkink, K. Keizer and A. J. Burggraaf. Permeation and separation studies on microporous sol-gel modified ceramic membranes, *Microporous Materials* 4 (1995) 169-186
- [7] R. M. de Vos and H. Verweij. Improved performance of silica membranes for gas separation, *J. Membr. Sci.* 143 (1998) 37-51
- [8] T. A. Peters, J. Fontalvo, M. A. G. Vorstman, N. E. Benes, R. A. v. Dam, Z. A. E. P. Vroon, E. L. J. v. Soest-Vercammen and J. T. F. Keurentjes. Hollow fibre microporous

- silica membranes for gas separation and pervaporation: Synthesis, performance and stability, *J. Membr. Sci.* 248 (2005) 73-80
- [9] J. Campaniello, C. W. R. Engelen, W. G. Haije, P. P. A. C. Pex and J. F. Vente. Long-term pervaporation performance of microporous methylated silica membranes, *Chemical Communications (Cambridge, England)* (2004) 834-835
- [10] M. C. Duke, J. C. Diniz da Costa, D. D. Do, G. Q. Lu and P. G. Gray. Hydrothermally robust molecular sieve silica for wet gas separation, *Advanced Functional Materials* Accepted - in press (2006)
- [11] M. C. Duke, J. C. Diniz da Costa, G. Q. Lu, M. Petch and P. Gray. Carbonised template molecular sieve silica membranes in fuel processing systems: permeation, hydrostability and regeneration, *J. Membr. Sci.* 241 (2004) 325-333
- [12] R. M. Barrer. Activated Diffusion in Membranes, *Transactions of the Faraday Society* 35 (1939) 644-656
- [13] R. S. A. de Lange, K. Keizer and A. J. Burggraaf. Analysis and theory of gas transport in microporous sol-gel derived ceramic membranes, *J. Membr. Sci.* 104 (1995) 81-100
- [14] A. J. Burggraaf. Single gas permeation of thin zeolite (MFI) membranes: theory and analysis of experimental observations, *J. Membr. Sci.* 155 (1999) 45-65
- [15] S. Sommer and T. Melin. Influence of operation parameters on the separation of mixtures by pervaporation and vapor permeation with inorganic membranes. Part 1: Dehydration of solvents, *Chemical Engineering Science* 60 (2005) 4509-4523
- [16] A. W. Verkerk, P. van Male, M. A. G. Vorstman and J. T. F. Keurentjes. Description of dehydration performance of amorphous silica pervaporation membranes, *Journal of Membrane Science* 193 (2001) 227-238
- [17] J. E. ten Elshof, C. R. Abadal, J. Sekulic, S. R. Chowdhury and D. H. A. Blank. Transport mechanisms of water and organic solvents through microporous silica in the pervaporation of binary liquids, *Microporous and Mesoporous Materials* 65 (2003) 197-208